DIELECTRIC STUDIES OF MOLECULES AND INTRAMOLECULAR RELAXATION PROCESSES

by

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Summary.

A new bridge technique for the measurement of the dielectric absorption of liquids and solutions at microwave frequencies has been described and its accuracy assessed. The dielectric data of the systems studied is discussed in terms of the relaxation processes contributing to the dielectric absorption and the apparent dipole moments.

Pyridine, thiophen and furan in solution have a distribution of relaxation times which may be attributed to the small size of the solute molecules relative to the solvent. Larger rigid molecules in solution were characterized by a single relaxation time as would be anticipated from theory.

The dielectric data of toluene, ethyl-, isopropyl- and t-butylbenzene as pure liquids and in solution were described by two relaxation times, one identified with molecular re-orientation and a shorter relaxation time. The subsequent work was an investigation of the possible explanations of this short relaxation process.

Comparable short relaxation times were obtained from the analysis of the dielectric data of solutions of p-chloro- and p-bromotoluene below 40°C, o- and m-xylene at 25°C and 1-methyl- and 2-methylnaphthalene at 50°C. Rigid molecules of similar shapes and sizes were characterized by a single relaxation time identified with molecular re-orientation. Contributions from a long relaxation process attributed to dipolar origins were reported for solutions of nitrobenzene, benzonitrile and p-nitrotoluene. A short relaxation process of possible dipolar origins contributed to the dielectric absorption of 4-methyl- and 4-t-butylpyridine in cyclohexane at 25°C.

It was concluded that the most plausible explanation of the short relaxation process of the alkyl-aryl hydrocarbons studied appears to be intramolecular relaxation about the alkyl-aryl bond.

Finally the mean relaxation times of some phenylsubstituted compounds were investigated to evaluate any shortening due to contributions from the process of relaxation about the phenyl-central atom bond. The relaxation times of triphenylsilane and phenyltrimethylsilane were significantly short.

Preface

The work described in this thesis was carried out at the University of Aston in Birmingham from October 1963 to September 1966 under the supervision of Dr. S. Walker M.A., D.Sc., D.Phil., F.R.I.C. whom I would like to thank for his encouragement and for many helpful discussions.

I would also like to thank Dr. A. W. P. Jarvie B.Sc., Ph.D. who supervised the preparation of the organosilicon compounds and with whom I have had interesting and useful discussions.

My sincere thanks are also due to Mr. M. D. Magee B.Sc. who provided the programmes for the Elliot 803 computer and to Mr. B. K. Morgan for his invaluable technical assistance.

W. F. Hassell

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Introduction

This thesis is an account of some dielectric studies at microwave frequencies of the relaxation processes of some polar organic molecules, either as pure liquids or in solution in a non-polar solvent. In recent years dielectric measurements have been used extensively to study the behaviour of molecules in the liquid state or in solution. A notable worker in this field, who has employed similar frequencies to those available for this work, is Professor C. P. Smyth of Princeton University and many references to his work are included in the subsequent discussions.

The basic theory of dielectric relaxation is outlined in Chapter 1 and references to more detailed accounts are given.

A new microwave bridge technique was developed which made possible the accurate measurement of the dielectric absorption of some systems having a low dielectric loss and sufficient frequencies became available which enabled a detailed analysis of the dielectric data to be made. The applicability of the apparatus to the measurement of the dielectric absorption of weakly polar molecules was utilized in a study of some aromatic hydrocarbons and related compounds. The work reported is an investigation of the relaxation processes contributing to the dielectric absorption of these molecules.

Chapter 1

Experimental Methods and Basic Theory

1.1 The Measurement of Dielectric Constant and Loss Factor at Five Microwave Frequencies

Dielectric Constant and Loss[1,2,3].

When small polar molecules are in solution in an alternating field of frequency less than about 10^8 c/sec. the electric dipole interacts with the electric field component of the electromagnetic radiation and the dipole responds instantly to the field variation. At significantly higher frequencies there is a time lag between the response of the dipole to the behaviour of the alternating field. The polar molecules of the system, under the influence of the field, move toward an equilibrium distribution in molecular orientation with a corresponding dielectric polarization. However, the rotation of the molecules is not sufficiently rapid for equilibrium with the field to be attained. The polarization then acquires a component out of phase with the field and the displacement current acquires a conductance component in phase with the field which results in thermal dissipation of energy.

In an ideal condenser of capacitance C_o in which the polarization is instantaneous, the charging or capacitive current, $E\omega\epsilon' C_o$, is 90° out of phase with the alternating potential, (see Fig. 1.1a).

Fig. 1.1 (a) Current - Voltage Diagram of a Dielectric with Loss.

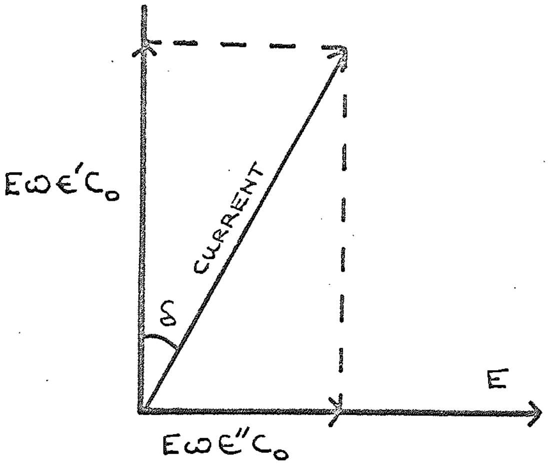


Fig. 1.1 (b) Cole - Cole Plot of a System Described by a Single Relaxation Time.

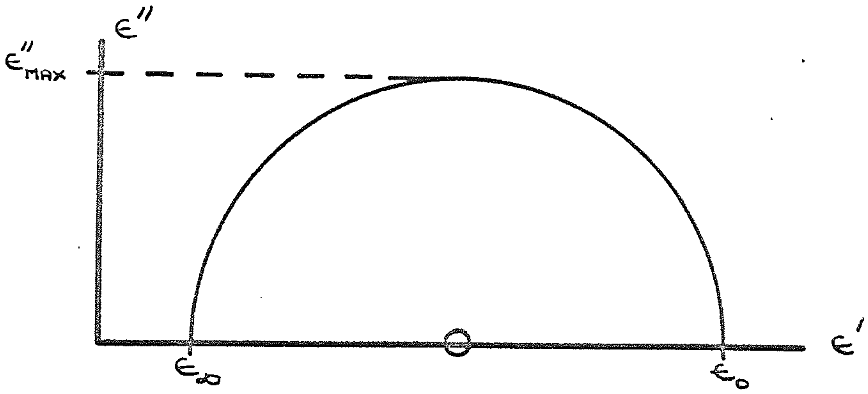
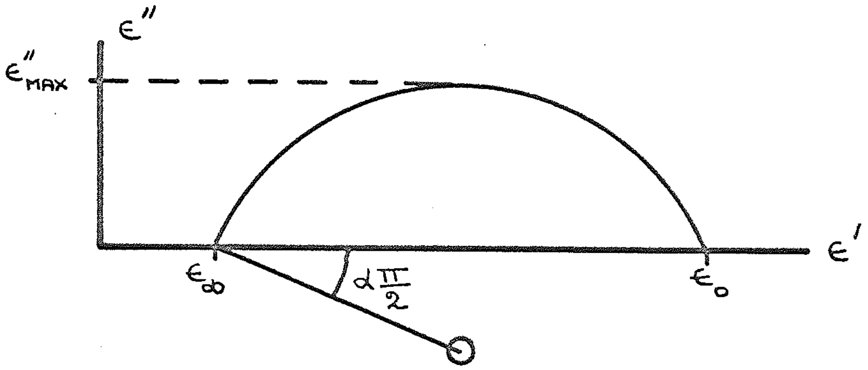


Fig. 1.1 (c) Cole - Cole Plot of a System having a Distribution of Relaxation Times.



where E is the alternating potential defined by

$$E = E^{o} \cos \omega t \qquad 1.1$$

E^{o} is independent of time t, ω is the angular frequency and ϵ' is the dielectric constant of the dielectric or the medium filling the condenser. In a condenser in which dielectric loss occurs the current also has a component $E\omega\epsilon''C_o$ in phase with the potential, where ϵ'' is the loss factor of the medium filling the condenser. This loss current, which measures the dielectric absorption, is due to the thermal dissipation of energy. From Fig. 1.1a, it can be seen that the total current is the sum of the charging current and the loss current. The angle δ between the vectors representing the total current and the charging current is known as the loss angle. Thus the tangent of this angle, or loss tangent is defined by

$$\tan \delta = \frac{\text{LOSS CURRENT}}{\text{CHARGING CURRENT}} = \frac{\epsilon''}{\epsilon'} \qquad 1.2$$

A complex dielectric constant is defined by

$$\epsilon^{*} = \epsilon' - i\epsilon'' \qquad 1.3$$

Attenuation and Phase Shift

If E^o is the electric field strength at time $t = 0$ at a point X in the path of an electromagnetic wave, then the electric field strength at point X at time $= t$ is from eqn. 1.1.

$$E = E^o e^{i2\pi f t} \tag{1.4}$$

where f is the frequency of the wave. At a distance Z from the point X in the direction of wave propagation, if the wave is travelling through a liquid (or solution) of propagation coefficient ∂, the electric field intensity is

$$E_z = E^o e^{i2\pi f t} e^{-\partial z} \tag{1.5}$$

which expands to

$$E_z = \left[E^o e^{-\alpha^* z}\right]\left[\cos(2\pi f t - \beta z) + i \sin(2\pi f t - \beta z)\right] \tag{1.6}$$

where $\partial = \alpha^* + i\beta$.

α^*, is the attenuation constant and is a measure of the diminuation of the intensity of the electric wave due to absorption by the liquid. The units of α^* are nepers cm.$^{-1}$. β is the phase constant for the liquid filled guide and the units are radians cm.$^{-1}$.

Determination of ϵ' and ϵ'' from α^* and β.

The basic equation is

$$\gamma = \alpha^* + i\beta = \frac{2\pi}{\lambda_0}\left[\left(\frac{\lambda_0}{2a}\right)^2 - \epsilon' + i\epsilon''\right]^{1/2} \qquad 1.7$$

where λ_0 is the wavelength in cm. of the radiation in vacuum and 'a' is the inner broad side width of the cross section of the waveguide.

From eqn. 1.7 it can be shown that

$$\epsilon'' = \left(\frac{\lambda_0^2}{4\pi^2}\right) 2\alpha^*\beta \qquad 1.8$$

$$\epsilon' = \left(\beta^2 - \alpha^{*2}\right)\frac{\lambda_0^2}{4\pi^2} + \left(\frac{\lambda_0}{2a}\right)^2 \qquad 1.9$$

Thus if α^* and β are determined for a known wavelength λ_0, from a knowledge of the dimensions of the waveguide ϵ'' and ϵ' may be obtained.

Apparatus; The Bridge Method[4]

A block diagram of the circuit is given in Fig. 1.2. The four arms of each magic T are labelled a, b, c and d. The individual items in the bridge were, excepting the cell, obtained from various manufacturers. The cells were made by the engineers of the Chemistry Department from rectangular waveguide.

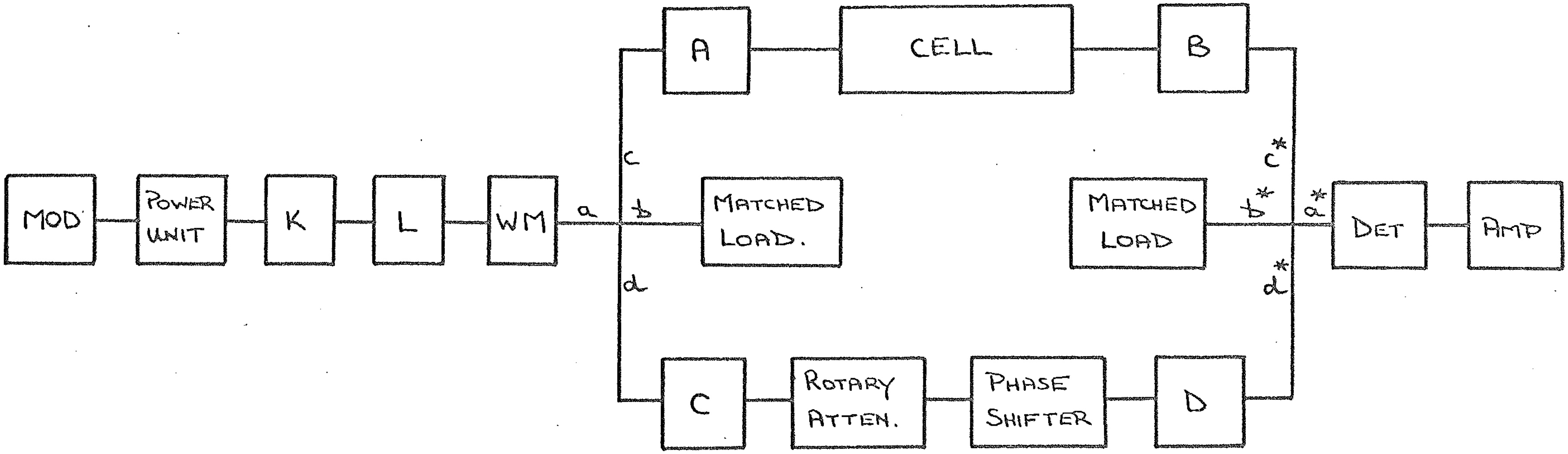
The monochromatic microwave radiation is generated by a klystron (K) to which square-wave reflector modulation of 3 Kc/sec. is applied. The wave is propagated along a rectangular waveguide. The range of frequencies which may be propagated along a waveguide of given cross section is limited and is listed in Table 1.1 for the bands used in this work.

Table 1.1 Waveguide Internal Cross Section Dimension, Frequency Range of Propagation and Frequency Employed.

Waveguide Internal Cross Section in Inches	Frequency Range in Gc/sec.	Frequency Employed in Gc/sec.
0.122 x 0.061	60.0 - 90.0	70.00
0.280 x 0.140	26.5 - 40.0	34.86
0.420 x 0.170	18.0 - 26.5	23.98
0.622 x 0.311	12.4 - 18.0	16.20
0.900 x 0.400	8.2 - 12.4	9.313

However, even these small variations of frequency are

Fig. 1.2 Block Diagram of the Bridge Apparatus.



barely permissible for accurate measurement of attenuation and phase shift owing to the variable behaviour of some of the measuring components at the different frequencies. Thus, although it was possible to obtain small variations in the frequency generated by the klystron, each band was operated at one frequency, also listed in Table 1.1. Before each series of measurements on any band the klystron was allowed to stabilize by running for one hour.

The attenuator or isolator at (L) protects the klystron from any reflected power. The wavelength of the propagated wave is read directly on a wavemeter (WM) and if necessary the klystron adjusted to give the required reading. At 'a' the power is split into two equal halves by the magic T. One half along arm 'c' through the cell containing the liquid or solution and the other half along arm 'd' through the calibrated variable attenuator and phase shifter. Any power passing along arm 'b' is matched out by the matched load. The liquid or solution in the cell shifts the phase and attenuates the wave. By adjustment of the variable attenuator and phase shifter it is possible to achieve the condition that at the output magic T the combining waves from arms 'c*' and 'd*' are of equal amplitude and 180° out of phase. With the fields so adjusted the vector sum in the output arm 'a*' is zero and the bridge is balanced. The high gain low noise amplifier and voltmeter connected to the crystal detector then registers zero reading.

For measurements on low loss solutions and liquids it is important to minimise reflections in the circuit. It was found that by the introduction of isolators or attenuators at points A, B, C and D reflections were minimised. This was assessed by determining the standing wave ratio at 'c*' and 'd*' using a standing wave indicator employing minimum probe depth.

The standing wave ratio ρ is defined as

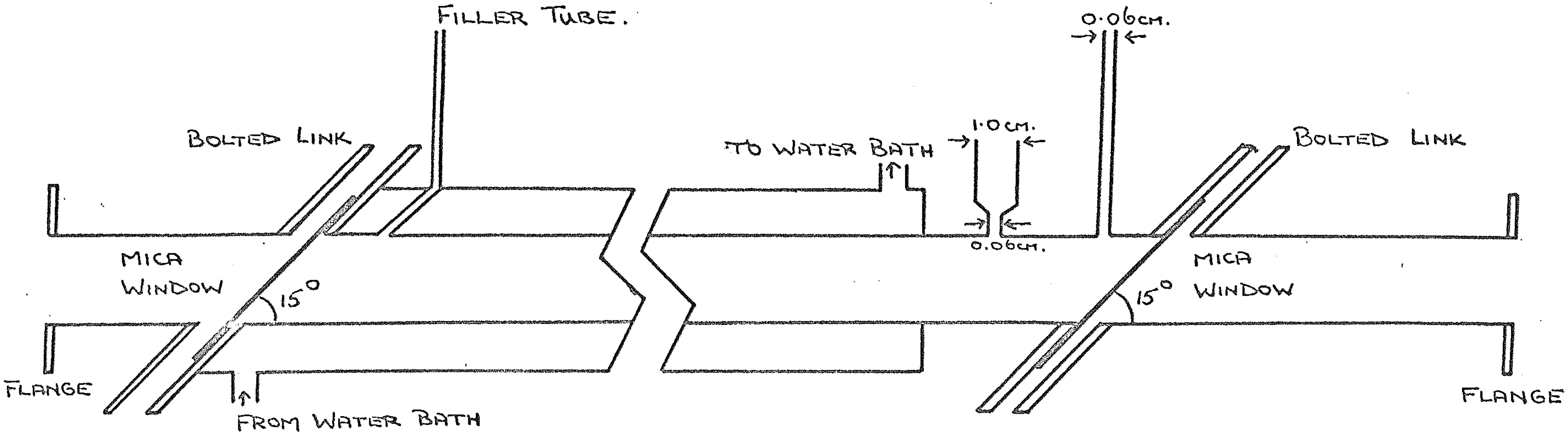
$$\rho = \frac{a_1 + a_2}{a_1 - a_2} \qquad 1.10$$

where a_1 is the amplitude of the forward wave and a_2 the amplitude of the reflected wave. Thus in an ideal circuit $a_2 = 0$ and $\rho = 1$. A value of less than 1.1 for ρ is acceptable in practice.

Isolators are particularly effective in obtaining good matches at 'c*' and 'd*' because they usually have low ρ values and also restrict wave propagation to the forward direction. They were employed whenever they were available.

The circuit was mounted on a board inclined at 15° from the horizontal, the klystron being at the lower end. Basic details of the cell are shown in Fig. 1.3. The windows are of mica and are

FIG. 1.3. DIAGRAM OF THE CELL



inclined at 15° to the direction of wave propagation so that the electric field component is introduced gradually into the cell and reflections are minimised. The temperature of the cell was controlled to ± 0.01°C by water circulating from a thermostat bath through the water jacket. The cell is filled through the narrow metal tube of 0.06 to 0.03 cm. inner diameter which enters the cell, remaining flush with the wall, in the middle of the broad side of the guide close to the bottom mica window. The tubes fitted near the top window allow the cell to be drained of test solution and washed with a volatile solvent. The cell is dried by blowing air through it from a pump.

A water jacketed 'Agla' micrometer syringe is employed for filling the cells of the bands operated at 70.00, 34.86 and 23.98 Gc/sec. The syringe is filled from a temperature controlled container. The cell of the 70.00 Gc/sec. band was modified because of its small size. It is filled through a 0.03 cm. inner diameter tube fitted close to the top window of the cell. A short tube fits close to the bottom window and is sealed before each series of measurements with a soldered needle. The cells of the circuits working at 16.20 and 9.313 Gc/sec. are filled from a grade A burette which is fitted with a water jacket. The burette of the 16.20 Gc/sec. band is connected to the filler tube by a short length of polythene tubing. Additions to the 9.313 Gc/sec. cell are made directly through the wide ended tube terminating in a 0.06 cm. diameter hole sited in the middle of the broad side of the waveguide at the top end of the cell. The filler tube at the bottom of the cell is not fitted.

The solution is run into the cell until the mica window is covered. The bridge is balanced and the attenuator and phase shifter readings are taken. Enough solution to give a phase shift of 360° is then added to the cell and the readings again taken. This is continued as many times as possible. The solution is added in aliquots to give 360° of phase shift because the phase shifter itself introduces attenuation which varies according to the setting. The phase shifter was calibrated by measuring its attenuation at settings of 10° intervals and it was found that for ± 10° settings the attenuation introduced can be considered to be constant.

The attenuation in nepers is plotted against the length of added solution in cms. The length of solution is known from the volume added and the cross section of the waveguide. The slope of this plot is α^* the attenuation constant.

The phase shift in radians is plotted against the length of added solution. The slope of the straight line plot is $\beta_{MEAS.}$. This value is not the phase constant of the solution because an equivalent volume of air has been displaced and this has a significant phase shift.

Thus,

$$\beta_{\text{SOLN.}} = \beta_{\text{MEAS.}} + \beta_{\text{AIR}} \qquad 1.11$$

β_{AIR} is a constant for any wavelength and is obtained from the equation

$$\beta_{\text{AIR}} = \frac{2\pi}{\lambda_g} \qquad 1.12$$

where λ_g is the wavelength in the guide.

The slopes of the plots were evaluated from the equation

$$\text{Slope} = \frac{\sum xy - \bar{y}\sum x}{\sum x^2 - \bar{x}\sum x} \qquad 1.13$$

where x = volume added

y = attenuation or phase change.

ϵ' and ϵ'' were then obtained by substitution of α^* and $\beta_{\text{SOLN.}}$ into eqns. 1.8 and 1.9.

To illustrate the procedure of evaluation of the dielectric constant and loss factor a typical example of experimental data is shown in Table 1.2 and the evaluation of ϵ' and ϵ'' is set out below.

Table 1.2. Experimental Readings from the Microwave Bridge Method

Operating at 9.313 Gc/sec.

Total Volume of Solution in Cell (mls.)	Phase Change (deg.)	Attenuation (db)
16.0	361.5	2.98
27.1	712.0	4.23
38.6	1075.0	5.53
50.1	1436.0	6.85
61.6	1799.5	8.16
72.9	2156.6	9.44

From the data given in Table 1.2 and eqn. 1.13 the slopes of Phase Change and attenuation against volume of solution added to the cell are determined.

Slope of Phase change = 31.5203 deg. ml^{-1}

Slope of Attenuation = 0.11361 db. ml^{-1}

The cross sectional area of the waveguide of the band operating at 9.313 Gc/sec. is 2.3237 cm^2, 1 neper = 8.686 decibels and 1 degree = 0.01745 radians.

Therefore,

$$\alpha^* = \text{Slope of Attenuation} \times \frac{2.3237}{8.686} = 0.03039 \text{ neper cm}^{-1}$$

$$\beta_{\text{MEAS.}} = \text{Slope of Phase Change} \times 2.3237 \times 0.01745$$

$$= 1.2781 \text{ radians cm.}^{-1}$$

from eqns. 1.11 and 1.12,

$$\beta_{\text{SOLN.}} = \beta_{\text{MEAS.}} + \beta_{\text{AIR}} = \beta_{\text{MEAS.}} + \frac{2\pi}{\lambda_g}$$

$$\lambda_g = \text{wavelength in the guide} = 4.546 \text{ cm.}$$

therefore,

$$\beta_{\text{SOLN.}} = \beta_{\text{MEAS.}} + 1.3834 = 2.6615$$

λ_o , the wavelength in vacuum = 3.22 cm. 'a' the inner broad side width of the cross section of the waveguide = 2.236 cm., therefore, eqns. 1.8 and 1.9 reduce to

$$\epsilon'' = 0.52526\, \alpha^* \beta_{\text{SOLN.}}$$

$$\epsilon' = 0.26263\left(\beta^2_{\text{SOLN.}} - \alpha^{*2}\right) + 0.49579$$

and substitution of $\beta_{\text{SOLN.}}$ and α^* gives

$$\epsilon'' = 0.0425$$

$$\epsilon' = 2.356$$

Static Dielectric Constant ϵ_o.

The static dielectric constants were measured at 2 Mc/sec. using a heterodyne beat apparatus. The instrument used was a Wiss-Tech-Werkstatten Dipolmeter, Type DM01.

The cell was calibrated with air and pure cyclohexane and measurements were checked by determining the dielectric constant of p-xylene at the same time as the solutions.

Density.

The densities of the solutions, when required, were determined using a pykometer similar to that employed by Cumper, Vogel and Walker[5]. Its volume was about 10 ml. and the weights were reproduceable to 0.1 mg.

Refractive Index.

The refractive indices were measured on a Bellingham and Stanley refractometer of the Pulfrich type reading to 0.00001.

Viscosity.

The viscosities were determined using an Ostwald Viscometer with a flow time of about five minutes for a liquid with a viscosity of 1 cp.

1.2 Analysis of the Dielectric Data

Equations.

As indicated earlier, at significantly higher frequencies than 10^8 c/sec. there is a time lag between the response of small polar molecules in solution to the behaviour of an applied field. This is measured in terms of the relaxation time, τ . τ may be defined as the time for the orientation polarization (P) to decay to $\frac{1}{e}$ times its original value (P_o), e being the natural logarithmic base, when the field is removed. This is deduced from the relationship,

$$P = P_o e^{-t/\tau} \qquad 1.14$$

for the case $t = \tau$.

For molecules whose dielectric absorption is characterized by a single relaxation time, Debye[6] developed the relationship of the relaxation time to the complex dielectric constant.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{1 + i\omega\tau} \qquad 1.15$$

where ϵ_o is the static dielectric constant, ϵ_∞ the optical dielectric constant or dielectric constant measured at very high frequencies and ω is the angular frequency of the applied field. Substitution of eqn. 1.15 into eqn. 1.3 and separation of real and imaginary parts gives

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \qquad 1.16$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \qquad 1.17$$

It can be seen from eqn. 1.17 that ϵ'' approaches zero for very large and very small values of $\omega\tau$, while at the maximum value of ϵ'',

$$\omega\tau = 1 \qquad 1.18$$

For molecules whose dielectric absorption is characterized by more than one relaxation time, Cole and Cole[7] modified eqn. 1.15 to give

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \qquad 1.19$$

where τ_0 is the most probable relaxation time corresponding to the frequency at which ϵ'' has a maximum value and α is the distribution coefficient which can have values between 0 and 1. α is a measure of the distribution of relaxation times.

Separation of eqn. 1.19 into real and imaginary parts yields the following equations[7].

$$\epsilon' = \epsilon_\infty + \frac{[\epsilon_0 - \epsilon_\infty][1 + (\omega\tau_0)^{1-\alpha}\cos(1-\alpha)\pi/2]}{[1 + 2(\omega\tau_0)^{1-\alpha}\cos(1-\alpha)\pi/2 + \omega\tau_0^{2(1-\alpha)}]} \qquad 1.20$$

$$\epsilon'' = \frac{\left[(\epsilon_0 - \epsilon_\infty)(\omega\tau_0)^{1-\alpha} \sin(1-\alpha)\pi/2\right]}{\left[1 + 2(\omega\tau_0)^{1-\alpha}\cos(1-\alpha)\pi/2 + \omega\tau_0^{2(1-\alpha)}\right]} \qquad 1.21$$

when $\alpha = 0$ these equations reduce to eqns. 1.16 and 1.17

For systems that have several discrete relaxation times contributing to the dielectric absorption eqns. 1.17 can be modified to[8]

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_i \frac{c_i}{1 + (\omega\tau_i)^2} \qquad 1.22$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \sum_i \frac{c_i\omega\tau_i}{1 + (\omega\tau_i)^2} \qquad 1.23$$

where C_i is the relative weight of the contribution of each relaxation process of relaxation time τ_i to the dielectric absorption as a whole and

$$\sum c_i = 1 \qquad 1.24$$

Internal Field Corrections.

The Debye[6] equations which take into account the effect of the internal field on the molecular relaxation process relate the microscopic or molecular relaxation time (τ_μ) to the macroscopic or measured relaxation time (τ_M) by the equation,

$$\tau_M = \frac{(\epsilon_0 + 2)}{(\epsilon_\infty + 2)} \tau_\mu \qquad 1.25$$

Powles[9] has proposed an expression for the internal field in a dielectric subjected to an alternating electric field which leads to

$$\tau_M = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \tau_\mu \qquad 1.26$$

Miller and Smyth[10] have shown that the Powles' equation appears to be the best approximation.

For the relatively low loss liquids and solutions studied in this work ($\epsilon_0 - \epsilon_\infty$) is about 0.2 or less. This leads to a Powles' correction which is less than the experimental error in the macroscopic relaxation time. Therefore the difference in the two relaxation times has been neglected and no internal field corrections have been applied to the relaxation times given in the following chapters.

The Cole-Cole Plot.

Cole and Cole[7] showed that by elimination of $\omega\tau$ from eqns. 1.16 and 1.17 the equation of a circle is obtained

$$\left[\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2}\right]^2 + \epsilon''^2 = \left[\frac{\epsilon_0 - \epsilon_\infty}{2}\right]^2 \qquad 1.27$$

and that a plot of ϵ'' against ϵ' in the complex plane gives a semicircle whose intercepts with the abscissa are ϵ_0 and ϵ_∞.

For systems characterized by a single relaxation time the semicircle, or Cole-Cole plot, has its diameter along the abscissa. Systems with more than one relaxation time, either two or more discrete relaxation times or a distribution of relaxation times about a most probable value, display a Cole-Cole plot whose diameter has been displaced about ϵ_∞ in a clockwise direction by an angle $\alpha\frac{\pi}{2}$ (See Figs. 1.1 b & c).

The accurate fitting of the Cole-Cole plot to the experimental data is important as it provides the value of ϵ_∞ which is used in the subsequent evaluation of dipole moments and relaxation times. The ϵ_∞ and α values have been evaluated by fitting the experimental data to eqns. 1.20 and 1.21, using an Elliot 803 computer programmed to minimise the square of the difference between the experimental values of ϵ' and ϵ'' at any frequency and the calculated values at the same frequency. The value of τ_0 , the most probable relaxation time, is also obtained from this programme.

For systems measured with τ_0 values of less than $\sim 2.5 \times 10^{-12}$ sec., that is with all the experimental points lying to the right of $\epsilon''_{MAX.}$ on the low frequency side of the Cole-Cole plot, it was found that, because the programme was written with a slight constraint to provide minimum α values, the ϵ_∞ values were invariably too large. This was indicated by the extremely low dipole moment values which were evaluated from $(\epsilon_0 - \epsilon_\infty)$ and eqn. 1.36. For these systems the ϵ_∞ values were obtained by graphical extrapolation. When this has been done is indicated in the following chapters.

Determination of Relaxation Times

τ_0, The Most Probable or Mean Relaxation Time

For most systems τ_0 was obtained from eqns. 1.20 and 1.21 using the Elliot 803 computer, as outlined previously. When this was not possible the angular frequency at which ϵ'' had its maximum value was determined by a method given by Smyth[1] using the relationship[7]

$$\frac{V}{u} = (\omega\tau_0)^{1-\alpha} \qquad 1.28$$

in which V and U are the distances between an experimental point and ϵ_0 and ϵ_∞ respectively.

A plot of log $\frac{V}{U}$ against log ω is a straight line whose intercept with the abscissa at log $\frac{V}{U}$ = 0 gives log ω_{MAX}. τ_0 was evaluated from the equation

$$\tau_0 = \frac{1}{\omega_{MAX.}} \qquad 1.29$$

Evaluation of Discrete Relaxation Times

For systems characterized by a single relaxation time $\alpha = 0$ and the methods used to evaluate τ_0 give the value of the single relaxation time.

For a system with two mutually independent relaxation times (τ_1 and τ_2), Bergmann[11, 12] developed a chord method of analysis in which eqns. 1.22 and 1.23 are modified to

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1 + (\omega\tau_1)^2} + \frac{C_2}{1 + (\omega\tau_2)^2} \qquad 1.30$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1\omega\tau_1}{1 + (\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1 + (\omega\tau_2)^2} \qquad 1.31$$

Estimates of τ_1, τ_2 and C_1 obtained from the chord method were fed into the Elliot 803 computer programmed to minimise the square of the difference between the experimental points at any frequency and the calculated values, from the variable τ_1, τ_2, C_1 values and the constants ϵ_0 and ϵ_∞, obtained from eqns. 1.30 and 1.31 at the same frequency. The accuracy of the analysis was checked by comparison of the experimental and calculated points when the minimisation was complete.

The Free Energy of Activation and Enthalpy of Activation of the Relaxation Process

From the relaxation times the free energy barrier, $\Delta G^{\ddagger}$, separating the two equilibrium positions of the relaxing dipole was evaluated from transition state theory as[13,14]

$$\frac{1}{\tau} = \kappa \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} \qquad 1.32$$

where h is Planck's constant, k the Boltzmann constant, T the absolute temperature and κ the transmission coefficient normally taken to be 1. This corresponds with the case of the re-orienting unit which each time it is excited to the top of the energy barrier continues to move in the same direction to the next minimum position. From eqn. 1.32 it follows that

$$\log \tau T = \frac{1}{T} \cdot \frac{\Delta H^{\ddagger}}{2.303 R} + \left[\log \frac{h}{k} - \frac{\Delta S^{\ddagger}}{2.303 R} \right] \qquad 1.33$$

where $\Delta H^{\ddagger}$ is the enthalpy and $\Delta S^{\ddagger}$ the entropy of activation. $\Delta H^{\ddagger}$ was obtained from the slope of the plot of $\log \tau T$ against $\frac{1}{T}$. If m is the slope of this plot, the enthalpy of activation is given by

$$\Delta H^{\ddagger} = 2.303 Rm - RT \qquad 1.34$$

The extra term RT in eqn. 1.34 arises from the absence of one degree of freedom in the transition state.

The entropy of activation, $\Delta S^{\ddagger}$, is obtained from

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad 1.35$$

Dipole Moments

For the solutions of high weight fraction (w_2), the apparent dipole moments have been evaluated from the Debye equation

$$\mu = 0.012812 \left[\frac{3T(\epsilon_0 - \epsilon_\infty)}{C(\epsilon_0 + 2)(\epsilon_\infty + 2)} \right]^{\frac{1}{2}} \qquad 1.36$$

in which C is the concentration in moles/ml. and T the absolute temperature.

$$C = \frac{w_2 d_{12}}{M_2} \qquad 1.37$$

where d_{12} is the density of the solution and M_2 is the molecular weight of the solute.

For dilute solutions, the dipole moments have been evaluated by extrapolation to infinite dilution at which

$$(\epsilon_0 + 2)(\epsilon_\infty + 2) = (\epsilon_1 + 2)^2 \qquad 1.38$$

and $d_{12} = d_1$

where ϵ_1 is the static dielectric constant of the solvent and d_1 the density of the solvent. Eqn. 1.36 then becomes

$$\mu = 0.012812 \left[\frac{3T(\epsilon_0 - \epsilon_\infty) M_2}{(\epsilon_1 + 2)^2 w_2 d_1} \right]^{\frac{1}{2}} \qquad 1.39$$

1.3 Preparation and Purification of Materials

Solvents

The distillation of all solvents was through a two foot column packed with glass rings.

Cyclohexane and p-xylene were purified by refluxing over sodium followed by distillation. They were stored in well closed amber bottles over sodium wire.

'Analar' benzene was shaken with several batches of sulphuric acid (d.1.84) until no darkening of the acid occurred. It was then well washed with distilled water and dried over sodium hydroxide pellets. It was finally distilled from sodium and stored in a similar manner to cyclohexane.

The purification of carbontetrachloride followed a method described by Vogel[15]. It was stirred under reflux with an aqueous ethanolic solution of potassium hydroxide for half an hour. This was repeated, then it was well washed with distilled water. Washing with concentrated sulphuric acid was then carried out until the washings were colourless. After further washings with distilled water, the carbontetrachloride was dried over anhydrous calcium chloride and distilled. 15% of the volume was rejected as a first fraction.

Solutes

The purification of the commercially available solutes is summarised in Table 1.3. The solutes are listed in subsections (a) to (g) each of which contains the compounds discussed in Chapters 2 to 8 respectively of this thesis.

Liquids were dried over a suitable drying agent when necessary and distilled on a 30 theoretical plate spinning band column. A small, constant boiling point, centre fraction was collected and the purity confirmed by gas-liquid chromatography.

Solids were recrystallised twice, or until a constant melting point was obtained.

Table 1.3 Purification of Solutes

Solute	Solid		Liquid	
	Solvent for recrystallisation	M.pt. (°C).	Drying Agent	B.pt. (°C).
a) Bromobenzene	-	-	Phosphorus Pentoxide	156
b) Pyridine	-	-	Phosphorus Pentoxide	115
Thiophen	-	-	-	83
Furan	-	-	-	32
Camphor	Sublimed	178	-	-
4-Cyanopyridine	p-Xylene	82	-	-

Table 1.3 continued

Solute	Solid		Liquid	
	Solvent for recrystallisation	M.pt. (°C).	Drying Agent	B.pt. (°C)
c) Toluene	-	-	Purified by Vogel's method[15]	111
Ethylbenzene	-	-	Purified by the method of Cumper, Vogel and Walker[16]	136
Isopropylbenzene	-	-		152
t-Butylbenzene	-	-		169
d) Fluorobenzene	-	-	Calcium Chloride	85
Chlorobenzene	-	-	Calcium Sulphate	132
Bromobenzene	See Section (a)			
Iodobenzene	-	-	-	188
Nitrobenzene	-	-	-	211
Benzonitrile	-	-	-	191
e) p-Chlorobenzene	-	-	Calcium Sulphate	162
p-Bromotoluene	-	-	Calcium Sulphate	184
p-Nitrotoluene	Cyclohexane	54	-	-
4-Methylpyridine	-	-	Potassium Hydroxide	143
4-t-Butylpyridine	Pure sample prepared by A.N.Sharpe[17]			
f) Benzocyclobutene	Pure sample prepared by J.B.F.Lloyd[18]			

Table 1.3 Continued

Solute	Solid		Liquid	
	Solvent for recrystallisation	M.pt. (°C).	Drying Agent	B.pt. (°C).
f) o-Xylene	-	-	Sodium Wire	144
m-Xylene	-	-	Sodium Wire	139
o-Dichlorobenzene	-	-	-	181
m-Dichlorobenzene	-	-	-	172
1-Methylnaphthalene	-	-	-	241
2-Methylnaphthalene	-	-	-	241
2-Bromonaphthalene	Aqueous Ethanol	57	-	-
g) Diphenylmethane	-	-	-	261
Triphenylphosphine	Cyclohexane	80	-	-
Triphenyl-phosphineoxide	p-Xylene	156	-	-
Triphenylarsine	Aqueous Ethanol	60	-	-
Triphenylamine	Cyclohexane	127	-	-

Phenyltrimethylsilane was prepared by the dropwise addition of an ether solution of phenylmagnesiumbromide Grignard reagent to a stirred solution of trimethylchlorosilane in ether. Reflux was maintained for six hours after the addition was completed. Excess dilute hyrochloric acid was added to the stirred, cooled reaction mixture. The ether layer was separated, washed twice with water and dried over anhydrous magnesium sulphate. After evaporation of the solvent the crude product was distilled at atmospheric pressure. The fraction collected boiled at 169-170°C.

Diphenyldimethylsilane was prepared from methylmagnesiumiodide Grignard reagent and diphenyldichlorosilane by the method outlined above. The crude product was distilled under reduced pressure. B.pt. 78-80°C at 0.3 mm. pressure.

Triphenylsilane was prepared by the dropwise addition of an ether solution of phenyllithium to a stirred solution of silicochloroform in ether. Reflux was continued for four hours. After filtration of the lithium halides the solvent was evaporated off and the crude product distilled under reduced pressure. B.pt. 126°C at 0.15 mm. pressure.

1.4 Experimental Results

Correction Applied to ϵ' and ϵ''.

The volume of liquid retained by the filler tube fitted to cells of the bands operating at 34.86 Gc/sec. and 23.98 Gc/sec. (see Fig.1.3) caused a small consistent error in the measurement of the dielectric constant at these frequencies. The error in the measured loss factors was negligible. To account for the error in ϵ' the apparent dielectric constant of pure cyclohexane was measured by the microwave bridge method at these frequencies and subsequent measurements of the dielectric constant of solutions were corrected by $+\left[\epsilon_{o\,\text{cyclohexane}} - \epsilon'_{\text{cyclohexane}}\right]$. These corrections to $\epsilon'_{\text{MEAS.}}$ were + 0.012 and + 0.003 for the bands operating at 34.86 Gc/sec. and 23.98 Gc/sec. respectively.

p-Xylene has a small but detectable dielectric absorption and corrections for this were made to measurements on solutions employing this solvent. The dielectric constant and loss factors of the same batch of p-xylene used in making the solutions were determined at the same temperature and frequencies used for the subsequent solution measurements. The measured dielectric constants and loss factors of the solutions were then corrected by $+\left[\epsilon_{o\,\text{p-xylene}} - \epsilon'_{\text{p-xylene}}\right]$ and $-\epsilon''_{\text{p-xylene}}$ respectively, where $\epsilon'_{\text{p-xylene}}$ and $\epsilon''_{\text{p-xylene}}$ were determined at the same frequency as the solution values.

Presentation of Experimental Results

All relevant experimental results are included in Chapter 2.

For subsequent chapters the relevant static dielectric constant, dielectric constant at very high frequency, distribution coefficient, dipole moment and relaxation time data are given in tabular form within each chapter and the experimentally determined dielectric constants $\epsilon'_{MEAS.}$ and loss factors $\epsilon''_{MEAS.}$ are tabulated in the appendix to this thesis. Tables 1 to 6 of the appendix correspond to Chapters 3 to 8 respectively. So that an assessment of the accuracy of the analysis of the dielectric data can be made, when appropriate, the tables in the appendix include $\epsilon'_{CALC.}$ and $\epsilon''_{CALC.}$ the dielectric constants and loss factors calculated from eqns. 1.30 and 1.31 and the $\tau_1, \tau_2, C_1, \epsilon_0$ and ϵ_∞ data given in the respective chapters. Density data is also included in the appendix.

Chapter 2

An Assessment of the Bridge Method

Introduction

Although certain bridge techniques have been employed to determine the dielectric constant and loss of solutions,[19,20] the apparatus described in Chapter 1 had not been used previously and an assessment of its reliability and accuracy was required.

At the time of this work the wavebands in use were those operating at 34.86, 23.98 and 9.313 Gc/sec. For the band at 23.98 Gc/sec. a phase shifter was not available and the solution was employed in that capacity. By addition of the solution in small amounts and balancing the bridge after each addition it was found that it was possible to add sufficient solution to shift the phase 360°. The detector recorded a zero reading at this point.

Bromobenzene in cyclohexane at 20°C was chosen as the test system because the relaxation time obtained by different workers was available for comparison[21,22,23]. The reported dipole moment value of 1.58D[24] meant that a wide range of concentrations could be measured. Also with only three wavebands available a system characterized by a single relaxation time was desirable. It was considered that an accurate analysis of the dielectric data into two relaxation times would be difficult with only three experimental points.

An important factor in assessing the accuracy of the dielectric data was the ability to determine the value of ϵ_∞. This was reflected in the apparent dipole moment calculated from eqn. 1.39 and $\epsilon_0 - \epsilon_\infty$. The dipole moment of bromobenzene in cyclohexane at 20°C was determined by the methods of Guggenheim[25] and Halverstadt and Kumler[26] to compare with previously reported values and the value obtained from the microwave method.

The assessment of the bridge technique was done with other workers who used pyridine/carbontetrachloride, 4-methylpyridine/cyclohexane and acetone/p-dioxane test systems[27].

Discussion

The dielectric constant $\epsilon'_{\text{MEAS.}}$ and loss factor $\epsilon''_{\text{MEAS.}}$ of a solution, of weight fraction $w_2 = 0.04900$, of bromobenzene in cyclohexane were measured at 20°C at frequencies of 34.86, 23.98 and 9.313 Gc/sec. by the bridge method. The measurements were repeated three times so that an appreciation of the reproducibility of results from the bridge apparatus could be obtained. The results are given in Table 2.1, $\Delta\epsilon'$ and $\Delta\epsilon''$ are the 95% confidence limits of $\epsilon'_{\text{MEAS.}}$ and $\epsilon''_{\text{MEAS.}}$ respectively, based on deviations from linearity of the plots of phase shift and attenuation against the length of added solution. It can be seen in Table 2.1 that the measurements of $\epsilon'_{\text{MEAS.}}$ were reproduceable to 0.001, but were within confidence limits of ± 0.004.

Table 2.1* Measurements on Bromobenzene in Cyclohexane at 20°C.

w_2 = 0.04900.

Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\Delta\epsilon'$	$\epsilon''_{\text{MEAS.}}$	$\Delta\epsilon''$
34.86	2.0365	0.0030	0.02274	0.00119
	2.0357	0.0008	0.02284	0.00204
	2.0359	0.0009	0.02285	0.00098
	2.0362	0.0014	0.02276	0.00094
23.98	2.0562	0.0035	0.02661	0.00132
	2.0556	0.0041	0.02743	0.00161
	2.0559	0.0039	0.02756	0.00191
	2.0564	0.0037	0.02694	0.00176
9.313	2.0846	0.0014	0.02794	0.00084
	2.0848	0.0012	0.02839	0.00091
	2.0855	0.0012	0.02838	0.00113
	2.0845	0.0024	0.02848	0.00115

* Accuracy of measurement of $\epsilon'_{\text{MEAS.}}$ and $\epsilon''_{\text{MEAS.}}$ is not claimed for all the places after the decimal point as shown in Table 2.1. They are included only for comparison.

Measurements of $\epsilon''_{\text{MEAS.}}$ were reproduceable to 0.001 within confidence limits of ± 0.002.

The dielectric constant and loss factors were then measured for four different concentrations of bromobenzene in cyclohexane. They are listed as $\epsilon'_{\text{MEAS.}}$ and $\epsilon''_{\text{MEAS.}}$ in Table 2.2. Plots of $\epsilon'_{\text{MEAS.}}$ and $\epsilon''_{\text{MEAS.}}$ against the weight fraction of the solute are shown in Fig. 2.1. Smyth[28] has shown that for dilute solutions of a polar solute in a non-polar solvent the dielectric constant and loss are proportional to the solute concentration expressed as weight fraction, w_2, of the solute.

i.e.

$$\epsilon' = \epsilon_1 + a' w_2 \qquad 2.1$$

$$\epsilon'' = a'' w_2 \qquad 2.2$$

$$\epsilon_0 = \epsilon_1 + a_0 w_2 \qquad 2.3$$

where ϵ_1 is the dielectric constant of the solvent. Although weight fractions up to 0.2 were employed, the plots in Fig. 2.1 did not appear to deviate from linearity. The $\epsilon'_{\text{MEAS.}}$ values were within 0.005 of the line determined by the method of least mean squares (see eqn. 1.13) and $\epsilon''_{\text{MEAS.}}$ were within 0.002. This agreed with the magnitude of the confidence limits in Table 2.1.

The Cole Cole plots of the four solutions are shown in Fig. 2.2 and it can be seen that no experimental point was greatly removed from the semicircular plot. It has been shown[28] that a' and

FIG: 2.1 PLOTS OF ϵ' AND ϵ'' AGAINST WEIGHT FRACTION W_2 FOR BROMOBENZENE IN CYCLOHEXANE AT 20°C.

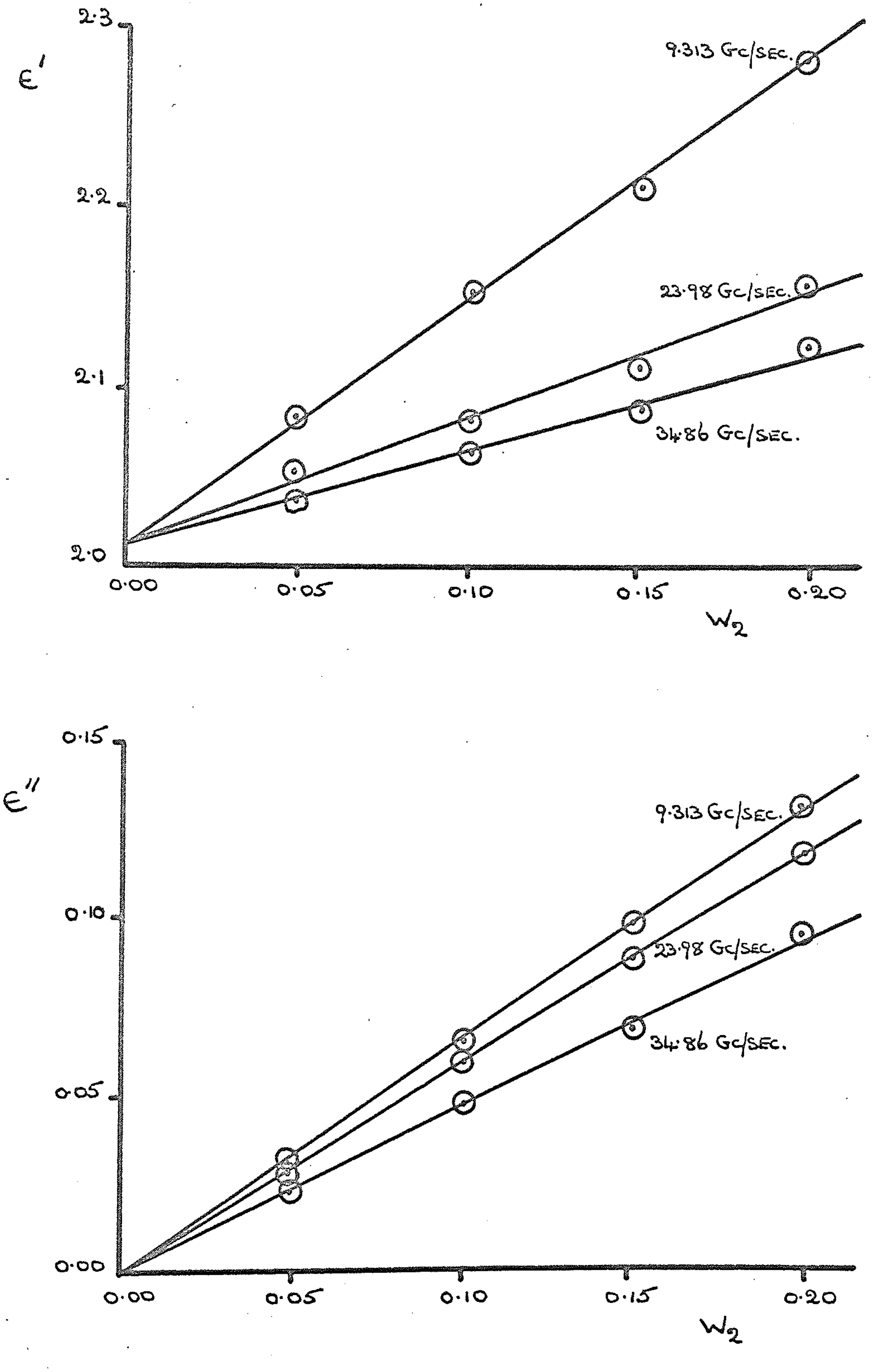
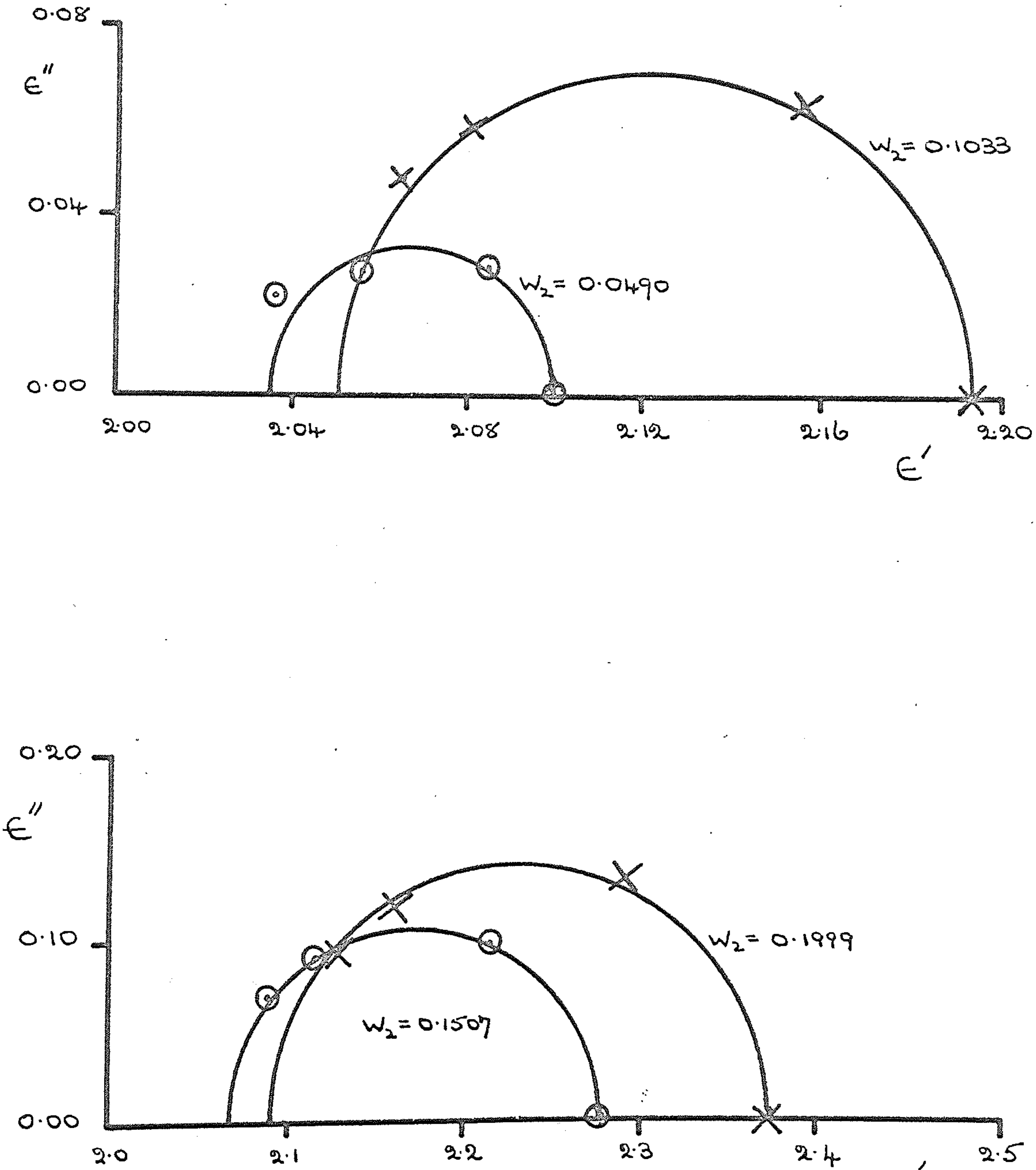


FIG. 2.2 COLE-COLE PLOTS OF BROMOBENZENE IN CYCLOHEXANE AT 20°C., AT WEIGHT FRACTIONS W_2



α'', the slopes of the plots in Fig.2.1 with α_0 the slope evaluated from eqn. 2.3, can be used to formulate a Cole-Cole plot of α'' against α'. This has the advantage that individual errors in particular values of dielectric constant or loss factor are minimised. Such a plot is shown in Fig. 2.3a.

Elimination of ϵ_∞ from eqns. 1.16 and 1.17 gives[29].

$$\epsilon' = \epsilon_0 - \tau\omega\epsilon'' \qquad 2.4$$

and on substitution from eqns. 2.1, 2.2 and 2.3

$$\alpha' = \alpha_0 - \tau\omega\alpha'' \qquad 2.5$$

Thus a plot of α' against $\omega\alpha''$ is a straight line of slope $-\tau$ whose intercept with the ordinate is α_0. This plot is shown in Fig. 2.3b. The relaxation time of bromobenzene in cyclohexane at 20°C obtained from this plot was 12.0×10^{-12} sec. This is to be compared with reported values of 10.6×10^{-12} sec. and 10.4×10^{-12} sec. in benzene and cyclohexane respectively at 20°C[21] and 10.0×10^{-12} sec.[22] or 10.5×10^{-12} sec.[23] in benzene solution at 19 ± 1°C.

The dielectric data of the four solutions WERE analysed for τ_0, α and ϵ_∞ using the Elliot 803 computer programmed to minimise on eqns. 1.20 and 1.21 as described in Chapter 1. α the distribution coefficient was zero for the four solutions indicating the presence of only one relaxation time. Therefore τ_0 the mean relaxation time is equal to τ the relaxation time of the single relaxation process.

FIG. 2.3. a', a'' PLOTS FOR BROMOBENZENE IN CYCLOHEXANE AT 20°C.

FIG. 2.3 (a) COLE-COLE PLOT.

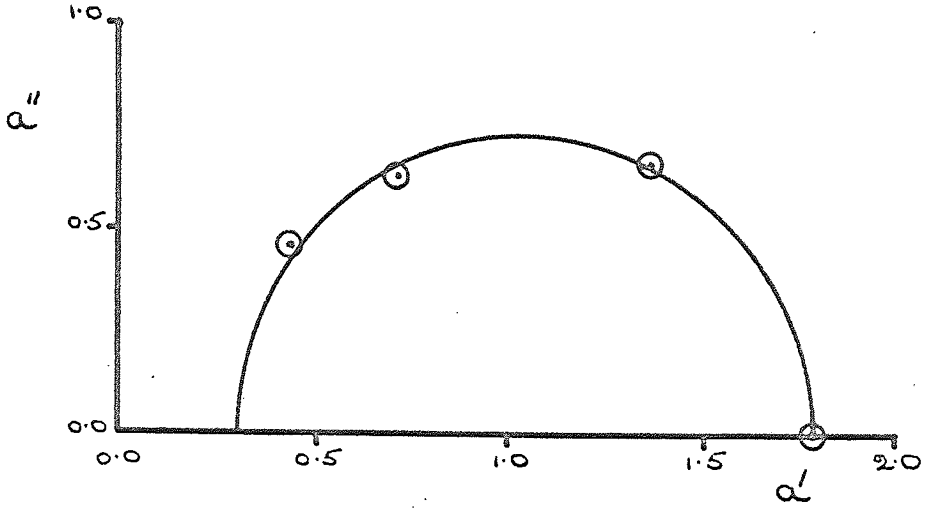
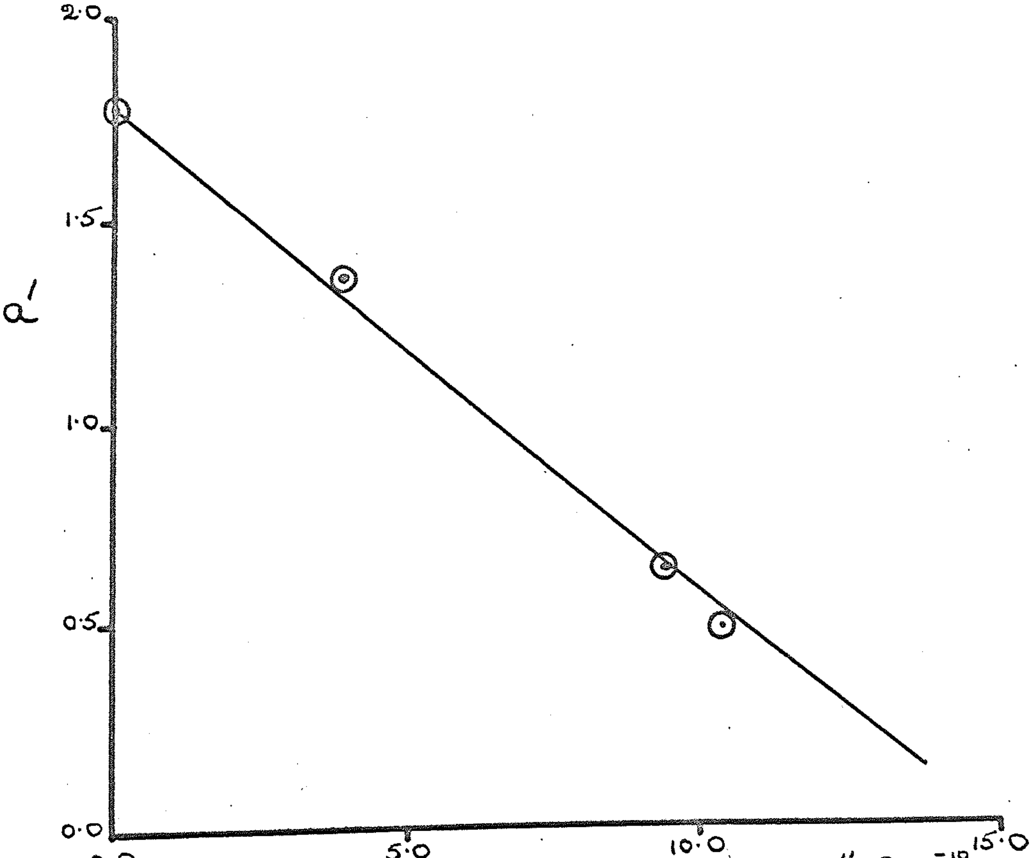


FIG. 2.3 (b) a' AGAINST $a''\omega$.



The values of τ and ϵ_∞ obtained are listed in Table 2.2. The values of τ were in good agreement with 12.0×10^{-12} sec. obtained from the graphical method that eliminated any individual errors.

The $\epsilon'_{\text{CALC.}}$ and $\epsilon''_{\text{CALC.}}$ values listed in Table 2.2 were obtained by substitution of the ϵ_∞ and τ values into eqns. 1.16 and 1.17. The agreement of experimental and calculated points is within $\pm$ 0.01 for ϵ' and $\pm$ 0.002 for ϵ'' .

The accuracy of the fit of the Cole-Cole plots and the analysis of the dielectric data in terms of a single relaxation time depended on the ϵ_∞ value obtained. Therefore the success of the method, apart from consistency, was evaluated in terms of the dipole moments obtained.

The dipole moment of bromobenzene in cyclohexane was evaluated by the methods of Guggenheim[25] and of Halverstadt and Kumler[26] from the data given in Table 2.3. Assuming the sum of the atom polarization P_A and the electron polarization P_E was equal to the molar refraction R_D a value of 1.62D was obtained by both methods. This did not compare with the value of 1.58D obtained by Cowley and Partington[24] for bromobenzene in cyclohexane at 20°C.

To minimise the errors in any one series of microwave measurements the dipole moment was evaluated from the maximum value

Table 2.2 The Measured and Calculated Dielectric Constants and Loss Factors, Relaxation Times, Dipole Moments, ϵ_0 and ϵ_∞ values for solutions of Bromobenzene in Cyclohexane at 20°C.

w_2	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$	ϵ_0	ϵ_∞	τ ($\times 10^{12}$ sec.)	μ (D)
0.0490	34.86	2.036	0.0228	2.043	0.0220	2.101	2.035	12.0	1.56
	23.98	2.056	0.0271	2.050	0.0281				
	9.313	2.085	0.0283	2.079	0.0302				
0.1033	34.86	2.064	0.0481	2.071	0.0478	2.193	2.052	11.7	1.57
	23.98	2.081	0.0596	2.087	0.0605				
	9.313	2.156	0.0649	2.148	0.0656				
0.1507	34.86	2.090	0.0678	2.094	0.0686	2.278	2.069	12.2	1.58
	23.98	2.117	0.0884	2.116	0.0878				
	9.313	2.217	0.0981	2.207	0.0991				
0.1999	34.86	2.129	0.0952	2.126	0.0941	2.373	2.090	12.0	1.59
	23.98	2.163	0.1187	2.157	0.1198				
	9.313	2.291	0.1319	2.280	0.1327				

Table 2.3 The Static Dielectric Constant ϵ_{12}, Density d_{12}, and Square of Refractive Index n_{12}^2 of solutions of Weight Fraction w_2, of Bromobenzene in Cyclohexane at 20°C.

w_2	ϵ_{12}	d_{12}	n_{12}^2
0.000000	2.0230	0.77746	2.03308
0.009904	2.0399	0.78109	2.03470
0.020215	2.0563	0.78499	2.03693
0.029900	2.0729	0.78862	2.03841
0.040087	2.0895	0.79251	2.04047
0.050711	2.1059	0.79658	2.04258
0.075095	2.1469	0.80618	2.04776

$$\epsilon_{12} = 2.023 + 1.654\, w_2$$

$$d_{12} = 0.77746 + 0.3746\, w_2$$

$$n_{12}^2 = 2.03308 + 0.1908\, w_2$$

v_{12} The Specific Volume $= \dfrac{1}{d_{12}} = 1.2861 - 0.6077\, w_2$

$P_{2\infty} = 89.02$ cc $\quad R_D = 34.47$ cc.

of α'' in Fig. 2.3a using a modified form of eqn. 1.39.

$$\mu = 0.012812 \left[\frac{6 T \alpha''_{MAX.} M_2}{(\epsilon_1 + 2)^2 d_1} \right]^{\frac{1}{2}} \qquad 2.6$$

where $\alpha''_{MAX.}$ is the maximum value of α'' .

The value of the dipole moment of bromobenzene in cyclohexane at 20°C obtained from the microwave measurements in this way was 1.57D. The dipole moments were then evaluated for each solution, using the values of ϵ_0 and ϵ_∞ given in Table 2.2 and eqn. 1.39. The values obtained were 1.57 ± 0.02D and are listed in Table 2.2.

It was considered that the slightly lower value of the dipole moment obtained from the microwave bridge method compared with that obtained by the Guggenheim and Halverstadt and Kumler approaches could possibly arise because in the former method no approximation for $P_A + P_E$ was involved. When $P_A + P_E$ was equated to 1.1 R_D a dipole moment value of 1.57D was obtained from the data in Table 2.3.

It was concluded that a value of 1.57D for the dipole moment of bromobenzene in cyclohexane solution at 20°C was acceptable and that the fit of the Cole-Cole plots and subsequent analyses were correct within the limits of experimental error and that the microwave bridge technique employed gave values of the dielectric constant ϵ'

accurate to ± 0.01 and the loss factor ϵ'' accurate to ± 0.002. This accuracy compared favourably with the impedance method of Smyth who quotes an accuracy of ± 2% for ϵ' and ± 0.05 on measured values of ϵ'' for low loss solutions[30].

Shortly after the work reported in this chapter was completed, the wavebands operating at 70.00 and 16.20 Gc/sec. were obtained, together with a phase shifter for the waveband at 23.98 Gc/sec. Other workers assessed the accuracy of this equipment[31] and the analysis of the dielectric data into one or two discrete relaxation times when measurements at five frequencies were available[32]. It was again concluded that the accuracy of ϵ' was ± 0.01 and ϵ'' ± 0.002.

Chapter 3.

Relaxation Processes of Some Small Solute Molecules in Solution.

Introduction

Preliminary measurements of the dielectric absorption of a dilute solution of pyridine in cyclohexane at 25°C gave a Cole-Cole plot with a significant distribution coefficient of 0.11, which indicated a distribution of relaxation times. This distribution is not consistent with the conclusions of the Perrin theory[33] that if the dipole moment of an ellipsoidal molecule lies along one axis of the ellipsoid the dielectric absorption is characterized by a single relaxation time.

It was thought necessary to investigate the distribution coefficient of the pyridine-cyclohexane solution and assess its physical significance as in subsequent studies the Cole-Cole plot was to have an important role in the appraisal of the experimental data.

Discussion

The experimental points lay to the low frequency side of $\epsilon''_{MAX.}$ on the Cole-Cole plot of pyridine in cyclohexane solution at 25°C and the ϵ_{∞} was obtained by a graphical extrapolation of the plot. It was pointed out in Chapter 1 that when all the experimental points are to the right of $\epsilon''_{MAX.}$ the evaluation of ϵ_{∞}, τ_0 and α by means of the Elliot 803 computer, programmed to minimise on eqns. 1.20 and 1.21, was not possible. The graphical extrapolation

Table 3.1 Static Dielectric Constant, Dielectric Constant at Very High Frequency, Relaxation Time, Distribution Coefficient and Dipole Moment Data for Solutions of Weight Fraction w_2 of Pyridine, Thiophen, Furan, Camphor and 4-Cyanopyridine.

Solute	Solvent	w_2	t (°C)	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	C_1	α	μ (D)
						$\times 10^{12}$ sec.					
Pyridine	Cyclohexane	0.01998	25	2.1273	2.021	3.1				0.11	2.22
		0.01790		2.1147	2.020	2.9				0.09	2.22
		0.02093	50	2.0767	1.979	2.1	2.1	-	1.00	0	2.23
		0.02014		2.0708	1.977	2.0	2.0	-	1.00	0	2.22
	Benzene	0.01962	25	2.4215	2.283	4.6				0.08	2.26
	p-Xylene	0.01989		2.4009	2.268	4.3				0.13	2.23
	Carbontetra-chloride	0.01180		2.3997	2.233	5.0				0.09	2.40
Thiophen	p-Xylene	0.48826	25	2.4706	2.312	2.8				0.11	0.47
	Carbontetra-chloride	0.42110		2.5127	2.298	3.2				0.15	0.54

Table 3.1 Continued

Solute	Solvent	W_2	t	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	C_1	α	μ
			(°C)			$\times 10^{12}$ SEC.					(D)
Furan	Cyclohexane	0.52997	25	2.4255	2.050	1.9				0.08	0.69
Camphor	Cyclohexane	0.02136	25	2.1309	2.021	7.4	7.4	-	1.00	0	3.02
4-Cyano-pyridine	p-Xylene	0.05057	25	2.4079	2.286	20.9	20.9	-	1.00	0	1.54
		0.05416	25	2.4244	2.292	20.9	20.9	-	1.00	0	1.55

to ϵ_∞ was also carried out for all the subsequent measurements on solutions of pyridine, thiophen and furan. The dipole moments obtained from the microwave technique compare with the range of reported values which are given in Table 3.2 and give support to the ϵ_∞ values and to the fit of the Cole-Cole plots to the experimental data.

Table 3.2 Reported Values of the Dipole Moments of Pyridine, Thiophen and Furan in Solution[34].

Solute	Solvent	Dipole Moment (D)
Pyridine	Cyclohexane	2.22 - 2.28
	Benzene	2.20 - 2.28
	Carbontetrachloride	2.35 - 2.39
Thiophen	Benzene	0.52 - 0.55
	Carbontetrachloride	0.54 - 0.56
Furan	Benzene	0.63 - 0.71

The τ_0 values of the pyridine, thiophen and furan solutions, given in Table 3.1, were obtained from the plot of log $\frac{V}{U}$ against log ω as described in Chapter 1 and the values of α, the distribution coefficient, were determined from the Cole-Cole plots.

The measurements of pyridine in cyclohexane solution at 25°C were repeated and the distribution coefficient confirmed (see Table 3.1). The Cole-Cole plots of pyridine in benzene, p-xylene and carbontetrachloride solution at 25°C also showed appreciable distribution coefficients and indicated that the non-Debye absorption was a characteristic of the solute molecule and was not due to a particular solvent effect.

Holland and Smyth[35] reported that the Cole-Cole plots of pyridine in n-heptane had distribution coefficients of 0.05, 0.04 and 0.06 at 1, 20 and 40°C respectively, whereas Miller and Smyth[36] reported zero distribution coefficients for solutions of pyridine in benzene at 20, 40 and 60°C. It is considered that these results for the benzene solutions conflict with those given in Table 3.1 because although the measurements of the dielectric loss at 70.00 Gc/sec. reported here show clearly that the Cole-Cole plots display distribution coefficients outside the limits of experimental error, the longest frequency employed by Smyth et al was 34.86 Gc/sec. and the flattening of the Cole-Cole plot is not readily apparent from their measurements.

The Cole-Cole plot of pyridine in carbontetrachloride solution at 25°C does not agree with the early work of Hassell, Magee, Tucker and Walker[27] which for this system at 25°C show $\alpha = 0$. This disagreement is probably due to the earlier results being obtained from measurements at only the three frequencies of 9.313, 23.98 and 34.86 Gc/sec.

To ascertain whether this non-Debye behaviour was peculiar to pyridine in solution or was common to similar molecules, thiophen and furan in solution at 25°C were also studied. The Cole-Cole plots of these systems in which the solute molecules, although slightly smaller, are similar in shape to pyridine also had appreciable distribution coefficients (see Table 3.1).

The distribution coefficients of the pyridine, thiophen and furan solutions indicate that the dielectric absorption is due either to contributions from more than one discrete Debye process or to a non-Debye absorption of a distribution of relaxation times about a most probable value.

For these small rigid molecules no detectable intramolecular relaxation process would seem feasible, however, contributions from some form of relaxation motion relating to the presence of aggregates of the solute molecules due to dipolar association could give rise to the observed distribution coefficients. For example, a rate process connected with the dissociation of one molecule from the aggregate or some form of lattice vibration connected with such aggregates.

No satisfactory analyses of the dielectric data into contributions from two relaxation times was possible for these systems and it was apparent that this procedure was invalid.

A comparison of the relaxation times in Table 3.1 with 2.4×10^{-12} sec., 2.3×10^{-12} sec. and 1.8×10^{-12} sec. the molecular re-orientation relaxation times of cyclopentanone[37], pyrrole[38] and thiacyclopentane[37] respectively in cyclohexane at 25°C indicates that the τ_0 values of pyridine, thiophen and furan are as would be anticipated for the molecular re-orientation of molecules of this size. The decrease in relaxation time along the series pyridine, thiophen and furan is consistent with the decrease in molecular size. The variation of the relaxation time of pyridine in different solvents might be accounted for the variations in the interaction of the solute with the solvent. Sharpe and Walker[39] have shown that the difference in dipole moment of pyridine in cyclohexane (or benzene) and carbontetrachloride can be attributed to a weak form of donor-acceptor interaction with the pyridine acting as the donor and the polarizable carbontetrachloride as the acceptor. Morcom and Travers[40] have recently confirmed this from thermochemical measurements.

Pitt and Smyth[41] pointed out that the dielectric relaxation time of a polar molecule in solution is dependent on the solute size and shape, on the position of the dipole moment within the solute and on the viscous interaction of the solute and solvent molecules during the orientation process. Pyridine, thiophen and furan are similar in shape and have their dipole moments along the main axis. Another common factor in their solutions is the small size of the solute molecules.

The Debye theory[6] is based on the assumption that the dipolar molecules are surrounded by a uniform homogenous field and Meakins[42] has shown that when the solute molecule is at least three times as large as the solvent molecule the solutions give good experimental agreement with the Debye equation written in the form $\tau = 3V\eta/kT$, where η is the viscosity and V the molecular volume.

The small size of the pyridine, thiophen and furan molecules compared with that of the solvent suggests that particular solute molecules might experience varying local enviroments. This would result in a variation in the energy barriers to molecular re-orientation and give rise to a distribution of relaxation times.

Kalman and Smyth[43] have suggested that the non-homogeneity of the enviroment of the solute molecule could account for the distribution coefficients of 0.10, 0.10 and 0.06 that they reported for Camphor in Nujol solution at 20, 40 and 60°C respectively and

Vaughan, Purcell and Smyth[44] have concluded for pure liquids that, "the small distribution commonly observed for such (ellipsoidal) molecules presumably arises from variation of the internal friction coefficient according to the axis about which the molecule turns."

From the above considerations an increase in the size of the rigid solute molecule would be expected to lead to Debye behaviour in solution and a Cole-Cole plot with zero distribution coefficient, unless some relaxation process of dipolar origins contributed to the dielectric absorption.

Measurements on the relatively larger camphor molecule in dilute cyclohexane solution at 25°C gave a Cole-Cole plot with $\alpha = 0$ and there was good agreement between the experimental points and those calculated, based on a single relaxation time of 7.4×10^{-12} sec. (see Table 3.1 and Appendix, Table 1).

The average interaction energy E_{D-D} between two dipoles of moment μ at a distance r apart is given by[3]

$$E_{D-D} = \frac{-2\mu^4}{3kTr^6} \qquad 3.1$$

Thus it might be anticipated from the dipole moment values given in Table 3.1 that any distribution of relaxation times due to interactions of the dipoles in dilute solutions of pyridine in cyclohexane would also be observed in cyclohexane solutions of camphor at the same temperature. The non-Debye behaviour of camphor in Nujol solution compared with its Debye behaviour in cyclohexane supports the suggestion that variations in the local enviroment of the polar solute molecule can give rise to significant distribution coefficients.

4-Cyanopyridine in p-xylene solution at 25°C also gave a Cole-Cole plot with $\alpha = 0$ described by a single relaxation time. As the main difference between this solute molecule and pyridine is the increase in the length of the main dipolar axis, these results give further indication that the explanation of the non-Debye behaviour of pyridine, thiophen and furan in solution at 25°C is to be found in a consideration of the small size of the solute molecule relative to that of the solvent.

At 50°C the Cole-Cole plots of pyridine in cyclohexane solution showed $\alpha = 0$ and the dielectric absorption was characterized by a single relaxation time of $\sim 2 \times 10^{-12}$ sec.(see Table 3.1). With increasing temperature, local interactions between the solute and neighbouring molecules would decrease and the surroundings of the small orienting dipole would approach the homogeneous enviroment assumed by Debye, hence agreement of the dielectric absorption with that predicted by the Perrin theory[33] would be anticipated.

From a consideration of the experimental evidence described above and especially from the τ_0 values of pyridine, thiophen and furan in solution at 25°C being as would be anticipated for molecular re-orientation it was concluded that the distribution of relaxation times, indicated by the Cole-Cole plots of these systems, can be accounted for by the small size of the solute molecules relative to those of the solvent, which results in variation in the local enviroment of the dipoles.

From the results of camphor and 4-cyanopyridine in dilute solution at 25°C it would be expected that only very small solute molecules would show this non-Debye behaviour with molecular re-orientation in dilute solution in the solvents employed. For the relatively larger molecules studied in the following chapters any distribution coefficient shown by the Cole-Cole plots would suggest contributions by more than one relaxation process, rather than a non-Debye absorption due to the size of the solute molecule. A consideration of the τ_0 values should in general confirm this, as τ_0 will not compare with the anticipated relaxation time of molecular re-orientation if there are significant contributions by relaxation times different to that of molecular re-orientation.

The importance of τ_0 in assessing the dielectric data is readily appreciated by an inspection of Table 3.3. The data given in

Table 3.3 were obtained from the normalized Cole-Cole plots drawn through the theoretical points obtained by substitution into eqns. 1.30 and 1.31 of the values of C_1, C_2, τ_1 and τ_2 listed in Table 3.3 and the frequencies used in this work. τ_0 was evaluated from the plot of $\log \frac{V}{U}$ against $\log \omega$ described in Chapter 1 and α, the distribution coefficient, was measured on the normalized Cole-Cole plots.

It can be seen that the larger the contribution of the second relaxation process (as indicated by C_2) to the dielectric absorption, the larger the difference in τ_0 and τ_1.

Significant contributions by a shorter or longer relaxation process than that of molecular re-orientation result in the respective shortening or lengthening of τ_0 compared with the relaxation time anticipated and hence τ_0 is invaluable in confirming significant contributions to the overall dielectric absorption by processes other than that of molecular re-orientation.

Table 3.3 τ_0 and α Data for the Theoretical Cole-Cole Plots of the Dielectric Absorption of Two Relaxation Processes τ_1 and τ_2 with the Respective Weight Factors C_1 and C_2.

(All Relaxation Times in this Table are given x 10^{12} sec.).

A) $\tau_1 = 2.0$: $\tau_2 = 10.0$

C_1	C_2	τ_0	α
1.0	0.0	2.0	0.00
0.9	0.1	2.2	0.04
0.8	0.2	2.5	0.10
0.7	0.3	3.0	0.12
0.6	0.4	3.7	0.15
0.5	0.5	4.5	0.16
0.4	0.6	5.5	0.14
0.3	0.7	6.7	0.12
0.2	0.8	7.9	0.08
0.1	0.9	9.1	0.04
0.0	1.0	10.0	0.00

B) $\tau_1 = 3.0$: $\tau_2 = 10.0$

C_1	C_2	τ_0	α
2.0	0.0	3.0	0.00
0.9	0.1	3.3	0.04
0.8	0.2	3.7	0.06
0.7	0.3	4.1	0.08
0.6	0.4	4.8	0.10
0.5	0.5	5.5	0.11
0.4	0.6	6.3	0.10
0.3	0.7	7.3	0.08
0.2	0.8	8.2	0.06
0.1	0.9	9.1	0.03
0.0	1.0	10.0	0.00

C) $\tau_1 = 4.0$: $\tau_2 = 10.0$

C_1	C_2	τ_0	α
2.0	0.0	4.0	0.00
0.9	0.1	4.3	0.02
0.8	0.2	4.7	0.05
0.7	0.3	5.2	0.06
0.6	0.4	5.7	0.06
0.5	0.5	6.3	0.07
0.4	0.6	6.9	0.06
0.3	0.7	7.6	0.06
0.2	0.8	8.4	0.04
0.1	0.9	9.2	0.02
0.0	1.0	10.0	0.00

Table 3.3 Continued

D) $\tau_1 = 6.0$: $\tau_2 = 10.0$

C_1	C_2	τ_0	α
1.0	0.0	6.0	0.00
0.9	0.1	6.3	0.01
0.8	0.2	6.6	0.01
0.7	0.3	7.0	0.02
0.6	0.4	7.4	0.02
0.5	0.5	7.8	0.02
0.4	0.6	8.2	0.02
0.3	0.7	8.6	0.02
0.2	0.8	9.0	0.01
0.1	0.9	9.5	0.01
0.0	1.0	10.0	0.00

E) $\tau_1 = 8.0$: $\tau_2 = 10.0$

C_1	C_2	τ_0	α
1.0	0.0	8.0	0.00
0.9	0.1	8.1	0.00
0.8	0.2	8.3	0.00
0.7	0.3	8.5	0.01
0.6	0.4	8.7	0.01
0.5	0.5	8.9	0.01
0.4	0.6	9.1	0.01
0.3	0.7	9.4	0.01
0.2	0.8	9.7	0.00
0.1	0.9	9.9	0.00
0.0	1.0	10.0	0.00

Chapter 4

Relaxation Processes of Four Monoalkylbenzenes.

Introduction

The dielectric absorption of liquid toluene has been measured previously and a distribution coefficient of zero or of the order of the experimental error obtained.[1,23,45,46] The relaxation times quoted have been taken to be the molecular relaxation time. The values of the relaxation time evaluated for toluene 7.3 - 7.6 x 10^{-12} sec. appeared to be short when compared with the value of 12.0 x 10^{-12} sec. for the relaxation time of bromobenzene in cyclohexane at 20°C, reported in Chapter 2. This difference in the relaxation times was not expected as the bromine atom and methyl group exhert a similar steric effect,[47] the van der Waal radii being 1.95 and 2.0 Å respectively[48]. Although the viscosity of toluene is less than cyclohexane (0.552 and 0.898 cp. respectively at 25°C[49]), which alone might account for the difference, dipole-dipole interactions would be expected to cause an increase in the toluene relaxation time compared with that of bromobenzene which was obtained from measurements on dilute solutions. The possibility of two relaxation processes in the toluene system has not been reported, but if a short timed relaxation process was also present the result would be a decrease in the observed relaxation time compared with that due to a molecular rotation.

It seemed worthwhile examining the dielectric absorption of some monoalkylbenzenes and their solutions to determine whether such ellipsoidal molecules, in which the direction of the permanent dipole coincides with one of the principle axes of the molecular ellipsoid, could have more than one relaxation time. From the Perrin theory[33] only one relaxation time would be expected for such molecules if they were rigid. Liquid toluene and t-butylbenzene and solutions in cyclohexane were measured. Ethyl- and isopropylbenzene were also measured as it was considered that the small dipole moment component normal to the main dipole axis would lead to negligible dielectric absorption and could be neglected.

Discussion

The mean relaxation time, τ_0 , of pure toluene at 25°C was determined as 6.9×10^{-12} sec. (see Table 4.1). This confirmed the reported shortness when compared with the relaxation time of 12.0×10^{-12} sec. for bromobenzene in cyclohexane at 20°C. The distribution coefficient, α , was not zero for the pure liquid and a study of solutions of toluene in the non-interacting solvent cyclohexane and also in p-xylene and carbontetrachloride solution revealed significant α values. These are listed in Table 4.1. This suggested the presence of a distribution of relaxation times. Reported measurements on liquid aromatic hydrocarbons have shown finite

Table 4.1 Static Dielectric Constant, Dielectric Constant at Very High Frequency, Relaxation times, Distribution Coefficient and Dipole Moment Data for some Alkylbenzenes and Their Solutions.

Solute	Solvent	t ($^\circ$C)	w_2	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	C_1	α	μ (D)
							$\times 10^{12}$ SEC.				
Toluene	Cyclohexane	15	0.6932	2.2713	2.175	7.0	9.9	1.8	0.55	0.14	0.35
			0.5946	2.2312	2.146	7.1	10.2	1.6	0.55	0.14	0.35
		25	1.0000	2.3795	2.259	6.9	9.5	4.3	0.55	0.03	0.31
			0.9015	2.3324	2.226	6.8	9.5	3.7	0.55	0.04	0.32
			0.7838	2.2843	2.184	6.4	9.2	2.5	0.55	0.13	0.34
			0.6932	2.2440	2.150	6.3	9.0	1.6	0.55	0.13	0.35
			0.5946	2.2070	2.126	6.3	9.0	1.6	0.55	0.16	0.36
			0.4969	2.1780	2.107	6.6	9.0	1.6	0.55	0.19	0.36
			0.4078	2.1390	2.084	6.5	9.0	1.6	0.55	0.18	0.36

Table 4.1 Continued.

Solute	Solvent	t (°C)	w_2	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	C_1	α	μ (D)
						$\times 10^{12}$ sec.					
Toluene	Cyclohexane	25	0.2996	2.1012	2.061	6.1	9.0	1.6	0.55	0.19	0.36
			0.2141	2.0767	2.049	6.4	9.0	1.6	0.55	0.17	0.36
		40	0.6932	2.2260	2.127	4.7	8.0	1.1	0.55	0.23	0.38
			0.5946	2.1870	2.103	4.8	8.0	1.1	0.55	0.24	0.37
		60	0.6932	2.1776	2.093	4.1	6.6	1.1	0.55	0.22	0.38
			0.5946	2.1420	2.070	4.3	6.6	1.1	0.55	0.25	0.39
	p-Xylene	25	0.6992	2.3491	2.245	6.5	9.0	1.6	0.55	0.15	0.36
	Carbontetra-chloride	25	0.4817	2.3367	2.249	7.5	14.0	3.5	0.55	0.13	0.34

Table 4.1 Continued.

Solute	Solvent	t	w_2	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	c_1	α	μ
		(°C)				$\times 10^{12}$ sec.					(D)
Ethylbenzene	Cyclohexane	25	1.0000	2.4011	2.246	12.2	18.8	6.2	0.60	0.09	0.39
			0.7003	2.2584	2.160	12.0	16.4	7.6	0.60	0.02	0.39
			0.6027	2.2201	2.138	12.1	16.2	8.0	0.60	0.03	0.39
Isopropylbenzene	Cyclohexane	25	1.0000	2.3761	2.229	15.6	21.5	8.4	0.67	0.06	0.40
			0.7004	2.2451	2.147	14.1	24.2	6.7	0.67	0.11	0.41
			0.6035	2.2058	2.130	14.1	20.4	8.1	0.67	0.07	0.39
t-Butylbenzene	Cyclohexane	25	1.0000	2.3588	2.239	21.2	27.4	9.2	0.75	0.04	0.39
			0.6931	2.2306	2.154	19.9	26.0	10.4	0.75	0.06	0.39
			0.5927	2.1940	2.126	19.7	30.0	8.5	0.75	0.09	0.40

distribution coefficients e.g. ethylbenzene $\alpha = 0.12$, isopropylbenzene $\alpha = 0.13$ at 20°C[46] and diphenylmethane $\alpha = 0.08$ at 40°C[50], but analyses of the dielectric data into discrete relaxation times have not been carried out. The measurements reported in this chapter on liquid ethylbenzene, isopropylbenzene, t-butylbenzene and their solutions in cyclohexane showed that all exhibit appreciable distribution coefficients which are listed in Table 4.1.

For liquid diphenylmethane DiCarlo and Smyth[50], obtained a longer value of the mean relaxation time than that previously reported but stated that, even for the revised values, the relaxation time was too short to result entirely from the rotation of the molecule as a whole. They suggested that hyperconjugation of the methylene group could give a small shift of electronic charge and the consequent moment would change somewhat in size with ring rotation. However, the low loss diphenylmethane data could not be analysed into individual relaxation time contributions and no definite evidence for an intramolecular relaxation process was obtained.

For molecules such as toluene in which the dipole moment vector lies along one of its rotational axes, the Perrin theory[33] predicts that if the molecules were rigid they would be characterized by a single relaxation time. A plot of ϵ' against $\epsilon''\omega$ is sometimes useful for indicating the presence of more than one relaxation time[29]. For Debye behaviour the plot is a straight line of slope $-\tau$ but for two relaxation times sufficiently distinct it is a curve, the limiting slopes of which are $-\tau_1$ and $-\tau_2$ the individual relaxation times[52]. The ϵ' against $\epsilon''\omega$ plots shown in Fig. 4.1 suggest the presence of two relaxation times. The accuracy of determining τ_1 and τ_2 from the limiting slopes of this plot is dependent on the number and distribution of the experimental points and on the ratio of $\frac{\tau_1}{\tau_2}$. In general it is to be expected that the resulting τ_1 value would be too short and the τ_2 values too long. To obtain even an estimate of τ_2 from these plots for the alkylbenzenes measured, experimental data at frequencies higher than 70.00 Gc/sec. would be required. The subsequent analysis of the dielectric data, by the method described in Chapter 1, confirmed the presence of two relaxation times in all the alkylbenzene systems measured. The τ_1, τ_2 and C_1 values are listed in Table 4.1.

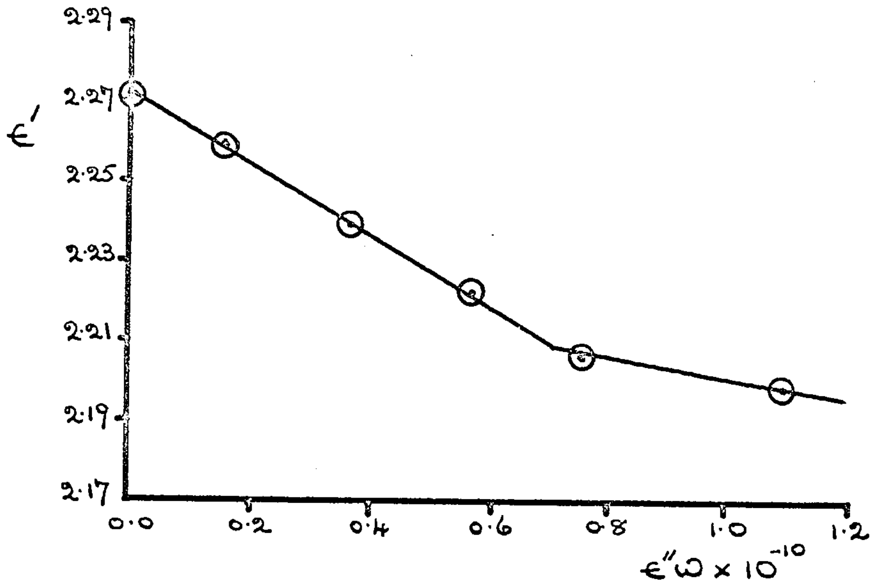
Possible explanations of the two relaxation times in the monoalkylbenzene systems are,

i) The orientation of the molecule as a whole.

ii) Some form of relaxation motion relating to the presence of aggregates of polar solute molecules, e.g. a rate process connected

FIG. 4.1 PLOTS OF ϵ' AGAINST $\epsilon''\omega$ FOR VARIOUS WEIGHT FRACTIONS W_2 OF A, TOLUENE AT 15, 25, 40, AND 60°C.; B, ETHYLBENZENE AT 25°C.; C, ISOPROPYLBENZENE AT 25°C.; D, t-BUTYLBENZENE AT 25°C.; IN CYCLOHEXANE SOLUTION.

A(i) TOLUENE AT 15°C., $W_2 = 0.6932$



A(ii) TOLUENE AT 25°C., $W_2 = 0.6932$

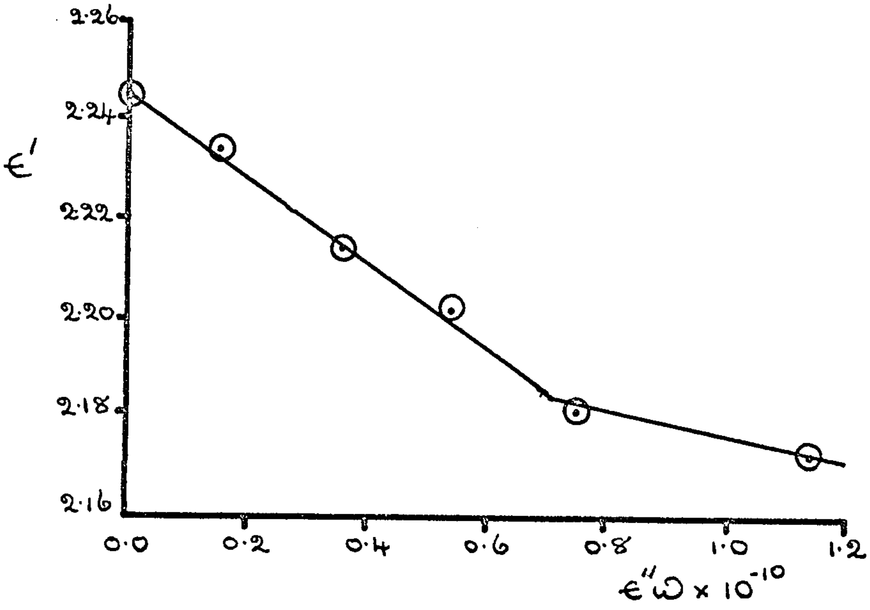
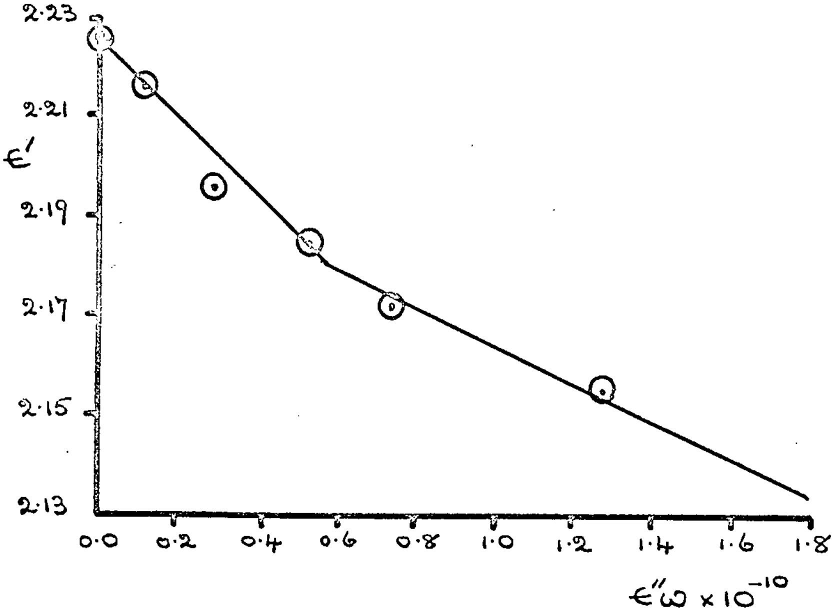


FIG. 4.1 CONTINUED.

A (iii) TOLUENE AT 40°C., $W_2 = 0.6932$



A (iv) TOLUENE AT 60°C., $W_2 = 0.6932$

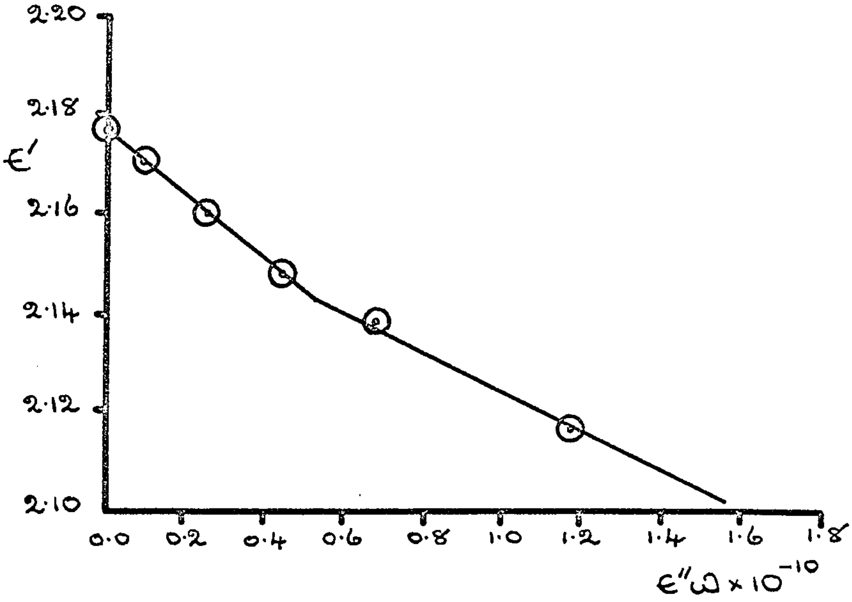
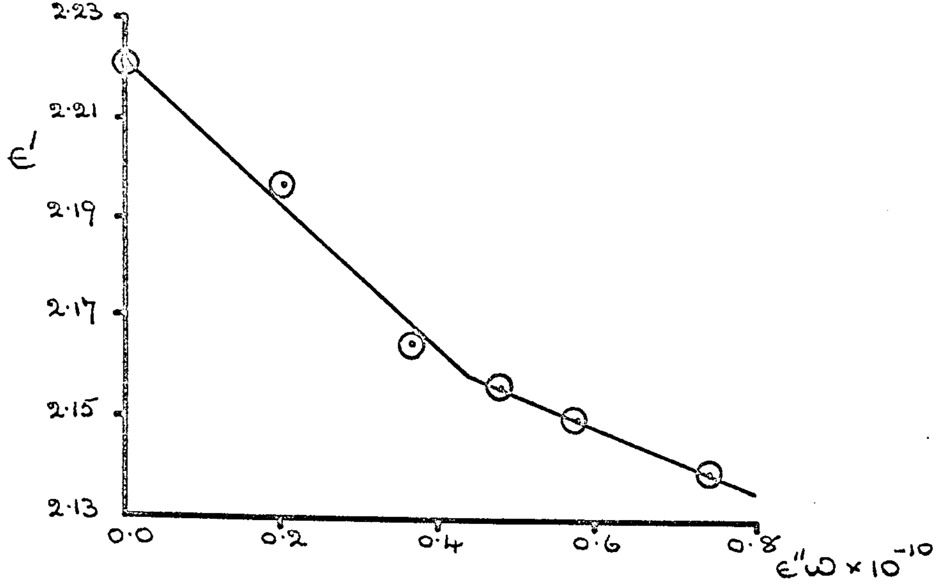
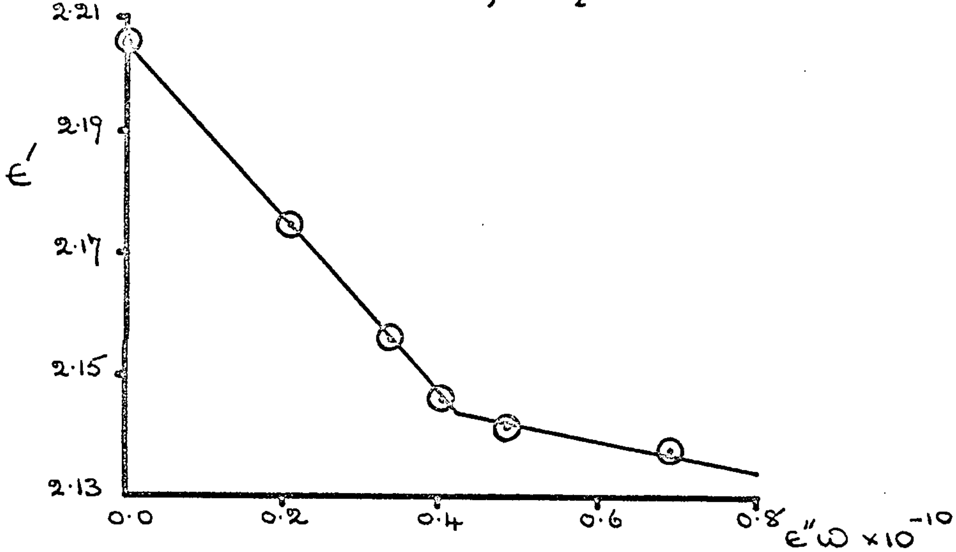


FIG. 4.1 CONTINUED

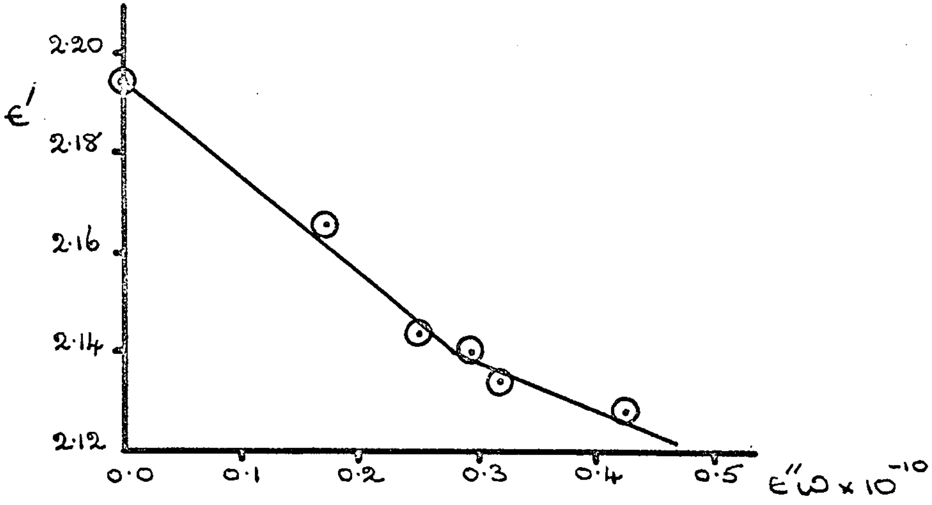
B ETHYLBENZENE AT 25°C., $W_2 = 0.6027$



C ISOPROPYLBENZENE AT 25°C., $W_2 = 0.6035$



D t-BUTYLBENZENE AT 25°C., $W_2 = 0.5927$



with the dissociation of one molecule from the aggregate or some form of lattice vibration associated with such aggregates.

iii) An intramolecular relaxation process.

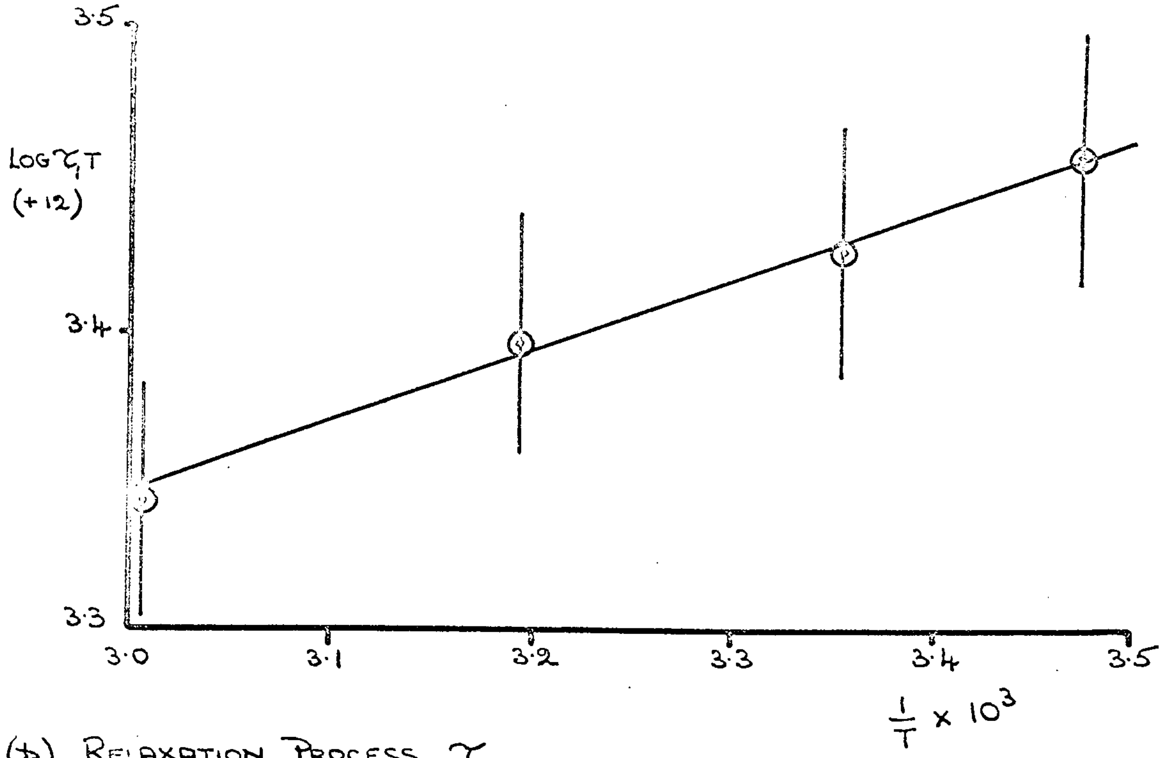
The dielectric data for liquid toluene at 25°C was resolved into two relaxation times $\sim 9 \times 10^{-12}$ sec. and $\sim 4 \times 10^{-12}$ sec. The longer value lies between those of chlorobenzene[53] and bromobenzene in cyclohexane 7.8×10^{-12} and 12.0×10^{-12} sec. respectively, at 20°C. On dilution of the toluene with cyclohexane the longer relaxation time remained constant within the limits of experimental error. It might be that with increasing dilution the long range interaction forces decrease while the viscosity increases from 0.552 cp. for pure toluene towards 0.898 cp. for cyclohexane[49], or alternatively that the relaxation time is insensitive to such a change in the macroscopic viscosity. The longer relaxation time of t-butylbenzene in cyclohexane is $\sim 28 \times 10^{-12}$ sec., this is to be compared with the molecular relaxation time of 23×10^{-12} sec. for benzotrichloride in cyclohexane at 25°C[54]. Since the van der Waal's radius of the methyl group is effectively larger than the chlorine atom (2.0 and 1.8 Å respectively[48]) this value appears to correspond with a similar type of relaxation. The assignment of the longer relaxation time to molecular re-orientation is supported by the reasonable increment of τ_1 with increasing size of alkyl substitutent.

From eqn. 1.33 and the plot of log. $\tau_1 T$ against $\frac{1}{T}$, shown in Fig. 4.2 (a), the enthalpy of activation for the τ_1 process of toluene in cyclohexane was found to be 1.1 k.cal.mole^{-1}, compared with a value of 1.3 k.cal.mole^{-1} for chlorobenzene in cyclohexane at 20°C[53]. This gives further support to the identification of τ_1 with process (i). In addition the ratio of the values of τ_1 for toluene in cyclohexane and in carbontetrachloride is 1.6 and within Higasi's[55] limits of 1.5 - 2.1 for molecular relaxation of a variety of solutes in the two solvents. It was concluded that the τ_1 relaxation process was that of overall molecular re-orientation.

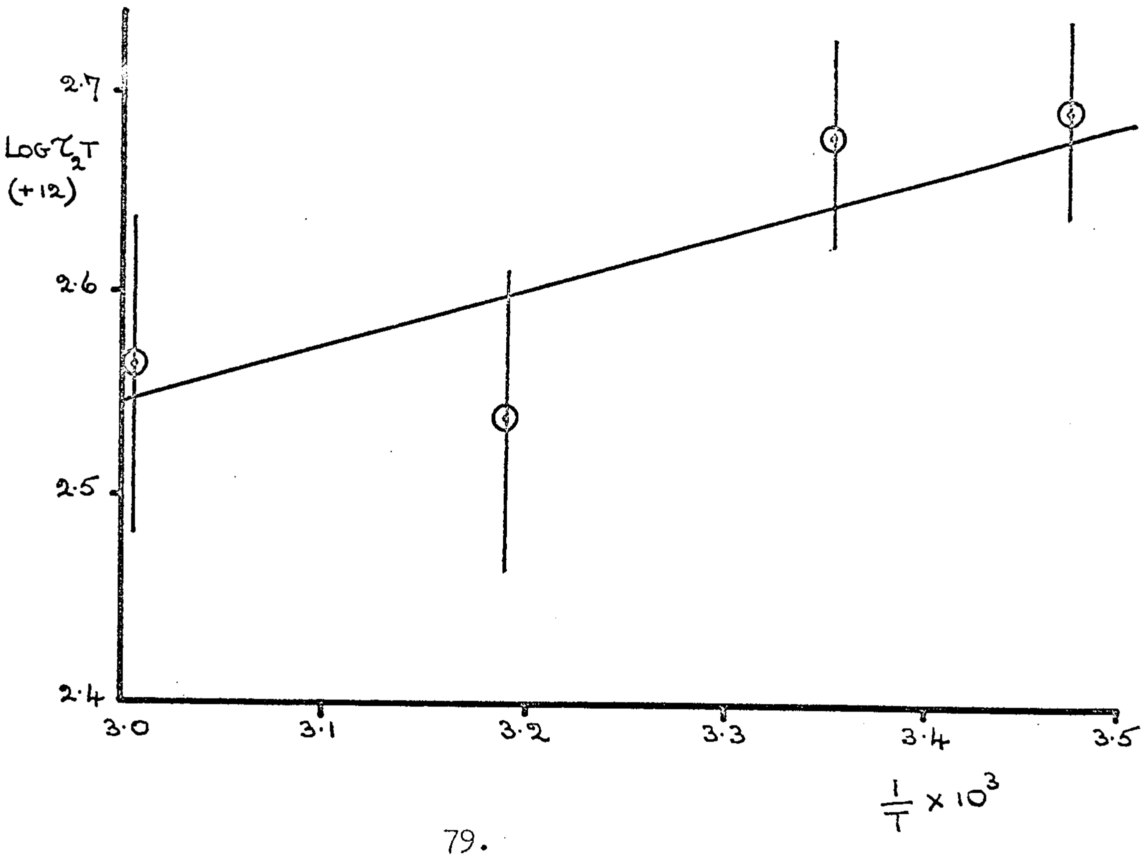
Relaxation processes arising from the presence of aggregates of polar solute molecules in the solutions would be directly concerned with long-range interaction forces. In concentrated solutions of molecules such as toluene, where the dipole acts along the main axis, the tendency would be for the molecules to align antiparallel with each other. This would give rise to a measured moment less than the true value. With increasing dilution the measured moment should rise to a constant value when interactions become no longer detectable. Table 4.1 shows that for toluene in cyclohexane at 25°C the measured dipole moment increases from 0.31D at $w_2 = 1.0000$ to an apparent constant value of 0.36D at $w_2 = 0.5946$, whereas the τ_2 value shortens

FIG. 4.2 PLOTS OF LOG τT AGAINST $\frac{1}{T}$ FOR THE RELAXATION PROCESSES OF TOLUENE IN CYCLOHEXANE SOLUTION.

(a) RELAXATION PROCESS τ_1



(b) RELAXATION PROCESS τ_2



and becomes constant at that concentration. These facts suggest that some dipolar association is present in, at least, the more concentrated solutions. In the more dilute solutions the effect has either become negligible or changes in the amount of association are no longer detectable. However, re-orientation of dimeric species or local aggregates would lead to much longer relaxation times than those in Table 4.1 and would be unacceptable as an explanation of the shorter relaxation time.

If the τ_2 process could be explained by a rate process involving dissociation of solute dimers or dissociation from local aggregates it would be expected that the C_2 value would have been temperature and concentration dependent. For toluene in cyclohexane over a 45°C temperature range and also an appreciable concentration range C_2 is apparently constant. The C_2 values determined for the other alkylbenzenes also are apparently independent of the concentration and that of toluene seems to be independent of the solvent.

The four monoalkylbenzenes have dipole moments of similar magnitude and the dipole-dipole interaction energy was estimated from[3]

$$E_{D-D} = -\frac{2}{3}\cdot\frac{1}{r^6}\cdot\frac{\mu^4}{kT} \qquad 4.1$$

where r is the interdipolar distance and k the Boltzmann constant.

Substitution of reasonable values of r , between 3 and 5 Å, into eqn. 4.1 indicated that E_{D-D} was less than 0.1 k.cal.mole^{-1}. This was supported by estimates of the dipolar contribution (which includes dipole-dipole and dipole-induced dipole interactions) to the cohesion energy of the pure liquids. This was obtained from the equations[3],

$$W = -\frac{4}{3}\pi\frac{d}{M}N^2\frac{(\epsilon_0 - 1)}{2\epsilon_0 + n_D^2}\cdot\left(\frac{n_D^2+2}{3}\right)\mu^2 \qquad 4.2$$

$$W = -RT\frac{(\epsilon_0 - 1)(\epsilon_0 - n_D^2)}{(n_D^2+2)} \qquad 4.3$$

where d is the density, M the molecular weight, N Avagadro's number and n_D the refractive index for the NaD line. Values obtained from eqns. 4.2 and 4.3 are listed in Table 4.2. A dipole moment value of 0.4D was used for all calculations involving eqn. 4.2.

The values of W indicate the order of magnitude of the energy required to cause infinite separation of the dipoles if dipolar forces alone were present. It would be expected that the change in free energy accompanying a relaxation process involving dissociation of a polar molecule from a local aggregate of solute molecules would be smaller as the distance of eventual separation of the dipoles would be considerably less.

Table 4.2 Estimate of the Dipolar Contribution to the Cohesion Energy of some pure Alkylbenzenes at 25°C.

	$-W$ (eqn. 4.2) k.cal.mole^{-1}	$-W$ (eqn. 4.3) k.cal.mole^{-1}
Toluene	0.015	0.012
Ethylbenzene	0.013	0.014
Isopropylbenzene	0.012	0.013
t-Butylbenzene	0.010	0.011

The τ_2 values of toluene and t-butylbenzene at 25°C are about 4×10^{-12} and 9×10^{-12} sec. respectively which correspond to free energies of activation of 1.9 and 2.4 k.cal.mole^{-1}. Thus it seemed unlikely that dipolar forces alone could be responsible for the τ_2 process.

The London dispersion energies of the monoalkylbenzenes were estimated from the equation[3],

$$E_L = -\frac{3}{4}\frac{\alpha_1^6}{r^6} I \qquad 4.4$$

where α_1 is the polarizability and I the ionization potential. A rough estimate of the cohesive energies was obtained using Hildebrande's equations[56]

$$\Delta H^{V}_{298}(\text{CAL.MOLE}^{-1}) = -2950 + 23.7T_b + 0.020T_b^2 \qquad 4.5$$

$$\Delta E^{v}_{T} = \Delta H^{v}_{T} - RT \qquad 4.6$$

where ΔE^{v}_{T} is the internal energy of vaporization, which is approximately equal to the cohesive energy, ΔH^{v}_{T} is the heat of vaporization at temperature $T\,^{o}K$ and T_b is the boiling point in ^{o}K.

Values of E_L obtained from eqn. 4.4 using reasonable values of I[57] and values of α_1 obtained from the Lorenz-Lorentz equation[47], for various values of r and also ΔE^{v}_{298} values obtained from eqns. 4.5 and 4.6 are listed in Table 4.3. Also listed is r', the value of the intermolecular distance at which the London dispersion energy equals the cohesive energy.

Table 4.3 Comparison of estimated Cohesive Energies and values of Dispersion Energies (in k.cal.mole^{-1}) for three Intermolecular Distances (r), r' is the value of r at which $E_L = \Delta E^{v}_{298}$.

	ΔE^{v}_{298}	E_L			r'
		3Å	4Å	5Å	(Å)
Toluene	8.5	31.7	5.6	1.5	3.9
Ethylbenzene	9.5	42.4	7.5	2.0	3.9
Isopropylbenzene	10.2	54.1	9.6	2.5	4.0
t-Butylbenzene	10.8	67.0	11.9	3.1	4.2

The van der Waal's radii of the methyl and phenyl groups are 2.0 and 1.85Å respectively[48], i.e. about $\frac{r'}{2}$ in Table 4.3. From this and the order of magnitude of the dipolar forces estimated from eqns. 4.1, 4.2 and 4.3 it was concluded that London dispersion forces are the predominating factor in intermolecular forces in the four monoalkylbenzenes. The order of magnitude of these forces is such that the free energies of activation observed for the τ_2 process could be due to a rate process involving London dispersion forces. Nevertheless, if such forces alone governed the τ_2 relaxation process, p-xylene would be expected to show an absorption of a similar magnitude despite the absence of a permanent dipole moment. However, p-xylene shows only an extremely weak absorption.

Chantry and Gebbie[58] have reported absorption bands with maxima in the 20 - 50 cm.$^{-1}$ region for the liquid halobenzenes and state that a "natural interpretation of these bands is that they are liquid lattice bands". Whether such a lattice vibration would cause absorption by the alkylbenzenes, in the pure state and in solution in a non-polar solvent, and whether such an absorption would occur in the microwave region is not yet clear. The concentrations of the weakly polar alkylbenzenes examined were very high and even between weight fractions $w_2 = 0.01$ to 0.1 the static dielectric constant has a parabolic dependence on w_2[16]. Such behaviour might indicate some molecular interaction[59].

If τ_2 could be explained by an intramolecular relaxation process the probable source would seem to be relaxation about the alkyl-aryl bond. The microwave spectrum of gaseous toluene yielded an energy barrier of $\sim$0.5 k.cal.mole^{-1} for rotation of the methyl group about the $C_{aryl} - C_{alkyl}$ bond[60]. In solution this value may well differ but undoubtedly rotation about the alkyl-aryl bond should take place readily. However, since there is no component of the dipole moment perpendicular to the $C_{aryl} - C_{alkyl}$ axis of rotation in toluene and t-butylbenzene, relaxation about this axis would not directly contribute to the dielectric absorption. The very small component of the dipole normal to the alkyl-aryl bond in ethylbenzene and isopropylbenzene would not alone cause an absorption of the magnitude observed for the τ_2 process. In fact the absorption due to this would be negligible.

If the alkyl-aryl bond was not a pure single bond, but had some double bond character due to π- electron resonance involving charge migration from the alkyl group to the ring, then during rotation about the alkyl-aryl bond the overlap of the group orbitals of the alkyl group with the π-electrons of the ring might vary. This would cause a rapid movement of charge to and fro between the alkyl group and the π-electron cloud of the phenyl group and implies oscillation of negative charge with an associated change in mesomeric moment. If the free energy of such a process was of a suitable magnitude the dielectric absorption would take place in the microwave region. The enthalpy of activation of the τ_2 process for toluene in cyclohexane was found to be 1.3 ± 1 k.cal.mole^{-1} which is of a similar order of magnitude to that reported for methyl rotation in the gaseous state.

In terms of Eyring and Fröhlich theories[61] the process would consist of a dipole oscillating along or parallel to the $C_{aryl} - C_{alkyl}$ bond, separated from its equilibrium positions by an energy barrier. This energy barrier should depend on (a) local interaction between adjacent molecules and (b) steric factors within the molecule. With regard to (a), the τ_2 values for toluene in cyclohexane at 25°C decrease with increasing dilution to a constant value of 1.6×10^{-12} sec. This is consistent with the apparent dipole moment increasing to a constant value as changes in interactions become no longer detectable at a weight fraction of 0.6. The τ_2 value for toluene in carbontetrachloride of 3.5×10^{-12} sec. compared with that of 1.6×10^{-12} sec. in cyclohexane together with the decrease in the dipole moment in carbontetrachloride might be explained by interaction between the solvent and solute molecules that causes an increase in the energy barrier to relaxation about the alkyl-aryl bond.

With respect to (b), the τ_2 values increase from toluene to ethylbenzene and are approximately constant within the experimental error for ethyl-, isopropyl-, and t-butylbenzene, possibly showing a slight increase with increasing size of alkyl substituent. It would be expected that steric interference to rotation would increase from methyl to ethyl although from ethyl to isopropyl to t-butyl the relaxation time might not alter appreciably from the view point solely of the volume swept out.

For two mutually independent relaxation processes, $C_1 \propto \mu_1^2$ and $C_2 \propto \mu_2^2$ where μ_1 is the molecular dipole moment and μ_2 would be related to the movement of charge due to such an intramolecular process and should reflect the magnitude of the mesomeric moment. A decrease in this moment from toluene through ethyl- and isopropyl- to t-butylbenzene would be expected from one concept of hyperconjugation in the monoalkylbenzenes[62]. This is in harmony with the relative magnitudes of C_2 found for the four monoalkylbenzenes, 0.45 toluene, 0.40 ethylbenzene, 0.33 isopropylbenzene and 0.25 t-butylbenzene, and lends support to the identification of τ_2 with an intramolecular relaxation process.

In conclusion it would seem that although the work presented in this chapter confirms the presence of two relaxation processes in the pure monoalkylbenzenes and their solutions in cyclohexane it is not possible to identify positively any one mechanism with the shorter relaxation process. The work described in the subsequent chapters is an investigation of the most probable causes of the τ_2 relaxation time which are either an intramolecular process or a relaxation process having its origins in intermolecular associations.

Chapter 5

Relaxation Processes of the Monohalo-, Cyano- and Nitrobenzenes in Dilute Solution

Introduction

When possible explanations of the shorter relaxation process of the monoalkylbenzenes were considered in Chapter 4, it was suggested that the short relaxation time might be attributed to lattice vibrations in local aggregates of polar solute molecules or to a rate process involving dissociation of a solute molecule from an aggregate. The work presented in this chapter was carried out to investigate the existence of any such aggregate formation in solutions of other monosubstituted benzenes and to establish whether contributions by a similar short relaxation process could be detected in the dielectric absorption of solutions of these rigid molecules in which there was no possibility of an intramolecular relaxation process.

Dielectric absorption studies by Poley et al[63,64,65] on liquid halobenzenes have indicated the presence of a second high frequency region of absorption. Its presence was inferred from the magnitude of the $\epsilon_\infty - n_D^2$ difference and attributed to a vibration of a molecule, trapped in a cage, about a temporary equilibrium position. Hill[66] in a theoretical treatment accounts for this high frequency dispersion. Gebbie et al[67], from measurements of the refractive index at 0.34 mm. wavelength of the four monohalobenzenes, considered that the Cole-Cole plots indicated the existence of an absorption process in addition to that predicted by the Debye equation. However, other workers have concluded that the dielectric absorption of the pure monohalobenzenes[68] and solutions in hexane and benzene of chloro-, bromo- and iodobenzene[69] can be explained by a single relaxation time. Also Garg and Smyth[70] have indicated that the $\epsilon_\infty - n_D^2$ difference for liquid fluoro-, chloro- and bromobenzene was negligible, although distribution coefficients of 0.03 at 21°C, 0.04 at 25°C and 0.07 at 25°C were obtained for fluoro-, chloro- and bromobenzene respectively.

The conflicting opinions and experimental work summarized above presented a confused picture of the dielectric absorption of the pure halobenzenes at high frequencies and did not confirm or deny the existence of a high frequency absorption region.

The work reported here was a study of solutions of the monohalobenzenes to determine whether such systems are characterized by a single relaxation time as predicted by the Perrin theory[33]. In addition, more accurate dielectric measurements were sought to determine whether the dielectric data could be adequately accounted for in terms of contributions from one or more Debye terms[6]. The measurements at 70.00 Gc/sec. and 34.86 Gc/sec. frequencies were considered to be of particular importance in providing an exacting test as to any contribution from a shorter relaxation process.

p-Xylene was chosen as solvent because its shape and structure favoured the formation of any quasi-crystalline pattern with the monosubstituted benzene solute. With increasing size of the halogen atom the polarizability of the C-halogen group significantly increases[71] while the dipole moment is roughly constant at 1.5D and, thus, the variability of solute polarizability was studied. The effect of the dipole moment was observed by also examining nitrobenzene and benzonitrile which have appreciably greater dipole moments of ~ 4D. This work, therefore, examined two of the basic factors which might influence the formation of quasi-crystalline patterns within solution, while temperature was the third variable.

Discussion

The Cole-Cole plots of the four monohalobenzenes in p-xylene solution at 15°C and 60°C were semicircular with the diameter lying along the abscissa and when the dielectric data was analysed in terms of τ_0, α and ϵ_∞, as described in Chapter 1, the distribution coefficient was determined as zero. This indicated that the dielectric absorption was characterized by one relaxation time as would be anticipated from the Perrin theory. There was good agreement between the experimental values of the dielectric constant and loss factor and those calculated based on a single relaxation time, see Appendix Table 3.

Table 5.1 Static Dielectric Constant, High Frequency Dielectric Constant, Square of Refractive Index (NaD Line), Relaxation Times, Weight Factor C_1, Distribution Coefficient α, and Dipole Moment Data for Solutions of Weight Fraction w_2 of Six Monosubstituted Benzenes.

Solute	Solvent	w_2	t (°C)	ϵ_0	ϵ_∞	n_D^2	τ_0	τ_1	τ_2	C_1	α	μ	$\mu_{\text{LIT.}}^{47}$
							$\times 10^{12}$ SEC.						
Fluorobenzene	p-Xylene	0.04418	15	2.3906	2.292	2.241	6.8	6.8	-	1.00	0	1.39	1.48
		0.04290	60	2.2898	2.212		4.2	4.2	-	1.00	0	1.40	
Chlorobenzene	p-Xylene	0.05042	15	2.4164	2.294	2.248	10.2	10.2	-	1.00	0	1.56	1.58
		0.05010	60	2.3075	2.213		6.0	6.0	-	1.00	0	1.55	
Bromobenzene	p-Xylene	0.04849	15	2.3760	2.289	2.250	14.0	14.0	-	1.00	0	1.59	1.56
		0.05018	60	2.2796	2.208		7.6	7.6	-	1.00	0	1.58	
Iodobenzene	p-Xylene	0.05700	15	2.3561	2.296	2.253	18.0	18.0	-	1.00	0	1.39	1.40
		0.06561	60	2.2705	2.215		9.2	9.2	-	1.00	0	1.39	

Table 5.1 Continued

Solute	Solvent	w_2	t (°C)	ϵ_0	ϵ_∞	n_D^2	τ_0	τ_1	τ_2	C_1	α	μ	$\mu^{47}_{\text{LIT.}}$
							— $\times 10^{12}$ SEC.		—				
Nitrobenzene	p-Xylene	0.01988	15	2.5763	2.296	2.246	15.3	13.0	35.0	0.80	0.03	3.94	4.01
		0.02005	60	2.4425	2.221		9.0	9.0	-	1.00	0	3.90	
Benzonitrile	p-Xylene	0.02022	15	2.6423	2.294	2.246	20.1	15.0	40.0	0.68	0.06	3.99	4.05
		0.02039	60	2.4900	2.218		10.6	9.0	26.0	0.76	0.03	3.99	
Nitrobenzene	Cyclohexane	0.01959	25	2.2453	2.025		9.9	8.2	33.0	0.84	0.06	4.03	
Nitrobenzene	Carbontetrachloride	0.01102	15	2.5554	2.267		17.8	15.0	40.0	0.80	0.06	3.97	
Benzonitrile	Cyclohexane	0.02033	15	2.3300	2.048		14.9	12.0	35.0	0.75	0.06	3.99	

The agreement at 70.00 Gc/sec. and 34.86 Gc/sec. indicated that there was no detectable contribution from a high frequency absorption for the halobenzene solutions.

The difference between ϵ_∞ and n_D^2, which Poley[64] has used as evidence for a high frequency absorption region was only ~ 0.05 for these dilute solutions at 15°C and showed no increment with increasing dipole moment as he observed in his study on the pure liquids. The square of the refractive index and ϵ_∞ are listed in Table 5.1. The small differences observed could be accounted for by the atomic polarization of the solute molecules which for fluoro-, chloro- and bromobenzene has been shown to be approximately 5 to 7% of $P_A + P_E$[70] and this would be inadequately allowed for in the n_D^2 term. This is supported by comparing the values of the dipole moment obtained from the microwave measurements, which are listed in Table 5.1, with values obtained by the Halvestadt and Kumler method[26] based on $P_A + P_E = 1.07\ R_D$. For bromobenzene in cyclohexane at 25°C from the data given in Chapter 1 a value of 1.58D is obtained and for chlorobenzene, which has the most reliably established value by this procedure for solution in benzene at 25°C[47], 1.55D is the value obtained. These agree within the experimental error with the microwave values in Table 5.1. For nitrobenzene and benzonitrile since $P_{2\infty} \gg (P_A + P_E)$ an allowance of 1.1 R_D as opposed to R_D makes no difference to the values calculated by the Halvestadt and Kumler method and agreement between dipole moment values obtained by the two methods should be within experimental error. The agreement between the two sets of dipole moments for all six solutes by the different methods gives strong support to the correctness of the dielectric data since the ϵ_∞ value employed in eqn. 1.39 is obtained by extrapolation. Quoted[47] values of the dipole moments have been listed in Table 5.1 as $\mu_{\text{LIT.}}$ so that direct comparison can be made.

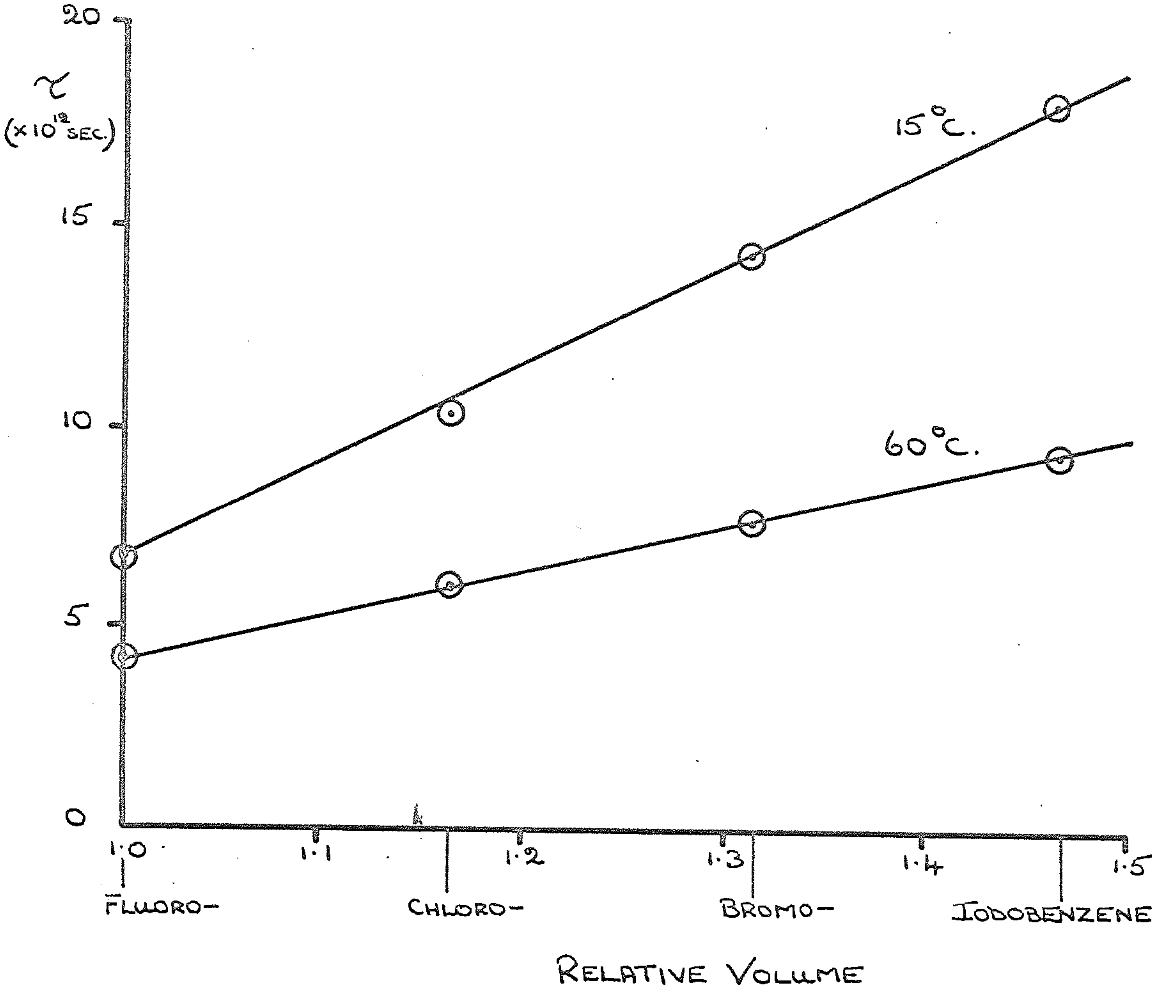
Fischer[72] has employed the relationship

$$\tau = \frac{4\pi abc\,\eta^* f}{kT} \qquad 5.1$$

for an ellipsoidal molecule where a, b and c are the lengths of the semi-axes of the molecular ellipsoid, η^* is an empirical viscosity, f a molecular structure factor and k the Boltzmann constant. τ is the relaxation time associated with molecular re-orientation. The volume of the ellipsoid is given by $V = 4\pi\ abc/3$. The shape factors for the monohalobenzenes may be taken as approximately equal and as the dipole moments and hence local force fields around the solute molecule are very similar, the viscosity term η^* should scarcely differ for the four molecules in dilute p-xylene solution at a given temperature. Thus a plot of molecular relaxation time against the volume of the molecular ellipsoid should be linear. The volumes of the molecules were estimated from Courtauld models and the plots of τ against relative volume are shown in Fig. 5.1. The good linearity of these plots supports the characterization of the dielectric absorption of the monohalobenzenes in p-xylene solution at 15°C and 60°C solely in terms of one molecular relaxation process. Furthermore, rough estimates of the enthalpy of activation of fluoro-, chloro-, bromo- and iodobenzene can be made from the relaxation times at 15°C and 60°C and these $\Delta H^{\ddagger}$ values, 0.8, 1.0, 1.4 and 1.6 ± 0.4 k.cal.mole^{-1} respectively at 25°C, are of the magnitude to be expected for molecular re-orientation of molecules of this size and shape. They are to be compared with the enthalpy of activation of the molecular re-orientation of toluene in cyclohexane at 25°C which is 1.1 k.cal mole^{-1} (see Chapter 4).

The Cole-Cole plot for nitrobenzene in p-xylene at 60°C has $\alpha = 0$ and the dielectric absorption is described by a single relaxation time, 9.0×10^{-12} sec. The volume of the nitrobenzene molecule is approximately the same as that of chlorobenzene and so from Fig. 5.1 it follows that the relaxation time of 9.0×10^{-12} sec. appears to be longer than anticipated. However, Jurinski and de Maine[73] have shown

FIG. 5.1 PLOT OF RELAXATION TIME AGAINST RELATIVE VOLUME FOR THE FOUR MONOHALOBENZENES IN p-XYLENE SOLUTION AT 15 AND 60°C.



that nitrobenzene interacts with toluene in carbontetrachloride solution, forming a weak charge transfer complex. Toluene acts as the donor and nitrobenzene as the acceptor. With other nitro-aromatic compounds they have shown that the donor ability of aromatic hydrocarbons increases with the number of methyl substituents. Such interaction would cause an increase in the viscosity term η^* in eqn. 5.1 and would lead to a longer τ value. There is no evidence for a high frequency absorption as the dipole moment which is dependent on the value of ϵ_∞ agrees, within the experimental error, with the established literature value. Furthermore, there is close agreement of the experimental and calculated dielectric constant and loss factor data given in Table 3 of the Appendix. Thus at 60°C the apparently longer relaxation time of nitrobenzene in p-xylene than that which might be anticipated from comparison with the halobenzenes is not to be attributed to a contribution from an additional relaxation process but to a longer η^* term than that of the halobenzenes.

Nitrobenzene at 15°C and benzonitrile at 15°C and 60°C all in p-xylene solution have significant distribution coefficients which suggest the presence of more than one relaxation process. The τ_0 values of 15.3×10^{-12}sec. for nitrobenzene in p-xylene at 15°C and 20.1×10^{-12}sec. and 10.6×10^{-12}sec. for benzonitrile in p-xylene solution at 15°C and 60°C respectively, appear too long for molecular re-orientation. This indicates a contribution to the dielectric absorption from a relaxation time longer than that for molecular re-orientation. The dielectric data for these systems have been analysed into contributions from the two relaxation times τ_1 and τ_2 listed in Table 5.1. Table 3 of the Appendix shows the good agreement between the experimental and calculated dielectric constants and loss factors. Similarly the data for nitrobenzene and benzonitrile in cyclohexane solution and that for nitrobenzene in carbontetrachloride solution analysed into two relaxation times with good agreement between the experimental and calculated points.

From the magnitude of the shorter relaxation time it apparently may be attributed to molecular re-orientation. Its progressive lengthening along the series of cyclohexane to p-xylene to carbontetrachloride as solvents for nitrobenzene is consistent with this, (see Table 5.1). Furthermore the enthalpy of activation of the shorter relaxation process of benzonitrile in p-xylene, estimated as 1 ± 0.8 k.cal.mole^{-1}, supports its identification with molecular re-orientation.

The existence of the longer relaxation process in different solvents eliminates the possibility that it might be due to some form of individual solvent effect. The vibration of a molecule trapped in a cage mechanism can be rejected as a possible explanation of this relaxation time as such a process would lead to a much shorter relaxation time than the τ_2 values in Table 5.1[66].

The polarizabilities of nitrobenzene and benzonitrile lie between those of fluoro- and bromobenzene while that of iodobenzene is significantly larger[71]. Thus the origin of the second relaxation time in nitrobenzene and benzonitrile is unlikely to be due to their polarizabilities and is more likely to arise from the much higher dipole moment that these two molecules have when compared with those of the monohalobenzenes. Possible ways of accounting for the longer relaxation time are,

i) re-orientation of a small polar aggregate of solute molecules.

ii) a rate process connected with the formation or (and) dissociation of the aggregate.

In Table 5.1 it can be seen that the contribution of the longer relaxation process to the dielectric absorption as a whole is temperature dependent, its weight factor decreasing with increasing temperature. This is consistent with the relaxation process being dependent on aggregates of solute molecules since an increase in thermal energy would oppose aggregate formation.

Within the limits of analysis the ratio of τ_2/τ_1 for the benzonitrile and nitrobenzene solutions is about 3/1 and from eqn. 5.1 this suggests that a re-orienting unit with three times the volume of the solute monomer would account for the τ_2 process. However, the shape factor could differ between the monomer and an associated species and, for example, a dimer could hardly be ruled out on these grounds. It is difficult though to envisage a likely dimeric species that would be polar and thus exhibit dielectric absorption. However, as Smith pointed out[47], "There is no reason of course, why association (of nitrobenzene) should be restricted to the formation of dimers." The free energies of activation $\Delta G_2^{\ddagger}$ corresponding to the longer relaxation time is about 3 k.cal.mole^{-1} and compares with a value of 3.3 k.cal.mole^{-1} for p-phenylacetophenone and 2.9 k.cal.mole^{-1} for p-phenylphenol both in benzene solution at 20°C[74] and these would be something of the order of the dimer or trimer in size.

Estimates of the dipolar contribution to the cohesion energy have been made to assess whether its magnitude is sufficient to give rise to the τ_2 process. For the pure polar liquid the dipolar contribution is the energy (W) required to cause infinite separation of the molecules if dipolar forces alone were present. Estimates of W obtained from eqns. 4.2 and 4.3, together with an estimate of the total cohesive energy, ΔE^{v}_{298}, obtained from Hildebrand's equations[56] (4.5 and 4.6) are given in Table 5.2. The dipolar forces are appreciably greater for nitrobenzene and benzonitrile, and the contribution of these forces to the cohesive energy is of the order of the free energy of activation for the longer relaxation process.

Table 5.2 Estimates of the Cohesive Free Energy and the Contributions of Dipolar Forces at 25°C. The units are k.cal.mole^{-1}.

	-W(eqn.4.2)	-W(eqn.4.3)	ΔE^{v}_{298}
Fluorobenzene	0.42	0.38	7.5
Chlorobenzene	0.46	0.37	9.7
Bromobenzene	0.44	0.32	10.3
Iodobenzene	0.32(20°C)	0.20(20°C)	11.7
Nitrobenzene	4.2	3.0	12.6
Benzonitrile	4.1	4.2	11.8

The enthalpy of activation for the longer relaxation process of benzonitrile in p-xylene estimated from the τ_2 values at 15 and 60°C is $\sim 1 \pm 1$ k.cal.mole^{-1} (the wide range of error being related to the small C_2 of ~ 0.3 and the low contribution to the dielectric loss, at the frequencies measured, of the long relaxation time.) It follows that this process is accompanied by a decrease in the entropy of activation. Molecular relaxation processes are usually characterized by a decrease in entropy whereas rate processes seem to be accompanied by an increase in entropy[75,76]. However, insufficient is known about such rate processes to rule out such an explanation on this alone.

It can be concluded that the work described in this chapter gives no evidence of a high frequency absorption in the six monosubstituted benzenes in solution and the values of $\epsilon_\infty - n_D^2$ obtained for the liquid halobenzenes by Garg and Smyth[70] are very similar to those obtained in p-xylene solution. The two sets of results differ in that in p-xylene solution the distribution coefficient is zero as opposed to a small but definite value for liquid bromobenzene. The dielectric absorption of the monohalobenzenes in p-xylene solution is described by a single Debye term, as predicted by the Perrin theory.

For nitrobenzene and benzonitrile, the two molecules with relatively large dipole moments of $\sim$4D, a relaxation process attributable to dipolar origins was observed. This was manifest as a relaxation time longer than that attributable to molecular re-orientation. A shorter relaxation process similar to that found for the monoalkylbenzene systems, described in Chapter 4, was not observed in any of the rigid monosubstituted benzene molecules in p-xylene solution.

Chapter 6

Relaxation Processes of Some Substituted Toluenes and Pyridines in Dilute Solution.

Introduction

In Chapter 4 it was shown that the dielectric absorption of toluene in cyclohexane and p-xylene solution was characterized by two relaxation times. The longer relaxation time was identified with molecular re-orientation and the shorter relaxation process was attributed either to an intramolecular relaxation process or to some relaxation time arising from the presence of aggregates of solute molecules in the solutions. The work reported in Chapter 5 investigated the existence of any comparable short relaxation process in solutions of the monohalobenzenes. The chlorobenzene molecule is similar in size and shape to toluene and although there is no possibility of intramolecular relaxation, the larger dipole moments of the monohalobenzenes would facilitate dipolar aggregation when compared with the alkylbenzenes. The dielectric data of the halobenzene solutions gave no indication of a short relaxation process and was described by a single relaxation time attributed to overall molecular re-orientation. Evidence for a relaxation process due to aggregates of solute molecules was obtained from measurements on solutions of nitrobenzene and benzonitrile in which the solute molecules had much larger dipole moments of $\sim 4D$. However, this second relaxation process was about three times longer than that of molecular re-orientation and no detectable contribution by a short relaxation time was observed in the dielectric data.

The above considerations suggested that in solutions of the weakly polar toluene molecules, aggregate formation would not be likely to cause a dielectric absorption contribution as large as that observed for the short τ_2 relaxation process and that the process could probably be ascribed to an intramolecular relaxation process. However, a major difference between the alkyl- and halobenzene systems was the concentrations of the solutions measured.

It was thought that measurement of the dielectric absorption of solutions of some parasubstituted toluenes might be useful to assess the significance of any concentration effect. The dipole moments of the parasubstituted toluenes are ~0.4D greater than the corresponding monohalobenzenes and therefore the dipolar forces exerted by the solute molecules will be somewhat larger. The main dipole vector lies along the major axis of the parasubstituted toluene molecules examined and from the Perrin theory[33] only one relaxation time would be expected if the molecules were rigid. However, reported measurements on pure p-chlorotoluene gave $\alpha = 0.01$ at 20, 40 and 60°C and solutions in p-xylene and benzene at 20, 40 and 60°C and in p-dichlorobenzene at 60°C have shown distribution coefficients greater than 0.1[46]. No attempt was made to analyse the dielectric data in terms of two relaxation times.

Smyth et al have reported distribution coefficients for some pure alkylsubstituted pyridines e.g. 2-methylpyridine α = 0.06 4-ethylpyridine α = 0.02 at 20°C[46] also 2.4-dimethylpyridine α = 0.10, 2.6-dimethylpyridine α = 0.03 at 20°C[77] and 4-methylpyridine α = 0.05 at 20°C[35]. It was thought that measurements of the dielectric absorption of dilute solutions of some 4-alkylpyridines would be worthwhile to see if there was evidence of a short relaxation process similar to that found in the alkylbenzene systems.

Discussion

The contribution of the shorter relaxation process to the dielectric absorption as a whole of toluene in cyclohexane had a weight factor C_2 = 0.45 (see Table 4.1). If it is assumed that this τ_2 process is due to an intramolecular relaxation process about the alkyl-aryl bond and that it is independent of the overall molecular re-orientation then an estimate of the mesomeric moment involved can be obtained from the relationship

$$\frac{C_1}{C_2} = \frac{\mu_1^2}{\mu_2^2} \qquad 6.1$$

where μ_1 is the dipole moment of the molecule and μ_2 the moment associated with the τ_2 process.

Substitution of C_1, C_2 and dipole moment values for toluene in cyclohexane at 25°C from Table 4.1 into eqn. 6.1 gives a value of 0.33D for μ_2. Quoted dipole moments of p-bromo- and p-chlorotoluene are 1.96 and 1.95D respectively[47]. Substitution of these values as μ_1 and 0.33D as μ_2 in eqn. 6.1 shows that if a similar relaxation process should occur in p-chloro- and p-bromotoluene a C_2 of 0.03 would be expected for the weight of the contribution of the intramolecular relaxation process to the total dielectric absorption. This assumes that any interaction between the parasubstituents is negligible and that the interaction moment ($\mu_{INT.}$) is zero. For p-nitrotoluene with a reported dipole moment of 4.42D[47] a C_2 value of 0.006 is obtained. Only very small α values for p-chloro-and p-bromotoluene and no detectable effect on the Cole-Cole plot of p-nitrotoluene would be anticipated for these contributions to the dielectric absorption as a whole.

p-Chloro-, p-bromo- and p-nitrotoluene in cyclohexane and p-xylene solution were measured and the values of α are listed in Table 6.1.

The Cole-Cole plots of p-nitrotoluene in cyclohexane and p-xylene solution at 40°C had $\alpha = 0$ and the dielectric data was

Table 6.1 Static Dielectric Constant, High Frequency Dielectric Constant, Relaxation Times, Weight Factor C_1, Distribution Coefficient α , and Dipole Moment Data for Solutions of Weight Fraction w_2 of Three Parasubstituted Toluenes and Two Alkylpyridines.

The values of τ_1 and τ_2 are quoted to the number of figures shown for comparison purposes only.

Solute	Solvent	w_2	t	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	C_1	α	μ
			(°C)			$\times 10^{12}$ sec.					(D)
p-Chlorotoluene	Cyclohexane	0.05089	15	2.1812	2.045	19.0	19.2	1.5	0.95	0.04	1.94
		0.05087	25	2.1590	2.031	16.4	16.8	1.6	0.93	0.04	1.93
		0.05089	32.5	2.1427	2.020	14.5	14.6	1.9	0.97	0.03	1.93
		0.05397	40	2.1318	2.010	13.2	13.2	-	1.00	0	1.91
	p-Xylene	0.05093	25	2.4337	2.279	17.0	18.4	2.0	0.94	0.03	1.91
		0.05093	40	2.3909	2.249	14.0	14.0	-	1.00	0	1.90
p-Bromotoluene	Cyclohexane	0.06831	15	2.1835	2.049	22.9	23.7	1.9	0.95	0.04	1.94
		0.05497	25	2.1340	2.030	19.9	21.0	2.1	0.97	0.03	1.95
		0.06831	32.5	2.1458	2.024	17.8	18.1	2.0	0.97	0.02	1.93
		0.06716	40	2.1249	2.010	16.1	16.1	-	1.00	0	1.93

Table 6.1 Continued

Solute	Solvent	w_2	t	ϵ_0	ϵ_∞	τ_0	τ_1	τ_2	C_1	α	μ
			(°C)			$\times 10^{12}$ sec.					(D)
p-Bromotoluene	p-Xylene	0.06811	25	2.4368	2.278	22.3	23.0	3.0	0.93	0.04	1.94
		0.06811	40	2.3936	2.248	17.4	17.4	-	1.00	0	1.93
p-Nitrotoluene	Cyclohexane	0.01995	15	2.3006	2.045	22.3	20.0	90	0.85	0.06	4.43
		0.02015	25	2.2749	2.028	19.6	17.8	80	0.90	0.03	4.44
		0.01995	32.5	2.2535	2.019	18.2	16.6	75	0.94	0.02	4.44
		0.01990	40	2.2300	2.012	15.5	15.5	-	1.00	0	4.37
	p-Xylene	0.02001	25	2.5863	2.281	24.0	21.0	90	0.85	0.04	4.44
		0.02001	40	2.5285	2.256	18.8	18.8	-	1.00	0	4.36
4-Methylpyridine	Cyclohexane	0.01999	25	2.1442	2.020	7.2	7.6	1.1	0.88	0.06	2.61
		0.02996	25	2.2117	2.024	7.1	8.4	2.3	0.80	0.05	2.62
4-t-Butylpyridine	Cyclohexane	0.01856	25	2.1049	2.019	15.8	20.1	3.9	0.89	0.04	2.71

described by a single relaxation time. The comparison of calculated and experimental points gave no indication of a second relaxation process. The single relaxation time obtained was attributed to molecular re-orientation as would be anticipated from the Perrin theory. However, solutions of p-nitrotoluene below 40°C gave Cole-Cole plots with definite distribution coefficients suggesting the presence of more than one relaxation time. The experimental points lay to the left of the maximum on the Cole-Cole plot, ϵ_∞ was estimated to within close limits and the α values though small were outside the experimental error.

The distribution coefficient of solutions of p-nitrotoluene in cyclohexane decreased with increasing temperature and there was a significant decrease in the measured dipole moment at 40°C when $\alpha = 0$ in both solvents. In these respects the measurements paralleled those of solutions of nitrobenzene in p-xylene, where the observed α became zero at a high temperature with an accompanying small decrease in the observed dipole moment (see Table 5.1).

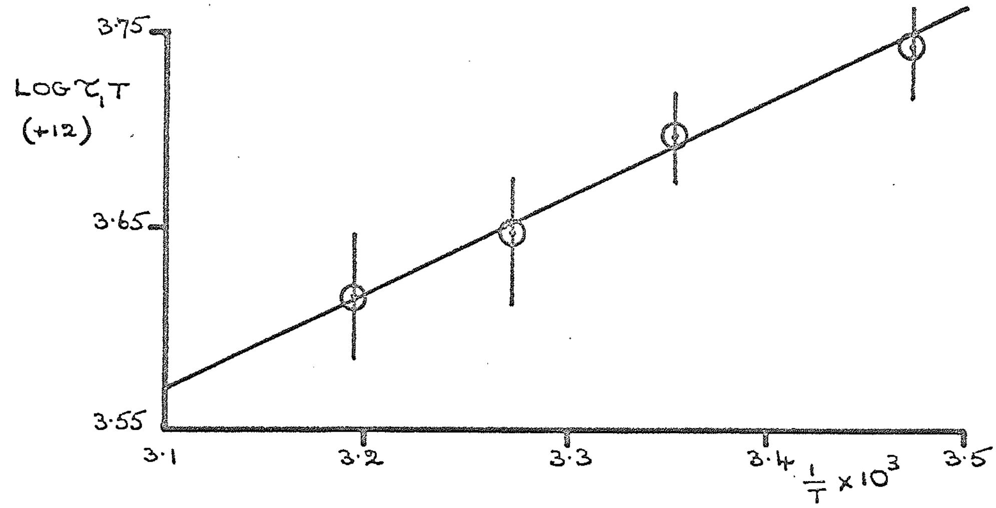
Although the plots of ϵ' against $\epsilon''\omega$ did not deviate from linearity outside the experimental error and gave no evidence of more than one relaxation process, because of the close similarity in the behaviour of the results of the p-nitrotoluene solutions with those of nitrobenzene in p-xylene it was considered that the dielectric data of the solutions below 40°C should be analysed in terms of two relaxation processes. The values of τ_1 , τ_2 and C_1 obtained are given in Table 6.1. The good agreement between the experimental and calculated dielectric constants and loss factors lends support to the analysis (see Appendix, Table 4).

It is apparent from the size of the shorter relaxation time, τ_1 , that it may be identified with molecular re-orientation. The enthalpy of activation, $\Delta H_1^{\ddagger}$, for the τ_1 process of p-nitrotoluene in cyclohexane obtained from the slope of Fig. 6.1 (c), is 0.6 k.cal.mole^{-1} at 25°C. This is apparently low when compared with a value of 1.1 k.cal.mole^{-1} for the enthalpy of activation of molecular re-orientation of toluene in cyclohexane at 25°C. However, it compares favourably with the estimate of 0.4 k.cal.mole^{-1} for nitrobenzene in p-xylene obtained from the τ_1 values in Table 5.1.

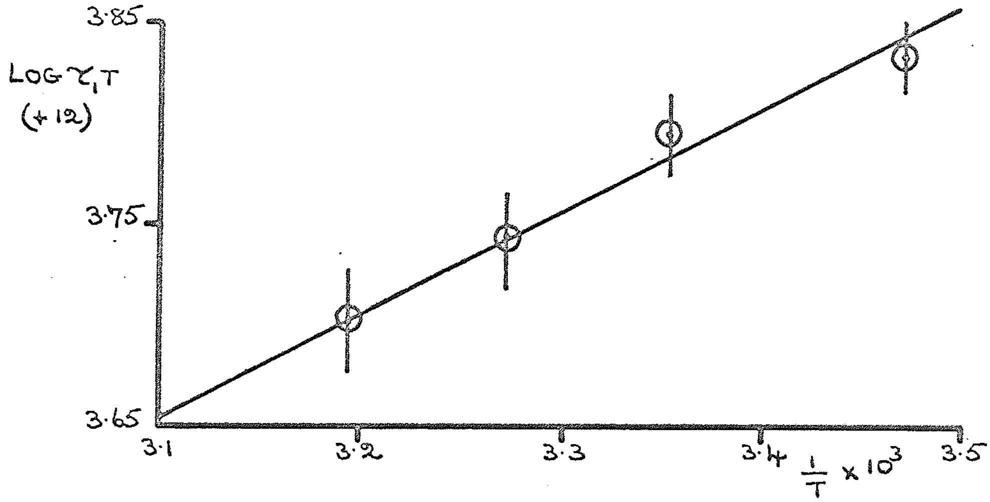
The long τ_2 process of the p-nitrotoluene solutions below 40°C might be attributed to a similar process to that of solutions of nitrobenzene and benzonitrile. The contribution of this process to the dielectric absorption of the p-nitrotoluene solutions decreases with increasing temperature as would be expected if it was due to some form of aggregation of solute molecules. The large dipole moment

FIG. 6.1 PLOTS OF LOG $\tau_1 T$ AGAINST $\frac{1}{T}$ FOR THREE PARASUBSTITUTED TOLUENES IN CYCLOHEXANE SOLUTION.

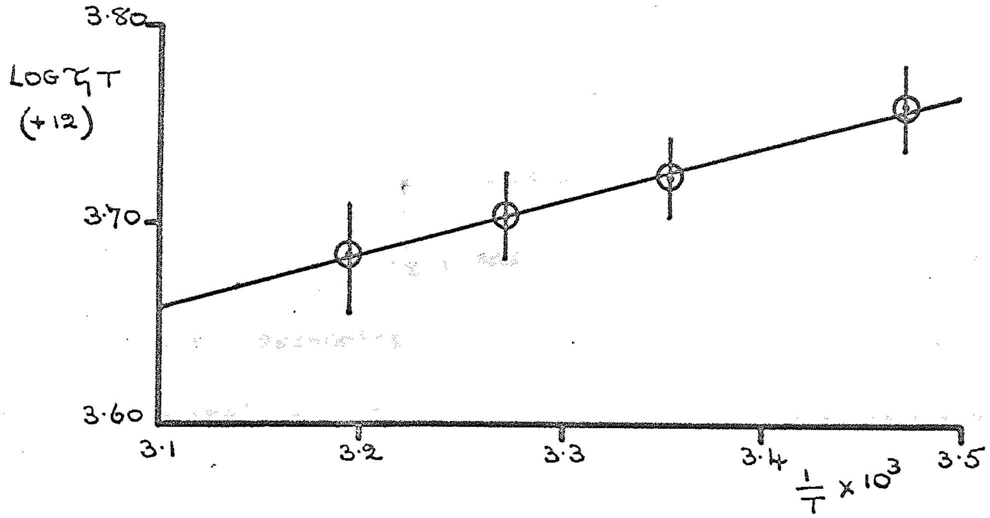
(a) p-CHLOROTOLUENE



(b) p-BROMOTOLUENE



(c) p-NITROTOLUENE



would facilitate dipolar aggregation and Sobhanadri[78], from measurements at 3.26 cm. of disubstituted toluenes as pure liquids and in solution, has concluded that the presence of a nitro group in a molecule appears to contribute considerably to the dipole interaction energy. The apparently constant value of 4.44D for the measured dipole moment of p-nitrotoluene in solutions whose Cole-Cole plots indicate a distribution of relaxation times and the decrease in the observed dipole moment to 4.36D at 40°C when $\alpha = 0$ suggests that any alignment of the dipoles is not in the antiparallel, non-polar, dimeric arrangement that might be anticipated, as this would lead to an increase in the measured moment until interaction became no longer detectable (cf. toluene in cyclohexane at 25°C, Table 4.1). The arrangement of the dipoles must be in some form of polar aggregate that leads to an increase in the apparent dipole moment.

Lattice vibrations in any such aggregate of solute molecules would lead to a very much shorter value of τ_2 than those obtained[66]. Re-orientation of a small polar aggregate of solute molecules could give rise to relaxation times of this size. However, because of the low weight factor and long τ_2, the contribution to the dielectric absorption at the frequencies measured by the longer relaxation process is very small and thus the τ_2 values listed in Table 6.1

for the p-nitrotoluene solutions can only be considered to indicate the presence of a relaxation process significantly longer than that attributed to molecular re-orientation.

It is concluded that the dielectric absorption of p-nitrotoluene in cyclohexane solution at 15, 25 and 32.5°C and in p-xylene at 25°C is described in a similar manner to that of the nitrobenzene and benzonitrile solutions, namely by two relaxation times, one attributable to molecular re-orientation and a much longer relaxation time probably of dipolar origins. There is no indication of a shorter relaxation process comparable with that observed in measurements on toluene solutions.

The Cole-Cole plots of p-chloro- and p-bromotoluene in cyclohexane and p-xylene solution at 40°C also showed $\alpha = 0$ and were described by a single relaxation time, whereas measurements at temperatures below 40°C showed small but definite distribution coefficients. They differed from the Cole-Cole plots of the monohalobenzenes in p-xylene solution which had $\alpha = 0$ at all the temperatures employed. The measured dipole moments of p-chloro- and p-bromotoluene were constant within ± 0.02D and showed no marked decrease when $\alpha = 0$. The measured values were slightly lower than the reported[47] values of 1.95 and 1.96D for p-chloro- and p-bromotoluene respectively in benzene solution. However, using reported measurements and equating $P_A + P_E$ to 1.1 R_D dipole moments of 1.91D for p-chlorotoluene in benzene at 20°C[79] and 1.93D for p-bromotoluene in benzene at 25°C[80] are evaluated. These values are in good agreement with the dipole moments obtained from the microwave technique in p-xylene solution. It is assumed that the difference between the reported values and the dipole moments listed in Table 6.1 is due to an inadequate allowance for the P_A term when equating $P_A + P_E$ to R_D in the traditional method of dipole moment determination. The good agreement of the individual measurements listed in Table 6.1 lends support to the dipole moment values obtained and hence the ϵ_∞ values.

The dielectric data of the p-chloro- and p-bromotoluene solutions below 40°C were analysed into contributions from two relaxation processes with good agreement between calculated and experimental points. The τ_1, τ_2 and C_1, values are shown in Table 6.1.

The size of the τ_1 values suggest that they may be attributed to molecular re-orientation. This is supported by the relative increase in τ_1 obtained from the measurements in cyclohexane and p-xylene solution at the same temperature. Furthermore, the enthalpies of activation of the τ_1 process of p-chloro- and p-bromotoluene in cyclohexane at 25°C are determined as 1.6 and

1.8 k.cal.mole^{-1} respectively from the slopes of Fig. 6.1 (a) and (b) and are as might be expected for molecular re-orientation when compared with values of 1.0 and 1.4 ± 0.4 k.cal.mole^{-1} for the enthalpy of activation of molecular re-orientation of chloro- and bromobenzene respectively in p-xylene solution at 25°C (see Chapter 5).

The outstanding difference in the analyses of the dielectric data of the p-chloro- and p-bromotoluene solutions when compared with those of p-nitrotoluene is that the relaxation process accompanying molecular re-orientation of the former is very short, whereas it is much longer than τ_1 in the p-nitrotoluene systems. The τ_2 value of $\sim 2 \times 10^{-12}$ sec. for the p-chloro- and p-bromotoluene solutions below 40°C compares with the τ_2 of 1.6×10^{-12} sec. reported for toluene in cyclohexane at 25°C (see Table 4.1). The C_2 values do not show any significant variation with temperature except at 40°C when no contribution from the shorter relaxation process is apparent. However the value of C_1 below 40°C is about 0.97 which is that estimated at the beginning of this discussion, when an intramolecular process similar to that suggested for the τ_2 process of the toluene solutions was assumed for p-chloro- and p-bromotoluene.

The decrease of the distribution coefficient with increasing temperature to zero is not inconsistent with reported measurements on molecules in which there is a well established intramolecular relaxation process. Fong and Smyth[74] reported α values of 0.09, 0.07, 0.01, and 0.11, 0.07 and 0.0 for p-phenylphenol and 2.6 dimethylphenol respectively at 20, 40 and 60°C. The τ_0 values were short because of-OH group orientation and all the measurements, including those for 2.6 dimethylphenol at 60°C which had zero distribution coefficient, were analysed in terms of two relaxation times. Roberti and Smyth,[81] in reporting low α values of 0.01, 0.01 and 0.00 for pure p-chloroanisole at 20, 40 and 60°C, concluded that the large fixed moment of the molecule placed greater emphasis on molecular rotation and reduced the effect of orientation by the methoxy group and so a small distribution coefficient was observed.

However, although an intramolecular relaxation process of relaxation about the alkyl-aryl bond with an associated mesomeric moment change of $\sim$ 0.3D would account for the shorter relaxation process of the p-chloro-and p-bromotoluene solutions, because of the small contribution of this relaxation process to the dielectric absorption at the frequencies employed, large errors are to be expected in the resulting τ_2 values. Therefore the possibility of an alternative mechanism such as a rate process involving the dissociation or (and) association of a polar solute molecule from a local aggregate or a lattice vibration associated with such an aggregate cannot definitely be ruled out. Nevertheless, it might have been expected that if such an explanation was correct, a similar process would have been observed in the halobenzene solutions at 15°C.

The Cole-Cole plots of 4-methylpyridine and 4-t-butylpyridine solutions in cyclohexane at 25°C also showed small but definite α values (see Table 6.1). The measured dipole moments of 2.61 and 2.71D for 4-methyl- and 4-t-butylpyridine respectively agree with the reported[82] values of 2.60 and 2.73D in benzene solution at 25°C. This supports the ϵ_∞ values and the fit of the Cole-Cole plots to the experimental points.

Substitution of a value of 0.33D for μ_2 and the measured dipole moment as μ_1 into eqn. 6.1 gives a C_2 value of 0.02 for 4-methylpyridine. Therefore if $\mu_{INT.} = 0$ only a very small effect on the measured dielectric absorption would be anticipated for an intramolecular process involving relaxation about the alkyl-aryl bond in 4-methylpyridine. From the C_1, C_2 and dipole moment data of t-butylbenzene in cyclohexane at 25°C (see Table 4.1), a mesomeric moment change of 0.23D would accompany the τ_2 process if relaxation about the alkyl-aryl bond gave rise to the shorter relaxation time. From eqn. 6.1 and the measured dipole moment of 2.71D for

4-t-butylpyridine in cyclohexane at 25°C it can be shown that a similar relaxation process would contribute a weight factor of 0.007 to the total dielectric absorption. It would be anticipated that such a contribution would have no measureable effect on the experimental values of the dielectric constants and loss factors of the solution of 4-t-butylpyridine measured.

The dielectric data of pyridine in solution displayed Cole-Cole plots with large distribution coefficients attributed to a distribution of relaxation times about a most probable τ_o value, whereas the Cole-Cole plot of 4-cyanopyridine in p-xylene at 25°C had $\alpha = 0$ and was described by a single relaxation time of 20.9×10^{-12}sec. (see Chapter 3). The disappearance of a significant distribution coefficient with the increased length of the main dipolar axis suggests that the distribution coefficients of 4-methylpyridine and 4-t-butylpyridine in cyclohexane at 25°C might be due to the presence of more than one relaxation process rather than a distribution of relaxation times about τ_o. Furthermore the τ_o values of $\sim 7 \times 10^{-12}$sec. and $\sim 16 \times 10^{-12}$sec. for 4-methyl- and 4-t-butylpyridine respectively both in cyclohexane solution at 25°C are short when compared with the relaxation times of $\sim 9 \times 10^{-12}$sec. and $\sim 28 \times 10^{-12}$sec. (see Chapter 4) for the molecular re-orientation of cyclohexane solutions of toluene and t-butylbenzene respectively at the same temperature. This is indicative of a shorter relaxation process (or processes) together with that of molecular re-orientation describing the dielectric absorption and resulting in the short τ_0 values.

An analysis of the dielectric data of the 4-alkylpyridine solutions measured into contributions from two discrete relaxation processes gave the τ_1 , τ_2 and C_1 values listed in Table 6.1.

The values of τ_1 and τ_2 for the 4-methylpyridine solutions show a resemblance to those obtained for toluene in cyclohexane at 25°C and the size of the τ_1 value obtained from the 4-t-butylpyridine data suggests that it could be attributed to molecular re-orientation, however the τ_2 value is not comparable with the τ_2 of 9×10^{-12} sec. for t-butylbenzene in cyclohexane at 25°C (see Table 4.1).

If the shorter relaxation process was ascribed to an intramolecular relaxation process about the alkyl-aryl bond the C_2 values obtained from the analyses would correspond to a mesomeric moment change of 0.96D and 0.95D for 4-methyl- and 4-t-butylpyridine respectively along the alkyl-aryl bond. These are much too large, for although the electron affinity increases from benzene to pyridine, an extensive study[82] of the dipole moments of substituted benzenes and pyridines has revealed no evidence of increased mesomerism in substituted pyridines due to hyperconjugation of the methyl and t-butyl groups. Therefore an intramolecular relaxation process is unable to account for the τ_2 values of the 4-alkylpyridine solutions measured.

Possible mechanisms giving rise to the short τ_0 values could be associated with the dissociation and (or) association of a solute molecule from a local aggregate of solute molecules and (or) a liquid lattice vibration within such an aggregate. Although no evidence of a similar distribution of relaxation times was observed for solutions of 4-cyanopyridine in cyclohexane at 25°C the larger dipole moments of the 4-alkylpyridines measured would facilitate any dipolar aggregation. The Free Energy barrier and hence relaxation time of a rate process involving association or dissociation of a solute molecule from a local aggregate would depend on the inter-dipolar forces. The dipole moments of 4-methyl- and 4-t-butylpyridine only differ by 0.1D and it might be expected that the dipolar forces would be similar. The τ_2 values of 4-methyl- and 4-t-butylpyridine are consistent with this interpretation of a rate process. However, the good agreement of the dipole moments obtained from the microwave technique and those from the traditional methods of dipole determination, which were obtained from measurements on very dilute solutions, is not compatible with a large amount of dipolar association in the solutions measured.

It is concluded that there is no common explanation for the distribution coefficients observed in the measurements reported in this chapter.

The most probable relaxation processes that describe the dielectric absorption of the p-nitrotoluene solutions are overall molecular re-orientation and a temperature dependent long relaxation process of dipolar origins.

A shorter relaxation time than that attributed to molecular re-orientation was obtained from the analysis of the dielectric data of solutions of p-chloro- and p-bromotoluene below 40°C. It is apparently described adequately by the concept of relaxation about the alkyl-aryl bond, although a short relaxation process of dipolar origins cannot definitely be ruled out.

Finally, the dielectric absorption data of 4-methyl- and 4-t-butylpyridine in cyclohexane solution at 25°C display small but definite distribution coefficients and give τ_0 values shorter than the relaxation times anticipated for molecular re-orientation. An intramolecular relaxation process cannot account for this and the dielectric loss is attributed to overall molecular re-orientation and a short relaxation process (or processes) possibly of dipolar origins.

Chapter 7

Relaxation Process of o- and m-Xylene, 1- and 2-Methylnaphthalene and Related Compounds in Cyclohexane Solution.

Introduction

The measurements reported in the previous chapter cast some doubt on the validity of attributing the shorter relaxation process of the monoalkylbenzenes to an intramolecular relaxation process.

The shorter relaxation time of p-chloro- and p-bromotoluene solutions below 40°C can be explained adequately by an intramolecular relaxation about the alkyl-aryl bond. However, the decrease of the distribution coefficient with increasing temperature to $\alpha = 0$ at 40°C and the difficulty in determining accurately the values of τ_2, because of the small C_2 factor, meant that an alternative dipolar mechanism could not be discounted. Furthermore, the short τ_0 values of the 4-alkylpyridine solutions could only be explained if a short relaxation process (or processes) of possible dipolar origins contributed to the dielectric absorption. An intramolecular relaxation process did not account for these short τ_0 values.

The existence of the short τ_2 relaxation processes that have been observed in the aromatic systems measured appears to be dependent upon an alkyl substituent and a permanent dipole moment in the solute molecule, as a similar process was not detectable in measurements on solutions of the monohalobenzenes and also p-xylene and mesitylene have no comparable dielectric loss.

Alkyl substitution increases the ability of the phenyl group to act as an electron donor in charge-transfer complex formation[83]. This is explained by the increase in the charge density of the π- electrons of the ring due to electron release from the alkyl substitutent. Any possible aggregate formation in the alkylsubstituted aromatic systems measured could involve the permanent dipolar forces and interactions of the charge cloud on the phenyl group. The possible requirement of a high charge density on the phenyl group might explain why no short relaxation process was detectable in solutions of the monohalobenzenes.

The dipole moments of toluene, ethyl-, isopropyl- and t-butylbenzene are similar and it might be expected that the activation free energy of any relaxation process involving association or (and) dissociation of a local aggregate depending on both dipolar forces and interaction of the phenyl charge clouds would be similar in solutions of the four monoalkylbenzenes and give rise to similar relaxation times. However the τ_2 values listed in Table 4.1 are not comparable for the four molecules and moreover the contribution of the τ_2 process to the total dielectric absorption of toluene in cyclohexane solution is apparently independent of the temperature, which is inconsistent with the process arising from any local aggregates of the solute molecules.

Further measurements on alkyl-aryl compounds were required to ascertain the correct explanation of this short relaxation process. Petro and Smyth[46] have reported α values of 0.08, 0.07 and 0.04 for pure o-xylene and 0.11, 0.06 and 0.04 for pure m-xylene at 20, 40 and 60°C respectively, but an analysis of the experimental results into contributions from two relaxation times was not reported. It was considered that measurements on cyclohexane solutions of o- and m-xylene and any subsequent analysis of the dielectric data into contributions from two Debye terms might prove useful in characterizing the τ_2 process of the monoalkylbenzenes, p-chloro- and p-bromotoluene. Any contribution to the dielectric absorption of the o- and m-xylene solutions from a relaxation process concerned with interaction of the charge cloud of the phenyl group might be enhanced by the presence of two charge donating methyl groups.

The comparison of the dielectric data of solutions of o-xylene with those from solutions of benzocyclobutene was hoped to be particularly useful in assessing the origins of any shorter relaxation process because in the latter molecule an intramolecular relaxation is impossible and both molecules would be expected to pack in a similar manner into any local aggregates of solute molecules in the solutions measured.

Studies by Rampolla and Smyth[77] have shown distribution coefficients of 0.10, 0.08 and 0.05 for pure 1-methylnaphthalene at 20, 40 and 60°C and 0.16 and 0.17 for pure 2-methylnaphthalene at 40 and 60°C whereas 1.2.3.4-tetrahydronaphthalene had $\alpha = 0$ at 20, 40 and 60°C. Measurements on cyclohexane solutions of the monomethylnaphthalenes and related halo compounds were made to investigate the existence of any shorter relaxation process in the methylnaphthalene systems.

Discussion

The Cole-Cole plots of o-dichloro- and m-dichlorobenzene in cyclohexane solution at 25°C showed zero distribution coefficients. The dipole moments obtained from the microwave technique agreed with the quoted values of 2.27D and 1.49D for o-dichloro- and m-dichlorobenzene respectively in benzene and n-heptane solution at 25°C[34]. This supports the extrapolated ϵ_∞ value and the fit of the Cole-Cole plot to the experimental points. The agreement between the experimental dielectric constants and loss factors and those calculated from the single relaxation times given in Table 7.1 showed no indication of a distribution of relaxation times (see Appendix, Table 5). From the zero distribution coefficient and a comparison of the single

Table 7.1 Static Dielectric Constant, High Frequency Dielectric Constant, Viscosity (η) Relaxation Times, Distribution Coefficient, C_1 and Dipole Moment Data of o- and m-Xylene, 1- and 2-Methylnaphthalene and Related Compounds.

The solvent was cyclohexane for all the solutions in this table.

Solute	w_2	t	ϵ_0	ϵ_∞	η	τ_0	τ_1	τ_2	C_1	α	μ
		(°C)			(cp.)		$\times 10^{12}$ sec.				(D)
Benzocyclobutene	0.78921	20	2.4640	2.317		11.6	11.6	-	1.00	0	0.40
	0.78921	40	2.4261	2.287		9.2	9.2	-	1.00	0	0.41
o-Xylene	0.69932	25	2.3840	2.185		8.3	11.4	5.4	0.50	0.04	0.54
	0.71108	50	2.3264	2.154		6.1				0	0.53
m-Xylene	0.69151	25	2.2335	2.166		9.3	11.8	2.6	0.70	0.06	0.32
	0.71759	50	2.1917	2.135		5.9				0	0.31
o-Dichlorobenzene	0.04128	25	2.1541	2.031		9.4	9.4	-	1.00	0	2.27

Table 7.1 Continued.

Solute	W_2	t ($^\circ$C)	ϵ_0	ϵ_∞	η (cp.)	τ_0	τ_1 $\times 10^{12}$ SEC.	τ_2	C_1	α	μ (D)
m-Dichlorobenzene	0.08096	25	2.1451	2.041		10.0	10.0	-	1.00	0	1.49
1-Methylnaphthalene	0.69751	25	2.5121	2.370	1.57	29.3				0.22	0.48
	0.59972	25	2.4252	2.311	1.38	24.8				0.19	0.48
	0.70466	50	2.4640	2.339	1.06	17.8	26.6	4.7	0.75	0.16	0.47
2-Methylnaphthalene	0.69540	25	2.4981	2.374	1.37	36.0				0.25	0.45
	0.69651	50	2.4314	2.325	0.93	19.1	26.9	3.0	0.77	0.20	0.45
2-Bromonaphthalene	0.08356	25	2.1777	2.048	0.92	25.5				0.08	1.86
	0.09164	50	2.1337	2.016	0.63	16.1	16.1	-	1.00	0	1.82

relaxation times of 9.4×10^{-12}sec. and 10.0×10^{-12}sec. for the solutions of o-dichloro- and m-dichlorobenzene respectively with those of 9×10^{-12}sec. and 7.8×10^{-12}sec. for the respective molecular re-orientation relaxation times of toluene at 25°C and chlorobenzene[21] at 20°C in cyclohexane solution, it is concluded that the dielectric absorption of the dichlorobenzene solutions measured is characterized by the single relaxation process of molecular re-orientation.

The Cole-Cole plots of benzocyclobutene in cyclohexane solution at 20°C and 40°C also had $\alpha = 0$ and there is good agreement between the experimental and calculated points when the calculations are based on the single relaxation times listed in Table 7.1. These measurements were supported by those of Crossley[54] who for the pure liquid at 25°C obtained a Cole-Cole plot with $\alpha = 0$ and described by a single relaxation time of 12.6×10^{-12}sec. The apparent dipole moment of the pure liquid was 0.40D at 25°C which agrees with those obtained from the measurements on the 70% solutions in cyclohexane given in Table 7.1.

A comparison of the relaxation times of the benzocyclobutene solutions, $\tau = \sim 11 \times 10^{-12}$sec. at 25°C, with that of the molecular re-orientation of o-dichlorobenzene, $\tau = 9.4 \times 10^{-12}$sec. at 25°C, suggests the identification of the former with a similar relaxation process. The enthalpy of activation obtained from the τ values of the benzocyclobutene solutions at 20 and 40°C and eqn. 1.31 is 1.0 ± 0.6 k.cal.mole^{-1}, which, compared with a value of 1.1 k.cal.mole^{-1} for toluene in cyclohexane, gives further support to the identification of the relaxation time of benzocyclobutene with molecular re-orientation.

The Cole-Cole plots of o- and m-xylene in cyclohexane solution at 25°C had distribution coefficients of 0.04 and 0.06 respectively indicating a distribution of relaxation times but at 50°C the Cole-Cole plots had $\alpha = 0$. The reported dipole moments of o-xylene range from 0.50 - 0.54D for the pure liquid and 0.52 - 0.58D for benzene solutions and those of m-xylene are 0.30 - 0.36D for the pure liquid and 0.37 - 0.46D for solutions in benzene[34]. The dipole moments obtained by the microwave technique, given in Table 7.1, are in accord with the ranges quoted for the pure liquids and are acceptable for measurements on $\sim$ 70% solutions. This gives some support to the ϵ_∞ values and the fit of the Cole-Cole plots to the experimental data.

The τ_0 values of 8.3×10^{-12}sec. for o-xylene and 9.3×10^{-12}sec. for m-xylene both in cyclohexane solution at 25°C are shorter than 9.4×10^{-12}sec. and 10.0×10^{-12}sec. respectively, which are the relaxation times identified with molecular re-orientation of the corresponding dichlorobenzenes. As the van der Waal's radii of the methyl group and the chlorine atom are 2.0 Å and 1.80 Å respectively[48], it would be anticipated that the relaxation time of the molecular re-orientation of a methylsubstituted compound would be longer than that of the corresponding chloro compound. This is shown by the relaxation times of 9.0×10^{-12} sec. and 7.8×10^{-12} sec. for the molecular re-orientation of toluene at 25°C and chlorobenzene at 20°C[21] respectively in cyclohexane solution. Also the τ_0 of the o-xylene solution at 25°C is appreciably shorter than 11×10^{-12} sec. which is the interpolated relaxation time for the molecular re-orientation of benzocyclobutene in cyclohexane at 25°C. The apparent shortness of the τ_0 values of the o- and m-xylene solutions at 25°C indicates that a short relaxation process is contributing to the dielectric absorption.

The dielectric data of the o- and m-xylene solutions at 25°C were analysed into contributions from two Debye terms and the τ_1 , τ_2 and C_1 values are listed in Table 7.1. The difference of the τ_1 values and the relaxation times of the corresponding dichlorobenzenes indicates that the τ_1 process of the xylene solutions at 25°C may be identified with molecular re-orientation. The τ_1 of 11.4×10^{-12} sec. for o-xylene is similar to the 11×10^{-12} sec. estimated for the molecular re-orientation of benzocyclobutene in cyclohexane at 25°C. and supports the assignment of τ_1 with the overall molecular relaxation process.

From the conclusions of the preceding chapters, possible explanations of the τ_2 process of the o- and m-xylene solutions at 25°C are an intramolecular relaxation about the alkyl-aryl bond with an accompanying mesomeric moment change along these bonds, or a short relaxation process relating to the dissociation and (or) association of a solute molecule from a local aggregate of solute molecules within the solution, or some form of lattice vibration associated with such aggregates. However, a single relaxation process explains the dielectric absorption of the benzocyclobutene solutions measured. In these systems no intramolecular relaxation process is possible and because of the similarity in shape, concentration and dipole moment of the solute molecule in these solutions and those of o-xylene, it might be anticipated that any dielectric loss due to a relaxation process arising from local aggregates of solute molecules would have a similar effect on the dielectric absorption of both molecules in solution. Furthermore, Crossley's[54] measurements on a 60% solution of Indane in cyclohexane at 25°C gave a Cole-Cole plot with $\alpha = 0$, described by a single relaxation time of 12.6×10^{-12} sec. The absence of any indication of a short relaxation process in a solution of this solute and solutions of benzocyclobutene, in which there is no possibility of an intramolecular relaxation process and in which the factors influencing any aggregate formation are comparable to those in the solutions of o- and m-xylene, indicates that the short relaxation process does not depend on the local aggregation of solute molecules but rather on an intramolecular relaxation process.

2.6×10^{-12}sec., the τ_2 of m-xylene in cyclohexane at 25°C, is slightly longer than the $\tau_2 = 1.6 \times 10^{-12}$sec. for solutions of toluene in cyclohexane at 25°C below a weight fraction of ~ 0.7. However the τ_2 value of the toluene solutions increased with increasing concentration above $w_2 = 0.7$ (see Table 4.1). It was suggested that if the τ_2 process was an intramolecular relaxation about the alkyl-aryl bond, increased local interactions between adjacent molecules might account for the variation of τ_2 in the solutions of toluene at very high concentration. This was consistent with the apparent dipole moment of toluene increasing to a constant value as changes in interactions became no longer detectable at $w_2 = \sim 0.7$. The small difference in the τ_2 of m-xylene and toluene solutions of weight fraction ~ 0.7 might be accounted for by increased local interactions in the m-xylene solution.

The free energy of activation, $\Delta G_2^{\ddagger}$, evaluated from eqn. 1.32 and the τ_2 values of toluene and m-xylene in cyclohexane solution of weight fraction $\sim$ 0.7 at 25°C, is 1.3 and 1.6 k.cal.mole^{-1} respectively. Therefore, in terms of the free energy of activation of the τ_2 process, the difference in relaxation times is small.

The τ_2 of o-xylene in cyclohexane at 25°C of 5.4×10^{-12} sec. corresponds to a free energy of activation of 2.1 k.cal.mole^{-1}. This increase in τ_2 from that of m-xylene is consistent with the process being that of an intramolecular relaxation. The steric effect of the adjacent methyl group would be expected to raise the energy barrier to relaxation about the alkyl-aryl bonds of the o-xylene compared with that of m-xylene.

With the presence of two methyl substitutents the physical significance of the C_2 value obtained from the analysis of the dielectric data of the o- and m-xylene solutions at 25°C is not readily apparent. However, the contribution of the τ_2 process to the dielectric absorption as a whole is appreciable and compares with the C_2 values of other hydrocarbon systems measured.

Although the dielectric data of o- and m-xylene solutions at 25°C are apparently described by contributions to the total dielectric absorption from a molecular re-orientation process and a shorter relaxation process probably that of relaxation about the alkyl-aryl bonds, the Cole-Cole plots at 50°C for cyclohexane solutions of both compounds show no distribution coefficients. The τ_0 of $\sim 6 \times 10^{-12}$ sec. for the o- and m-xylene solutions at 50°C is shorter than 7.9×10^{-12} sec. and 7.3×10^{-12} sec. which are the extrapolated relaxation times of molecular re-orientation of benzocyclobutene and toluene (see Table 4.1) respectively in cyclohexane at 50°C. This indicates that the τ_0 values of the o- and m-xylene solutions at 50°C are shorter than the relaxation times that would be expected for the molecular re-orientation of molecules of this size and shape in cyclohexane solutions at $w_2 = \sim 0.7$ and suggests that a short relaxation process is contributing to the dielectric absorption as a whole although the Cole-Cole plots give no indication of a distribution of relaxation times.

The zero distribution coefficient of the o- and m-xylene solutions at 50°C, although unexpected, perhaps helps to account for the Cole-Cole plots of the p-chloro- and p-bromotoluene solutions which had $\alpha = 0$ at 40°C but for which no evidence of the continued presence of a short relaxation process at 40°C could be obtained from the values of τ_0, because in these systems τ_1 approached τ_0 since $C_1 \gg C_2$ (see Chapter 6).

It is concluded that the shorter relaxation process of the o- and m-xylene solutions in cyclohexane at 25°C cannot be attributed to a relaxation mechanism relating to local aggregates of solute molecules but may be adequately described by an intramolecular relaxation process about the alkyl-aryl bonds and that the τ_0 values from the measurements at 50°C indicate that a shorter relaxation process contributes to the total dielectric absorption of the systems, although this is not apparent from the Cole-Cole plots at this temperature.

The Cole-Cole plots of 1-methyl- and 2-methylnaphthalene in cyclohexane solution at 25 and 50°C showed large distribution coefficients (see Table 7.1). Because of the long τ_0 values the experimental points lay to the left of $\epsilon''_{MAX.}$ on the Cole-Cole plots and ϵ_∞ was extrapolated to within close limits. The apparent dipole moments listed in Table 7.1, when compared with quoted values of 0.51D and 0.42D for the pure 1-methyl- and 2-methylnaphthalenes respectively and 0.23D for 1-methylnaphthalene in benzene solution at 20°C[34], are acceptable for measurements on solutions of $\sim$ 0.7 weight fraction.

Grubb and Smyth[84] reported that the Cole-Cole plots of 1-chloro- and 1-bromonaphthalene in decalin solution showed considerable distribution coefficients (all greater than 0.1) which decreased with increasing temperature over the range 20 - 60°C. Recently Fong and Smyth[85] have reported that $\alpha = 0$ for solutions of 1-fluoronaphthalene in benzene at 20, 40 and 60°C and measurements by Forest and Smyth[30] of benzene solutions of 1-chloro- and 1-bromonaphthalene at 25°C have shown that both systems are characterized by a single relaxation time of 18.2×10^{-12} sec. and 23.1×10^{-12} sec. respectively. However, the Cole-Cole plot of 1-chloronaphthalene in cyclohexane at 25°C from measurements by Magee[86] shows $\alpha = 0.06$ and $\tau_0 = 17.6 \times 10^{-12}$ sec. Measurements on 2-bromonaphthalene in cyclohexane at 25°C gave a Cole-Cole plot with a definite distribution coefficient but at 50°C $\alpha = 0$ (see Table 7.1).

The high viscosities of the methylnaphthalene solutions measured compared with those of the halonaphthalene solutions in cyclohexane (see Table 7.1) would lead to a relative increase in the observed relaxation times of the former. This difference in viscosity together with the difference in concentration makes direct comparison of the τ_0 values impossible.

Although no evidence of a shortening of the τ_0 of the methylnaphthalenes can be obtained from a consideration of the relaxation times of the related halo compounds, the results of the toluene, o- and m-xylene systems and the large distribution coefficients of the methylnaphthalene solutions at 25°C and 50°C suggest that the dielectric data of these monomethylnaphthalene systems might analyse into contributions from two relaxation processes. Because of the small but definite distribution coefficients of the Cole-Cole plots of 1-chloro- and 1-bromonaphthalene in cyclohexane solution at 25°C, it was considered that any analysis of the dielectric data of the monomethylnaphthalene systems into contributions from two Debye terms should be attempted only for those measurements carried out at 50°C.

The τ_1, τ_2 and C_1 values obtained from the analyses are given in Table 7.1. The good agreement between the calculated and experimental points gives support to the analyses (see Appendix Table 5).

The τ_1 values are such that they might be attributed to molecular re-orientation. The long τ_1 of 2-methylnaphthalene compared with 16.1×10^{-12} sec. for 2-bromonaphthalene in cyclohexane at 50°C might be accounted for by the $\sim$ 50% increase in the viscosity of the former system compared with that of the latter and also solute-solute interactions in the more concentrated solution.

The τ_2 value of 2-methylnaphthalene is comparable to that of m-xylene in cyclohexane solution. The slightly longer τ_2 of

1-methylnaphthalene is consistent with attributing the τ_2 process to an intramolecular relaxation about the alkyl-aryl bond, as the steric effect of the 8 - H atom would increase the energy barrier to relaxation about the alkyl-aryl bond in 1-methylnaphthalene.

If it is assumed that the τ_2 process can be attributed to relaxation about the alkyl-aryl bond, it can be estimated from eqn. 6.1 and the dipole moment and C_1 data given in Table 7.1 for the monomethylnaphthalenes in cyclohexane at 50°C that a mesomeric moment change along the alkyl-aryl bond of 0.27D and 0.25D for 1-methyl- and 2-methylnaphthalene respectively would accompany the τ_2 process. These values compare with the 0.33D mesomeric moment change estimated to accompany the τ_2 process of toluene when similar assumptions are made. (see Chapter 4).

It is concluded that the work presented in this chapter supports the identification of the τ_2 process of the alkyl substituted hydrocarbons with an intramolecular relaxation about the alkyl-aryl bonds. The absence of any evidence of a comparable process in the solutions of benzocyclobutene and indane does not support the suggested τ_2 mechanisms related to local aggregates of solute molecules.

Although the Cole-Cole plots of o- and m-xylene solutions at 50°C showed no evidence for a distribution of relaxation times, the τ_0 values were too short to be identified with molecular re-orientation and this indicates the continued contribution of a short relaxation process to the dielectric absorption. It was suggested that a similar effect might have been observed in the Cole-Cole plots of p-chloro- and p-bromotoluene at 40°C (see Chapter 6), although no evidence of this could be obtained from the τ_0 values of these solutions.

The τ_2 relaxation time of 1-methyl- and 2-methylnaphthalene in cyclohexane at 50°C and of o- and m-xylene in cyclohexane at 25°C was described adequately by the proposed intramolecular relaxation mechanism and supports the hypothesis that a mesomeric moment change accompanying relaxation about an alkyl-aryl bond can account for the shorter relaxation process of the alkylsubstituted hydrocarbons studied.

Chapter 8

Relaxation Processes of Some Phenylsubstituted Compounds.

Introduction

The work reported in Chapters 4 to 7 shows that contributions to the overall dielectric absorption from a short relaxation process, namely relaxation about the alkyl-aryl bond with an accompanying change in mesomeric moment along that bond, is the most plausible explanation of the short τ_0 and distribution coefficients of the alkyl-aryl hydrocarbons studied.

From this it might be anticipated that relaxation about any bond with partial double bond character, that is dependent upon the relative orientation of the groups about this bond, would be accompanied by a mesomeric moment change and if the free energy of activation of this process was of a suitable magnitude it would give rise to dielectric absorption in the microwave region. To ascertain if contributions from such an intramolecular relaxation process could be observed in the dielectric absorption of molecules other than the simple alkyl-aryl hydrocarbons previously studied, measurements of τ_0 , reported in this chapter, were carried out on some phenylsubstituted compounds in which some double bond character would be anticipated for the phenyl-central atom bond.

A difference in τ_0 and the relaxation time expected for molecular re-orientation indicates contributions by some other relaxation process (or processes). If the mesomeric moment change accompanying relaxation about the phenyl-central atom is small, the relationship $C_1/C_2 = \mu_1^2/\mu_2^2$ indicates that for molecules with a small dipole moment the relative contribution to the overall dielectric absorption by such an intramolecular relaxation process would be larger than that for molecules with a large dipole moment. Therefore any difference in τ_0 and the expected molecular re-orientation relaxation time, due to contributions from such a process, would be more readily apparent for molecules with a small dipole moment. For molecules with a large dipole moment, if there was no contributions from other relaxation processes, τ_0 would approach the molecular re-orientation relaxation time.

Di- and triphenylmethane in cyclohexane solution were also studied as it was considered that the short relaxation process of the toluene systems should also be apparent in these solutions, unless the steric effect of the neighbouring phenyl groups prevents relaxation about the alkyl-aryl bonds of these molecules.

Discussion

DiCarlo and Smyth[50] repeated earlier work of Roberti, Kalman and Smyth[51] on the dielectric absorption of pure diphenylmethane and reported τ_0 values of 13×10^{-12}sec. and 7×10^{-12}sec. at 40 and 60°C

Table 8.1 Static Dielectric Constant, High Frequency Dielectric Constant, Viscosity (η), Relaxation Time, Distribution Coefficient and Dipole Moment Data of some Phenylsubstituted Molecules.

All Measurements in this Table were at 25°C.

Solute	Solvent	w_2	ϵ_0	ϵ_∞	τ_0 $\times 10^{12}$ sec.	η (cp.)	τ_0/η	α	μ (D)
Diphenylmethane	Cyclohexane	0.88121	2.4741	2.423	8.3	2.11	3.9	0.25	0.27
		0.78691	2.4182	2.366	7.8	1.80	4.3	0.27	0.29
		0.78689	2.4058	2.363	7.2	1.80	4.0	0.24	0.27
Phenyltrimethylsilane		1.00000	2.3533	2.308	13.8	0.89	15.5	0.25	0.25
Triphenylsilane	p-Xylene	0.25962	2.4091	2.358	54	0.99	54	0.24	0.66
		0.23184	2.3908	2.346	52	0.93	56	0.21	0.66
Triphenylarsine	Cyclohexane	0.09976	2.0986	2.059	78	1.02	77	0.12	1.15

Table 8.1 Continued.

Solute	Solvent	w_2	ϵ_0	ϵ_∞	τ_0 $\times 10^{12}$ sec.	η (cp.)	τ_0/η	α	μ (D)
Triphenylphosphine	p-Xylene	0.22811	2.5779	2.353	81	0.97	83	0.15	1.45
		0.19319	2.5244	2.340	71	0.90	80	0.14	1.44
		0.15633	2.4736	2.328	63	0.82	76	0.12	1.44
Triphenylphosphineoxide	p-Xylene	0.00818	2.3352	2.267	78	0.71	110	0.19	4.63
Triphenylamine	p-Xylene	0.13679	2.3516	2.337	3 (approx.)			0	0.48 (approx.)

respectively with a distribution coefficient of 0.08 at both temperatures. They showed that the observed relaxation times are too short to result entirely from rotation of the molecule as a whole.

The Cole-Cole plots of solutions of diphenylmethane in cyclohexane at 25°C showed large distribution coefficients and the τ_0 values were short when compared with 18.5×10^{-12} sec. the relaxation time of benzophenone in dilute benzene solution at 25°C[87] (see Table 8.1). As benzophenone is approximately the same size and shape as diphenylmethane and moreover as the relatively high viscosity of the concentrated diphenylmethane solutions measured would be expected to increase the molecular re-orientation relaxation time compared with that in dilute solution, these measurements confirm that a shorter relaxation process (or processes) than that of molecular re-orientation makes an important contribution to the dielectric absorption of this system.

The work presented in Chapters 4 to 7 indicates that the mesomeric moment change accompanying relaxation about an aryl-methyl bond is ~ 0.3D and that the relaxation time associated with such a process is $\sim 2 \times 10^{-12}$ sec. The apparent dipole moment of diphenylmethane in cyclohexane is ~ 0.28D (see Table 8.1), therefore, from the relationship $C_1/C_2 = \mu_1^2/\mu_2^2$, it would be anticipated that relaxation about the alkyl-aryl bonds of diphenylmethane might result in some shortening of the mean relaxation time.

To account for the very short τ_0 of 2.8×10^{-12} sec. for diphenylether in benzene at 25°C[88], Fong[89] has proposed a mechanism of molecular re-orientation by co-ordinated internal rotations about the phenyl-oxygen bonds. Recent studies by Anderson and Smyth[90] and by Nelson and Smyth[91] have concluded that the experimental results of diphenylether and some substituted diphenylethers seem to be best explained by this double internal rotation mechanism predominating in the overall dielectric absorption of the diphenylethers. Fong[89] showed how this mechanism could account for the short τ_0 of liquid diphenylmethane.

The mechanism described by Fong, although dependent upon the energy barrier to internal rotation, results in molecular re-orientation and the weight factor of its contribution to the dielectric absorption should be independent of the dipole moment of the solute molecule. Di-p-nitrophenylmethane has a dipole moment of 4.32D in benzene solution[34] and it would be expected that contributions to the dielectric absorption from an intramolecular relaxation process with an associated mesomeric moment change of ~ 0.3D would be negligible. The energy barrier to relaxation about the alkyl-aryl bonds would be similar to that in the diphenylmethane, therefore contributions by the Fong mechanism would be anticipated to have a similar effect on the τ_0 of each molecule. Purcell and Smyth[92] have reported a mean relaxation time of 22.8×10^{-12} sec. for di-p-nitrophenylmethane in dilute benzene solution at 20°C which approaches the $\sim 25 \times 10^{-12}$ sec. anticipated for molecular re-orientation of this molecule. However the distribution coefficient of 0.11 reported by Purcell and Smyth[92] suggests that contributions from more than one relaxation process describes the dielectric absorption of di-p-nitrophenylmethane. Work at present in progress in this laboratory by Farmer[93] suggests that a shift of mesomeric charge with phenyl group rotation, as well as coupled internal rotations, contributes to the dielectric absorption of molecules of the type $(\text{phenyl})_2X$, where $X = CH_2$, O and S and that for molecules with a low dipole moment the former mechanism can offer a significant contribution.

It is concluded that the dielectric absorption of diphenylmethane is possibly more complex than that described by two discrete Debye terms. However, the large difference in τ_0 between diphenylmethane and di-p-nitrophenylmethane suggests that relaxation about the alkyl-aryl bond is at least one factor contributing to the short mean relaxation times observed for the diphenylmethane solutions.

Measurements on solutions of triphenylmethane were carried out in order to assess any significant contribution to the dielectric absorption by a short relaxation process. Unfortunately the dielectric absorption of these solutions was of the magnitude of the experimental error and even an estimate of the mean relaxation time was impossible.

The dielectric absorption of some phenylsilanes was measured to ascertain whether the relaxation times of these compounds showed a similar behaviour to the analogous carbon compounds. The atomic radii of the carbon and silicon atoms are 0.77 and 1.17 Å respectively[48] and it would be expected that the relaxation times of molecular re-orientation of the silicon compounds would be slightly longer than the corresponding carbon compounds.

The τ_0 for pure phenyltrimethylsilane at 25°C is 13.8×10^{-12} sec. (see Table 8.1) which is very short when compared with $\sim 28 \times 10^{-12}$ sec. and 23×10^{-12} sec. for the molecular re-orientation of t-butylbenzene and benzotrichloride[54] respectively in cyclohexane at 25°C, especially since the tendency of the solvent would be to shorten the relaxation time compared with the value in the pure liquid state. This indicates that some short relaxation process (or processes) makes an appreciable contribution to the dielectric absorption of phenyltrimethylsilane.

The apparent dipole moment of 0.25D obtained by the microwave technique for the pure liquid at 25°C is low when compared with 0.44D, the reported dipole moment of phenyltrimethylsilane in benzene solution at 25°C[34]. For toluene the moment was lowest in the pure liquid and gradually increased on dilution with cyclohexane (see Chapter 4). This was attributed to some antiparallel alignment of the dipoles in the pure liquid. Estimates of the dipolar contribution to the cohesive energy of pure phenyltrimethylsilane at 25°C from eqns. 4.2 and 4.3 are -0.011 and -0.026 $k.cal.mole^{-1}$ respectively, and the cohesive energy obtained from eqn. 4.6 is 10.9 $k.cal.mole^{-1}$. This small dipolar contribution to the cohesive energy compares with 0.01 $k.cal.mole^{-1}$ estimated as the dipolar contribution to the cohesive energy of t-butylbenzene. This indicates that the dipolar forces are of similar significance in both liquids. The work reported in Chapter 7 gave no support to the identification of the short relaxation process of the alkylsubstituted hydrocarbons measured with a mechanism associated with dipolar forces and it is thought that this is unlikely to be the explanation of the short τ_0 of phenyltrimethylsilane.

Dipole moment studies[94,95] of some substituted phenyltrimethylsilanes have indicated that the phenyl-silicon bond of these compounds has some double bond character. This is attributed to $d_{\pi} - p_{\pi}$ bonding in which the π-electrons of the phenyl ring enter the d-orbitals of the silicon atom[96]. If the amount of interaction of the π-cloud with the d-orbitals was dependent upon the orientation of the phenyl group, relaxation about the phenyl-silicon bond would cause a movement of charge along the bond with an associated change in mesomeric moment. Dipole moment studies[97,98] of some alkylhalosilanes have indicated that alkyl groups release electrons towards silicon atoms much more strongly than towards carbon atoms and it has been suggested that this indicates that delocalised electrons of the C-H bond can enter into the d-orbitals of the silicon atom and that there are contributions from hyperconjugated structures of the type $H^{+}CH_{2}{=}\bar{S}i{\equiv}$. The silicon-carbon bond lengths reported for the methylsilanes[99] are shorter than would be expected from the sum of the covalent radii and it has been suggested that this also could be due to some double bond character in the methyl-silicon bond[100]. If the interaction of the electrons of the C-H bonds with the d-orbitals of the silicon atom varies with the relative orientation of the methyl group, relaxation about the methyl-silicon bond would be accompanied by a change in mesomeric moment along this bond.

Relaxation about any of the bonds to the central silicon atom in phenyltrimethylsilane might be accompanied by a change in mesomeric moment and contribute to the dielectric absorption. From the relationship $C_1/C_2 = \mu_1^2/\mu_2^2$ and the low dipole moment of phenyltrimethylsilane it would be anticipated that any such intramolecular relaxation process (or processes) would have an appreciable contribution to the overall dielectric absorption. Such an effect, if characterized by a short relaxation time (e.g. $\sim 9 \times 10^{-12}$ sec. for t-butylbenzene in cyclohexane at 20°C), could lead to significant shortening of the relaxation time compared with that of a rigid molecule. If both these intramolecular processes involving rotation about the two types of carbon-silicon bond contribute to the dielectric absorption of phenyltrimethylsilane then three relaxation times may be involved. An analysis of the dielectric data given in Appendix Table 6 into contributions from three terms is not feasible.

Measurements on pure diphenyldimethylsilane were attempted, but the extremely low dielectric absorption of this compound was comparable to the experimental error and no estimate of τ_0 could be made.

The Cole-Cole plots of triphenylsilane in p-xylene at 25°C had significant distribution coefficients with $\tau_o \sim 53 \times 10^{-12}$ sec. (see Table 8.1). The measured dipole moment of 0.66D agrees with 0.66 ± 0.04D reported for triphenylsilane in carbontetrachloride solution at 25°C[34] and supports the fit of the Cole-Cole plots to the dielectric data. The mean relaxation time of triphenylsilane appears short when compared with the relaxation time of 78×10^{-12} sec. for triphenylarsine in cyclohexane at 25°C (see Table 8.1). The silicon atom is slightly smaller than arsenic, the atomic radii being 1.17 and 1.21 Å respectively[48], however the van der Waals radius of arsenic is 2.0 Å[48] and the length of the Si-H bond is 1.5 Å [96] and the van der Waals radius of the H atom is 1.2 Å [48]. From these figures it follows that triphenylsilane is greater in size than triphenylarsine. The molecules are of similar shape with the molecular moment lying along a similar axis, therefore, the molecular relaxation time of triphenylsilane should not be shorter than that of triphenylarsine and it follows that the dielectric absorption of triphenylsilane contains at least one contribution from a short relaxation process.

The measured dipole moments of triphenylsilane and triphenylarsine are 0.66D and 1.15D respectively and from the consideration given in the introduction to this chapter it would be expected that any shortening of τ_0 by contributions from an intramolecular relaxation process with an accompanying small mesomeric moment change in both molecules would be more apparent in triphenylsilane. It is considered that relaxation about the phenyl-silicon bonds might be a factor contributing to the difference in the mean relaxation times of triphenylsilane and triphenylarsine.

The data for solutions of triphenylphosphine, triphenylphosphineoxide and triphenylarsine are given in Table 8.1. The experimental points lay on the extreme high frequency side of the Cole-Cole plots and the ϵ_∞ values were extrapolated within close limits. The reported[34] dipole moments are 1.40 - 1.46D, 4.34D and 1.08D for triphenylphosphine, triphenylphosphineoxide and triphenylarsine respectively in benzene solution. Although the dipole moment of triphenylphosphine obtained from the microwave technique is comparable with the range of values quoted, there is not very good agreement between the dipole moments of triphenylphosphineoxide and triphenylarsine given in Table 8.1 and the literature values.

Errors in the τ_0 determined for these systems might be expected as the experimental points are far removed from $\epsilon''_{MAX.}$ on the Cole-Cole plot. However the mean relaxation times of triphenylphosphine and triphenylarsine compare with values reported by other workers which are given in Table 8.2.

Table 8.2 Literature Values of the Relaxation Times of Triphenylphosphine and Triphenylarsine in Solution.

Solute	Solvent	t(°C)	$\tau \times 10^{12}$ sec.	Ref.
Triphenylphosphine	Xylene	18	79	101
			63	101
	Benzene	20	71	90
			60	102
Triphenylarsine	Benzene	20	77	102
	Xylene	18	90	101

Meakins[42] has concluded that when the solute molecule is at least three times the size of the solvent molecule the Debye equation $\tau = 3V\eta/kT$ is in good agreement with experimental results. Therefore a comparison of the reduced relaxation times τ_0/η of triphenylphosphine, triphenylphosphineoxide and triphenylarsine given in Table 8.1 should be valid. From a consideration of molecular volumes it would be anticipated that the molecular re-orientation relaxation times of triphenylphosphine and triphenylarsine would be similar and that of the larger triphenylphosphineoxide molecule be longer. The reduced relaxation times follow the expected trend and from a comparison of the relaxation time of 70×10^{-12} sec.

for triphenylchloromethane in benzene at 20°C[90] it is concluded that the predominant factor in the dielectric absorption of these systems is molecular re-orientation.

Short relaxation times of $\sim 0.7 \times 10^{-12}$ sec.[102] and 2×10^{-12} sec.[50] have been reported for triphenylamine in benzene solution. The data given in Table 8.1 for triphenylamine in p-xylene at 25°C supports these short values. Because of the very low absorption of the triphenylamine solution the extrapolation of the Cole-Cole plot to ϵ_∞ was subject to large error and the τ_0 and dipole moment values given in Table 8.1 can be regarded only as approximations.

Mansel Davies[103] has concluded that the short relaxation times of aniline and related compounds are due to nitrogen inversion rather than rotation about the phenyl-nitrogen bonds and more recently Knoblock and Stockhausen[102] concluded that the short relaxation time of triphenylamine is due to dipole orientation by inversion of the molecule about the nitrogen atom.

Marsden and Sutton[104] obtained mesomeric moments of 1.12D and 1.55D for aniline and N.N. dimethylaniline respectively, which indicates a high mesomerism in the phenyl-nitrogen bonding, however, Smith[47] concluded that these values should be taken as indicative rather than absolute. Nevertheless as the dipole moment of triphenylamine is only about 0.5D a mesomeric moment change of $\sim$1D accompanying relaxation about the phenyl-nitrogen bond might be expected to have a large contribution to the dielectric absorption and have a significant effect on the value of τ_0.

In conclusion, it is interesting to compare the difference in the mean relaxation time observed with that expected for the molecular re-orientation of a rigid molecule and the measured dipole moments of the compounds studied in this chapter.

Table 8.3 Reduced Mean Relaxation Times, Relaxation Times Estimated For Molecular Re-orientation in Dilute Solution and Measured Dipole Moments for Some Phenylsubstituted Compounds.

Compound	τ_0/η	$\tau_{EXP.}$	μ
	—— $\times 10^{12}$ SEC. —		(D)
Diphenylmethane	4	20	0.28
Phenyltrimethylsilane	15	30	0.25
Triphenylamine	3	70	0.48
Triphenylsilane	55	70	0.66
Triphenylarsine	77	80	1.15
Triphenylphosphine	80	80	1.44
Triphenylphosphineoxide	110	100+	4.63

Table 8.3 summarises this data. $\tau_{EXP.}$ is an estimate of the magnitude of the molecular re-orientation relaxation times in dilute solution. To take into account the viscosity differences of the systems measured, the reduced mean relaxation times $\tau_0 | \eta$ are listed for comparison purposes instead of the observed τ_0 values.

An inspection of Table 8.3 reveals that τ_0 is short for those molecules with dipole moments less than 1D. In the introduction to this chapter it was considered that any difference in τ_0 and the relaxation time expected for molecular re-orientation, due to contributions by relaxation about the phenyl-central atom bonds, would be more readily apparent for molecules with a small dipole moment. The results in Table 8.3 show the expected trend. However, the alternative possible explanations of the short relaxation times of diphenylmethane and triphenylamine complicate the interpretation of the τ_0 values of these systems. The short mean relaxation times of triphenylsilane and especially phenyltrimethylsilane are significant as there is apparently no alternative explanation of the τ_0 values other than contributions to the dielectric absorption by a short intramolecular relaxation process.

Suggestions for Further Work.

The work presented in this thesis has shown that a short relaxation process contributed to the dielectric absorption of the alkyl-aryl hydrocarbons measured. The most plausible explanation of this process is apparently relaxation about the alkyl-aryl bond accompanied by a change in mesomeric moment along this bond. In the absence of wider background of data, further work should be done to establish this short intramolecular relaxation process.

The difficulty in examining this process is that the molecules studied must have a low dipole moment for the short relaxation process to be readily apparent. However, apart from the study of other hydrocarbons such as 1.2- and 1.3-diethylbenzene, by choice of suitably substituted molecules such as those listed below further investigation should be possible.

The Reported[34] Dipole Moments of Some Substituted Toluenes in Benzene Solution.

Compound	μ (D)
2.5 Dinitrotoluene	0.58
2.4.6 Trichlorotoluene	0.55 - 0.66
2.4.6 Tribromotoluene	0.73

Measurements on molecules with substituents ortho to the alkyl group would be valuable in characterizing the short relaxation process as an intramolecular relaxation as the relaxation times associated with that process would be expected to be longer than those of the unsubstituted compounds because of steric hindrance to relaxation about the alkyl-aryl bond.

If the interpretation of the short relaxation process is correct, the weight factor of the contribution of the short relaxation time to the dielectric absorption, expressed as C_2, provides a measurement of the mesomeric moment change along the alkyl-aryl bond from the relationship $C_1/C_2 = \mu_1^2/\mu_2^2$. Dielectric studies might therefore be unique in providing a direct measurement of mesomeric moments, or at least their lower limits, and a more extensive study is required to establish the C_2 values accurately. Ideally this would involve measurements at more frequencies than have been employed in the work reported. However as, at the moment, this is not feasible, detailed studies over a range of concentrations and temperatures would be valuable not only in helping to confirm that the short relaxation process was that of relaxation about the alkyl-aryl bond but would yield more accurate estimates of the mesomeric moment changes associated with the intramolecular relaxation process.

Two other points arising from this thesis which suggest that further investigation might be worthwhile are,

i) The short τ_0 values of phenyltrimethylsilane and triphenylsilane indicate that an interesting field of study would be afforded by dielectric measurements of other organosilicon compounds.

ii) The dielectric data of 4-methylpyridine and 4-t-butylpyridine in cyclohexane at 25°C, reported in Chapter 6, showed small but definite distribution coefficients and analysed into contributions from two relaxation times. However it was shown that the contribution of the shorter relaxation time to the dielectric absorption was too large to be explained by a shift of mesomeric charge with relaxation about the alkyl-aryl bond. No satisfactory explanation of the dielectric data was readily apparent, although it was concluded that the short relaxation process might be of dipolar origins. To obtain an explanation of these results a more rigorous investigation of these and other alkylsubstituted pyridines in a variety of solvents and over a range of temperatures will have to be carried out.

In conclusion the improved accuracy of the microwave bridge technique and its application to systems having a relatively low dielectric loss suggests that this apparatus has a great potential in the study of inter- and intramolecular relaxation processes in solution.

Appendix.

1. Tables of Experimental Results.

Tables 1 to 6 of this Appendix contain the experimental data of the systems discussed in Chapters 3 to 8 respectively.

The dielectric constants and loss factors determined by the microwave bridge technique are tabulated under $\epsilon'_{\text{MEAS.}}$ and $\epsilon''_{\text{MEAS.}}$. Whenever an analysis of the dielectric data into discrete relaxation times has been carried out, $\epsilon'_{\text{CALC.}}$ and $\epsilon''_{\text{CALC.}}$ are given which are the dielectric constants and loss factors calculated from eqns. 1.30 and 1.31 (see Chapter 1) by substitution of the τ_1, τ_2, C_1, ϵ_0 and ϵ_∞ data tabulated in the relevant chapters. Weight fraction (w_2) and density (d) data are also given in the following tables.

The following notation has been used for the solvents employed.

Cyclohexane	Cyhx.
p-Xylene	pXyl.
Carbontetrachloride	CTC.
Benzene	Benz.

Table 1. Experimental Results Discussed in Chapter 3.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Pyridine	Cyhx.	25	34.86	2.089	0.0434		
w_2 = 0.01998			23.98	2.104	0.0350		
			16.20	2.114	0.0272		
			9.313	2.123	0.0158		
Pyridine	Cyhx.	25	70.00	2.063	0.0401		
w_2 = 0.01790			34.86	2.085	0.0388		
			23.98	2.099	0.0315		
			16.20	2.104	0.0236		
			9.313	2.112	0.0145		
Pyridine	Cyhx.	50	70.00	2.036	0.0429	2.032	0.0487
w_2 = 0.02093			34.86	2.063	0.0359	2.060	0.0371
			23.98	2.075	0.0276	2.068	0.0281
			16.20	2.073	0.0208	2.072	0.0200
			9.313	2.063	0.0130	2.075	0.0118
Pyridine	Cyhx.	50	70.00	2.036	0.0411	2.030	0.0465
w_2 = 0.02014			34.86	2.058	0.0344	2.056	0.0345
			23.98	2.068	0.0267	2.063	0.0259
			16.20	2.070	0.0183	2.067	0.0183
			9.313	2.066	0.0113	2.070	0.0108

Table 1 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	$\epsilon'_{MEAS.}$	$\epsilon''_{MEAS.}$
Pyridine	Benz.	25	70.00	2.307	0.0551
w_2 = 0.01962			34.86	2.352	0.0614
			23.98	2.379	0.0573
			16.20	2.399	0.0456
			9.313	2.413	0.0281
Pyridine	pXyl.	25	70.00	2.312	0.0484
w_2 = 0.01989			34.86	2.337	0.0558
			23.98	2.357	0.0506
			16.20	2.372	0.0411
			9.313	2.387	0.0279
Pyridine	CTC.	25	70.00	2.260	0.0594
w_2 = 0.01180			34.86	2.302	0.0728
			23.98	2.332	0.0686
			16.20	2.360	0.0595
			9.313	2.382	0.0405
Thiophen	pXyl.	25	70.00	2.382	0.0662
w_2 = 0.48826			34.86	2.413	0.0628
			23.98	2.434	0.0549
			16.20	2.446	0.0452
			9.313	2.462	0.0269

Table 1 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
Thiophen	CTC.	25	70.00	2.378	0.0792		
w_2 = 0.42110			34.86	2.437	0.0816		
d = 1.1334			23.98	2.459	0.0695		
			16.20	2.478	0.0493		
			9.313	2.492	0.0346		
Furan	Cyhx.	25	70.00	2.272	0.1608		
w_2 = 0.52997			34.86	2.365	0.1170		
d = 0.8385			23.98	2.395	0.0898		
			16.20	2.417	0.0651		
			9.313	2.421	0.0328		
Camphor	Cyhx.	25	70.00	2.031	0.0324	2.031	0.0307
w_2 = 0.02136			34.86	2.050	0.0480	2.052	0.0489
			23.98	2.065	0.0521	2.070	0.0544
			16.20	2.090	0.0522	2.091	0.0526
			9.313	2.118	0.0388	2.114	0.0399
4-Cyanopyridine	pXyl.	25	70.00	2.289	0.0158	2.287	0.0131
w_2 = 0.05057			34.86	2.290	0.0251	2.292	0.0254
			23.98	2.298	0.0340	2.297	0.0351
			16.20	2.308	0.0448	2.308	0.0469
			9.313	2.334	0.0592	2.335	0.0597

Table 1 Continued

Solute	Solvent	t ($^{\circ}$C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
4-Cyanopyridine	pXyl.	25	70.00	2.295	0.0167	2.294	0.0142
$w_2 = 0.05416$.			34.86	2.296	0.0258	2.298	0.0276
			23.98	2.304	0.0356	2.304	0.0382
			16.20	2.317	0.0499	2.316	0.0510
			9.313	2.332	0.0611	2.345	0.0649

Table 2. Experimental Results Discussed in Chapter 4

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Toluene	Cyhx.	15	70.00	2.198	0.0251	2.203	0.0327
w_2 = 0.6932			34.86	2.206	0.0353	2.222	0.0349
d = 0.8366			23.98	2.223	0.0376	2.232	0.0354
			16.20	2.238	0.0359	2.243	0.0342
			9.313	2.260	0.0281	2.258	0.0275
Toluene	Cyhx.	15	70.00	2.170	0.0217	2.174	0.0279
w_2 = 0.5946			34.86	2.172	0.0294	2.188	0.0293
d = 0.8280			23.98	2.186	0.0312	2.196	0.0300
			16.20	2.199	0.0297	2.206	0.0294
			9.313	2.222	0.0234	2.219	0.0241
Toluene	-	25	34.86	2.293	0.0525	2.300	0.0527
w_2 = 1.0000			23.98	2.310	0.0567	2.319	0.0556
d = 0.8623			16.20	2.339	0.0545	2.339	0.0528
			9.313	2.364	0.0392	2.361	0.0408
Toluene	Cyhx.	25	34.86	2.252	0.0469	2.266	0.0462
w_2 = 0.9015			23.98	2.273	0.0486	2.282	0.0478
d = 0.8512			16.20	2.301	0.0473	2.298	0.0449
			9.313	2.321	0.0336	2.317	0.0347

Table 2 Continued

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Toluene	Cyhx.	25	34.86	2.211	0.0395	2.229	0.0409
w_2 = 0.7838			23.98	2.235	0.0410	2.243	0.0410
d = 0.8380			16.20	2.251	0.0388	2.256	0.0382
			9.313	2.274	0.0287	2.271	0.0294
Toluene	Cyhx.	25	70.00	2.172	0.0260	2.181	0.0331
w_2 = 0.6932			34.86	2.181	0.0346	2.198	0.0341
d = 0.8280			23.98	2.205	0.0357	2.208	0.0343
			16.20	2.216	0.0344	2.219	0.0325
			9.313	2.235	0.0250	2.232	0.0253
Toluene	Cyhx.	25	70.00	2.153	0.0216	2.153	0.0285
w_2 = 0.5946			34.86	2.155	0.0294	2.168	0.0293
d = 0.8191			23.98	2.171	0.0304	2.176	0.0295
			16.20	2.179	0.0275	2.186	0.0279
			9.313	2.199	0.0208	2.197	0.0217
Toluene	Cyhx.	25	34.86	2.124	0.0229	2.143	0.0257
w_2 = 0.4969			23.98	2.139	0.0250	2.151	0.0259
d = 0.8090			16.20	2.148	0.0238	2.159	0.0245
			9.313	2.163	0.0170	2.169	0.0191

Table 2 Continued.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Toluene	Cyhx.	25	34.86	2.105	0.0191	2.112	0.0200
w_2 = 0.4078			23.98	2.108	0.0208	2.118	0.0202
d = 0.8012			16.20	2.112	0.0192	2.125	0.0191
			9.313	2.132	0.0142	2.132	0.0148
Toluene	Cyhx.	25	34.86	2.076	0.0140	2.082	0.0146
w_2 = 0.2996			23.98	2.078	0.0147	2.086	0.0147
d = 0.7930			16.20	2.082	0.0136	2.091	0.0139
			9.313	2.099	0.0097	2.096	0.0108
Toluene	Cyhx.	25	34.86	2.059	0.0096	2.064	0.0099
w_2 = 0.2141			23.98	2.059	0.0103	2.066	0.0099
d = 0.7832			16.20	2.065	0.0103	2.070	0.0094
			9.313	2.074	0.0071	2.073	0.0073
Toluene	Cyhx.	40	70.00	2.155	0.0292	2.167	0.0317
w_2 = 0.6932			34.86	2.172	0.0340	2.182	0.0335
d = 0.8145			23.98	2.185	0.0352	2.193	0.0339
			16.20	2.196	0.0292	2.204	0.0315
			9.313	2.216	0.0205	2.216	0.0237

Table 2 Continued

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Toluene	Cyhx.	40	70.00	2.215	0.0255	2.137	0.0270
w_2 = 0.5946			34.86	2.135	0.0280	2.150	0.0286
d = 0.8052			23.98	2.145	0.0283	2.159	0.0289
			16.20	2.161	0.0252	2.168	0.0269
			9.313	2.181	0.0172	2.179	0.0202
Toluene	Cyhx.	60	70.00	2.118	0.0264	2.129	0.0294
w_2 = 0.6932			34.86	2.139	0.0314	2.144	0.0306
d = 0.7966			23.98	2.148	0.0294	2.153	0.0296
			16.20	2.161	0.0249	2.163	0.0259
			9.313	2.171	0.0165	2.171	0.0182
Toluene	Cyhx.	60	70.00	2.087	0.0219	2.100	0.0249
w_2 = 0.5946			34.86	2.108	0.0261	2.113	0.0259
d = 0.7869			23.98	2.122	0.0256	2.121	0.0250
			16.20	2.122	0.0209	2.129	0.0219
			9.313	2.134	0.0137	2.137	0.0154
Toluene	pXyl.	25	34.86	2.275	0.0374	2.299	0.0377
w_2 = 0.6999			23.98	2.289	0.0395	2.309	0.0380
d = 0.8606			16.20	2.315	0.0384	2.322	0.0359
			9.313	2.337	0.0276	2.336	0.0279

Table 2 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Toluene	CTC.	25	34.86	2.275	0.0336	2.278	0.0334
w_2 = 0.4817			23.98	2.292	0.0358	2.289	0.0351
d = 1.1279			16.20	2.305	0.0358	2.300	0.0353
			9.313	2.319	0.0264	2.316	0.0316
Ethylbenzene	–	25	70.00	2.254	0.0320	2.255	0.0313
w_2 = 1.0000			34.86	2.271	0.0470	2.273	0.0511
d = 0.8626			23.98	2.286	0.0581	2.290	0.0603
			16.20	2.309	0.0668	2.311	0.0662
			9.313	2.349	0.628	2.343	0.0660
Ethylbenzene	Cyhx.	25	34.86	2.174	0.0302	2.175	0.0326
w_2 = 0.7003			23.98	2.182	0.0366	2.186	0.0399
d = 0.8300			16.20	2.200	0.0476	2.201	0.0449
			9.313	2.235	0.0407	2.224	0.0438
Ethylbenzene	Cyhx.	25	70.00	2.140	0.0168	2.141	0.0155
w_2 = 0.6027			34.86	2.150	0.0262	2.150	0.0271
d = 0.8205			23.98	2.156	0.0315	2.159	0.0334
			16.20	2.165	0.0356	2.171	0.0379
			9.313	2.198	0.0342	2.191	0.0371

Table 2 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Isopropylbenzene	-	25	70.00	2.243	0.0251	2.234	0.0226
w_2 =, 1.0000			34.86	2.242	0.0374	2.245	0.0405
d = 0.8575			23.98	2.252	0.0472	2.256	0.0514
			16.20	2.280	0.0616	2.274	0.0612
			9.313	2.320	0.0663	2.307	0.0671
Isopropylbenzene	Cyhx.	25	34.86	2.152	0.0252	2.159	0.0271
w_2 = 0.7004			23.98	2.166	0.0322	2.168	0.0330
d = 0.8277			16.20	2.182	0.0372	2.179	0.0380
			9.313	2.207	0.0421	2.197	0.0419
Isopropylbenzene	Cyhx.	25	70.00	2.137	0.0156	2.133	0.0122
w_2 = 0.6035			34.86	2.140	0.0218	2.139	0.0215
d = 0.8188			23.98	2.145	0.0265	2.145	0.0271
			16.20	2.156	0.0321	2.155	0.0320
			9.313	2.176	0.0349	2.172	0.0345
t-Butylbenzene	-	25	70.00	2.238	0.0183	2.241	0.0144
w_2 = 1.0000			34.86	2.241	0.0274	2.247	0.0265
d = 0.8624			23.98	2.256	0.0340	2.254	0.0347
			16.20	2.266	0.0419	2.265	0.0434
			9.313	2.287	0.0544	2.287	0.0528

Table 2 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
t-Butylbenzene	Cyhx.	25	34.86	2.156	0.0164	2.158	0.0169
w_2 = 0.6931			23.98	2.164	0.0225	2.163	0.0226
d = 0.8307			16.20	2.172	0.0286	2.170	0.0287
			9.313	2.192	0.0359	2.185	0.0351
t-Butylbenzene	Cyhx.	25	70.00	2.128	0.0096	2.128	0.0080
w_2 = 0.5927			34.86	2.133	0.0144	2.131	0.0146
d = 0.8213			23.98	2.139	0.0192	2.135	0.0189
			16.20	2.143	0.0242	2.141	0.0234
			9.313	2.165	0.0292	2.152	0.0286

Table 3. Experimental Results discussed in Chapter 5.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
Fluorobenzene	pXyl.	15	70.00	2.308	0.0307	2.302	0.0297
w_2 = 0.04418			34.86	2.319	0.0454	2.323	0.0457
			23.98	2.341	0.0489	2.340	0.0494
			16.20	2.362	0.0470	2.359	0.0462
			9.313	2.382	0.0336	2.377	0.0339
Fluorobenzene	pXyl.	60	70.00	2.224	0.0339	2.230	0.0326
w_2 = 0.04290			34.86	2.262	0.0376	2.254	0.0388
			23.98	2.273	0.0343	2.268	0.0352
			16.20	2.277	0.0272	2.278	0.0281
			9.313	2.289	0.0177	2.285	0.0180
Chlorobenzene	pXyl.	15	70.00	2.301	0.0289	2.300	0.0260
w_2 = 0.05042			34.86	2.313	0.0440	2.314	0.0456
			23.98	2.329	0.0536	2.330	0.0559
			16.20	2.355	0.0632	2.353	0.0612
			9.313	2.386	0.0533	2.384	0.0539
Chlorobenzene	pXyl.	60	70.00	2.225	0.0306	2.225	0.0315
w_2 = 0.05010			34.86	2.246	0.0453	2.247	0.0457
			23.98	2.267	0.0490	2.265	0.0472
			16.20	2.284	0.0412	2.282	0.0422
			9.313	2.303	0.0318	2.297	0.0297

Table 3 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Bromobenzene	pXyl.	15	70.00	2.294	0.0155	2.291	0.0136
w_2 = 0.04849			34.86	2.298	0.0252	2.297	0.0253
			23.98	2.300	0.0330	2.305	0.0333
			16.20	2.322	0.0404	2.317	0.0406
			9.313	2.342	0.0396	2.341	0.0427
Bromobenzene	pXyl.	60	70.00	2.214	0.0187	2.214	0.0196
w_2 = 0.05018			34.86	2.226	0.0303	2.227	0.0315
			23.98	2.244	0.0350	2.239	0.0354
			16.20	2.257	0.0351	2.253	0.0346
			9.313	2.276	0.0274	2.268	0.0265
Iodobenzene	pXyl.	15	70.00	2.301	0.0100	2.297	0.0075
w_2 = 0.05700			34.86	2.301	0.0151	2.299	0.0144
			23.98	2.303	0.0198	2.303	0.0197
			16.20	2.309	0.0268	2.309	0.0255
			9.313	2.322	0.0303	2.324	0.0303
Iodobenzene	pXyl.	60	70.00	2.215	0.0120	2.218	0.0130
w_2 = 0.06561			34.86	2.231	0.0213	2.226	0.0222
			23.98	2.240	0.0267	2.234	0.0264
			16.20	2.246	0.0292	2.245	0.0278
			9.313	2.265	0.0261	2.258	0.0233

Table 3 Continued.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Nitrobenzene	pXyl.	15	70.00	2.311	0.0430	2.302	0.0418
w_2 = 0.01988			34.86	2.319	0.0752	2.321	0.0774
			23.98	2.343	0.0964	2.344	0.1012
			16.20	2.392	0.1260	2.392	0.1227
			9.313	2.453	0.1315	2.453	0.1304
Nitrobenzene	pXyl.	60	70.00	2.236	0.0549	2.234	0.0526
w_2 = 0.02005			34.86	2.262	0.0878	2.266	0.0894
			23.98	2.302	0.1053	2.299	0.1058
			16.20	2.347	0.1121	2.341	0.1103
			9.313	2.394	0.0896	2.394	0.0913
Benzonitrile	pXyl.	15	70.00	2.310	0.0440	2.300	0.0415
w_2 = 0.02022			34.86	2.319	0.0758	2.316	0.0786
			23.98	2.339	0.1016	2.336	0.1056
			16.20	2.388	0.1364	2.372	0.1344
			9.313	2.453	0.1599	2.445	0.1578
Benzonitrile	pXyl.	60	70.00	2.232	0.0558	2.231	0.0567
w_2 = 0.02039			34.86	2.265	0.0959	2.264	0.0979
			23.98	2.301	0.1207	2.298	0.1184
			16.20	2.347	0.1348	2.343	0.1288
			9.313	2.418	0.1204	2.406	0.1190

Table 3 Continued.

Solute	Solvent	t ($^{\circ}$C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
Nitrobenzene	Cyhx.	25	70.00	2.032	0.0515	2.037	0.0474
w_2 = 0.01959			34.86	2.069	0.0790	2.065	0.0806
			23.98	2.099	0.0959	2.094	0.0959
			16.20	2.136	0.1017	2.131	0.1018
			9.313	2.183	0.0907	2.179	0.0897
Nitrobenzene	CTC.	15	70.00	2.273	0.0392	2.272	0.0375
w_2 = 0.01102			34.86	2.289	0.0708	2.287	0.0707
			23.98	2.303	0.0920	2.306	0.0946
			16.20	2.350	0.1176	2.340	0.1191
			9.313	2.402	0.1330	2.406	0.1352
Benzonitrile	Cyhx.	15	70.00	2.061	0.0467	2.056	0.0433
w_2 = 0.02033			34.86	2.080	0.0768	2.076	0.0793
			23.98	2.109	0.1003	2.100	0.1024
			16.20	2.145	0.1192	2.138	0.1220
			9.313	2.209	0.1289	2.203	0.1273

Table 4. Experimental Results Discussed in Chapter 6.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
p-Chlorotoluene	Cyhx.	15	70.00	2.052	0.0189	2.052	0.0182
w_2 = 0.05089			34.86	2.055	0.0299	2.058	0.0311
			23.98	2.064	0.0422	2.065	0.0414
			16.20	2.086	0.0539	2.079	0.0535
			9.313	2.108	0.0643	2.109	0.0648
p-Chlorotoluene	Cyhx.	25	70.00	2.034	0.0209	2.039	0.0202
w_2 = 0.05087			34.86	2.044	0.0327	2.048	0.0329
			23.98	2.052	0.0425	2.056	0.0426
			16.20	2.077	0.0551	2.078	0.0533
			9.313	2.098	0.0604	2.101	0.0602
p-Chlorotoluene	Cyhx.	32.5	70.00	2.020	0.0201	2.025	0.0199
w_2 = 0.05089			34.86	2.040	0.0350	2.034	0.0352
			23.98	2.044	0.0475	2.044	0.0458
			16.20	2.065	0.0559	2.061	0.0558
			9.313	2.088	0.0600	2.092	0.0592
p-Chlorotoluene	Cyhx.	40	70.00	2.021	0.0227	2.014	0.0204
w_2 = 0.05397			34.86	2.024	0.0378	2.023	0.0376
			23.98	2.035	0.0477	2.035	0.0489
			16.20	2.059	0.0579	2.053	0.0583
			9.313	2.086	0.0601	2.086	0.0589

Table 4 Continued.

Solute	Solvent	t ($^{\circ}$C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
p-Chlorotoluene	pXyl.	25	70.00	2.279	0.0231	2.286	0.0223
w_2 = 0.05093			34.86	2.289	0.0375	2.295	0.0374
			23.98	2.299	0.0509	2.304	0.0504
			16.20	2.321	0.0632	2.320	0.0622
			9.313	2.355	0.0744	2.356	0.0738
p-Chlorotoluene	pXyl.	40	70.00	2.259	0.0235	2.253	0.0225
w_2 = 0.05093			34.86	2.260	0.0410	2.263	0.0419
			23.98	2.275	0.0558	2.275	0.0550
			16.20	2.299	0.0673	2.296	0.0668
			9.313	2.328	0.0704	2.334	0.0695
p-Bromotoluene	Cyhx.	15	70.00	2.054	0.0158	2.054	0.0155
w_2 = 0.06831			34.86	2.056	0.0258	2.059	0.0261
			23.98	2.063	0.0348	2.065	0.0350
			16.20	2.081	0.0468	2.074	0.0465
			9.313	2.097	0.0614	2.099	0.0614
p-Bromotoluene	Cyhx.	25	70.00	2.033	0.0137	2.033	0.0121
w_2 = 0.05497			34.86	2.034	0.0216	2.037	0.0221
			23.98	2.038	0.0298	2.042	0.0299
			16.20	2.048	0.0391	2.051	0.0395
			9.313	2.075	0.0508	2.073	0.0500

Table 4 Continued.

Solute	Solvent	t ($^{\circ}$C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
p-Bromotoluene	Cyhx.	32.5	70.00	2.023	0.0169	2.028	0.0164
w_2 = 0.06831			34.86	2.039	0.0296	2.034	0.0294
			23.98	2.041	0.0396	2.041	0.0392
			16.20	2.058	0.0502	2.054	0.0503
			9.313	2.079	0.0608	2.083	0.0594
p-Bromotoluene	Cyhx.	40	70.00	2.016	0.0177	2.012	0.0159
w_2 = 0.06716			34.86	2.016	0.0298	2.019	0.0302
			23.98	2.028	0.0394	2.027	0.0405
			16.20	2.042	0.0512	2.041	0.0511
			9.313	2.070	0.0583	2.071	0.0574
p-Bromotoluene	pXyl.	25	70.00	2.279	0.0191	2.284	0.0198
w_2 = 0.06811			34.86	2.289	0.0336	2.291	0.0333
			23.98	2.295	0.0443	2.299	0.0435
			16.20	2.316	0.0576	2.311	0.0565
			9.313	2.339	0.0723	2.341	0.0726
p-Bromotoluene	pXyl.	40	70.00	2.255	0.0202	2.250	0.0187
w_2 = 0.06811			34.86	2.255	0.0353	2.257	0.0357
			23.98	2.270	0.0483	2.267	0.0484
			16.20	2.289	0.0615	2.283	0.0623
			9.313	2.317	0.0720	2.320	0.0728

Table 4 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
p-Nitrotoluene	Cyhx.	15	70.00	2.048	0.0304	2.048	0.0253
w_2 = 0.01995			34.86	2.060	0.0499	2.056	0.0491
			23.98	2.071	0.0674	2.067	0.0677
			16.20	2.103	0.0896	2.088	0.0901
			9.313	2.143	0.1146	2.138	0.1143
p-Nitrotoluene	Cyhx.	25	70.00	2.034	0.0316	2.032	0.0286
w_2 = 0.02015			34.86	2.044	0.0544	2.042	0.0549
			23.98	2.063	0.0750	2.055	0.0747
			16.20	2.080	0.0934	2.080	0.0970
			9.313	2.141	0.1169	2.136	0.1136
p-Nitrotoluene	Cyhx.	32.5	70.00	2.025	0.0335	2.023	0.0301
w_2 = 0.01995			34.86	2.040	0.0578	2.035	0.0572
			23.98	2.049	0.0771	2.049	0.0772
			16.20	2.086	0.0953	2.076	0.0984
			9.313	2.129	0.1125	2.133	0.1132
p-Nitrotoluene	Cyhx.	40	70.00	2.017	0.0348	2.017	0.0313
w_2 = 0.01990			34.86	2.025	0.0595	2.029	0.0591
			23.98	2.045	0.0789	2.046	0.0788
			16.20	2.077	0.0990	2.075	0.0986
			9.313	2.126	0.1085	2.132	0.1085

Table 4 Continued.

Solute	Solvent	t (^{o}C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
p-Nitrotoluene	pXyl.	25	70.00	2.293	0.0337	2.284	0.0289
w_2 = 0.02001			34.86	2.296	0.0560	2.298	0.0562
			23.98	2.306	0.0769	2.305	0.0779
			16.20	2.339	0.1034	2.328	0.1045
			9.313	2.386	0.1357	2.386	0.1354
p-Nitrotoluene	pXyl.	40	70.00	2.264	0.0355	2.260	0.0325
w_2 = 0.02001			34.86	2.274	0.0628	2.271	0.0625
			23.98	2.290	0.0849	2.286	0.0855
			16.20	2.325	0.1111	2.315	0.1119
			9.313	2.370	0.1323	2.379	0.1357
4-Methylpyridine	Cyhx.	25	70.00	2.038	0.0358	2.041	0.0357
w_2 = 0.01999			34.86	2.054	0.0520	2.063	0.0514
			23.98	2.068	0.0560	2.082	0.0563
			16.20	2.101	0.0530	2.103	0.0544
			9.313	2.129	0.0397	2.126	0.0414
4-Methylpyridine	Cyhx.	25	70.00	2.041	0.0565	2.053	0.0568
w_2 = 0.02996			34.86	2.070	0.0780	2.088	0.0782
			23.98	2.101	0.0842	2.115	0.0847
			16.20	2.147	0.0811	2.147	0.0825
			9.313	2.185	0.0605	2.182	0.0643

Table 4 Continued.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$	$\epsilon'_{\text{CALC.}}$	$\epsilon''_{\text{CALC.}}$
4-t-Butylpyridine	Cyhx.	25	70.00	2.022	0.0132	2.020	0.0131
w_2 = 0.01856			34.86	2.027	0.0215	2.026	0.0219
			23.98	2.035	0.0292	2.031	0.0278
			16.20	2.041	0.0357	2.040	0.0346
			9.313	2.066	0.0403	2.059	0.0412

Table 5. Experimental Results Discussed in Chapter 7.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
Benzocyclobutene	Cyhx.	20	70.00	2.309	0.0314	2.322	0.0278
w_2 = 0.78921			34.86	2.332	0.0481	2.337	0.0501
d = 0.9156			23.98	2.356	0.0611	2.353	0.0633
			16.20	2.387	0.0728	2.378	0.0725
Benzocyclobutene	Cyhx.	40	70.00	2.275	0.0329	2.295	0.0324
w_2 = 0.78921			34.86	2.311	0.0523	2.315	0.0554
d = 0.8970			23.98	2.335	0.0645	2.335	0.0660
			16.20	2.370	0.0720	2.361	0.0694
o-Xylene	Cyhx.	25	70.00	2.211	0.0523	2.204	0.0547
w_2 = 0.69932			34.86	2.239	0.0817	2.240	0.0834
d = 0.8394			23.98	2.268	0.0927	2.270	0.0920
			16.20	2.319	0.0910	2.304	0.0912
			9.313	2.341	0.0726	2.344	0.0745
o-Xylene	Cyhx.	50	70.00	2.167	0.0562		
w_2 = 0.71108			34.86	2.222	0.0819		
d = 0.8197			23.98	2.255	0.0875		
			16.20	2.293	0.0763		
			9.313	2.305	0.0566		

Table 5 Continued.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
m-Xylene	Cyhx.	25	70.00	2.168	0.0179	2.173	0.0182
w_2 = 0.69151			34.86	2.182	0.0251	2.185	0.0270
d = 0.8276			23.98	2.186	0.0284	2.194	0.0295
			16.20	2.202	0.0300	2.204	0.0297
			9.313	2.227	0.0247	2.218	0.0255
m-Xylene	Cyhx.	50	70.00	2.138	0.0187		
w_2 = 0.71759			34.86	2.154	0.0266		
d = 0.8093			23.98	2.174	0.0291		
			16.20	2.190	0.0264		
			9.313	2.191	0.0177		
o-Dichlorobenzene	Cyhx.	25	70.00	2.040	0.0292	2.038	0.0281
w_2 = 0.04128			34.86	2.055	0.0475	2.055	0.0484
			23.98	2.072	0.0584	2.072	0.0580
			16.20	2.104	0.0610	2.095	0.0615
			9.313	2.125	0.0520	2.126	0.0520
m-Dichlorobenzene	Cyhx.	25	70.00	2.046	0.0242	2.046	0.0225
w_2 = 0.08096			34.86	2.059	0.0396	2.059	0.0393
			23.98	2.072	0.0488	2.073	0.0479
			16.20	2.099	0.0522	2.092	0.0520
			9.313	2.114	0.0468	2.118	0.0454

Table 5 Continued

Solute	Solvent	t ($^\circ$C)	Frequency (Gc/sec.)	ϵ' MEAS.	ϵ'' MEAS.	ϵ' CALC.	ϵ'' CALC.
1-Methyl-naphthalene	Cyhx.	25	70.00	2.376	0.0178		
			34.86	2.383	0.0255		
w_2 = 0.69751			23.98	2.390	0.0309		
d = 0.9293			16.20	2.409	0.0368		
			9.313	2.424	0.0489		
1-Methyl-naphthalene	Cyhx.	25	70.00	2.319	0.0156		
			34.86	2.322	0.0240		
w_2 = 0.59972			23.98	2.327	0.0278		
d = 0.9035			16.20	2.335	0.0330		
			9.313	2.356	0.0425		
1-Methyl-naphthalene	Cyhx.	50	70.00	2.344	0.0200	2.346	0.0203
			34.86	2.361	0.0302	2.357	0.0315
w_2 = 0.70466			23.98	2.367	0.0372	2.366	0.0370
d = 0.9118			16.20	2.381	0.0442	2.376	0.0428
			9.313	2.391	0.0498	2.396	0.0506
2-Methyl-naphthalene	Cyhx.	25	70.00	2.385	0.0148		
			34.86	2.383	0.0207		
w_2 = 0.69540			23.98	2.385	0.0257		
d = 0.9200			16.20	2.389	0.0280		
			9.313	2.408	0.0408		

Table 5 Continued.

Solute	Solvent	t ($^{\circ}$C)	Frequency (Gc/sec.)	ϵ' meas.	ϵ'' meas.	ϵ' calc.	ϵ'' calc.
2-Methyl-naphthalene	Cyhx.	50	70.00	2.322	0.0189	2.335	0.0187
			34.86	2.346	0.0237	2.344	0.0247
w_2 = 0.69651.			23.98	2.356	0.0281	2.350	0.0282
d = 0.8995			16.20	2.364	0.0333	2.357	0.0332
			9.313	2.371	0.0415	2.372	0.0412
2-Bromo-naphthalene	Cyhx.	25	70.00	2.049	0.0144		
			34.86	2.050	0.0231		
w_2 = 0.08356			23.98	2.065	0.0322		
d = 0.7975			16.20	2.078	0.0418		
			9.313	2.092	0.0538		
2-Bromo-haphthalene	Cyhx.	50	70.00	2.016	0.0179	2.019	0.0165
			34.86	2.031	0.0305	2.025	0.0310
w_2 = 0.09164			23.98	2.041	0.0414	2.034	0.0413
d = 0.7764			16.20	2.051	0.0514	2.049	0.0518
			9.313	2.071	0.0590	2.078	0.0579

Table 6. Experimental Results Discussed in Chapter 8.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$
Diphenylmethane	Cyhx.	25	70.00	2.439	0.0137
w_2 = 0.88121			34.86	2.433	0.0153
d = 0.9683			23.98	2.434	0.0163
			16.20	2.455	0.0172
			9.313	2.460	0.0146
Diphenylmethane	Cyhx.	25	70.00	2.380	0.0133
w_2 = 0.78691			34.86	2.379	0.0154
d = 0.9443			23.98	2.387	0.0164
			16.20	2.399	0.0174
			9,313	2.403	0.0138
Diphenylmethane	Cyhx.	25	70.00	2.374	0.0119
w_2 = 0.78689			34.86	2.373	0.0131
d = 0.9443			23.98	2.375	0.0136
			16.20	2.400	0.0144
			9.313	2.390	0.0116
Phenyltrimethylsilane	-	25	34.86	2.317	0.0119
			23.98	2.320	0.0128
w_2 = 1.0000			16.20	2.329	0.0156
d = 0.8651			9.313	2.339	0.0145

Table 6 Continued.

Solute	Solvent	t (°C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$
Triphenylsilane	pXyl.	25	34.86	2.359	0.0059
w_2 = 0.25962			23.98	2.363	0.0080
d = 0.9034			16.20	2.366	0.0116
			9.313	2.371	0.0123
Triphenylsilane	pXyl.	25	34.86	2.345	0.0051
w_2 = 0.23184			23.98	2.351	0.0074
d = 0.8979			16.20	2.355	0.0101
			9.313	2.355	0.0114
Triphenylarsine	Cyhx.	25	34.86	2.059	0.0031
w_2 = 0.09976			23.98	2.060	0.0039
d = 0.8064			16.20	2.061	0.0062
			9.313	2.064	0.0086
Triphenyl-phosphine	pXyl.	25	34.86	2.356	0.0174
			23.98	2.363	0.0243
w_2 = 0.22811			16.20	2.366	0.0335
d = 0.9059			9.313	2.382	0.0489
Triphenyl-phosphine	pXyl.	25	34.86	2.346	0.0159
			23.98	2.342	0.0212
w_2 = 0.19319			16.20	2.354	0.0303
d = 0.8981			9.313	2.366	0.0430

Table 6 Continued.

Solute	Solvent	t ($^{\circ}$C)	Frequency (Gc/sec.)	$\epsilon'_{\text{MEAS.}}$	$\epsilon''_{\text{MEAS.}}$
Triphenyl-phosphine	pXyl.	25	34.86	2.331	0.0136
			23.98	2.337	0.0178
w_2 = 0.15633			16.20	2.338	0.0264
d = 0.8899			9.313	2.347	0.0371
Triphenyl-phosphineoxide	pXyl.	25	34.86	2.271	0.0055
			23.98	2.273	0.0080
w_2 = 0.00818			16.20	2.273	0.0123
			9.313	2.274	0.0150
Triphenylamine	pXyl.	25	70.00	2.344	0.0069
w_2 = 0.13679			34.86	2.345	0.0063
d = 0.8676			23.98	2.348	0.0056
			16.20	2.350	0.0041
			9.313	2.351	0.0020

2. Published Work

The following papers have been published, reprints of which are enclosed in the pocket inside the back cover.

i) New Microwave Procedure for Determining Dipole Moments and Relaxation Times.

W.F.Hassell, M.D.Magee, Miss.S.W.Tucker and S.Walker.

Tetrahedron, 20, 2137, (1964)

ii) Dielectric Studies, Part 4:- Relaxation Processes of Four Monoalkylbenzenes.

W.F.Hassell and S.Walker. Trans. Far. Soc., 62, 861, (1966)

iii) Dielectric Studies, Part 11:- Relaxation Processes of Six Monosubstituted Benzenes in Dilute Solution.

W.F.Hassell and S.Walker. Trans. Far. Soc., 62, 2695, (1966)

The following papers have been prepared for publication.

i) Dielectric Studies, Part 15:- Molecular and Additional Relaxation Process(es) of Some Phenylsubstituted Compounds.

W.F.Hassell, A.W.P.Jarvie and S.Walker.

ii) Dielectric Studies, Part 16:- Relaxation Processes of Some Small Solute Molecules in Solution.

W.F.Hassell and S.Walker.

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NEW MICROWAVE PROCEDURE FOR DETERMINING DIPOLE MOMENTS AND RELAXATION TIMES

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PART 11.—RELAXATION PROCESSES OF SIX MONOSUBSTITUTED BENZENES IN DILUTE SOLUTION