NEW MICROWAVE PROCEDURE FOR DETERMINING DIPOLE MOMENTS AND RELAXATION TIMES

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

Chemistry Department, College of Advanced Technology, Birmingham

Abstract—An improved bridge technique for dielectric absorption work at microwave frequencies has been evolved which yields electric dipole moments of polar solutes in non-polar solvents in excellent agreement with those derived by the Halverstadt and Kumler[1] approach in which the dielectric constant measurements are carried out at 1 Mc/s. An equation—based on Debye theory—has been developed to evaluate dipole moments, from microwave results for molecules with a single relaxation time. This equation does not involve atomic polarization approximations, and hence, might be expected to yield slightly lower moments than the Halverstadt–Kumler approach. This has proved to be so for bromobenzene in cyclohexane and pyridine in carbon tetrachloride. The relaxation time values are similar to those obtained by some of the other methods. On the whole, the dielectric data resulting from these measurements would seem not to be inferior to the other methods in current practice. In contrast to the impedance methods this approach should have certain appeal to physical-organic chemists because it involves more straightforward measurement and readily appreciated theory. The potential of dielectric absorption work for studying molecular interaction is considered briefly, particularly the use in examining the nature of intermolecular complexes and dipolar interaction at different concentrations. It would seem that such work has a unique approach to certain problems but has, so far, been surprisingly neglected.

INTRODUCTION

Numerous methods[2] of measuring the dielectric absorption of solutions at microwave frequencies have been known for almost twenty years. Although the method yields electric dipole moments and relaxation times, it has rarely found favour with chemists—especially for the evaluation of the former. Of the tried methods the ones which appeared to give the most reasonable relaxation time value with no serious approximations in the theory were those involving the measurement of impedance. On the whole, this is not a procedure of ready appeal to the chemist who prefers a somewhat more pictorial concept of waves. Partly with this in mind and also with a view to an improved accuracy we sought an approach which involved the attenuation and phase shift of the wave by the solution. From the measurement of this at more than one wavelength at a fixed temperature it then becomes feasible, in the case of simple molecules, to evaluate the dielectric constant, loss factor, relaxation time and electric dipole moment. The alternative approach of keeping the wavelength fixed and varying the temperature was not considered suitable since our object was to study molecular interaction which is itself temperature dependent. Apart from the work reported in 1946, we can find little trace of any dipole moment determination on solutions employing the microwave technique; this is not quite true, however, of relaxation times, although even here no significant bulk of data exists for dilute solutions. For pure liquids, though Smyth

[1] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.* **64**, 2988 (1942).
[2] C. G. Montgomery, *Technique of Microwave Measurements* Vol II. Radiation Laboratory Series. McGraw-Hill, New York (1947).

et al.[3] have made a major contribution to their study by means of relaxation times, and have made also some investigations of dilute solutions.[4] Scarcely any information appears to be available on intermediate concentrations.

With regard to the correspondence of dipole moments and also relaxation times (for a polar solute in a non-polar solvent) obtained by different workers, in the microwave region, the agreement on the whole has been fairly poor. The majority of results embodying both dipole moment and relaxation time as determined by one set of workers are listed in Table 1. These results were obtained by three sets of workers

TABLE 1. COMPARSION OF RELAXATION TIMES AND DIPOLE MOMENTS (IN D) BY MICROWAVE METHODS BY DIFFERENT WORKERS. THE DIPOLE MOMENTS ARE ALSO COMPARED WITH LITERATURE VALUES OBTAINED BY THE HALVERSTADT AND KUMLER APPROACH. BENZENE WAS THE SOLVENT IN ALL CASES

Solute	μ_{1it}	μ_M	$\tau \times 10^{12}$sec	Reference
Benzophenone		3·04	16·4	5
		2·88	22	6
		2·81	18·1	7
Nitrobenzene	4·01	3·96	11·6	5
		3·75	11·5	6
		3·88	13·0	7
Bromobenzene	1·55	1·64	10·5	5
		1·51	10	6
Chloroform	1·22	1·13	7·7	5
		1·23	2·4	6
Chlorobenzene	1·58	1·52	7·5	6
		1·51	10·8	7
Acetone	2·76*	2·58	3·2	6
		2·6	3·3	7
Ethyl benzoate		1·85	12	6
		2·02	17·6	7
Methyl benzoate	1·84	1·84	12	6
		1·83	13·0	7
Cyclohexanone		3·02	6·5	6
		2·90	10·5	7
Nitromethane	3·20	2·87	3·9	6
		2·81	4·36	7
Methyl acetate	1·67	1·65	3·1	6
		1·58	3·73	7

* See later in Discussion with regard to this value.

employing a resonant cavity (Jackson et al.[5]), a resonant cavity and a transmission method (Whiffen and Thompson[6]), and an impedance method (Cripwell and Sutherland[7]). No consistent agreement occurs between any two groups of these workers. In fact, only in the case of acetone and methyl benzoate is there a reasonable

[3] C. P. Smyth, Dielectric Behaviour and Structure. McGraw-Hill, New York and London (1955).

[4] W. Heston Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, J. Amer. Chem. Soc. 72, 3443 (1950).

[5] W. Jackson and J. G. Powles, Trans. Far. Soc. A42, 101 (1946). This work was carried out at 19 ± 1°.

[6] D. H. Whiffen and H. W. Thompson, Trans. Far. Soc. A42, 114 (1946). This work was carried out at 19 ± 1°.

[7] F. J. Cripwell and G. B. M. Sutherland, Trans. Far. Soc. A42, 149 (1946). This work was carried out at 18·5 ± 1°.

agreement for both the dipole moment and relaxation time by two sets of workers, but even with the acetone the moment appears much too low when compared with the non-microwave method.

In column 2 we have inserted the dipole moments determined by the non-microwave approach as quoted by Smith[8] and again no one set of microwave workers emerges as giving good agreement. It would seem that the accuracy achieved by these workers cannot compare with that obtained by the now traditional Halverstadt and Kumler approach—based on dielectric constant measurements at 1Mc/s of which the quoted accuracy is $\pm 0\cdot 01$D.

A variety of reasons may well be involved in explaining the divergences by different workers using different methods in the microwave region. It seemed that a detailed study of a few systems by one group of workers was required.

Of the methods available for the measurement of attenuation and phase shift of solutions the bridge method is one of the most straightforward. However, with a few exceptions[9,10] it has found little favour and appears never to have been employed in dipole moment determination.

In principle and practice the method is simple. Possibly what has deterred workers from its use in the accurate measurement of dielectric loss of solutions is that the method involves use of a variable attenuator and a variable phase shifter: adjustment of the attenuator introduces phase shift while alteration of the phase shifter adds unwanted attenuation. As regards the latter, even the best commercial phase shifters introduce sufficient attenuation on variation through 360° to rule out the method for most very dilute solution work. Clearly some modifications were required before the method could compete with those employing the measurement of impedance.

Our ultimate object is to study molecular interaction and solvation by means of changes of apparent dipole moments and relaxation times. The latter takes into account dipolar interaction, shape and steric factors and also the size of the complex. Thus, with suitably designed experiments the method offered a potential route to gaining more basic information on complexes not at present available by other methods. First of all, though, it was imperative to be assured that a method was available, or could be devised which would give repeatable and significant differences in moments and relaxation times for a polar solute in different interacting environments.

BASIC THEORY

(1) *The Concept of Dielectric Loss*[*]

For small polar molecules in solution at frequencies less than about 10^8 c/s the electric dipole interacts with the electric field component of the electromagnetic radiation, and the dipole responds instantly to the field variation with time ($E = E°e^{i\omega t}$ where E° is the electric field strength at t = 0 and $\omega = 2\pi \times$ frequency).

At significantly higher frequencies there is a time lag between the response of the dipole to the behaviour of the field, and this is measured in terms of relaxation time (τ). τ may be defined as the time after the removal of the electric field for the

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[*] References 2 and 3 provide a much more detailed and rigorous treatment than given here.

[8] J. W. Smith, *Electric Dipole Moments.* Butterworths, London (1955).

[9] F. H. Branin, Jr. *J. Applied Phys.*, 23, 990 (1952).

[10] T. J. Buchanan and E. G. Grant, *Brit. J. Appl. Phys.* 6, 64 (1955).

polarization (P) to decay $1/2 \cdot 718$ of its original value (P_0), the definition being deduced from the equation:

$$P = P_0 e^{-t/\tau}$$

for the case $t = \tau$. For small polar molecules in non-viscous solutions the relaxation time is $\sim 10^{-11}$ to 10^{-10} sec, and the corresponding frequency required for the dipole to alter its orientation would occur in the microwave region. For very large molecules the relaxation time may be as high as $\sim 10^{-6}$ sec which would require radiofrequency radiation.

At microwave frequencies—unlike the heterodyne beat frequency of 1 Mc/s—the current (I) and voltage (E) vectors of the wave are no longer at an angle of $\pi/2$ to each other and are inclined at $\pi/2 - \delta$. As a consequence Joule heating occurs which equals: E × component of I in step with voltage.

$$= E \times I \sin \delta$$

and this measures the dissipation of the energy of the field in a given medium. From this the concept of dielectric loss emerges, and the dielectric constant (ϵ^*) becomes a complex number: $\epsilon^* = \epsilon' - i\epsilon''$ in which ϵ' may be related to the usual picture of dielectric constant, whereas ϵ'' measures the ability of the medium to dissipate energy.

(II) *Attenuation and Phase Shift of Wave*

If $E°$ is the electric field strength at zero time ($t = 0$) at the point which the wave enters the solution, then at time t

$$E = E° e^{i2\pi ft}$$

At a distance z further down the solution the electric field intensity is diminished to:

$$E = E° e^{i2\pi ft} e^{-\nu z}$$

in which ν is known as the propagation coefficient of the solution and:

$$\nu = \alpha + i\beta$$

Hence:

$$E = (E° e^{-\alpha z}) \left[\cos(2\pi ft - \beta z) + i \sin(2\pi ft - \beta z) \right]$$

Since the term in round brackets is the amplitude of the wave, then it follows that the amplitude of the wave has been attenuated by the factor $e^{-\alpha z}$ in travelling through z cm of solution. Therefore α is known as the attenuation constant and is a measure of the diminution of electric intensity of the wave per cm of solution. Similarly it follows from the term in square brackets that the phase of the wave has been reduced by βz radians where β is known as the phase constant and is measured in radians/cm.

(III) *Essential Equations and Evaluation of Parameters*

(i) *Debye's equations*

For molecules which can be characterized by a single relaxation time the complex dielectric constant is related to relaxation time by:†

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau} = \epsilon' - i\epsilon'' \tag{1}$$

† For molecules with more than one relaxation time the factor has to be modified to $(i\omega\tau)^{1-\alpha}$ where the greater the value of α the wider the distribution of relaxation times. The subsequent methods of dipole moment evaluation (IVa and b) apply to the type of molecule which is characterized by a single relaxation time at the measured frequencies.

On separation of real and imaginary parts:

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

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{3}$$

The ratio ϵ''/ϵ' equals $\tan\delta$, and this is known as the loss tangent. This is related to the dipole moment (μ) and relaxation time by means of the following equation:

$$\tan\delta = \frac{(\epsilon_0 + 2)(\epsilon_\infty + 2)}{\epsilon'}\frac{4\pi cN\mu^2}{27kT}\frac{\omega\tau}{1 + \omega^2\tau^2} \tag{4}$$

in which ϵ_0 is the static dielectric constant (e.g. the value measured at 1 Mc/s frequency and for such a case $\tau = 0$) ϵ_∞ is the dielectric constant determined at very high frequencies when the molecules become unable to alter their orientation in the applied field, c = concentration in moles/cc, N = Avogadro number, T = absolute temperature. From evaluation of ϵ' $\tan\delta$, i.e. ϵ'' at different frequencies both μ and τ may be evaluated by manipulation of Eq. (4). See later.

(ii) *Cole–Cole plot*

Elimination of $\omega\tau$ between (2) and (3) gives the equation of a circle thus:

$$\left[\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2}\right]^2 + \epsilon''^2 = \left[\frac{\epsilon_0 - \epsilon_\infty}{2}\right]^2 \tag{5}$$

Hence, a graph of ϵ'' against ϵ' in the complex plane gives a semicircle, the so-called Cole–Cole.[11] Eqs. (2) and (3) together with this plot provide a basis for the interpretation of dielectric relaxation phenomena.

It has been found for dilute solutions of polar solute in non-polar solvent that the dielectric constant and loss is proportional to the solute concentration expressed as weight fraction (w_2) or mole fraction of solute[4] (f_2).

i.e.

$$\epsilon' = \epsilon_1 + a'w_2 \tag{6}$$

$$\epsilon'' = a''w_2 \tag{7}$$

$$\epsilon_0 = \epsilon_1 + a_0w_2 \tag{8}$$

$$\epsilon_\infty = \epsilon_1 + a_\infty w_2 \tag{9}$$

where ϵ_0 is the static dielectric constant and ϵ_1 is the dielectric constant of the solvent at the same frequency.

When Eqs. (6)–(9) are substituted into Eq. (5) the concentration terms are eliminated yielding:

$$\left[a' - \frac{a_0 + a_\infty}{2}\right]^2 + a''^2 = \left[\frac{a_0 - a_\infty}{2}\right]^2 \tag{10}$$

The slopes of the lines represented by Eqs. (6)–(9) can, therefore, be used to formulate

[11] K. S. Cole and R. H. Cole, *J. Chem. Phys.* 9, 341 (1941).

a Cole–Cole plot of a″ against a′ with the advantage that individual errors in particular values of dielectric constant or loss are minimized.

(iii) *Determination of relaxation times*

(a) *Whiffen's and Thompson's method.* These workers modified Eq. (4) by approximating $(\epsilon_0 + 2)(\epsilon_\infty + 2)$ to $(\epsilon_1 + 2)^2$ and, in addition, ϵ' was taken to be equal to ϵ_1. Thus, Eq. (4) reduced to:

$$\tan \delta = \frac{(\epsilon_1 + 2)^2}{\epsilon_1} \frac{4\pi cN\mu^2}{27kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{11}$$

When tan δ is plotted against log frequency a Gaussian form of curve results. If two measurements of tan δ are carried out on a dilute solution at frequencies f_A and f_B corresponding to points A and B, where A and B are two points in the region of the maximum then:

$$\frac{\tan \delta_A}{\tan \delta_B} = \frac{2\pi f_A \tau}{1 + (2\pi f_A \tau)^2} \times \frac{1 + (2\pi f_B \tau)^2}{2\pi f_B \tau} \tag{12}$$

In addition, if a graph is constructed of the ratio of the tan δ's against relaxation time, by inserting various values of τ into Eq. (12) for the two frequencies f_A and f_B, then from the experimental tan δ ratio the corresponding relaxation time can be read off.

(b) *A simple means of evaluating the relaxation time.* This follows from the equation:[3]

$$\frac{v}{u} = \omega\tau \tag{13}$$

in which v and u are the distances between an experimental point on the Cole–Cole plot and ϵ_0 and ϵ_∞ respectively.

(c) *From modification of the Debye equations.* On elimination of ϵ_∞ from Eqs. (2) and (3):

$$\epsilon' = \epsilon_0 - \tau\omega\epsilon'' \tag{14}$$

and on substitution from Eqs. (6), (7) and (8)

$$a' = a_0 - \tau\omega a'' \tag{15}$$

Hence, τ may be evaluated from Eq. (15) for each particular frequency providing a_0, a″, and a′ have been determined. However, a more satisfactory procedure is to plot a′ against $\omega a''$ for a few frequencies and determine τ from the slope.

(IV) *Dipole Moment Determination*

(a) We have deduced a new method of determining μ from Eq. (4) for the case when $w_2 \to 0$. The term $(\epsilon_0 + 2)(\epsilon_\infty + 2)\epsilon'$ is then equal to $(\epsilon_1 + 2)^2\epsilon'$ as is illustrated in Fig. (6). If a″ is plotted against a′, and a_M is the maximum value of a″, then for this value $\omega\tau = 1$, and it follows that Eq. (4) may be modified and rearranged to give:

$$\mu^2 = \frac{27}{2} \frac{kT}{\pi N} \frac{M_2}{(\epsilon_1 + 2)^2} \frac{a_M''}{d_1} \tag{16}$$

in which M_2 is the molecular weight of the solute and d_1 the density of the solvent. The concentration factor (in moles/cc) has been replaced by $w_2 d_1/M_2$ where w_2 is the

weight fraction of solute, and since the value of the moment has to correspond with the case of infinite dilution the density of the solution (d_{12}) may be replaced by that of the solvent. It must be stressed that this approach—unlike the Whiffen and Thompson—is not to be regarded as involving serious approximations.

(b) The value of τ determined by the Whiffen and Thompson approach may be substituted into Eq. (11) and the corresponding value of μ calculated. However, this method involves the definite approximations that in dilute solution:

$$\epsilon_0 = \epsilon_\infty = \epsilon' = \epsilon_1$$

Determination of ϵ' and ϵ''

(I) *Introduction*

Unlike most other fields of spectroscopy, each microwave spectrometer is capable of only small variations in frequency. The range of frequency which may be propagated along a waveguide of a given cross section is summarized in Table 2 for the bands which we employed, and the letter employed to designate the band is also given.

TABLE 2. WAVEGUIDE INTERNAL CROSS SECTION DIMENSION, FREQUENCY RANGE OF PROPAGATION AND LETTER EMPLOYED TO CHARACTERIZE BAND

Waveguide internal cross section diameter (inches)	Frequency range in Gc/sec (10^9c/s)	Letter characterizing Waveband
0·280 × 0·140	26·5 to 40·0	Q
0·420 × 0·170	18·0 to 26·5	K
0·900 × 0·400	8.2 to 12·4	X
1·372 × 0·622	5·85 to 8·20	C

However, even these small variations of frequency are barely permissible for accurate measurement of attenuation and phase shift owing to the variable behaviour of the measuring components at the different frequencies. Nevertheless, small alterations of frequency in this range cannot be ruled out as a useful procedure but as yet we have had only a limited success with this variable.

So far our work has been mainly at Q, K and X bands with a limited amount at C band.

(II) *The bridge method*

(a) A block diagram of the bridge circuit* is given in Fig. 1; the four arms of each magic T are labelled a, b, c and d. The monochromatic microwave radiation is generated by a klystron (K) (to which square-wave reflector modulation of 1000 c/s is applied) and propagated along a rectangular waveguide. An attenuator or isolator (L) prevents 'pulling of the klystron.' The wavelength is read directly on a wavemeter (WM). At 'a' the power is split into two equal halves by the magic T, one half passing through the cell containing the solution and the other half along the other side of the bridge through the calibrated variable attenuator and phase shifter. The polar solution shifts the phase and attenuates the wave; hence the procedure is to

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* We have not listed the source of each item since many manufacturers make almost equivalent equipment. Our apparatus has been purchased from six different sources. The best guide in choice is to study the accuracy quoted in relation to price and requirements.
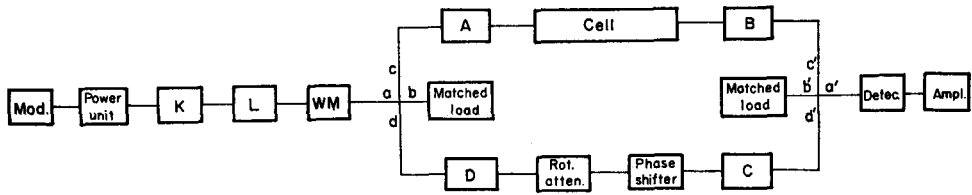
FIG. 1. Block diagram of bridge apparatus.

alter the phase and attenuation in the other side of the bridge and to achieve the condition in which, when the waves combine, the fields have been restored to equal antiphase conditions at the junction of arms c′ and d′ of the output magic T. With the fields so adjusted the vector sum in output in arm a′ is zero and the bridge is balanced. A crystal is connected to a unit which is some form of signal detection system which can be a high gain, low noise amplifier and voltmeter. At the balance point of the bridge the latter has a zero reading. Before any measurements were taken the klystron was left for an hour to stabilize. The wavelength of the radiation was checked by the resonant cavity wavemeter before and after the experiment.

Since the phase shifter itself introduces attenuation, which varies according to its setting, sufficient liquid was added to the cell each time to give a phase shift of about 360°. As a precaution the phase shifter was calibrated by measuring its attenuation at settings of 10° intervals. The calibration was not absolute, but the graph of attenuation of phase shifter against phase shift (in degrees) indicated those settings about which small variations in the 360° phase shift would not significantly alter the attenuation.

An outstanding justification of the fact that our employment of a phase shifter did not vitiate the attenuation results was obtained as follows. For K-band the phase shifter was dispensed with and the solution itself was employed in that capacity. By careful addition of solution from an Agla micrometer syringe and observation of a minimum of the detection needle it was found possible to add sufficient solution to shift the phase 360° for each unit of volume added. The solution was added in small amounts and the attenuation balanced at each addition and this was continued until a null point was obtained. The ϵ' and ϵ'' values evaluated from these phase shift and attenuation results for K-band lay on the Cole-Cole plot obtained from the ϵ_0, Q and X band results.

The attenuator similarly gives rise to phase shift, although to a lesser extent. To eliminate this the attenuator could be set at some convenient value of the attenuation and the minimum found while moving only the phase shifter. This lacks sensitivity when the attenuation of the liquid is far from the pre-set value. However, the range of sensitivity about the pre-set value is great enough to enable a satisfactory determination. Thus, the objection that the attenuator itself introduces phase shift may be overcome.

(b) *Modifications to basic circuit*. For very dilute solutions, when the attenuation is low, it is particularly important to minimize reflection. The magnitude of the reflections may be assessed by determining the standing wave ratio* using the standing

* If a_1 is the amplitude of the incident wave and a_2 that of the reflected wave then the standing wave ratio (ρ) may be defined as $\rho = a_1 + a_2/a_1 - a_2$. Thus, ideally, a_2 ought to be zero and ρ equal to one.

wave indicator employing a minimum probe depth. It is desirable to have a standing wave ratio as near to unity as is possible. This value may be approached by introducing isolators at points A, B, C and D or alternatively introducing four attenuators (set at about 3 db) or stub tuners. It can be worthwhile also to (i) match the detector by means of a stub tuner and (ii) ensure that the value of ρ in front of the incident cell window is $\not>$ about 1·1. The isolators often have an acceptable ρ and apart from minute reflections restrict propagation of the wave to the forward direction.

(c) *Details of cells*. Various types of cells have been tried employing mica, melanine windows and parallelogram teflon blocks, and, in general, we now have a preference for mica. It is readily apparent that the windows must be inclined or reflections from the window vitiate the results for dilute solutions. The angle of inclination of the windows to the direction of propagation of the microwave employed for the bands in Table 2 have ranged from ∼13 to 19°. This meant that for the H_{10} mode, in which the electric field is perpendicular to the broad side of the guide, the electric field component was introduced gradually into the cell and consequently reflection of the wave due to changes of medium were minimized.

If only one window is employed and the bridge circuit is set up on a board inclined at ∼15° to the horizontal—with the klystron at the lower end—then a window may be dispensed with at the upper end of the cell. However, if it is wished to eliminate the meniscus or to keep moisture out of the cell, an additional mica window is added. The resulting shape of liquid may be either a trapezium or a parallelogram. The cell is surrounded by a water jacket around which water is circulated and the temperature controlled to ±0·01°. The cell is filled through a narrow metal tube of 0·06 to 0·03 cm inner diameter which entered the cell—remaining flush with the wall—in the middle of the broad side of the guide close to the bottom mica window for Q and K bands and at the upper end of the cell for X and C bands. An agla micrometer syringe is then employed for filling the former cells and a grade A burette or a special micrometer burette for the X-band. The burettes are jacketted and water circulated. As regards Q and K bands, the solution is preheated in a tightly stoppered flask in a water bath. The micrometer syringe is itself kept in a sealed glass vessel immersed in the water bath and is removed only to insert solution into the cell. From the volume of solution added to a known cross section of the cell the length of the solution in the cell may be calculated. Electroformed wave guide may be employed to obtain a virtually constant cross sectional area.

Attention has also to be paid to the thickness of the mica windows, since, if the window is too thin in the waveguides of wider cross section, bowing of the window results with consequent reflection. Suitable thicknesses for Q and K bands were 0·0015 cm and for X band 0·0025 cm.

The solution* is run in until the mica window is covered. The bridge is balanced and attenuation and phase shift readings taken. Enough solution is added to give a phase shift of 360° and the readings are again taken. This is continued until sensitivity is lacking—usually about eight readings—which of course varies with the type of solute and its concentration.

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* The purification of solvents and pyridine and γ-picoline has been described previously.[19] The acetone and bromobenzene were purified by distillation in a 20-plate column and a small middle fraction selected.

The attenuation reading in nepers* is plotted against the length of added liquid in cms. The slope is α. The length of liquid is known from the volume added liquid and the cross section of the waveguide.

The phase shift in radians is plotted against the length of added liquid. The slope is β_{meas}†. The value of β_{meas} is not that of the liquid however, because an equivalent volume of air has been displaced and this too has a significant phase shift. Hence:

$$\beta_{liq.} = \beta_{meas} + \beta_{air}$$

β_{air} is a constant for any waveband and

$$\beta_{air} = \frac{2\pi}{\lambda_g}$$

where λ_g is the wavelength in the guide.

(d) *Determination of ϵ' and ϵ'' from α and β.* The basic equation is:

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

where λ_0 is the wavelength in cm of the radiation in vacuum as deduced from the wavemeter reading and "a" is the inner broad side width of the cross section of the waveguide.

From the above equation it follows:

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

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

Hence, since α, β, and λ_0 are measured and "a" is known the ϵ'' and ϵ' values follow for a particular wavelength.

RESULTS

Various values have been given for the accuracy in determining ϵ' and ϵ'' at microwave wavelengths. Smyth quoted $\pm 1\%$ for the former and $\pm 3\%$ for the latter with respect to his impedance method.[3] We have examined at the X-band wavelength bromobenzene in cyclohexane by both his and the bridge method. The agreement from the two approaches of ϵ' and ϵ'' was well within his quoted accuracy. The ϵ' values are determined by the Smyth method by simply measuring the wavelength in the dilute solution. For extremely dilute solutions (e.g. weight fractions less about 0·005) the bridge method has sometimes not yielded consistent values for ϵ'. The Smyth method does not appear to suffer this way. However, as regards the ϵ'' values we have found the bridge method significantly more satisfactory. Our present tendency for such dilute solutions is to determine the attenuation by the bridge method and the phase shift by the other method.

* The most recent rotary vane attenuators give the scale reading in decibels and if this is divided by 8·686 the value is converted to nepers.

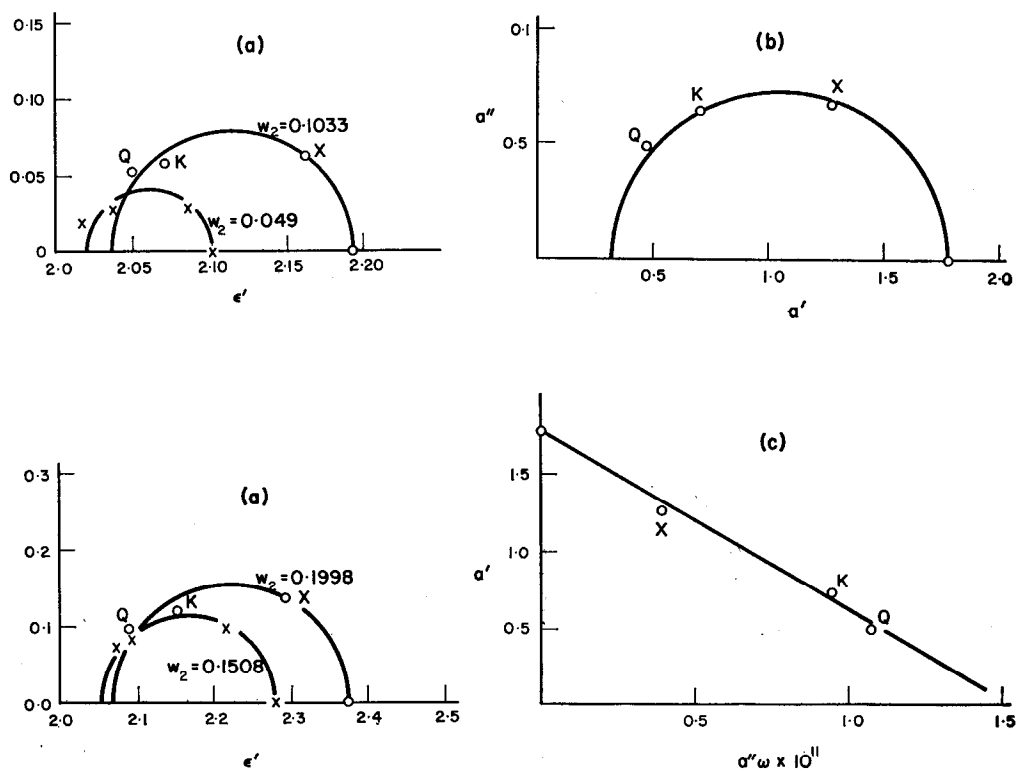† The slopes were determined by the method of least mean squares.

FIG. 2. (a) $\epsilon'' - \epsilon'$ plots for bromobenzene in cyclohexane* (at 20°C) at weight fractions of about 0·05, 0·10, 0·15 and 0·20, (b) the corresponding a″ — a′ plot, (c) the a′ — a″ω plot.

TABLE 3. DIPOLE MOMENT VALUES OBTAINED BY DIFFERENT PROCEDURES AND A COMPARISON WITH THE RANGE OF LITERATURE VALUES

Solute	Solvent	μ_{WT}	μ_{WT} mean	μ_M	$\mu_{1·1R_D}$	μ_{HK}	μ_G	μ_{11t}
Acetone	Dioxan	Q 2·78 K 2·84 X 2·95	2·85	2·85	2·84	—	2·84	—
Bromobenzene	Cyclohexane	Q 1·56 K 1·39 X 1·63	1·53	1·57	1·57	1·62	1·62	1·58†
Pyridine	Carbon tetrachloride	Q 2·30 K 2·33 X 2·29	2·31	2·34	2·33	—	—	2·37
γ-Picoline	Cyclohexane	Q 2·48 K 2·48 X 2·53	2·50	2·60	2·59	—	—	2·59

Relaxation time results obtained by the Whiffen and Thompson (τ_{WT}), the arc (τ_{arc}) and τ_{graph} from the slope of the plot of a′ — a″ω are given in Table 4.

* Higher weight fractions were employed in this determination since the change in ϵ' was small at low concentration variations.
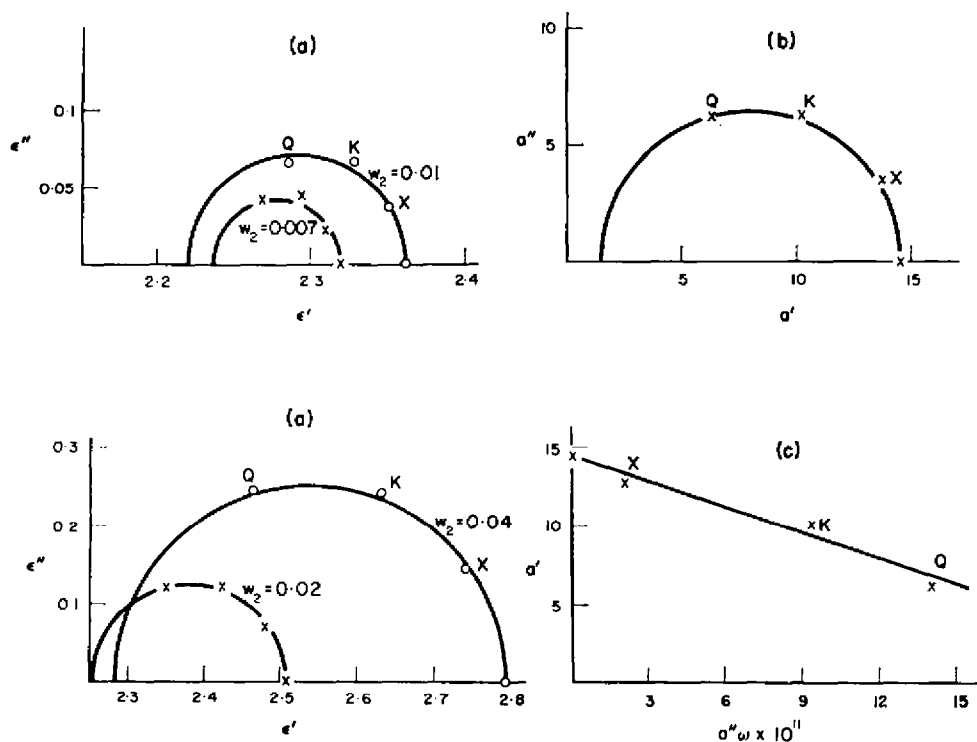
† Recalculated value.

FIG. 3. (a) $\epsilon'' - \epsilon'$ plot for pyridine in carbon tetrachloride (at 25°C) at weight fractions of 0·007, 0·01, 0·02 and 0·04, (b) the corresponding $a'' - a'$ plot, (c) the $a' - a''\omega$ plot.

TABLE 4. RELAXATION TIME VALUES OBTAINED BY DIFFERENT PROCEDURES

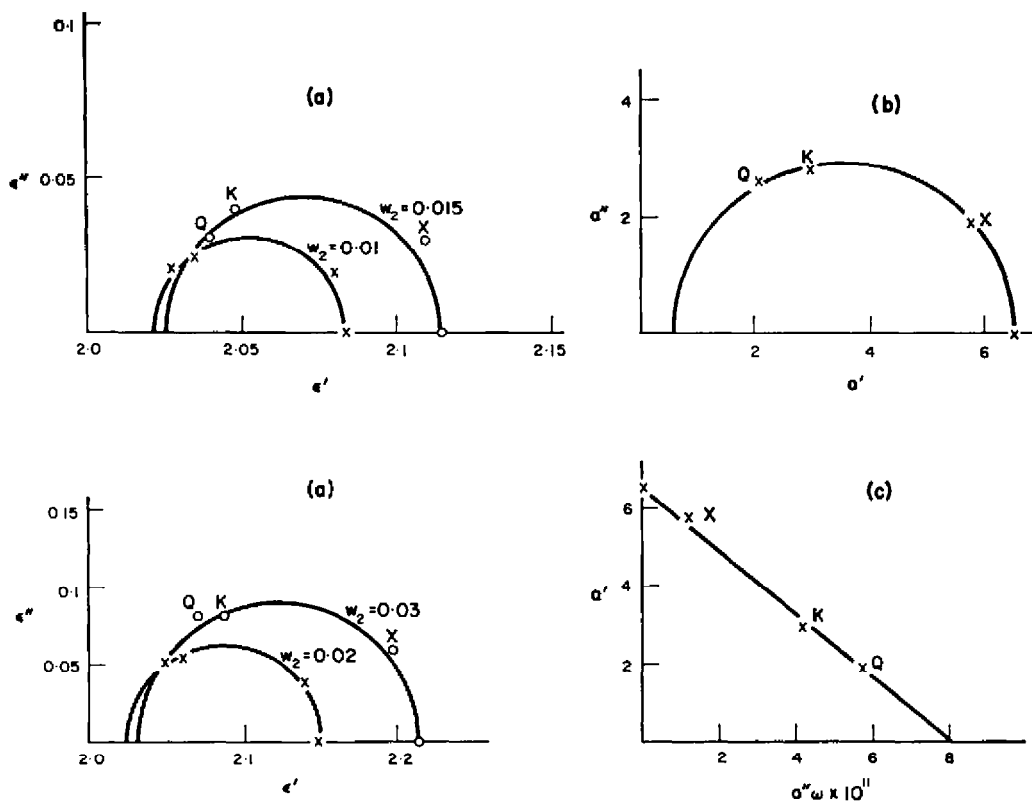| Solute	Solvent	τ_{WT}		τ_{arc}		τ_{graph}
Acetone	Dioxan	Q/K	3·6	Q	4·6	4·5
		Q/X	2·0	K	4·2	
		K/X	—	X	4·5	
Bromobenzene	Cyclohexane	Q/K	8·8	Q	13·5	12·0
		Q/X	10·3	K	12·1	
		K/X	11·2	X	9·4	
Pyridine	Carbon tetrachloride	Q/K	5·0	Q	6·0	5·8
		K/X	4·65	K	4·9	
		Q/X	5·2	X	5·7	
γ-Picoline	Cyclohexane	Q/K	6·0	Q	8·3	8·1
		K/X	7·0	K	8·5	
		Q/X	6·7	X	6·7	

FIG. 4. (a) $\epsilon'' - \epsilon'$ plot for γ-picoline in cyclohexane (at 25°C) at weight fractions of 0·01, 0·015, 0·02 and 0·03, (b) the corresponding $a'' - a'$ plot, (c) the $a' - a''\omega$ plot.

Rather than tabulate the data we thought it more illustrative of the consistency— if not the accuracy—of the method to present the data graphically. This has been done in the form of $\epsilon'' - \epsilon'$ and $a'' - a'$ Cole–Cole plots and the plot of $a' - a''\omega$ in Figs. (2–5).*

On comparison of the $\epsilon'' - \epsilon'$ and $a'' - a'$ plots the necessity of the latter type of procedure may be deduced. The $a' - a''\omega$ plots are quite revealing with regard to inaccurate data. On the whole the measurements have been reported as they occurred —rather than repeat the determination with a view to obtaining all the points on the Cole–Cole plot. However, remeasurement indicated that the deviations from the plot could be attributed to ϵ' rather than ϵ''. The worst divergences of ϵ' from the plot are of the order $\pm 0·5\%$.

The dipole moment results as obtained by the Halverstadt–Kumler† (μ_{HK}), the Guggenheim† (μ_{G}), the Whiffen and Thompson (μ_{WT}), and the microwave approach (μ_{M}) employing equation 16 are given in Table 3. A comparison is made with the range of literature value (μ_{lit}) when possible.

* Special weight has been placed on the a_0 points since this may be determined with greater accuracy.

† Details of the procedure employed in obtaining and evaluating such results are given in: P. A. Young, A. Holt and S. Walker, *Tetrahedron*. In press (1964).
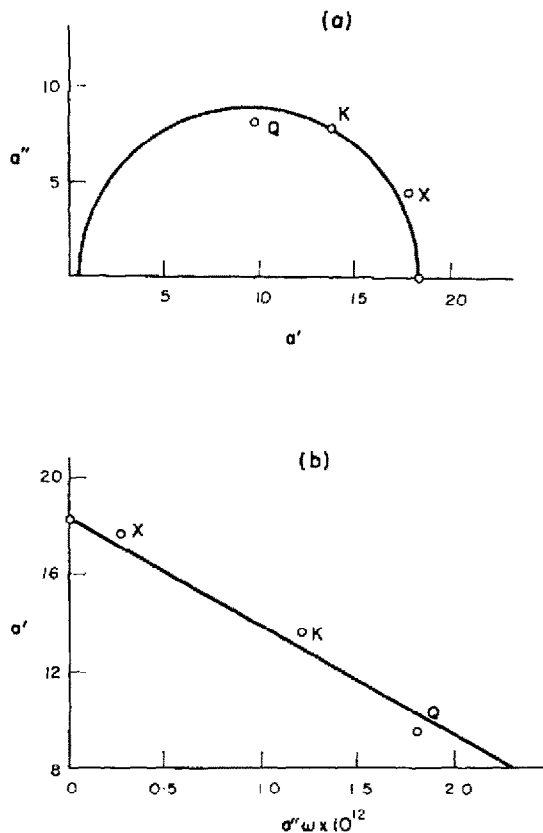
FIG. 5. (a) the $a'' - a'$ plot for acetone in dioxan (at 25°C). Since different sets of solutions were used for each band the $\epsilon'' - \epsilon'$ plot could not be formulated, (b) the $a' - a''\omega$ plot.

DISCUSSION

In order to test the bridge method and partly because we wished to study electric dipole moments (and relaxation times) we chose to evaluate the degree of success of the method—apart from consistency—in terms of dipole moments. The dipole moments of bromobenzene in cyclohexane and acetone in dioxan were measured by the microwave and also evaluated either by the Halverstadt and Kumler or the Guggenheim[13] (employing the Smith[14] correction factor) approaches in which the dielectric constants were determined by the heterodyne beat technique. The moments of pyridine in carbon tetrachloride and γ-picoline in cyclohexane had been determined previously by the Halverstadt and Kumler procedure.[12] The new results are given in Table 3. Rather to our surprise we can find no instance of another determination of dipole moments by the microwave and Halverstadt and Kumler or Guggenheim approaches by one set of workers.

For bromobenzene and pyridine the moments obtained by the microwave technique

[13] A. N. Sharpe and S. Walker, *J. Chem. Soc.* 2974 (1961).
[13] E. A. Guggenheim, *Trans. Far. Soc.* 45, M14 (1949).
[14] J. W. Smith, *Trans. Far. Soc.* 46, 394 (1950).

are slightly lower than those obtained by the Halverstadt and Kumler and Guggenheim approaches. However, the agreement is sufficiently close almost to be within the degree of experimental error experienced by the latter two methods. In fact, it would be rare to find such correspondence between two sets of workers employing the Halverstadt and Kumler approach to four determinations.

It is interesting to note that the low value of the dipole moment of acetone (in benzene) obtained by the workers quoted in Table 1 has not been obtained here. Because two groups of workers agreed on a value about 0·2D lower than that obtained by the Halverstadt–Kumler approach this indicated the necessity of special attention. On studying this solute in cyclohexane we also obtained a low dipole moment value and relaxation time similar to theirs. However, the points were low on the a_0 side of the Cole–Cole plot, and it was difficult to determine accurately the semi-circle. By altering the solvent to dioxan, however, the relaxation time was increased and the positions of the points on the Cole–Cole plot altered sufficiently to enable a fairly reasonable semi-circle (see Fig. 5). In general, if the distribution of the points on the Cole–Cole plot is poor, then the accuracy diminishes. However, this may be overcome by varying the solvent or the temperature or by having a good range of wavebands.

The dipole moment value of acetone requires further consideration since the value generally quoted in benzene is 2·76D. The most recent value for acetone in this solvent[15] is one by Buckingham and Le Fèvre of 2·83 ± 0·02D while the previous value of Cherrier was 2·85 ± 0·02D. The other five literature values ranged between 2·74 and 2·81D. Values of 2·74D and 2·85D in n-hexane and carbon tetrachloride were obtained by Wolf.[15] Altogether it would seem that the moment of acetone is not readily determined with accuracy. The wide range of moments in benzene emphasized the necessity of one group of workers measuring the same system by both techniques.

We remained somewhat uneasy with respect to our acetone in dioxan moment for the following reasons:

(i) No points lay on the a_∞ side of the Cole–Cole plot and, consequently, the semi-circle and a_M'' became more uncertain to determine.

(ii) Acetone loss from evaporation or moisture absorption were possibilities. A repeat determination was carried out employing the same solutions—as opposed to fresh solutions—for each band. In addition, we chose a weight fraction range of 0 to 0·015 as opposed to up to 0·04 in the first determination. We now feel, taking into account all the evidence, that the moment of acetone in dioxan is 2·83 ± 0·02D. It should be stressed, though, that this small inaccuracy is not an inherent defect of the method in general but of this system in particular.

Equation (16), which is a limiting one involving a_M'', appears to give the most satisfactory dipole moment results and such values involve no atomic polarization approximations as in the Halverstadt–Kumler approach. This may explain the (apparent) tendency to obtain slightly lower moments by the microwave procedure. As may be seen from Table 3 the agreement between the microwave and the other method values—based on $1·1R_D$ equals the sum of the atomic and electronic polarizations—is very good. However, much more work is required before definite conclusions can be drawn on this aspect. If, though, the microwave approach did eliminate (or reduce) this unfortunate atomic polarization factor and give true dipole

[15] A. L. McClellan, *Tables of Experimental Dipole Moments*. W. H. Freeman and Company, San Francisco and London (1963).

moment values relating to the solute in solution, it would be an attractive move forward.

The Whiffen and Thompson method gives dipole moment values which differ according to the wave bands selected, but the mean would seem to be of the order of that obtained from a_M''. This method depends upon the accuracy of the value of τ used and obtained as part of this procedure. Furthermore, the method is applicable only when the two frequencies used are in the neighbourhood of the tan δ maximum. This is especially clear for acetone in dioxan between K and X band when the relaxation time value obtained is unreal. For bromobenzene the relaxation time found between
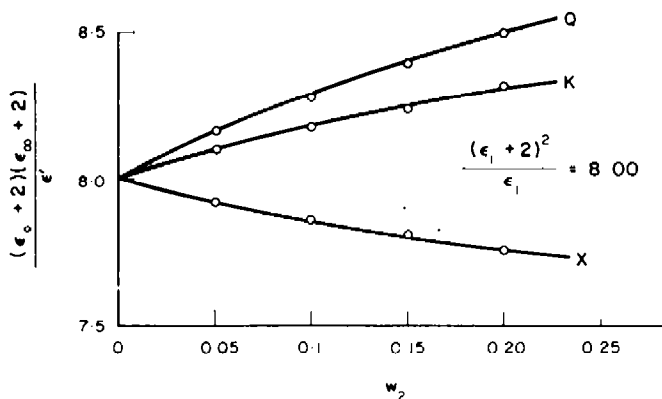

FIG. 6. The plot of $(\epsilon_0 + 2)(\epsilon_\infty + 2)/\epsilon'$ against weight fraction for bromobenzene in cyclohexane. The plot has been extrapolated to the $(\epsilon_1 + 2)^2/\epsilon_1$ value.

Q and K bands, which are both on the left hand side of the plot, also deviates appreciably from the value obtained by other methods. This, however, is applying the method outside its limits, but this may account for some of the deviations in Table 1.

Fig. 6 illustrates the limitations of the approximation made in the Whiffen Thompson method that $(\epsilon_\infty + 2)(\epsilon_0 + 2)/\epsilon'$ is equal to: $(\epsilon_1 + 2)^2/\epsilon_1$ for dilute solutions. This would seem to be true of bands near the maximum but not so for other bands except approximately so, in extremely dilute solutions.

Smyth commonly uses the arc method of Cole and Cole to find τ. The results show that this is probably as satisfactory a method as any if the mean of the τ obtained at different bands is used. Individual bands, however, can give misleading values.

The graphical method due to Cole would appear to give the best indication of the magnitude of τ since errors due to variations in individual solutions and at different bands are minimized. The $a'/a''\omega$ plot is useful also in that erroneous results fall off the line and immediately suggest remeasurement. It is worth noting that the a_0 value—obtained by the heterodyne beat method—can be determined more accurately than the microwave a' values. Since for the a_0 value $a'' = 0$, then this point on the ordinate axis can be fixed with reasonable certainty and is accordingly allotted special weight—as also in the Cole–Cole plot—when determining the slope of the straight line.

It would seem appreciably more difficult to obtain accurate relaxation time than dipole moment values. The range of literature values in Table 5 suggests an accuracy of the order $\pm 10\%$. Although our relaxation time values are of a similar magnitude to the best literature values, we do not feel that we have achieved yet the accuracy

of which the method is capable. Our next step in this direction will be to examine six to eight solutions for each point on the a″ — a′ plot and to extend our waveband range to include 4 mm and 2 cm equipment. In addition, this should result in even greater accuracy in the dipole moments and it may be worthwhile then determining the radius of the semi-circle (i.e. a_M'') mathematically. The 4 mm band should give a useful point towards the left hand side of the Cole–Cole plot for small polar molecules.

As assessed by both dipole moment and relaxation time data—compare tables (1, 3, 4, 5)—the modified bridge technique has attractive features. One of the assets of

TABLE 5. LITERATURE RELAXATION TIME, VALUES OF SOLUTES IN VARIOUS SOLVENTS

Solute	Solvent	T°C	$\tau \times 10^{12}$ sec	Solute	Solvent	T°C	$\tau \times 10^{12}$ sec
Chlorobenzene	Cyclohexane	20	7·8	Chloroform	Cyclohexane	20	3·2
Chlorobenzene	Benzene	20	8·3	Chloroform	Carbon	20	5·0
Chlorobenzene	Benzene	19	7·5		tetrachloride		
Chlorobenzene	Benzene	19	10·8	Chloroform	Benzene	20	7·1
Chlorobenzene	Benzene	23	10·6	Chloroform	Benzene	18	7·7
				Chloroform	Benzene	23	8·4
Bromobenzene	Cyclohexane	20	10·4	Chloroform	Carbon	20	2·7
Bromobenzene	Benzene	20	10·6		disulphide		
Bromobenzene	Benzene	19	10·0				
Bromobenzene	Benzene	19	11·0	Nitrobenzene	Cyclohexane	20	9·5
Bromobenzene	Benzene	19	10·5	Nitrobenzene	Carbon	20	15·2
Bromobenzene	Benzene	23	12·3		tetrachloride		
				Nitrobenzene	Benzene	20	12·8
Acetone	Benzene	19	3·2	Nitrobenzene	Benzene	19	11·5
Acetone	Benzene	20	3·3	Nitrobenzene	Benzene	19	11·6
Acetone	Benzene	19	3·3	Nitrobenzene	Benzene	19	11·3
Acetone	Benzene	19	3·3	Nitrobenzene	Benzene	19	13·0
Acetone	Benzene	23	3·3	Nitrobenzene	Benzene	23	13·2
Acetone	Benzene	23	2·5	Nitrobenzene	Carbon	20	8·6
					disulphide		

the procedure adopted is that the attenuation and phase shift are not dependent on just one reading but on several. Furthermore, the dipole moment and relaxation data are not based on results from just one solution. In general, we employed four solutions. If six to eight solutions had been employed, it may well be that negligible deviation would be detected on the Cole–Cole plots. Doubtless the bridge technique is still capable of improvement. A next step may be to place a cell in either side of the bridge containing, for example, different lengths of solution.

Debye developed a molecular concept of relaxation characterized by the relaxation time τ^* where τ^* is the molecular relaxation time and may be regarded as the time for the oriented dipoles to become random if the electric field influence was suddenly removed. The two relaxation times are related by the Eq :

$$\tau = \tau^* \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}$$

[16] Von A. Spernal and K. Wirtz, A. Naturforschg. 8a, 522 (1953).

τ^* (and also τ) must be dependent on:
  (i) the relative shapes of the solute and solvent molecules
  (ii) dipolar interaction which will vary according to the concentration
  (iii) molecular interaction which may be of the hydrogen bonding or donor acceptor type.

It is our intention to study all these factors—particularly (iii)—and to illustrate the potentiality of the method for such work we have chosen the following examples.

The relaxation time of pyridine at 25° is 7.0×10^{-12} sec whereas that of γ-picoline is 12.6×10^{-12} sec.[17] From the close similarity of the polar nature of these molecules it follows that the protruding methyl group hinders the re-orientation of the substituted molecule. For pyridine in benzene[18] and γ-picoline in cyclohexane the relaxation times fall to 3.0×10^{-12} and 8.1×10^{-12} sec respectively at 25°C. Evidently this fall in relaxation time for the polar molecule in dilute solution indicates the effect of the dipolar forces in the pure liquid. Since the relaxation time of the weakly polar toluene[6] is 7.3×10^{-12} sec at 19° which is fairly similar to that of γ-picoline in cyclohexane, this gives support to the idea that the similar shape and size of γ-picoline and toluene are governing the relaxation time value when the dipolar influences are small. Altogether, the micro-wave approach would appear a promising method for the study of the dipolar influences in solutions of increasing concentration.

The potentiality of the method for the study of hydrogen bonding may be gained from the relaxation time values in Table 5 of chloroform in three solvents. In the absence of molecular interaction, as is borne out by the results for chlorobenzene and bromobenzene, the relaxation time in cyclohexane is just slightly less than in benzene, and significantly less than the relaxation time in carbon tetrachloride. However, the relaxation time of chloroform in benzene is more than double that in cyclohexane and greater than that in carbon tetrachloride. We suggest that if the relaxation values may be relied on this is evidence for hydrogen bonding of the hydrogen atom in chloroform to the π electrons.

Sharpe and Walker[19] showed that the difference in moment of pyridine and substituted pyridines in cyclohexane (or benzene) and carbon tetrachloride could be attributed to a weak form of donor-acceptor interaction with the pyridine as the donor and the polarizable carbon tetrachloride as the acceptor. Later work showed that this was not an isolated instance but such interaction occurred with ethers, organic sulphides and phosphines which can act as donors to polyhalogenated hydrocarbons.[20] It is one of the present intentions to study the relaxation times for some of these systems to gain an additional insight as to the apparent size of the re-orienting unit.

An example illustrating the desirability of eliminating atomic polarization factor considerations may be related to our previous work. The difference in moment between pyridine in carbon tetrachloride and benzene is ~ 0.12D. Le Fèvre et al.[21] attributed the difference to an increase in atomic polarization of the pyridine in carbon tetrachloride. Sharpe and Walker, however, assigned it to donor-acceptor interaction

[17] R. S. Holland and C. P. Smyth, *J. Phys. Chem.* **59**, 1089 (1955).
[18] R. C. Miller and C. P. Smyth, *J. Amer. Chem. Soc.* **79**, 308 (1955).
[19] A. N. Sharpe and S. Walker, *J. Chem. Soc.* 157 (1962).
[20] A. N. Sharpe and S. Walker, *J. Chem. Soc.* In press (1964).
[21] Buckingham, Chau, Freeman, Le Fèvre, Narayan Rao and Tardif, *J. Chem. Soc.* 1405 (1956).

—possibly involving a transient increase in polarization as the carbon tetrachloride molecules approach the vicinity of the lone-pair electrons of the nitrogen atom. Such interaction could increase the total polarization of the system, partly by increasing the atomic polarization and partly by a change of dipole moment. The fact, that the dipole moment from the microwave method in carbon tetrachloride is significantly higher than the benzene value and virtually coincides with the Halverstadt–Kumler value based on $P_A + P_E = 1 \cdot 1 R_D$ must be considered as strong evidence favouring the explanation of the difference of moment being due to mainly a change in moment as opposed to an increase in atomic polarization.