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CONDUCTION PROCESSES IN THIN LAYERS
OF DIELECTRIC LIQUIDS

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by

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ABSTRACT.

The electrical properties of a range of organic liquids trapped in thin layers has been investigated. The conduction mechanisms relevant to such systems of thin liquid layers have been determined mainly by dielectric measurements.

A short review of dielectric properties, with particular reference to effects relevant to liquids is presented at the beginning of the thesis.

The development of a suitable measuring cell is described. With the apparatus, in its final form, measurements could be made over the temperature range -50°C to $+50^{\circ}\text{C}$. The lower practical limit on the thickness of the layer is of the order of $1\mu\text{m}$.

It has been found that, depending on conditions, the measured permittivity of a thin layer of liquid may either be greater or less than the relevant value for a bulk specimen of the liquid, although the low values of permittivity must be viewed with a certain amount of suspicion. The marked rise in permittivity found at low frequency has been related to an interfacial polarization effect. An approximate solution of the conduction-diffusion differential equations governing the motion of ionizable impurities has been advanced, which fits the observed data very well. This theory enables the mobility and concentration of the ionic impurity to be calculated from the dielectric response, measured at low field strength. Reproducibility of the measured parameters for a given electrode material and different samples of liquid was not good owing to their sensitivity to the amount of impurity present. In view of this, differences obtained with different electrodes are most likely due to variations in impurity concentration and not to the electrodes themselves. Stress dependence of the permittivity and loss factor

(Garton Effect) have been observed in the case of aluminium electrodes only and this conflicts with the fact that the experimental results indicate that aluminium, silver and gold electrodes are all blocking and thus one should expect to see the Garton Effect with all three electrode metals.

An apparent lowering of permittivity below bulk values has been found in the case of n-heptanol and Aroclor 1242. However in view of the limited amount of experimental evidence available this effect must be viewed with some suspicion. A speculative theory attributing the effect to a constraint on the rotation of the molecular dipoles present in the liquid has been advanced. However this theory requires oriented layers on the electrodes the indicated thicknesses of which are unrealistically large.

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CONTENTS.

	Page No.
Abstract.	2
Acknowledgements.	4
<u>Chapter 1.</u> <u>The Context of the Research.</u>	8
1.1 Introduction.	8
1.2 Mechanisms of Polarization.	10
1.3 Static Permittivity and Dipole Moment.	15
1.4 Orientational Polarization and Relaxation Processes.	16
1.5 Permittivity of Pure Liquids.	21
1.5.1 Non-polar Liquids.	21
1.5.2 Polar Liquids.	22
1.5.3. Hydrogen-bonded Liquids.	23
1.6 Dispersion and Absorption in Liquids.	25
1.7 The Role of "Structure" in Liquids.	28
1.8 Conclusions.	32
1.9 References.	33
<u>Chapter 2.</u> <u>Experimental Techniques.</u>	35
2.1 Introduction.	35
2.2 The Mercury Squeeze Film Cell.	35
2.2.1 The "Plate" Apparatus.	35
2.2.2 The "Ball" Apparatus.	37
2.2.3 Disadvantages of the Mercury Squeeze Film Apparatus.	37
2.3 The Micrometer Cell.	40
2.4 Cell Systems using Optical Flats.	42
2.5 Temperature Control Systems.	53
2.6 Cell Preparation.	56
2.7 Purification of the Liquids Used.	57

		Page No.
2.8	References.	64
<u>Chapter 3.</u>	<u>Results.</u>	65
3.1	Introduction.	65
3.2	Early Results.	65
3.3	Thickness and Frequency Behaviour of n-Heptanol on Gold Electrodes.	71
3.4	The Effects of Temperature on the Behaviour of the n-Heptanol, Gold Electrode System.	73
3.5	Thickness and Frequency Behaviour of n-Heptanol with Silver Electrodes.	85
3.6	The Effects of Temperature on the Behaviour of n-Heptanol with Silver Electrodes.	89
3.7	The Behaviour of n-Heptanol with Aluminium Electrodes.	98
3.8	The Effects of Temperature on the Behaviour of n-Heptanol with Aluminium Electrodes.	98
3.9	"Garton Effect" Measurements.	104
3.10	D.C. Conduction Currents.	105
3.11	References.	118
<u>Chapter 4.</u>	<u>Discussion of Results.</u>	119
4.1	Introduction.	119
4.2	Space Charge Effects.	119
4.3	Single Mobile Charge Carrier Theory.	120
4.4	Time-dependent Solution for the Single Mobile Carrier Theory.	126
4.5	Comparison of A.C. Theory with Data.	130
4.6	Calculation of Impurity Concentration and Mobility from Single mobile Carrier Theory.	133

		Page No.
4.7	Interpretation of Carrier Concentration and Mobility Values.	143
4.8	An Electron Injection Theory.	149
4.9	The Relative Merits of the Electron Injection and Single Mobile Carrier Theories.	152
4.10	D.C. Current-Voltage Curves.	156
4.11	Stress-dependent Loss Factor: The "Garton Effect".	158
4.12	Hindered Dipolar Rotation.	164
4.13	Summary.	170
4.14	References.	176
<u>Chapter 5.</u>	<u>Conclusions.</u>	178
5.1	Conclusions.	178
5.2	Areas for Further Research.	179
Appendix I.	The Wayne-Kerr B221 Universal Bridge.	182
Appendix II.	The Measurement of Film Thickness by Optical Interferometry.	185

CHAPTER 1

The Context of the Research.

1.1. Introduction.

For a number of years some types of capacitor have been made commercially by winding together thin sheets of solid dielectric materials with metallic electrodes. The thin sheets of dielectric have been, for example, various grades of paper tissues or plastics while the electrodes have been aluminium or tin foils (generally of thickness 5 or 6 $\mu\text{m}.$) or metallized paper or plastics sheets. Under normal room temperature and humidity conditions, paper contains approximately 5 per cent by weight of water. Most plastics contain very little water but may have some condensed or adsorbed on the surfaces. To improve the insulating properties of such capacitors it is usual to dry the windings very thoroughly (by heating and vacuum treatment) and to fill the internal spaces ("impregnation") with well de-gassed purified dielectric liquids, at temperatures of about 100°C. At room temperature the impregnants may still be liquid or they may have cooled to jellies or even hard solids. The presence of such impregnants, especially when still liquid, generally suppresses internal discharges within capacitors wherever they are stressed electrically under normal working conditions.

In order to meet modern demands there is a tendency to concentrate on the use of "high K" liquids (relative permittivity of the order of 6 or 7 at room temperature) coupled with increased working stresses and temperatures. Under these conditions the mobility of charge carrying contamination is greater than that experienced with earlier capacitors in which "low K" impregnants and lower stresses and lower maximum temperature conditions were specified.

During the past few years, work on impregnated paper capacitors at the Electrical Research Association and elsewhere¹ has shown that such charge carrying contamination can be involved in the degradation of electrodes and dielectric materials and that this can lead to premature failure of the dielectrics under duty. There is a move in present capacitor technology to use plastic foils in place of some (if not later all) of the paper tissues in certain designs of capacitor. However, if in such capacitors internal discharges must be suppressed, then the use of dielectric liquid impregnants will have to continue. This becomes particularly important whenever stress demands are increased. Although charge carrying contamination has been linked with failure of paper capacitors, it would be wise also to consider the possibility of damaging effects of such contamination on the electrodes of future impregnated plastic film capacitors under highly stressed conditions.

In 1941, C.G.Garton of the E.R.A. published a paper "Dielectric Loss in Thin Films of Insulating Liquids"² in which he related $\tan \delta$ measurements at various electrical stresses to the ionic concentration, mobility and radius present in certain capacitors. "Garton Effect" measurements now are used in determining whether or not capacitors are suffering from contamination, but it is still not practical to attempt identification of the types of contamination from these measurements.

It was suggested that it would be very helpful to the capacitor manufacturing industry if a method of electrical measurement of the properties of dielectric liquids in special cells or trapped in thin layers could be evolved in order easily and positively to identify various types of contamination.

In general, films down to the smallest measurable thickness, appear to exhibit bulk values of permittivity in the absence of

relaxation effects. This is because the permittivity is determined by the polarizability of the constituent ions and is very little affected by structure. A possible exception to this rule might be the case of a liquid material, such as an oil, with long polar molecules which rotate into orientation with the applied field.

On the one hand, because of their widespread use in electrical engineering, insulating oils have been extensively investigated in bulk form, while thin oil films have been extensively studied, from the point of view of their mechanical properties, in lubrication engineering. The lubrication work indicates that at thicknesses in the region of $2\mu\text{m}$. and less the oil film behaves as a quasisolid. Smith³ has demonstrated directly, by scanning electron micrograph, that a solid quasicrystalline adsorbed layer, of thickness up to $2.5\mu\text{m}$. may be formed by the oil on a metal surface in the presence of fatty acids.

Thus it may be expected that the dielectric properties of the oil may change from bulk values, at very low thicknesses. In particular, if the molecules are polar and the polarization is due to orientation effects, inhibition of their rotation in the adsorbed layer may reduce their polarizability. On the other hand, if the molecules are fixed in position, mechanisms applicable to solids, such as interfacial polarization, may be expected.

In order to set this work in context of its inception, this chapter will be concerned with a brief description of fundamental dielectric properties in general and more particularly effects of relevance to liquid dielectrics. Discussions of individual points in the published literature on this subject which have particular relevance to this work are confined to the appropriate later chapters.

1.2. Mechanisms of Polarization.

A brief description of mechanisms of polarization is given in

this section. For further information texts, such as those of reference 4, should be consulted.

It is an experimental fact that if a dielectric material is inserted between the plates of a charged capacitor the potential difference between the plates falls. Consider a capacitor with plane parallel electrodes, having uniform charge density of σ on each electrode and having vacuum as its dielectric. The electric flux density (D) is given, according to Gauss' theorem, by

$$D = \sigma \quad (1.1.)$$

Also, by definition, the electric field strength (E) is given by

$$E = D/\epsilon_0 = \sigma/\epsilon_0 \quad (1.2.)$$

When a dielectric material of relative permittivity ϵ' is inserted, the electric field falls to E_d .

$$E_d = \sigma/\epsilon'\epsilon_0 \quad (1.3.)$$

The change, in field (ΔE), caused by insertion of the dielectric medium is therefore

$$\Delta E = \frac{\sigma(\epsilon' - 1)}{\epsilon'\epsilon_0} \quad (1.4.)$$

The value of D, however, remains unchanged.

Therefore the contribution of E to D falls by an amount ΔE which, according to 1.3. is equal to $\frac{\sigma(\epsilon' - 1)}{\epsilon'}$. This quantity is termed the polarization, P, of the dielectric medium, and the equation for D is then written

$$D = \epsilon_0 E + P$$

$$\text{Where} \quad P = \frac{\sigma(\epsilon' - 1)}{\epsilon'} \quad (1.5.)$$

Combining 1.3. with 1.5. gives

$$P = (\epsilon' - 1)\epsilon_0 E_d = \chi\epsilon_0 E_d \quad (1.6.)$$

where $\chi = (\epsilon' - 1)$ is called the dielectric susceptibility of the

medium and is given by

$$\chi = \frac{(\text{Bound charge density})}{(\text{Free charge density})}$$

The measurement of the polarization of a material is based on 1.6. and consists of the measurement of χ or in practice of ϵ' .

The polarization flux density P is visualized as being induced in the dielectric by the orientation of existing permanent dipoles within the material, or by the induction of dipoles by separation of charges within otherwise non-polar molecules or atoms. Thus, on a molecular or atomic scale, the electric field exhibits large local variations, and the polarization of a dielectric depends not only upon the number of dipoles present and the ease with which they may be aligned by an electric field, but also on the local field within the dielectric, since this will, in general, control their magnitude. The link between microscopic and macroscopic descriptions of a dielectric medium is provided by assuming the polarized dielectric to be composed of N elementary dipoles per unit volume, each with a mean dipole moment $\bar{\mu}$. Thus, the total moment per unit volume is $N\bar{\mu}$. Now, in the polarized dielectric, there are P bound charges per unit area and if we take two such areas, separated by a distance ℓ , the moment due to a unit area will be

$$\mu = P\ell \quad (1.7.)$$

For unit distance between unit areas $\ell = 1$ and therefore $\mu = P$ per unit volume. Thus the polarization is identical with the electric moment per unit volume of material and therefore

$$P = N\bar{\mu} \quad (1.8.)$$

Furthermore, $\bar{\mu}$ may be assumed to be proportional to a local electric field inside the dielectric. If this is denoted by E_{int} , being the value of the field acting on the dipole, we define

$$\mu = \alpha E_{\text{int}} \quad (1.9.)$$

where α is called the polarizability of the dipole i.e. is the average

dipole moment per unit field strength. The dimensions of d are

$$\frac{(\text{sec}^2 \text{coul}^2)}{(\text{kilogramme})} = (\text{farad metre}^2) = (\epsilon \text{m}^3)$$

Thus we have

$$P = (\epsilon' - 1)\epsilon_0 E = N\alpha E_{\text{int.}} \quad (1.10.)$$

This is referred to as the Clausius Equation.

Since α is defined in terms of dipole moment, its magnitude will clearly be a measure of the extent to which electric dipoles are formed by the atoms and molecules. These may arise through a variety of mechanisms, any or all of which contribute to the value of α . Thus for convenience, it is usual to resolve α into components applicable to each mechanism.

An atom comprises a positively charged inner shell surrounded by electron clouds having symmetries determined by their quantum states. Under the influence of an applied electric field, the electron clouds may be displaced slightly with respect to the nucleus, causing the atoms to take on an induced dipole moment. This induced moment is equivalent to an assembly of dipoles produced by elastic displacement of electrons, which have natural frequencies, equal to or higher than, those of visible light. The strength of the induced moment, μ_e , for an atom is proportional to the local field in the region of the atom and is given by

$$\mu_e = \alpha_e E_{\text{int.}} \quad (1.11.)$$

where α_e is called the optical or electronic polarizability.

In cases where electronic polarization alone operates, it was shown by Maxwell that an identity exists between the square of the refractive index and the relative permittivity. This provides a useful test for the relative importance of electronic and other types of polarizability.

In diatomic molecules composed of two different atoms the nature

of the interactions between the atoms causes redistribution of the electrons of the outermost valence shells with a resulting permanent dipole moment aligned along the direction of the chemical bond between them. The distribution will be axially symmetrical (for diatomic molecules) around the line joining the nuclei, and the dipole will be in the direction of this line. Molecules composed of similar atoms, by virtue of their symmetry have no permanent dipole. Polar molecules having a dipole moment may interact with an applied field in two distinct manners, either by elastic displacement of the charges, or by rotation of the whole molecule resulting in partial or complete alignment of the dipole with the field. These interactions give rise to the atomic and orientational (or dipole) polarizabilities, α_a and α_d respectively. The atomic polarizability corresponds to oscillations with natural frequencies in the infra-red and gives rise to the infra-red absorption spectra, while orientational polarizabilities become effective in the radio frequency region of the electromagnetic spectrum. Clearly the atoms of polar molecules will also exhibit electronic polarizability.

These three mechanisms of polarization, characterized by an electronic polarizability α_e , an atomic polarizability α_a , and an orientational polarizability α_d , are due to charges that are locally bound in atoms, in molecules, or in the structures of solids and liquids, in addition, carriers that can migrate for some distance through the dielectric usually exist. When such carriers are impeded in their motion, either because they become trapped in the material or on interfaces, or because they cannot be freely discharged or replaced at the electrodes, space charges and a macroscopic field distortion result. Such a distortion appears to an outside observer as an increase in the capacitance of the sample and may be indistinguishable from a real rise in the dielectric permittivity.

Thus we have to add to our polarization mechanisms a fourth one, a space charge (or interfacial) polarization, characterized by a space charge (or interfacial) polarizability α_i . Assuming that the four polarization mechanisms act independently of each other, they can be lumped together in a phenomenological constant α , the polarizability, given by

$$\alpha = \alpha_e + \alpha_a + \alpha_d + \alpha_i \quad (1.12)$$

where each term may again represent a sum of contributions.

In Eq. 1.10. it was taken for granted that the polarizability α is a real quantity. Actually, in alternating fields, a temporal phase shift may occur between the driving field and the resultant polarization, and a loss current component appears. Thus α becomes complex and Eq. 1.10 has to be replaced by the more general formulation

$$P = (\epsilon^* - 1)\epsilon_0 E = NqE_{int} \quad (1.13.)$$

where ϵ^* is the complex permittivity.

Dielectric materials may then be classified according to which types of polarizability they exhibit. Those which have only electronic polarizability and show variations of permittivity in the optical range of frequencies only are termed non-polar, while those molecules with permanent dipole moments are termed polar or dipolar according to whether polarization is entirely due to elastic displacement of the dipoles, or whether rotation and orientation are also possible.

Of the four possible polarization mechanisms only orientational and interfacial polarizabilities can be expected to be affected by the thickness of the material.

1.3. Static Permittivity and Dipole Moment.

The static permittivity of a gas may be accurately calculated by

means of the Debye equation⁵ from the molecular polarizability and permanent dipole moment. The Debye equation may be used to calculate approximate values of the molecular dipole moment from the permittivities and densities of dilute solutions of the polar molecules in non-polar solvents. The small difference between these approximate solution values and the gas values may be calculated correctly as to magnitude and sign by the equations of Higasi⁶, of Conner and Smyth⁷, and of Ross and Sack⁸, but none of these equations takes strict account of all the factors involved. The Debye equation is not applicable to pure polar liquids, but the Onsager equation⁹ gives the approximate relation between the permittivity of a normal polar liquid and the molecular dipole moment. The dipole moment value calculated by it from the permittivity of the pure liquid is commonly only a little less approximate than the uncorrected Debye solution values. Kirkwood¹⁰ introduced a factor, into the Onsager equation, to take into account the restriction of molecular orientation by neighbouring molecules. In the usual absence of knowledge of liquid structure this factor is unknown and useful only as an empirical constant.

1.4. Orientational Polarization and Relaxation Processes.

Permittivity, $\epsilon = \epsilon_r \epsilon_0$ is defined as a property of a dielectric medium by means of Coulombs law, where ϵ_r is the relative permittivity. If a parallel-plate capacitor has a capacitance C_0 with vacuum as its dielectric and the space between the plates is filled by a medium of permittivity ϵ_r then, neglecting fringe effects, the capacitance becomes

$$C = \epsilon_r C_0 \quad (1.14.)$$

When an alternating electromotive force of value v is applied across the plates of the capacitor an alternating current i will flow, its

value being

$$i = j\omega\epsilon_r C_o v \quad (1.15)$$

provided that the dielectric is a "perfect" one. In general, however, an in-phase component of current will appear corresponding to a resistive current between the capacitor plates. Such a current is entirely due to the dielectric medium and is a property of it. We therefore characterize it by a component of permittivity by defining the relative permittivity as

$$\epsilon_r = \epsilon' - j\epsilon'' \quad (1.16)$$

The current in the capacitor then becomes

$$i = j\omega(\epsilon' - j\epsilon'')C_o v = \omega\epsilon''C_o v + j\omega\epsilon'C_o v \quad (1.17.)$$

and it has a real component. The magnitude of ϵ'' will be defined by the magnitude of the in-phase, or "loss", component of the current. It will be noted that this mode of definition requires no statement as to the type of loss mechanism envisaged in the dielectric.

It is conventional to describe the performance of a capacitor in terms of its loss angle δ , which is the phase angle between the total current i and the purely quadrature component i_c . If the in-phase component is i_L then

$$|i| = (|i_L|^2 + |i_c|^2)^{\frac{1}{2}}$$

$$\text{and} \quad \tan \delta = \frac{|i_L|}{|i_c|} = \frac{\omega\epsilon''C_o v}{\omega\epsilon'C_o v}$$

$$\text{i.e.} \quad \tan \delta = \frac{\epsilon''}{\epsilon'} \quad (1.18)$$

Eq. 1.17 may be regarded as the definition of ϵ'' and, at the same time, indicates the basis of its measurement. When the dielectric medium is "loss-free", ϵ'' will be zero.

It is sometimes convenient to use the concept of dielectric conductivity. The capacitance of an air-filled (vacuum), parallel-plate capacitor is

$$C_o = \frac{A\epsilon_o}{d} \quad \text{farads}$$

With an applied alternating electromotive force of v and a dielectric between the plates, the current is given by

$$i = j\omega(\epsilon' - j\epsilon'')\frac{A\epsilon_0 v}{d}$$

but the electric field strength $E = v/d$ and the current density $J = i/A$. Therefore

$$J = j\omega\epsilon_0\epsilon'E + \omega\epsilon_0\epsilon''E$$

Now by definition, the conductivity (which may be complex) is the ratio J/E and thus

$$J/E = j\omega\epsilon_0\epsilon' + \omega\epsilon_0\epsilon'' \quad (1.19.)$$

In the dielectric, however, the imaginary part is already accounted for by the capacitance. Thus a dielectric conductivity may be defined as the real part of the ratio J/E in Eq. 1.19.

$$\text{i.e. } \sigma_d = \omega\epsilon_0\epsilon'' \quad (1.20.)$$

Dielectric conductivity represents the sum of all the loss mechanisms in the material and is a measure of the performance of a dielectric as an insulator.

In general, the electric flux density, D , resulting from an applied alternating field E differs in phase from E . This is due to the inertia of polarization which, when the frequency becomes high enough, cannot follow the field variations, giving rise to a "relaxation" of the measured permittivity.

This behaviour may be stated formally by an equation of the type

$$\epsilon(\omega) = \epsilon_\infty + \int_0^\infty \alpha(t)e^{j\omega t} dt \quad (1.21)$$

in which ϵ_∞ is the value of permittivity at infinite frequency (which is a constant), and $\alpha(t)$ is some sort of decay factor accounting for the lagging of polarization behind the applied field. Clearly $\alpha(t)$ will be connected with the total permittivity such that it can be put in terms of the real and imaginary parts ϵ' and ϵ'' . Also Eq. 1.21 requires that $\alpha(t) \rightarrow 0$ as $\omega \rightarrow \infty$ since $\epsilon(\omega) = \epsilon_\infty$ as $\omega \rightarrow \infty$.

Since it accounts for the lagging of $D(\omega)$ with respect to $E(\omega)$, $\alpha(t)$ must describe the decay of polarization after the sudden removal of a steady field. It will also describe the increase of polarization towards its equilibrium value when a steady field is suddenly applied. It may therefore be summarized as being related to the time constant of polarization of a dielectric.

Debye⁵ proposed an exponential form for the decay factor

$$\alpha(t) = \alpha(0)e^{-t/\tau} \quad (1.22.)$$

where τ is a relaxation time, characteristic of the dielectric, which may be a function of temperature but not of time.

Inserting this into Eq. 1.21. we have

$$\epsilon_r(\omega) = \epsilon_\infty + \int_0^\infty \alpha(0) e^{(j\omega - 1/\tau)t} dt \quad (1.23.)$$

$$\epsilon_r(\omega) = \epsilon_\infty + \frac{\alpha(0)}{1/\tau - j\omega} \quad (1.24.)$$

At $\omega = 0$, $\epsilon_r(\omega) = \epsilon_s$ and we have

$$\epsilon_s = \epsilon_\infty + \tau \alpha(0) \quad (1.25.)$$

Putting Eq. 1.25. into Eq. 1.22. gives

$$\alpha(t) = \frac{(\epsilon_s - \epsilon_\infty)e^{-t/\tau}}{\tau} \quad (1.26)$$

while using Eq. 1.26. in Eq. 1.21. results in

$$\epsilon_r(\omega) = \epsilon_\infty + \int_0^\infty \frac{(\epsilon_s - \epsilon_\infty)}{\tau} e^{-t/\tau} e^{j\omega t} dt$$

Therefore $\epsilon_r(\omega) = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \quad (1.27)$

Equating real and imaginary parts in Eq. 1.27. gives

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (1.28)$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad (1.29)$$

and $\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{\epsilon_s + \omega^2\tau^2\epsilon_\infty} \quad (1.30)$

Equations 1.28 to 1.30 are known collectively as the Debye equations. This treatment makes no specific reference to the mechanism resulting in an exponential decay factor and there are several models which will account for this type of behaviour. For example, the potential double well model, described by Anderson^{4a} assumes a collection of non-interacting particles, each of which has two possible equilibrium positions, separated by a high potential barrier. Such a model would apply, for instance, to a dipole having equilibrium positions corresponding to its axis being at 0° and 180° to some given direction.

Dielectric relaxation, in which the frequency spectrum of permittivity is in general agreement with the Debye formulae, is often found in dipolar liquids. This suggests a mechanism of polarization involving an exponential decay factor and Debye⁵ proposed a model for this. Since, in a liquid, the molecules are not in fixed positions, it may be imagined that if one molecule turned from its equilibrium position, its neighbours would rearrange themselves to make the new position an equilibrium one. Their average motion might be described by treating them as a continuous medium, exerting a viscous frictional damping force on the original dipole. If the dipolar molecule has radius a and moves in a continuous viscous fluid of viscosity η , the frictional constant ξ is given by Stokes law as

$$\xi = 8\pi\eta a^3 \quad (1.31.)$$

If a field is applied, at an angle θ to the axis of the dipole, a torque will be produced on it such that

$$\Gamma = \xi \frac{d\theta}{dt} \quad (1.32.)$$

and the dipole will align itself with the field at a rate dependent upon the friction factor ξ . However, the molecular dipole is also subject to thermal fluctuations (Brownian motion) which affects the rate of

change of angle when the field is applied. Debye took account of this in his calculation and was able to deduce an expression for the relaxation time:

$$\tau = \xi/2kT = 4\pi\eta a^3/kT \quad (1.33.)$$

or
$$\tau = 3\eta V/kT \quad (1.34.)$$

where V is the volume of the molecular dipole. To obtain an absolute value for τ it is necessary to know the volume of a sphere having the same frictional constant as the dipolar molecule, which is not necessarily the same as the molecular volume. Thus it is not to be expected that Eq. 1.34 will predict accurately the experimental values of relaxation time. However some agreement is obtained; for water $\eta = 0.01$ poise at room temperature and the molecular volume is approximately $3.5 \times 10^{-23} \text{ cm}^3$, leading to a relaxation time $\tau \sim 0.25 \times 10^{-10} \text{ sec.}$ Since the maximum absorption (ϵ''_{max}) occurs at an angular frequency $\omega = 1/\tau$, we should expect relaxation in the region of 10^{10} Hz. , which is in agreement with experiment.

An interesting feature of Eq. 1.34 is its prediction that the variation, with temperature, of relaxation time, τ , should be the same as that of the coefficient of viscosity, η , divided by T . Experimentally η is related to temperature by

$$\eta \propto \exp(H_{\eta}/kt)$$

where H_{η} is a constant for a given liquid. Thus we may predict

$$\tau \propto \frac{1}{T} \exp(H_{\eta}/kt)$$

and this may be experimentally tested.

1.5. Permittivity of Pure Liquids.

1.5.1. Non-polar liquids

The permittivity of non-polar liquids is determined by the liquid density and by the atomic and electronic polarizations. The Clausius-

Mossotti equation predicts a constant molar polarization,

$$P = \left(\frac{\epsilon_s - 1}{\epsilon_s + 2} \right) \frac{M}{d} = \frac{4\pi N}{3} (\alpha_e + \alpha_a)$$

and adequately represents the permittivity changes produced by changes in the liquid density. Over limited temperature ranges the permittivity is linearly related to temperature

$$\epsilon(T_2) = \epsilon(T_1) - a(T_2 - T_1)$$

Contrary to the predictions of the Clausius - Mossotti theory, the polarization is dependent on the molecular state, and is smaller in the liquid than in the ideal gas phase¹¹. Deviations of the polarization of gases from a constant value with increasing pressure are explained by fluctuation effects and by changes in the polarizability of molecules caused by intermolecular interactions at high pressures. With increasing pressure, intermolecular interactions cause the polarizability to increase to a maximum and then to decrease when repulsion forces between the interacting molecules become significant. In liquids, fluctuation effects are largely suppressed, and the polarizability is less than in the gas phase, because of the increased intermolecular interactions produced by the higher density.

1.5.2. Polar liquids.

Calculation of the molecular dipole moment using the Debye equation gives values which are usually very different from those obtained from measurements in the gas phase. Intermolecular interactions in liquids produce deviations from the simple conditions envisaged by Debye, whose version of the internal field is now seriously in error. The Onsager equation⁹ gives a more satisfactory representation of the molecular dipole moment in non-associated liquids. For associated liquids, the Kirkwood¹⁰ and Fröhlich¹² treatments are more appropriate but require a detailed knowledge of the liquid structure before the correlation parameter g may be

calculated. The use of n_D^2 in the Onsager, Kirkwood and Fröhlich equations is strictly incorrect, and it should be replaced by ϵ_∞ . For non-associated systems, ϵ_∞ is approximately 5 to 10% greater than n_D^2 . For associated systems, few estimates of ϵ_∞ are available, and it is usual (erroneously) to use n_D^2 when evaluating the dipole moment.

The Onsager values for non-associated liquids agree with the gas values as well as do those from dilute solutions. The dipole moments of rigid molecules calculated by using Onsager's equation should be temperature-independent, but this is found not to be strictly true. Better agreement between the gas and liquid dipole moments is obtained when Onsager's spherical cavity is replaced by an ellipsoidal cavity of the same volume, with the dipole directed along one of the principal axes. If the volume of the cavity is temperature-independent, the modified Onsager equation gives a good representation of the temperature variation of permittivity¹³. Unfortunately calculations using the ellipsoidal-cavity model are complicated, and have not been widely used.

1.5.3. Hydrogen bonded liquids.

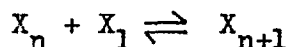
Short-range interactions described as hydrogen-bonding align the molecules either into chain-like structures (e.g. water, alcohols) or into anti-parallel arrangements (e.g. carboxylic acids). The atomic polarization increases, and in the latter case the orientation polarization decreases by mutual cancellation of the individual molecular dipoles, producing a liquid permittivity smaller than that calculated for a non-associating liquid of the same dipole moment. These short-range interactions are included in the Kirkwood and the Fröhlich evaluations of the permittivity by the correlation factor g , which may be calculated if the liquid structure is known. Oster and Kirkwood¹⁴ assumed the presence of infinitely long hydrogen-bonded chains in alcohols, each alcohol molecule having two nearest neighbours.

Assuming free rotation about the hydrogen-bonds, calculations gave $g = 2.57$ for normal alcohols, resulting in the values shown below

<u>Alcohol</u>	<u>ϵ_s (calc.)</u>	<u>ϵ_s (obs.)</u>
Methyl	29.2	32.8
Ethyl	21.3	24.6
Propyl	17.3	19.5
Butyl	14.6	18.0
Pentyl	12.8	15.8

Because of the lack of information concerning the structure of liquids, most evaluations of g are made by comparing the effective dipole moment ($g^{\frac{1}{2}}\mu$), calculated from the Kirkwood equation with the molecular dipole moment (μ), obtained from gas-phase measurements. The absolute magnitude of the g factor is not of great significance because of the uncertainty in the value of n^2 used in the Kirkwood equation, but the variation of the g factor within a series of measurements is often of structural value. The g factor for ethanol decreases from 3.34 at -133°C to 1.87 at 227°C ¹⁵, showing the decreasing association with increasing temperature. In the alcohols hydrogen-bonding decreases in the series normal butyl, secondary butyl and tertiary butyl alcohol. The g factors decrease in the same order.

Permittivity measurements are used to evaluate equilibrium constants in associated systems. Assume a molecule X associates into a series of multimers according to the equilibrium



The equilibrium constant $K = C_{n+1}/C_n C_1$ is assumed to be independent of n . If C_0 is the gross concentration measured as monomer then

$$C_0 = \sum_{n=1}^{\infty} n C_n = C_1 / (1 - KC_1)^2$$

The Kirkwood equation and the vapour dipole moment give the overall g factor for the liquid, which is the weighted average correlation factor for all the individual species in the liquid. This has been evaluated for alcohols¹⁶, N substituted amides¹⁵ and linear multimers¹⁷. The correlation factor for a linear chain of multimers equals n , the number of molecules in the chain, and the weighted average correlation factor is

$$g = \frac{\sum_{n=1}^{\infty} n^2 C_n}{C_0} = \frac{1 + KC_1}{1 - KC_1}$$

This leads to $KC_0 = (g^2 - 1)/4$, and a plot of $\log(g^2 - 1)$ against $1/T$ should be linear with gradient proportional to ΔH , the heat of association.

1.6. Dispersion and Absorption in Liquids.

First anticipations are that a non-polar liquid will show no dielectric absorption. This, in practice, is correct to a very high degree of approximation, but there are important qualifications.

Impurities in the liquid will give rise to apparent loss values in two regions. At low frequencies a significant loss factor will appear as a result of conductivity. A conductivity of $\sigma = 1 \times 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ will give

$$(\epsilon'' \times f) = 1.8 \times 10^{-2}$$

where f is in Hz. This is the minimum conductance-loss to be expected for non-polar solvents (e.g. benzene) in equilibrium with atmospheric moisture. Very careful drying and subsequent handling will move the conductance of hydrocarbons (n-heptane, cyclohexane) down to the region $\sigma = 1 \times 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$. Small traces of moisture have a large influence on the conductivity values, not only because water itself is a conducting species, but also because it will almost invariably increase the concentrations of ions in the medium. In addition the non-polar molecules may undergo some minute degree of

self-ionization, and current carrying ions will appear in a background of cosmic-rays and other radiations. Because of their chemical stability and poor solution powers, the saturated hydrocarbons readily give low conductances. Chlorinated hydrocarbons (carbon tetrachloride, tetrachloroethylene, etc.) suffer ultimately from the less stable character of the (C-Cl) bond. In this regard, the perfluorinated solvents prove more acceptable.

Any polar impurity will contribute its own loss to a solvent being measured. The order of magnitude of this contribution can be gauged in terms of $\epsilon''_{\max}$, the maximum value it will give rise to at $\omega\tau = 1$. Near room temperature an impurity having dipole moment μ (D), and a concentration of C (g. mol. litre⁻¹) would have

$$\epsilon''_{\max} \sim 60 \times 10^{-3} \mu^2 C$$

For water ($\mu = 1.85$ D) at a volume fraction of 1×10^{-5} , i.e.

$C = 5.5 \times 10^{-4}$, the value is $\epsilon''_{\max} \sim 1.1 \times 10^{-4}$.

Accordingly, particular care in preparing and handling solvents is needed if impurity losses of this order are not to be encountered in the microwave region.

Of far greater significance than the residual losses due to impurities is the finding that typically non-polar liquids do show a real absorption, albeit a very small one, in the microwave region. Early measurements¹⁸ using such solvents as benzene showed an apparent residual absorption, and this was thoroughly confirmed by Whiffen¹⁹. Whiffen suggested that the absorptions were due to the presence of temporary collision-induced dipoles of the order of 0.1D having an effective relaxation time c. 1×10^{-12} sec. ($\bar{\nu} \sim 7\text{cm}^{-1}$) determined by the time between collisions in the liquid. The polarization relaxes not by dipole rotation but by changing configurations of the molecular encounters which have given rise to it. In spectroscopic terms it

represents a breakdown of the selection rule forbidding absorption of microwave energy by a non-polar molecule. However, the appearance of absorptions forbidden by isolated molecule symmetry is a frequent occurrence in infra-red liquid spectra. In molecular dynamics it represents the limited rigidity of the structure whose non-polarity arises from a symmetrical pattern of polar bonds.

The majority of liquids formed by polar molecules lacking obvious flexible dipole elements give single dielectric absorptions, often conforming very well to the simple relaxation pattern of Debye. Most such liquids give an absorption with $\epsilon''_{\max}$ occurring between 0.1 and 10cm^{-1} .

Debyes original model led to the expression

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

for relaxation time, where V = volume of rigid polar molecule and η is an "effective" viscosity of the medium. Debye established at a very early stage²⁰ that the latter is significantly different from the macroscopic viscosity. From data obtained by Poley²¹ and estimated Van der Waals molecular volume imply that $\eta(\text{effective}) \sim 0.1 \eta$ (macroscopic) for molecules of the type $\text{C}_6\text{H}_5\text{X}$ (substituted benzenes).

Limited guidance on the variation of relaxation time can be sought from $\tau = \frac{3V}{kT} \eta$ according to Fischer²² by using $\eta(\text{effective}) = s \cdot \eta$ (macroscopic), where s itself varies with the system considered but is c.0.3. for such molecules as chlorobenzene in common organic solvents. This limited use implies equal temperature coefficients in any one medium of τ and η . Even over as restricted a range as 20 to 60°C , the ratio τ/η for pure polar liquids may vary by 20 per cent²³.

Dielectric relaxations are rate processes, and the relaxation time is the reciprocal of a mean rate coefficient. Such molecular

rate processes usually follow the temperature law associated with the name of Arrhenius, the origin of which is the Boltzmann energy-distribution function. The Arrhenius relation for rate coefficients

$$\text{is } k = A' \exp (-\Delta H_A^*/kT)$$

$$\text{or } \tau = A \exp (\Delta H_A^*/kT)$$

Here A ($=1/A'$) is a numerical constant, and ΔH_A^* is the Arrhenius activation enthalpy. (An enthalpy value is given when rates are measured at constant pressure rather than constant volume, which would give rise to the closely similar energy term. Because of the small difference ($\Delta H^* - \Delta E^*$) in these activation terms, the usually measured enthalpy term is frequently referred to as the "activation energy".) Whilst the Arrhenius equation assumes A to be independent of temperature, different models of rate processes incorporate a power of T , varying with the model, in the term A : but such is the predominance of the exponential factor, which they all share, that it is not easy to discriminate between them.

Over the usual temperature range of about 100 deg.C or less, many polar liquids and solutions of polar molecules will show scarcely any significant deviation from the Arrhenius relation.

1.7. The Role of "Structure" in Liquids.

Models based on systems of rigid dipoles of such a character that little specific interaction between one molecule and its neighbour arises lead to the simplest pattern of dielectric dispersion. The situation changes appreciably when hydroxyl-containing molecules are considered. Such molecules are known to have appreciable mobility of at least a large part of the total dipole within the molecule: thus, in the alcohols or phenols, the (OH) group is able to rotate about the axis of the (C-O) bond (Fig. 1.1a.) which joins it to the molecular skeleton. An approximate representation of the polar

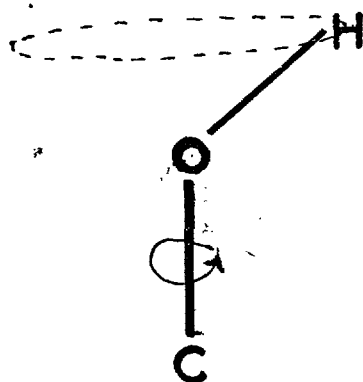


Figure I.l.a. Rotation of hydroxyl(O-H) group about a (C-O) single bond.

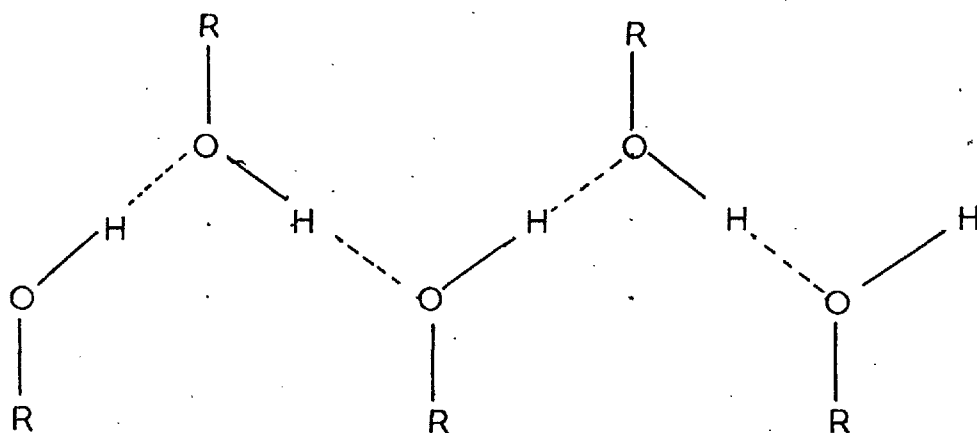


Figure I.l.b.Chain association of hydroxyl groups in hydroxylic compounds.

elements concerned emphasizes that perhaps 80 per cent of the total observed moment could relax intramolecularly. However, in the liquid phase, another over-riding factor dominates the situation. The hydroxyl groups of different molecules (sometimes two such groups within the same molecule) interact with one another, forming a hydrogen-bond, which links the molecules together. This hydrogen-bond develops essentially between the hydrogen atom of one hydroxyl group and the $(2p_z^2)$ lone-pair electrons of another hydroxyl oxygen: its energy, of the order of $5K \text{ cal.mole}^{-1}$, restricts the mobility of the hydroxyl groups, and as the bonding can continue through a chain of such groups (Fig. 1.1b) considerable 'structure' is produced in the liquid. The equilibrium in the association of such molecules, $n\text{ROH} \rightleftharpoons (\text{ROH})_n$ is a dynamic one, and a range of values of n , i.e. in the complexity of the multimer $(\text{ROH})_n$ is usually encountered. Clearly water (and hydrogen peroxide HO-OH) will represent a limiting state of such interactions.

The alcohols, of which there is a considerable variety, have attracted a great deal of study of their dielectric dispersion. In some of the first significant work to follow Drude's²⁴ pioneering measurements, Mizushima²⁵ examined the alcohols. French workers (from Girard and Abadie, 1932) took an interest which still continues, and work of R.H.Cole and his school, which has made an intensive study of these systems, provides a major contribution to a pattern which illuminates not only these processes of dielectric absorption but also some general aspects of the liquid state.

There are three major aspects of dielectric studies of the alcohols: firstly, the precise representation of the form of the main absorption: secondly, the question of the occurrence of subsidiary high-frequency processes; thirdly, the temperature behaviour of the absorptions. It may be mentioned that these aspects, which arise in

the case of any polar liquid, have received detailed study in the alcohols for sound practical reasons. The alcohols are reluctant to crystallize; so they can be studied in the liquid (and supercooled) states over a wide range of temperature and, especially at lower temperatures ($T < 200^{\circ}\text{K}$), the major dispersion, which is of considerable amplitude, is all within the frequency range of precise bridge measurement.

Certain associated liquids supercool easily and have a supercooled condition viscosities which class them as glassy solids rather than normal liquids. The most interesting liquids in this group are glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$ and related liquids, and mixtures of chlorinated diphenyls. The latter are of commercial interest, and known under trade names such as "aroclor" and "pyranol".

The chlorinated diphenyls are useful impregnants for paper capacitors because they combine a fairly high permittivity with chemical stability²⁶. They are mixtures based on diphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5$ and have substituted chlorine atoms in varying numbers and positions. Under the trade name Aroclor they are graded so that the last two digits of a four-digit code give the weight percentage of chlorine. For instance, type 1242 contains about three chlorine atoms per molecule.

The Aroclors have moderately wide relaxation peaks of the skewed type²⁷. The viscosity as a function of temperature shows a linear relationship between $\log \eta$ and $1/T^3$ at low temperature. The pressure dependence of the relaxation time is also exceptionally large.

The complicated relaxation behaviour of the aroclors may be appreciated in terms of structure, in so far as one may expect that different forms of clustering may be possible and thermo-dynamically about equally favourable. The chlorinated diphenyls can twist about the carbon-carbon bond joining the two rings, and the average

configuration of the two rings will in general be different for different isomers. The C-Cl groups are dipolar, and may form hydrogen-bonds²⁸ with adjacent C-H groups. Since aroclors are mixtures of isomers and of compounds with different chlorine contents, many patterns of short range order seem possible, and external variables such as the pressure may exert a strong influence on the structure.

1.8. Conclusions.

The foregoing equations are fundamental to the measurements described in this thesis.

The experiments were devised to investigate the extent to which a dielectric film could be reduced in thickness before its dielectric properties are affected, and to determine the dielectric properties of very thin films. The work is described in detail in the following chapters.

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CHAPTER 2

Experimental Techniques.

2.1. Introduction.

It is immediately apparent that one of the major difficulties is to produce a thin film of liquid upon which electrical measurements may be made. Several types of measuring cell were developed and these will be described below together with an evaluation of the performance of each system.

2.2. The Mercury Squeeze Film Cell.

Smith¹ in his work on boundary layer lubrication developed a mercury squeeze film viscometer and it was thought that this type of apparatus could be used in the present work. The squeeze film apparatus comprises two different forms, namely the "plate" apparatus and the "ball" apparatus. These two forms will be described separately.

2.2.1. "Plate" apparatus.

The cell consists of a glass chamber closed by a removable plate (see Fig.2.1.). The front plate has a pattern of thin metal electrodes on the inside surface. These electrodes were deposited by evaporation and condensation in vacuum. Connection to the electrodes was made via wires cemented with conducting epoxy resin into small holes drilled through the glass front plate.

In operation the cell is filled with the liquid to be tested and left for a period of time (of the order of 15 to 20 minutes) to allow the liquid time to adsorb onto the surface of the electrodes. The liquid is then displaced by introducing mercury from the reservoir into the cell, trapping a thin layer of the liquid between the mercury and the evaporated metal electrodes on the glass front plate. Connection to the other side of the liquid film is made via the

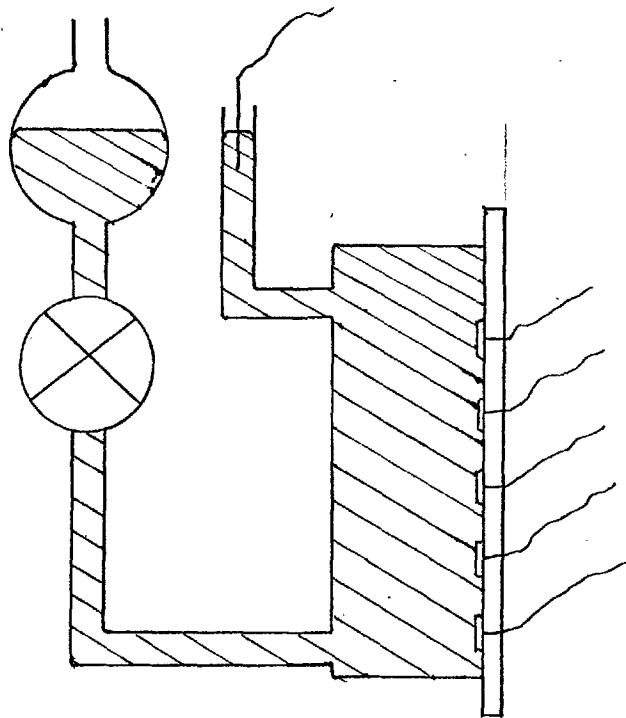
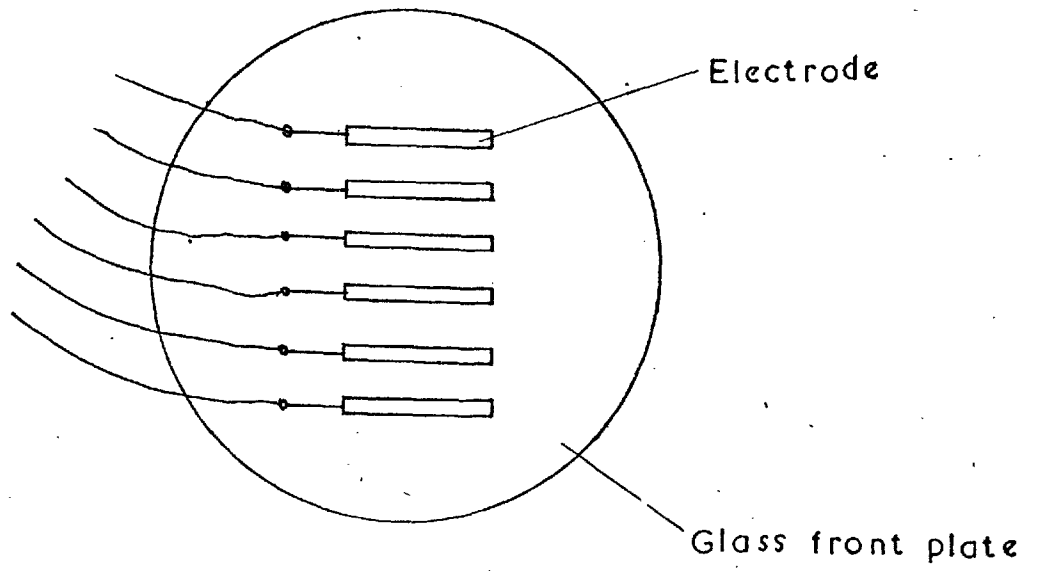


Figure 2.1. The Mercury Plate Apparatus.

mercury in the reservoir.

2.2.2. The "Ball" Apparatus.

The principal of operation is the same as the "Plate" apparatus but the form is slightly different. With reference to Figure 2.2, one electrode comprises a steel ball, which is approximately one half inch in diameter. This ball is suspended from a wire which also carries a guard coil, whose function is to protect the ball and film from damage. The cell consists of a small glass tube containing mercury covered by a layer of the liquid under investigation. The ball is lowered below the liquid into the mercury. As with the "Plate" form of the apparatus the second electrode is formed by the mercury.

2.2.3. Disadvantages of the Mercury Squeeze Film Apparatus.

The first and most serious objection to the Mercury Squeeze Film Apparatus is that it is difficult to measure the thickness of the liquid film. When this apparatus is used as a viscometer, capacitance measurements are made to determine the thickness of the liquid layer and from the work done by Smith¹ it is apparent that film thicknesses as low as a few tens of Angstrom units are obtained. However, for the purposes of the present work we require to know accurately both the capacitance of the system and the thickness of the liquid film independently of one another. It is possible to measure the thickness of the liquid layer by a laser interferometric technique for the plate apparatus but not in the case of the "Ball" apparatus. Despite this the problem still remains that in order to deduce the permittivity of the liquid layer the following assumptions must be made

1. That the refractive index of the thin liquid film is the same as that of a bulk sample of the liquid. This is a not unreasonable assumption and any error introduced will be small.
2. That the geometric electrode area is the area to be used in calculating capacitance. This assumption is not too unreasonable.

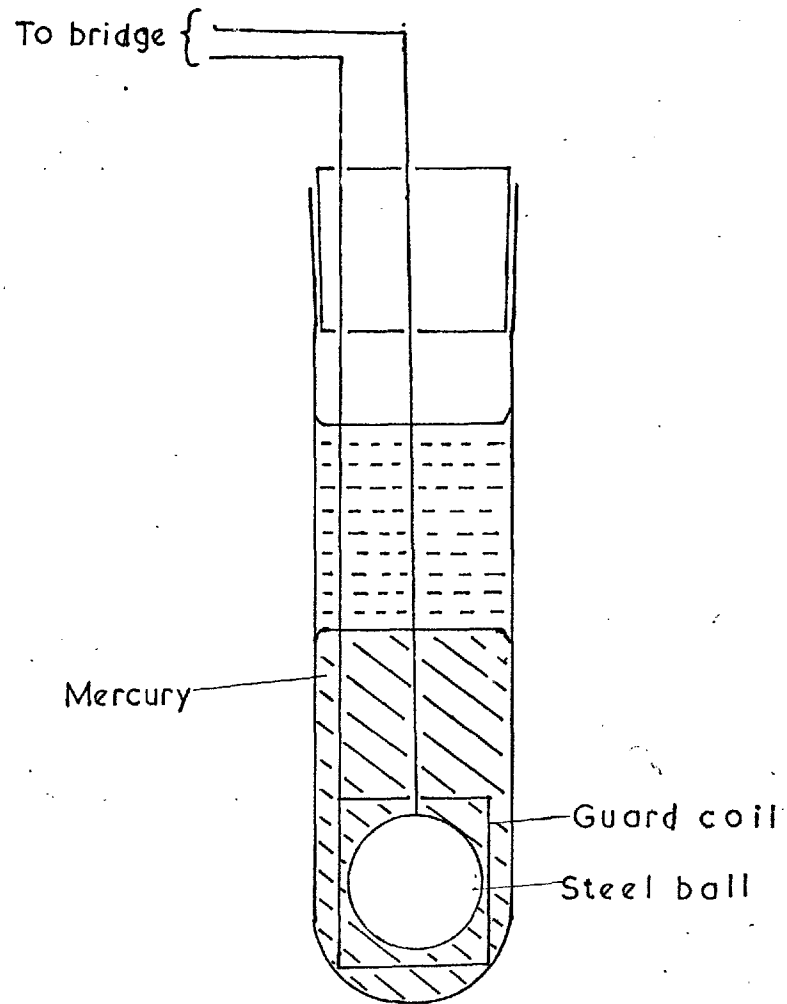


Figure 2.2 The Mercury Ball Apparatus.

in the case of the "Plate" apparatus where the glass front plate is flat and smooth, but even so the effects of stray capacitance have to be allowed for. In the case of the "Ball" form of the apparatus the correlation between "real" area and geometric area will depend on the surface finish of the steel balls.

As mentioned before the film thickness obtained with this form of apparatus is in the range $<100\text{\AA}$ to $20,000\text{\AA}$. The thickness of the film depends upon the liquid used, the hydrostatic pressure due to the mercury and the temperature. For a given liquid the pressure and temperature can be controlled but the variation in film thickness obtainable is limited.

Only in the "Plate" form of the mercury squeeze cell is it possible to make film thickness measurements independently of the capacitance measurements, but unfortunately the "Plate" apparatus does not adapt itself well to use at temperatures other than ambient. The temperature of the "Ball" apparatus can be varied easily by placing it in an oil bath, but the thickness of the film cannot be measured.

Another consequence of the very thin films produced is that their breakdown voltages are small. Difficulty was encountered in making capacitance measurements since the films broke down even with the lowest practical measuring voltage. Low frequency measurements were made on the samples using a Wayne - Kerr type B221 Transformer Ratio Arm Bridge. The voltage applied to the sample with this kind of bridge depends on the capacitance range being used, which is in turn dictated by the capacitance value of the sample. By using an external oscillator and detector it is possible to control the applied voltage on any range by varying the input voltage to the bridge, but the lower limit, which is set by the sensitivity of and the noise generated in the detector (General Radio, Tuned Amplifier and Null Detector, Type 1232-A), was found to be too high for the thinner films.

A consideration of the principal of operation of the transformer ratio arm bridge (see Appendix I) will show that an alternative method exists for reducing the voltage applied to the sample but the system must be designed to operate at one particular frequency and must be calibrated carefully before use and therefore its use is severely limited.

In view of the above arguments, along with several more minor points, it was decided that this form of apparatus was quite unsuitable for the work envisaged.

2.3. The Micrometer Cell.

This cell represented the first attempt to overcome some of the disadvantages of the mercury squeeze film apparatus. A diagram of the cell is shown in Fig. 2.3 and it can be seen that this cell again has an optically flat plate upon which an electrode may be deposited by evaporation and condensation in vacuum. In this case there is a single electrode, approximately 1cm. in diameter. Since a circular electrode is used in this cell a guard ring can also be deposited on the glass helping to reduce stray capacitance effects. The body of the cell was made from stainless steel and is fitted with a micrometer gauge head which carries the counter electrode.

The electrode spacing can be altered by means of the micrometer screw pushing against the counter electrode. This counter electrode can be made from any material required and silver was used in the prototype. The first major difficulty encountered with this cell was concerned with producing a surface which was sufficiently smooth and flat to permit it to be brought into close proximity to the evaporated electrode on the glass front plate without asperities causing short circuits. Quite a good finish could be obtained with the silver electrode by diamond lapping but because silver is a soft metal the

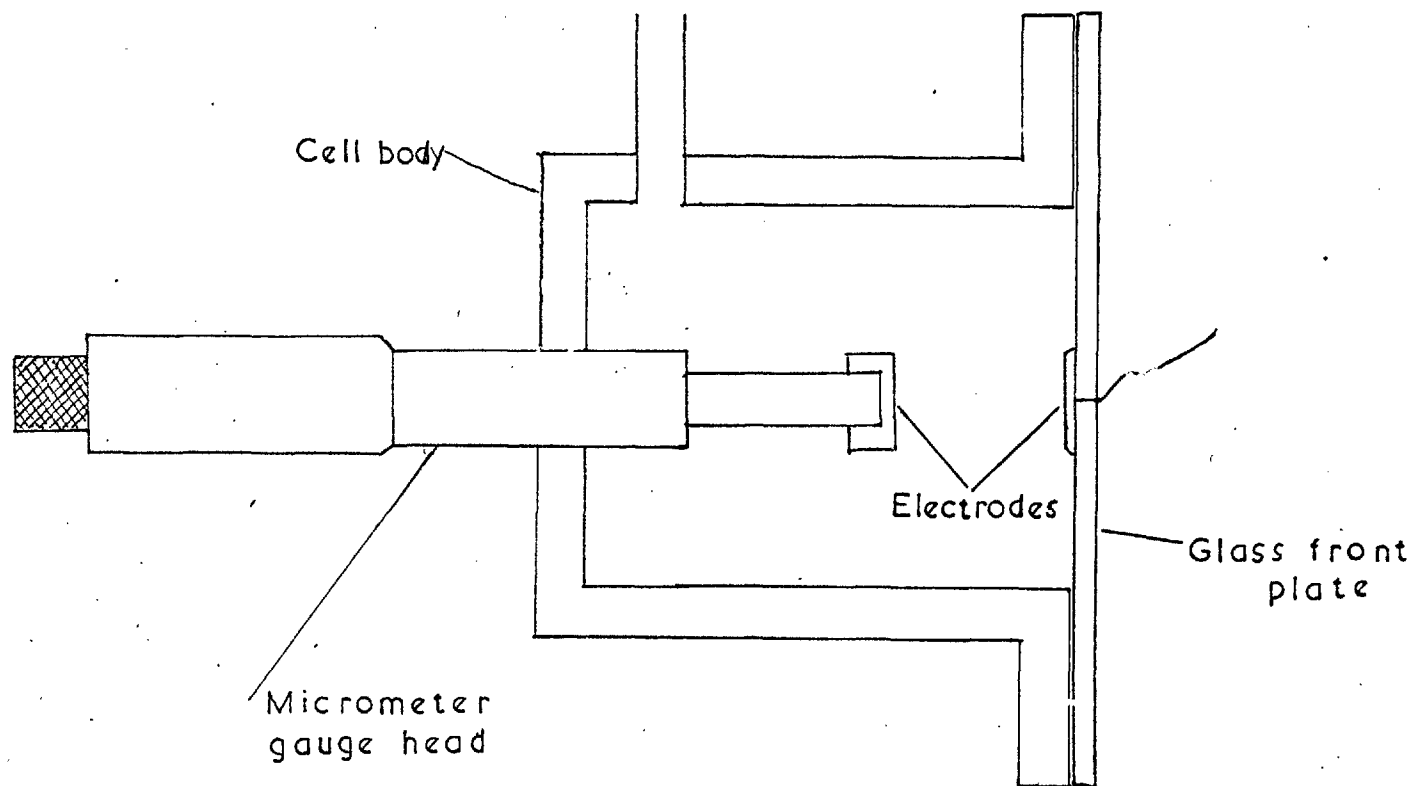


Figure 2.3 Micrometer Cell

lapping process tended to remove more material from the edges than at the centre and so a surface was produced that was flat over the central section but fell away towards the edges of the electrode.

It was decided that a lapped finish would be sufficient to test the viability of the cell and that if need be more refined finishing techniques such as electropolishing² could be tried. This cell has the great advantage that the capacitance of the electrode assembly may be measured with air as dielectric and then with the liquid added thus giving the relative permittivity directly from the relationship $\epsilon' = C_{\text{liquid}} / C_{\text{air}}$.

The electrode spacing may be measured by an interferometric method. The evaporated electrode is made semi-transparent and the spacing measured using "Fringes of Equal Chromatic Order" (see Appendix II). The angle between the two electrodes may be adjusted by means of the three screws which clamp the front plate to the cell and zero angle (i.e. electrodes parallel) can be detected by the shape of the interference fringes.

In practice it was very difficult and time consuming to adjust the cell correctly and the smallest electrode spacing obtainable was about 10 μ m. Presumably better results could have been obtained by improving the surface finish of the counter-electrode, but it was realized that a simpler solution would be to use two optically flat discs furnished with electrodes and clamped together with a suitable spacer.

2.4. Cell Systems using Optical Flats.

It was thought that using two optical flats with evaporated electrodes should reduce problems due to surface irregularities. In its first form the cell consisted of two glass discs 25mm. diameter with electrodes approximately 7mm. diameter. On one glass disc a

spacer layer of SiO was evaporated as shown in Fig.2.4. Several discs were produced with various thicknesses of SiO films in the range $0.5\mu\text{m}$ to $5\mu\text{m}$. The metal electrodes were made semi-transparent to permit the use of multiple-beam interferometry to measure their spacing. Several difficulties were encountered with this set-up two of which were fairly serious. Firstly, it is difficult to prepare SiO films greater than about $1\mu\text{m}$ thick without introducing mechanical stress which, ultimately, results in the film cracking, especially if the cell is temperature cycled. Secondly the glass discs used were only 1mm. thick and the clamping system used ~~to~~ caused them to flex, resulting in non-uniformity of the electrode spacing and poor stability of the spacing with temperature variations.

The above system then, although an improvement on previous attempts, is limited in the temperature range over which measurements could be made and also the range of thickness that could be covered. It was decided to improve these features by using much thicker optical flats (13mm.). A further improvement was effected by using rectangular flats and forming an optical wedge as shown in Fig.2.5. The optical flats used were 10cm. x 3.5cm. x 1.3cm. and had 45° chamfered edges on one face. This face was flat to within one eighth of a wavelength of the mercury green line over its whole surface. A pattern of electrodes was deposited on this face, and connection could be made to the electrodes where they extended onto the chamfered edges. The two flats were clamped together, with spring loaded clamps, with a suitable spacer at one end thus forming a wedge. The spacer used in most of the experiments was a piece of mica cleaved to a thickness $\sim 20\mu\text{m}$.

In this way several capacitors with different electrode spacing were formed and this represents a considerable saving in time and effort over the previous system whereby only one thickness at a time

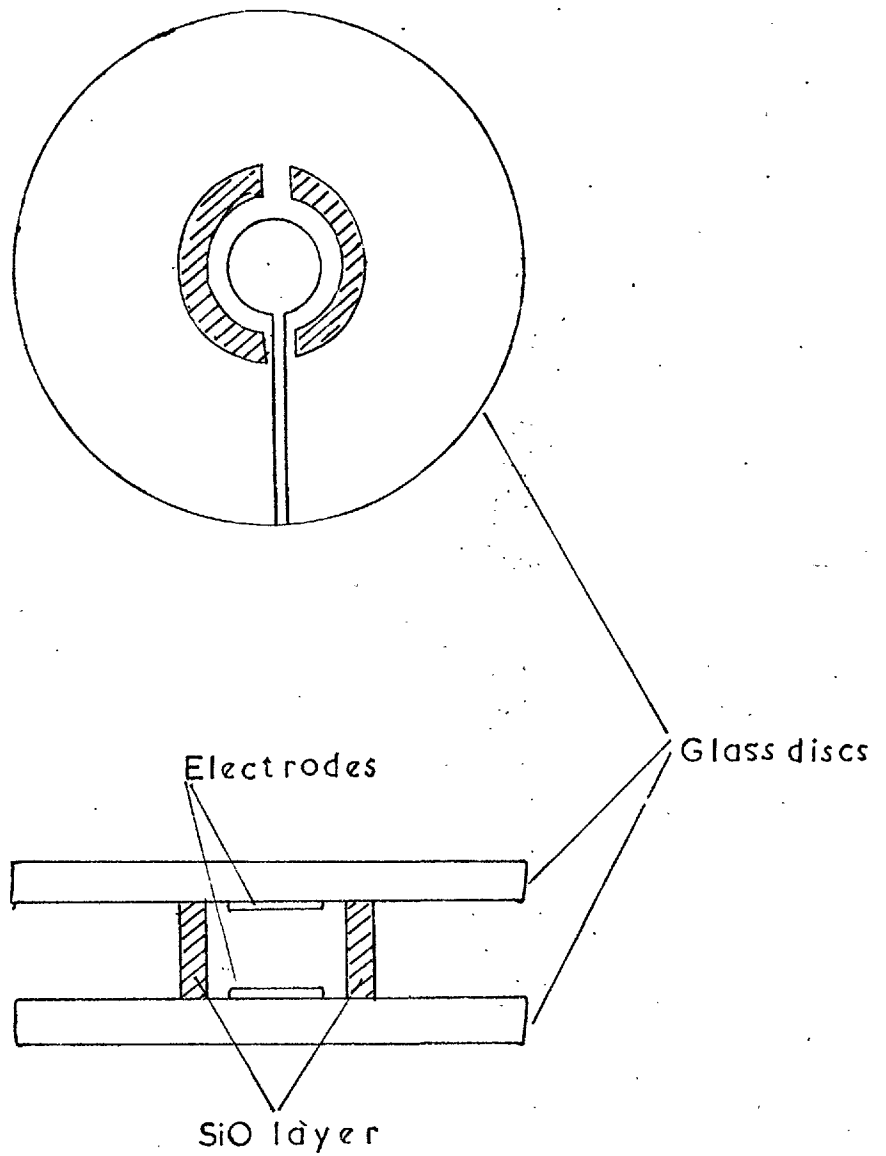
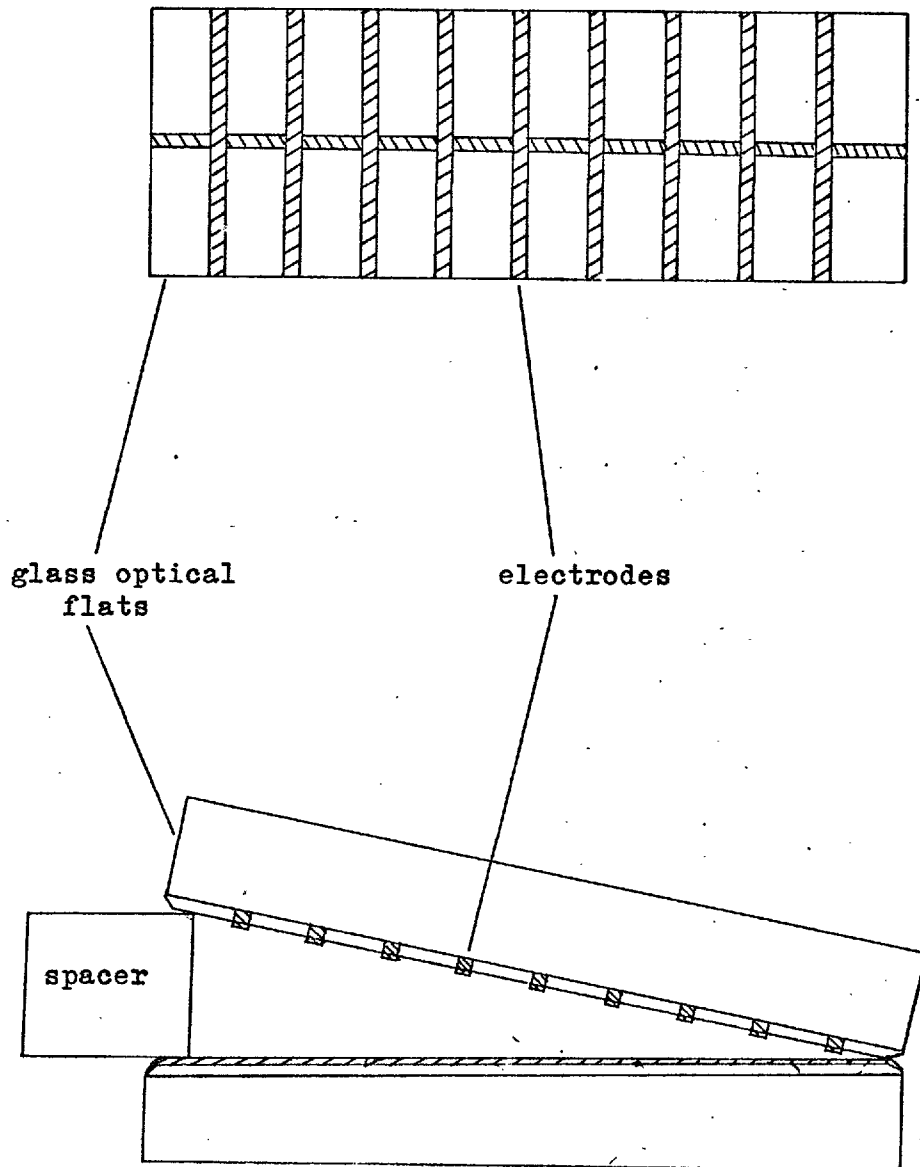


Figure 2.4 Early optical flat cell



*see Fig. 2.7. for photograph of assembled cell.

**wedge angle shown much exaggerated.

Figure 2.5. Optical wedge cell.

was realized. The use of an optical wedge also simplifies considerably the technique for measuring the electrode spacing.

With an optical wedge "fringes of equal thickness" may be formed simply by illuminating the wedge with monochromatic light. The fringes are localized within the wedge and so can be focussed upon with a microscope. The optical set up for thickness measurements is shown in simplified form in Fig.2.6.

The cell was illuminated by a mercury lamp fitted with a green filter which only allows the mercury green line ($\lambda = 5461 \text{ \AA}$) through. The "mono-chromatic" light is arranged to fall, at normal incidence, onto the cell system thus producing localized fringes within the wedge. The fringes were observed by means of a travelling microscope and a half-silvered mirror placed between the light source and the wedge. By using a travelling microscope the fringe spacing may be measured.

The procedure for measuring the electrode spacings is then as follows. After deposition of the electrode patterns on each glass block, they are assembled with the spacer placed at one end between them to create the wedge. Care must be exercised to ensure that dust is excluded as far as is practicable when assembling the wedge, also contamination from finger marks etc. is to be avoided at all costs.

The assembled cell is then placed under the mercury lamp and the fringes observed. The fringes represent constant height contours in the wedge and when first observed are at some angle to the wedge direction (Fig.2.7.)

The adjusting screws on the clamps are used to make the fringes straight lines perpendicular to the wedge direction. This means that the two flats are parallel to one another in the direction perpendicular to the wedge angle. The straightness of the fringes

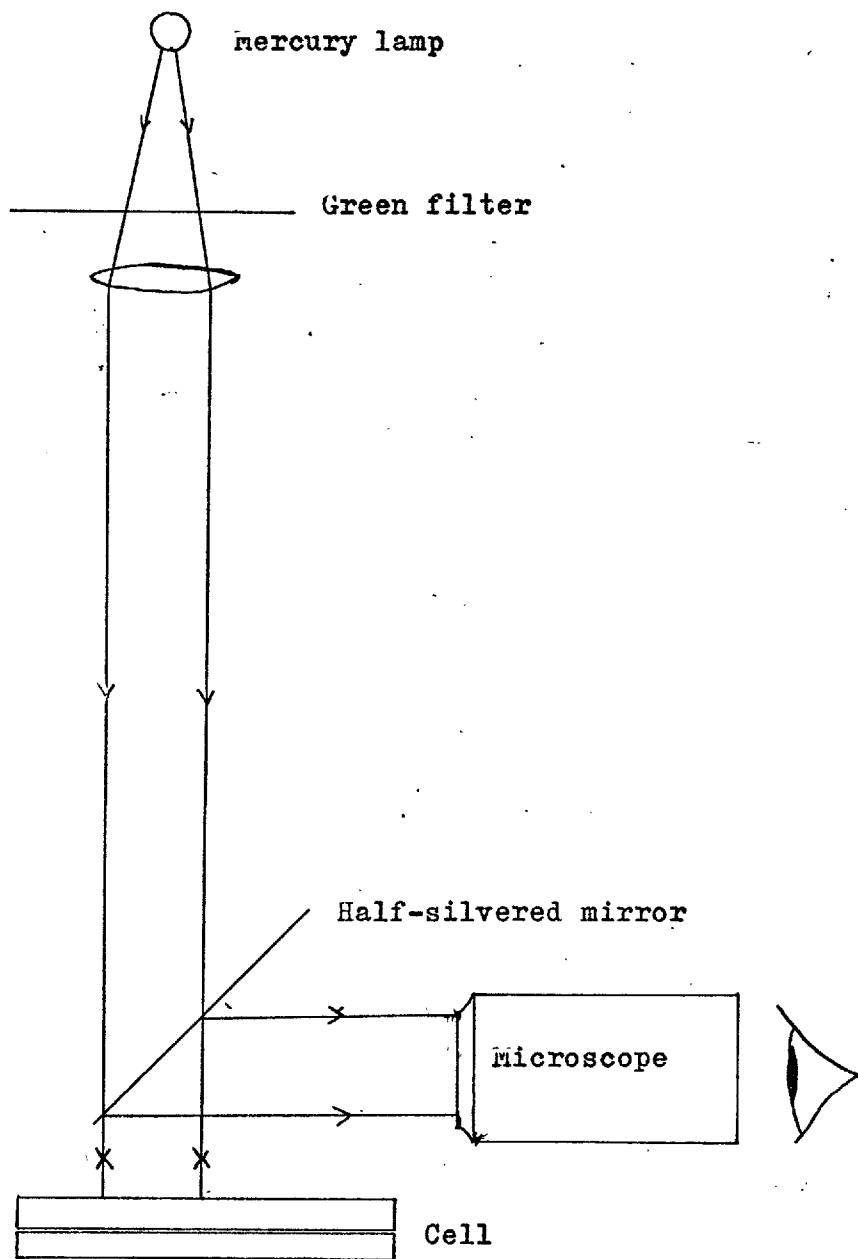


Figure 2.6. Optical system for thickness measurements.

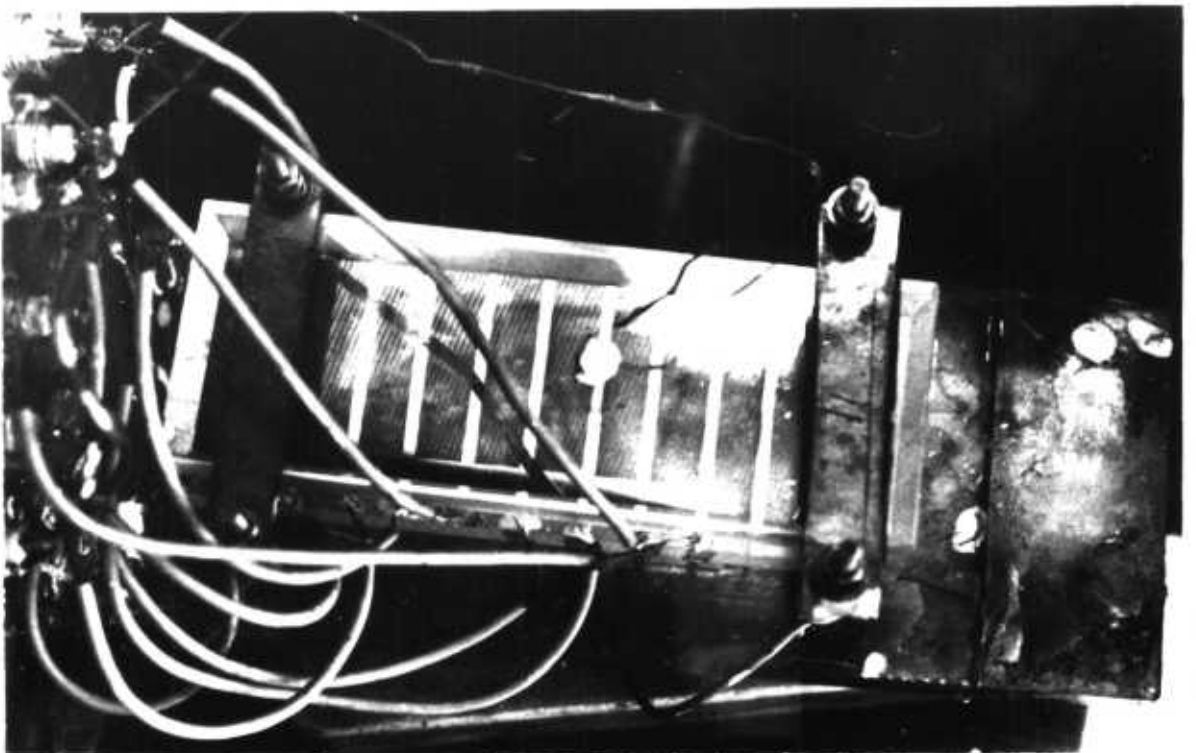


Figure 2.7. Optical wedge cell showing
interference fringes

At the point of contact between the flats the zero order fringe could not be seen and so the distance of the electrodes from the edges of the flats was measured being careful that these edges coincide. Using this method there is the possibility of a constant error on each thickness, but relative measurements will not be affected.

is a measure of the flatness of the glass blocks.

Having adjusted the wedge as described above the spacing between adjacent fringes is measured using the travelling microscope. The average over several fringes is used and the measurements repeated at various positions along the wedge to ensure accuracy. In this way the fringe spacing may be measured with an uncertainty of less than 1%. The distance between the two edges of each transverse electrode and the point of contact between the two flats is then measured again using the travelling microscope.

The formula relating to the fringe spacing is³

$$2\mu t \cos \theta = n\lambda \quad (2.1.)$$

Normal incidence is used in this case therefore $\theta = 90^\circ$ and $\cos \theta = 1$

thus $2\mu t = n\lambda \quad (2.2.)$

where μ = refractive index of medium in wedge (=1 for air)

t = wedge thickness

λ = wavelength of light used

n = order of fringe.

If y is the distance between any two fringes, say n and $n+1$, then we have, assuming $\mu = 1$

$$2t_n = n\lambda \quad (2.3.)$$

and $2t_{n+1} = (n+1)\lambda \quad (2.4.)$

combining (2.3.) and (2.4.) gives

$$t_{n+1} - t_n = \lambda/2 \quad (2.5.)$$

In other words the increase in thickness of the wedge in going from one fringe to the next is half the wavelength of the light used (=0.273 μ m. for the mercury green line). Thus measurement of the spacing gives the wedge angle θ . Actually the tangent of this angle is measured (Fig.2.8.)

$$\tan \theta = \frac{\lambda}{2y} \quad (2.6.)$$

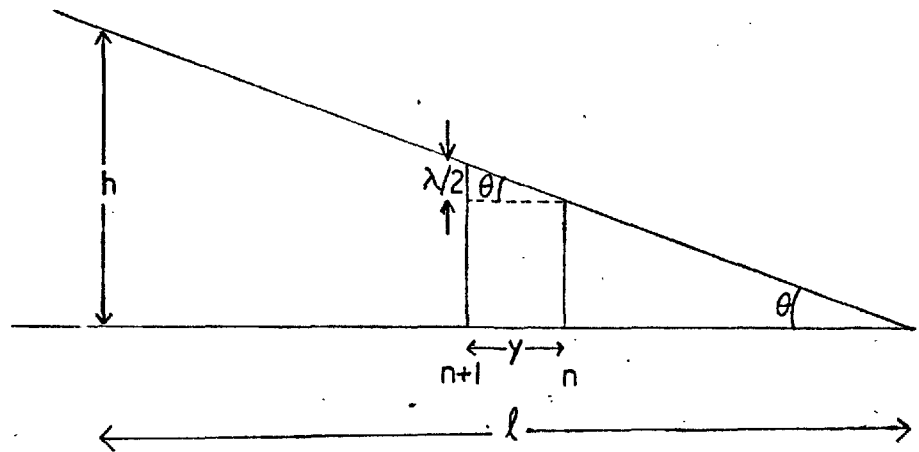


Figure 2.8. Film thickness

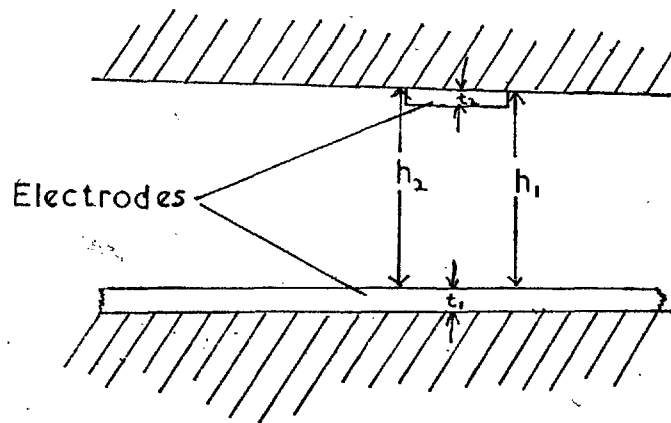


Figure 2.9 Correction for electrode thickness

The distance between the two flats h at a distance ℓ from the point of contact is then simply given by

$$h = \ell \tan \theta = \frac{\ell \lambda}{2y}$$

$$h = \frac{\ell \lambda}{2y} \quad (2.7.)$$

Thus the inter-electrode spacing for each capacitor along the length of the cell may be determined with good accuracy. However the distance measured is the one between the inside glass faces while the distance between the faces of the two electrodes is required (see Fig. 2.9.). Also since the capacitors are formed on a wedge the thickness is not constant across the width of an electrode. To minimize this the electrodes were made narrow (1.5mm. wide approximately) and the average spacing taken. The thickness of the electrode layers (typically 0.1 μ m) were measured after experiments were completed. Two methods of measuring the thickness of the electrodes were available:

1. The Talysurf
2. Multiple beam interferometry using a Fizeau microscope.

Referring to Fig. 2.9. the inter-electrode spacing was taken to be

$$\ell = \frac{h_1 + h_2}{2} - (t_1 + t_2) \quad (2.8.)$$

After making the thickness measurements the assembled cell was placed on a glass table as shown in Fig. 2.10.

The glass table contains embedded thermocouples for temperature measurements. Since the glass blocks of the cell are 1.3cm. thick and the gap between them too small to permit the introduction of a thermocouple the table was made to double as a carrier for the cell and also a "dummy" cell for accessing the temperature in the interior of the cell itself. A further thermocouple was attached to the top of the cell to permit comparison with the embedded thermocouples in

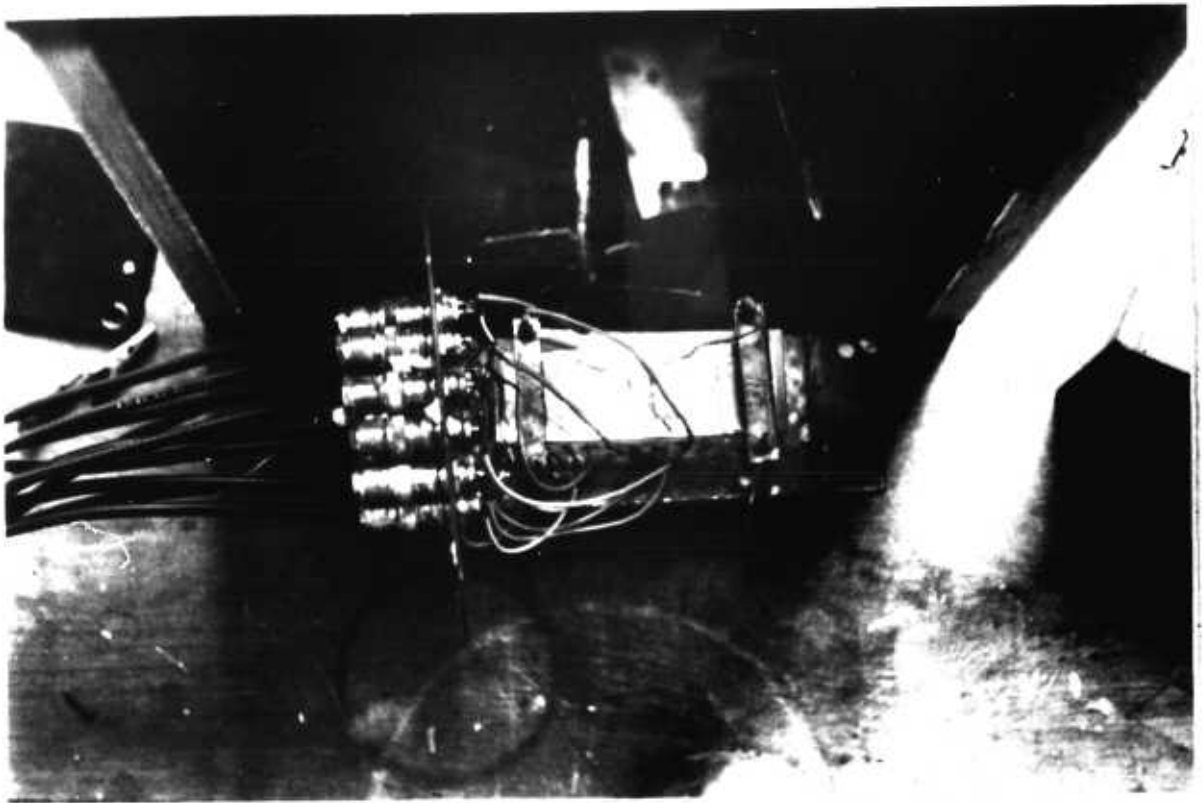


Figure 2.10 Assembled cell

the table. In practice all the thermocouples gave readings of temperature within $\pm 2^{\circ}\text{C}$ of one another provided sufficient time was allowed for the system to reach equilibrium. The time taken to reach equilibrium in the system used was of the order of 30 minutes.

The support table was affixed to a brass disc at one end as shown. The thermocouple wires pass through small holes sealed with epoxy resin. The disc also carries eleven "bnc" sockets ("bnc" connectors are constant-impedance connectors with beryllium-copper contacts and silver-plated brass bodies having weatherproof bayonet locking construction. P.T.F.E. insulation permits 500V peak working and frequencies of 10,000MHz with $50\ \Omega$ impedance) by means of which connections can be made to the measuring apparatus. The sockets were connected to the electrodes on the cell using fine silver wires (5 thousandths of an inch diameter) affixed to the electrodes using "silver dag." This method was found to be unsatisfactory owing to stray capacitance. Typical values of capacitance obtained with the cell, with air dielectric, were in the range 2pF to 20pF and using silver wire interconnections the stray capacitance was of the same order as the lower values obtained. To avoid the affects of strays, fine screened wire was used in preference to plain silver wire. The outer screens of the cable were connected to the brass plate and the screening maintained to as near the point of connection to the electrodes as possible. The use of the screened cable reduced strays to an acceptable level.

2.5. Temperature Control System.

The assembled cell system, after assessing the electrode spacing of the capacitors in the cell and making connections to the electrodes, could be placed inside a chamber as shown in Fig.211. The whole chamber was surrounded by a thermally insulating material and was fitted with an inlet and an outlet to allow an inert gas (N_2) to be

passed through. This gas is also utilized in taking the cell below room temperature. This is accomplished as follows. A large dewar of liquid nitrogen was modified in order that the nitrogen could be boiled off at a controlled rate (Fig.2.12).

A resistor was immersed in the liquid nitrogen dewar and the current through the resistor controlled using a variable voltage transformer (Variac) connected to the a.c. mains. The amount of power supplied to the resistor controls the rate of boiling of the liquid nitrogen. The dry nitrogen gas thus produced was passed through a coil of copper tubing which was immersed in liquid nitrogen. This coil was mounted close to the chamber and provided further cooling to make up for heat exchanges along the connecting tubes. From the cooling coil the gas is passed through the chamber over the cell thus providing cooling. The exhaust gas from the chamber was passed through a flowmeter to monitor the rate of flow of gas and to act as a detector for blockages in the tubes or exhaustion of the liquid nitrogen in the reservoir.

A given value of current through the resistor thus produces a certain flow of gas and assuming that the ambient conditions do not change then the system will reach equilibrium at some particular temperature. In practice the temperature drifts continually with this open-loop control system, however by making minor adjustments to the current flowing through the heater resistor in the liquid nitrogen, the temperature of the cell could be held within $\pm 1^{\circ}\text{C}$ of any desired temperature for a period of several hours if necessary.

For measurements above room temperature the cell chamber was fitted with heating tape below the glass table. This heating tape was connected to a Eurotherm temperature controller. One of the thermocouples in the chamber was connected to the controller to provide a closed-loop control system and it was only necessary to set the

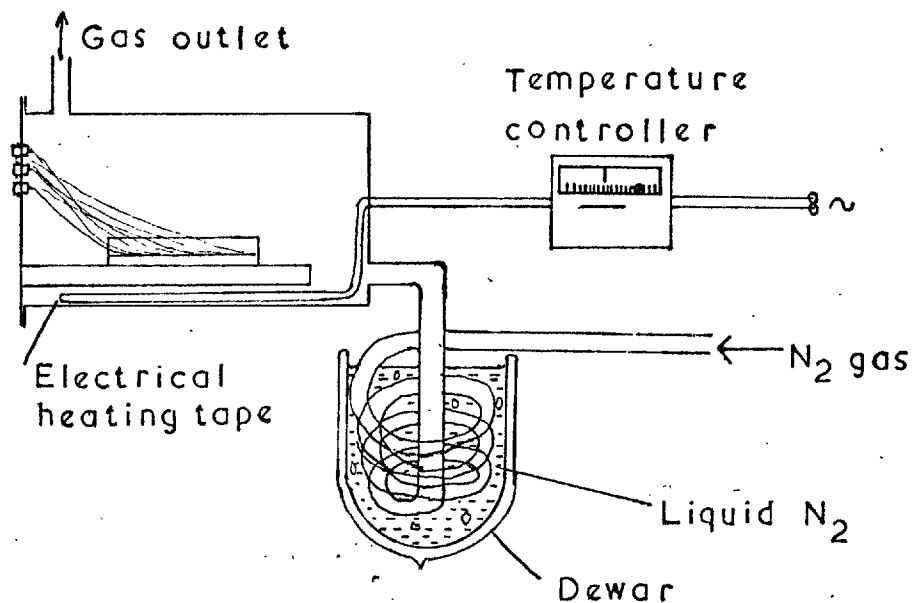


Figure 2.11. Temperature control system

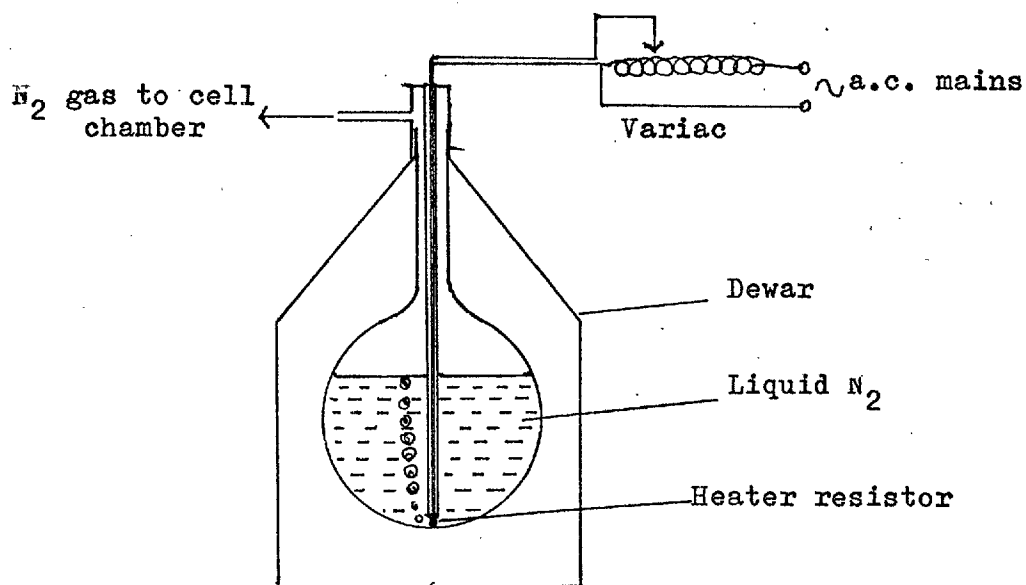


Figure 2.12. Cold nitrogen generator.

required temperature on the controller.

2.6. Cell Preparation.

The optically flat glass blocks were cleaned, prior to laying down the metal electrodes, as follows. The blocks were placed in a solution of "Teepol" detergent and water and agitated for a period of approximately ten minutes in an ultrasonic bath. This can be expected to remove gross amounts of contamination. After rinsing thoroughly with tap water the ultrasonic treatment was repeated using a 2% solution of "Decon 90" in distilled water, followed by a thorough rinse using distilled water.

The pre-cleaned blocks were then given a final clean by vapour de-greasing. This operation was carried out using a Soxhlet extraction apparatus. The medium used to effect the vapour de-greasing was an azeotropic mixture of water and iso-propyl alcohol. This mixture can be expected to remove surface contamination, antioxidants and ionizable inorganic salts.

After final treatment in the Soxhlet apparatus the glass blocks were immediately placed in a vacuum chamber which was then evacuated. When the chamber had been exhausted to a pressure of the order of $1 \text{ to } 3 \times 10^{-6}$ torr the electrode pattern was deposited onto the glass flats by evaporation of the electrode material from a suitable source and subsequent condensation onto the glass block through a suitable mask.

The masks for the electrode patterns consisted of molybdenum sheet, three thousandths of an inch thick, with the required electrode pattern etched away. This was done by means of a photo-lithographic technique.

Having deposited the electrodes, the vacuum chamber was allowed to return to atmospheric pressure and the glass blocks removed. The cell was then assembled as described earlier.

2.7. Purification of the Liquids used.

For the initial experiments a commercial capacitor impregnant was used. The Aroclor (Aroclor is a Registered Trade mark) dielectrics are a range of chlorinated diphenyls produced by Monsanto for the manufacture of impregnated paper capacitors. These products are generically known as "Askarels", that is, synthetic, fire resistant insulating liquids which, if decomposed by an electric arc, evolve only non-explosive gaseous mixtures. There are three grades of Aroclor, identified by their code numbers; Aroclor 1242, Aroclor 1248, and Aroclor 1252. Aroclor is made by the chlorination of diphenyl to predetermined chlorine contents which are indicated as a percentage by the last two digits in the code number e.g. Aroclor 1248 contains 48% chlorine by weight.

In the present experiments Aroclor 1242 was used (commercially known as Trichlorodiphenyl). The Aroclor 1242, as received in a drum, is said to be suitable for filling into capacitors after vacuum treatment. However the manufacturers state that, if there is any possibility that the liquid may have been contaminated in any way the vacuum treatment should be preceded by earth treatment.

The earth treatment can be carried out in two principal ways. In the first place Fullers earth is contained in a column and the liquid is circulated until the contamination is removed. Alternatively activated earth is added to the liquid in a container and it is stirred to ensure intimate mixing and the earth is subsequently filtered out. In both cases either Fullers Earth or activated alumina may be used and each must be thoroughly dried. It has been found by experience in the manufacturer's laboratory tests that the earth may be passivated by heating to excessive temperatures, and the optimum treatment has been found to be about 150°C for 6 hours. The activated material is then added to the Aroclor to be treated at a level of 0.2% to 2% by weight.

The earth treatment may be expected to remove ionic contamination and the liquid was subsequently treated to remove dissolved gases, water and particulate contamination. The purification plant was designed for use with the "Plate" form of the mercury squeeze film apparatus. Since this form of apparatus was difficult to clean the plant was designed to incorporate the cell in which measurements were to be made and provision made for re-circulating the oil in an attempt to obtain as low a concentration of contaminants as possible.

Aroclor 1242 is very susceptible to contamination and consequently the materials with which it comes into contact during purification must be carefully selected. The plant used was a modification of a design used by Martin and Thompson⁴ and is shown in Fig. 2.13.

The earth treated liquid, after being left for some time to allow most of the earth to settle out, is passed through a pre-filter and then through a sintered glass filter into a glass coil. The region below the filter is evacuated to a pressure of a few centimetres of mercury and the function of the coil is to allow the liquid to present a large surface area of liquid to the vacuum to ensure adequate de-gassing and dehydrating of the liquid. The liquid was then given a final filter before passing into the reservoir from where it could be pumped through the measuring cell and back to the start of the cycle if required.

In the final filter a membrane filter was used. These are available from Millipore (U.K.) Ltd.. These filters exhibit an absolute surface retention, that is all particles larger than the pore size of the filter are retained on its surface. The filters are easily clogged by liquid-borne particles, which are of the order of the size of the filter pore, and by stable gels. Consequently a prefilter was used to increase the life of the membrane filter.

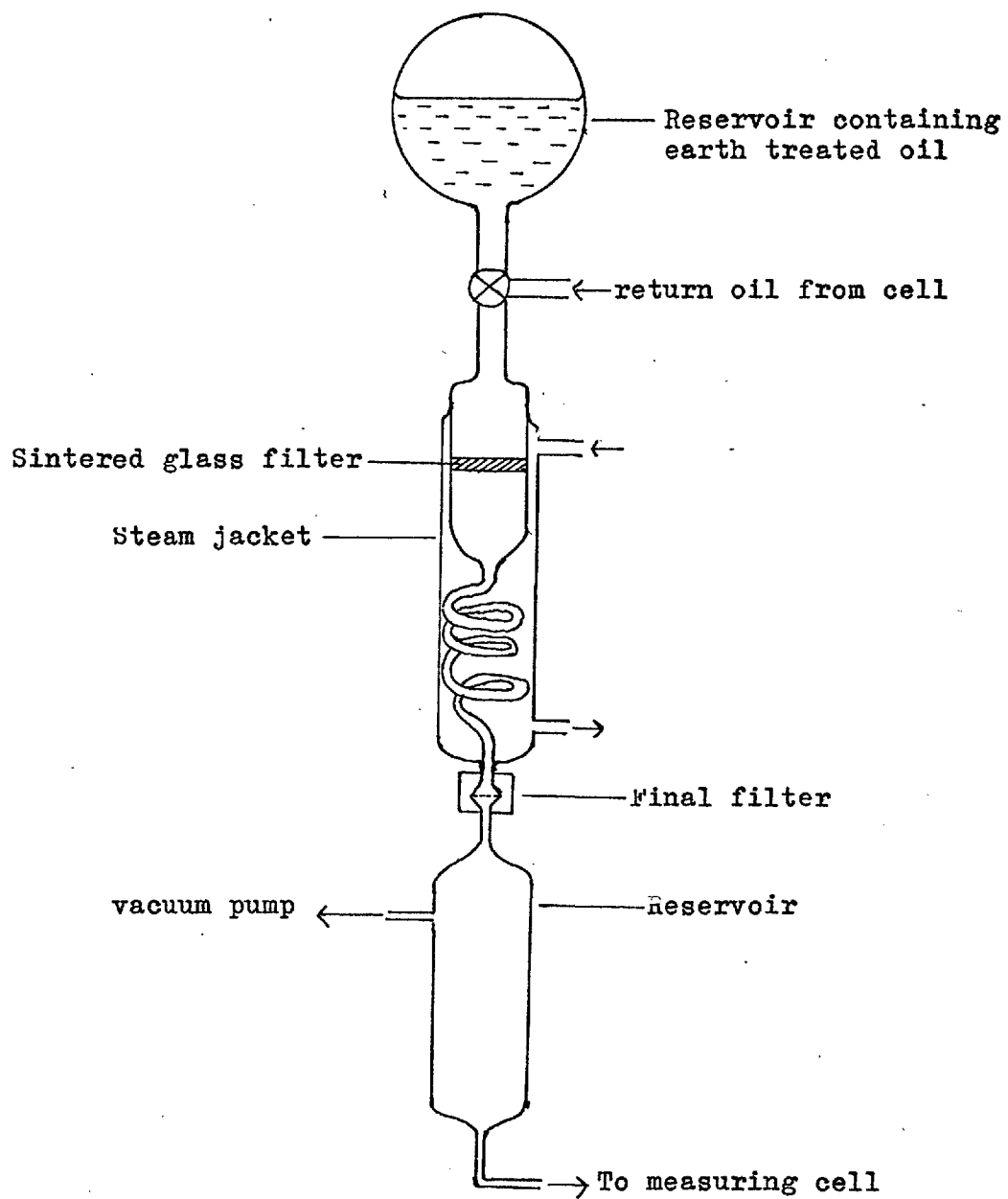


Figure 2.13. Purification system for aroclor.

These membrane filters are available with pore sizes down to $0.01 \pm 0.002 \mu\text{m}$. However with the filter holder used the flow rate obtained with a $0.01 \mu\text{m}$ filter at 20°C under a differential pressure of 1 atmosphere would be of the order of 1000 hrs/litre of Aroclor. This is rather an unrealistic figure and it was decided to try $0.2 \mu\text{m}$ Celotate filters which gave a flow rate of about 40 ml /hr. and $1 \mu\text{m}$ Duralon filters which gave a flow rate of the order of 500 ml/hr.

In later work a range of simple organic compounds was used, the main one being n-heptanol and it was decided that a purification plant was needed for this liquid. At the time of designing this plant it had been decided that the most important contaminant is that of an ionic nature.

Unlike hydrocarbon and some mildly polar compounds, the numerous strongly polar liquids of organic chemistry have been hitherto neglected both in research and engineering. This lack of interest may be ascribed to the considerable sensitivity of these liquids to electrolytic pollution, which has made them quite unmanageable until recently. At present, however, modern ion exchangers, coupled with efficient dehydration techniques, allow the resistivities of such liquids to be improved by several orders of magnitude. In two important cases, methyl and ethyl alcohols, the measured conductivity matches the theoretical expectation within 10%.

Much work has been done in the past few years by Professor N.J. Felici in order to determine a) the relative efficiency of ion exchange techniques compared with conventional methods in de-ionizing polar liquids, and b) whether ion-exchange techniques can completely de-ionize polar liquids to their natural state of autolytic ionization.

The apparatus used to purify the n-heptanol for use was based on one proposed by N.J. Felici⁵. A block diagram of the system is given in Fig. 2.14, while a more detailed diagram of the system may be found

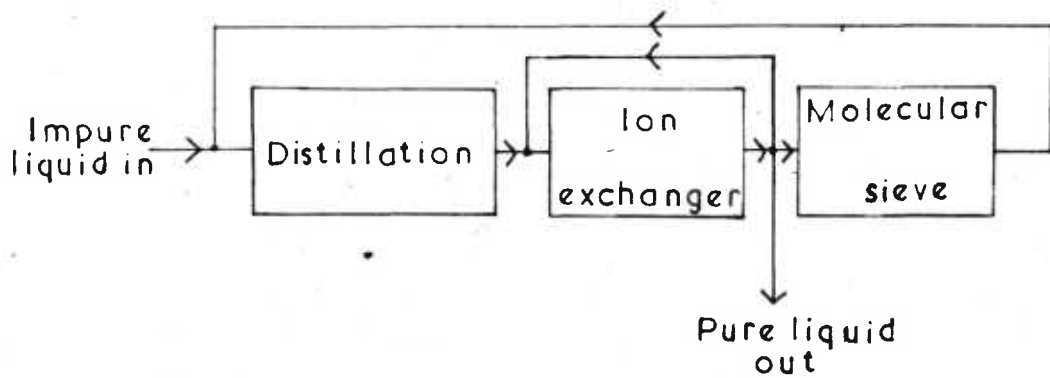
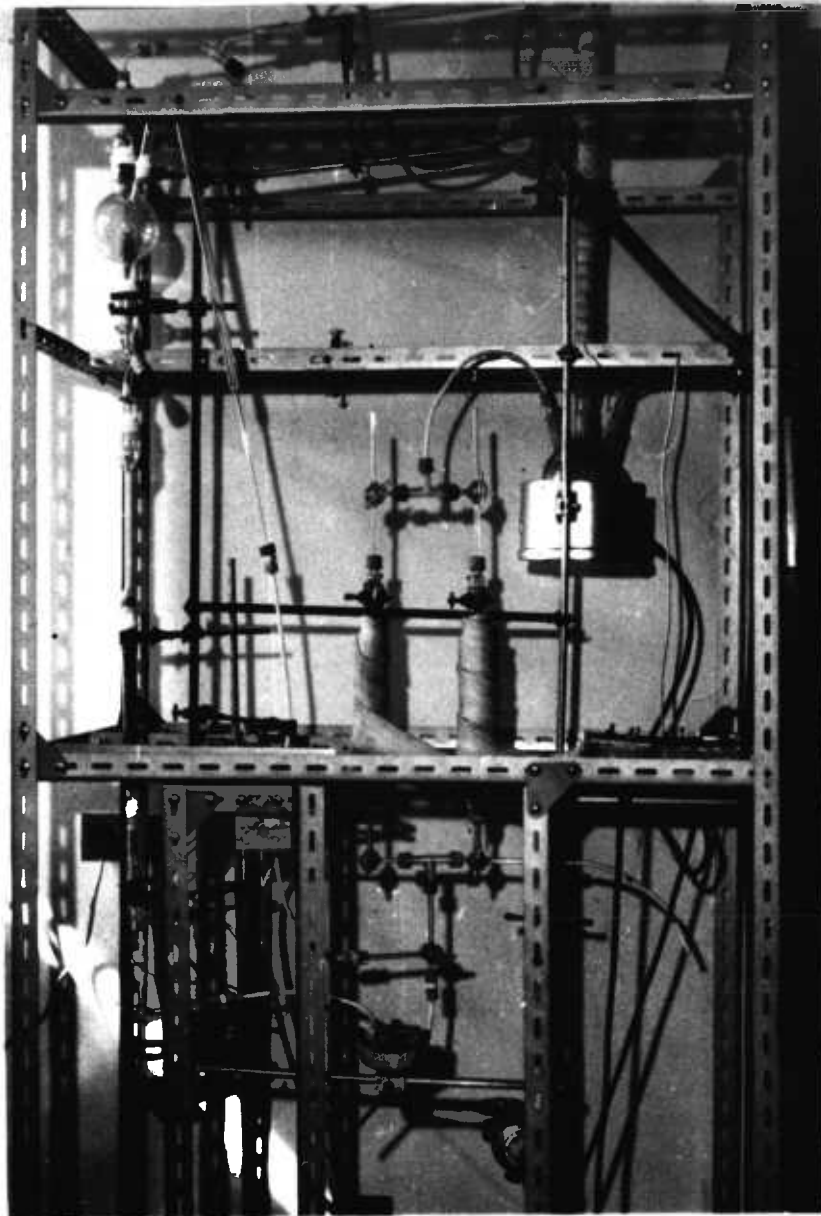


Figure 2.14. Purification plant for n-heptanol

in the paper by N.J.Felici.

First of all, it was necessary to remove water from the ion exchange resin, since commercial ion exchangers are usually soaked with water. For de-ionization a mixed-bed ion exchanger was used, consisting of the strongest acidic and strongest basic types available. To remove water from the ion exchanger the procedure recommended by Felici was followed. Preliminary repeated saturation and regeneration cycles were performed in ordinary aqueous solutions. This is useful in freeing the exchanger of impurities which would impede the de-ionization process.

Dehydration of ion exchangers is a rather difficult task. Since decomposition sets in at temperatures as low as 40°C , they may not be dehydrated by heating. Washing off the adsorbed water by some hydrophilic agent is the only practicable method. Dioxane is recommended by Felici mainly because of its unlimited miscibility with water. For dehydration, about one pound of ion exchanger beads were put into a Pyrex vessel and flooded with anhydrous dioxane, which was drawn off after an hour or so and replaced by fresh dehydrant. To achieve sufficient removal of moisture, the process was repeated 15 times in all, requiring approximately 2 gallons of dioxane. This amount could be considerably reduced by previous vacuum drying of the beads at room temperature. This procedure, however, is not recommended since the beads are very sensitive to environment. Removal of water without provision of another liquid in exchange causes shrinkage and then swelling when the beads are flooded with dioxane. They are very likely to shatter under the strain, and would then lose most of their exchanging efficiency.

For de-ionization purposes, both acidic and basic ion exchangers must be used, and the best results are achieved by mixing

the beads of both kinds intimately in the same column ("mixed-bed" technique). Regeneration of an exhausted mixed-bed is not easy, but this inconvenience was immaterial since the amounts of ions to be removed were always negligible.

Dehydration of the liquid under investigation was achieved by molecular sieve material. This technique is to be preferred to any other, provided that the amount of liquid to be treated is modest. Molecular sieves can thoroughly dry (down to 10p.p.m. of water) the most hydrophilic liquids and do not give rise to unwanted chemical reactions. One must, however, take into account the tendency of molecular sieves to form colloidal solutions, which soon poison the ion exchanger. The dehydrated liquid must therefore be submitted to distillation before being presented to the ion exchanger. The liquid was drained off several times, in order to eliminate the last traces of water and to wash out the walls and electrodes of the conductivity monitoring cell. Continuous recycling is then performed for several days until no further improvement in conductivity could be effected. The equivalent parallel conductance at an angular frequency of 10^4 radians sec^{-1} was used as a measure of purity.

After the liquid has passed through the ion exchanger column it can be recirculated or drawn off through a stopcock. To introduce the liquid into the cell the outlet arm of the stopcock is flushed out for several seconds with the purified liquid before allowing a drop to fall onto the assembled cell. The liquid then fills the inter-electrode space by capillary action. This method of filling the cell suffers from the disadvantage that stray impurities, especially in the form of dissolved gases from the atmosphere, may be introduced into the liquid. It would have been more satisfactory to include the cell system in the purification plant.

2.8. References.

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2. "Electrolytic Polishing and Bright Plating of Metals," Wernick, S., Alwin and Redman, London, (1948).
3. "Multiple-Beam Interferometry," Tolansky, S., OUP, (1948); "An Introduction to Interferometry," Tolansky, S., Longmans, London (1955).
4. Martin, R.G., and Thompson, C.N., Brit. J. Appl. Phys., 2, 222, (1951).
5. Felici, N.J., Brit. J. Appl. Phys., 15, 801 (1964).

It is worth stressing from the outset that the measured dielectric properties are highly sensitive to contamination of the liquid by stray impurities. In all the results described below reproducibility was good for a given sample of liquid. However the magnitudes of the measured dielectric parameters should not be viewed too critically since they vary with changes in the liquid test samples. The frequency behaviour of the permittivity and loss factor show a consistent trend.

CHAPTER 3

Results.

3.1. Introduction.

It will be evident from the discussion of the evolution of measuring cells that results from early cell systems were inconclusive. Measurements using the mercury squeeze film cells were beset by many difficulties, the major ones being breakdown of the films and troublesome thickness measurements.

The micrometer cell contributed to the development of the cell systems using optical flats, but in retrospect that was its only virtue. The "optical-wedge" form of apparatus gave the first acceptable results, and all the results presented in this chapter were obtained using this form of cell.

3.2. Early Results.

Initial experiments were made using "Aroclor 1242". This is a dipolar liquid, belonging to the "askarel" family of synthetic insulating liquids, which is widely used as a capacitor impregnant.

The real and imaginary parts of the permittivity as a function of thickness for Aroclor 1242 between silver electrodes, measured at 1KHz, is shown in Figure 3.1.. These initial results show two interesting features: 1). The relative permittivity and relative loss factor are both thickness dependent and, 2). The values of permittivity measured are all less than 6, which is the permittivity of a bulk specimen of this liquid under these conditions. The bulk permittivity of Aroclor 1242 at 23°C is constant over the frequency range 60Hz to 20KHz Fig. 3.2. shows the frequency behaviour for a thickness of 4.3μm.

At this stage it was decided that an investigation of other liquids

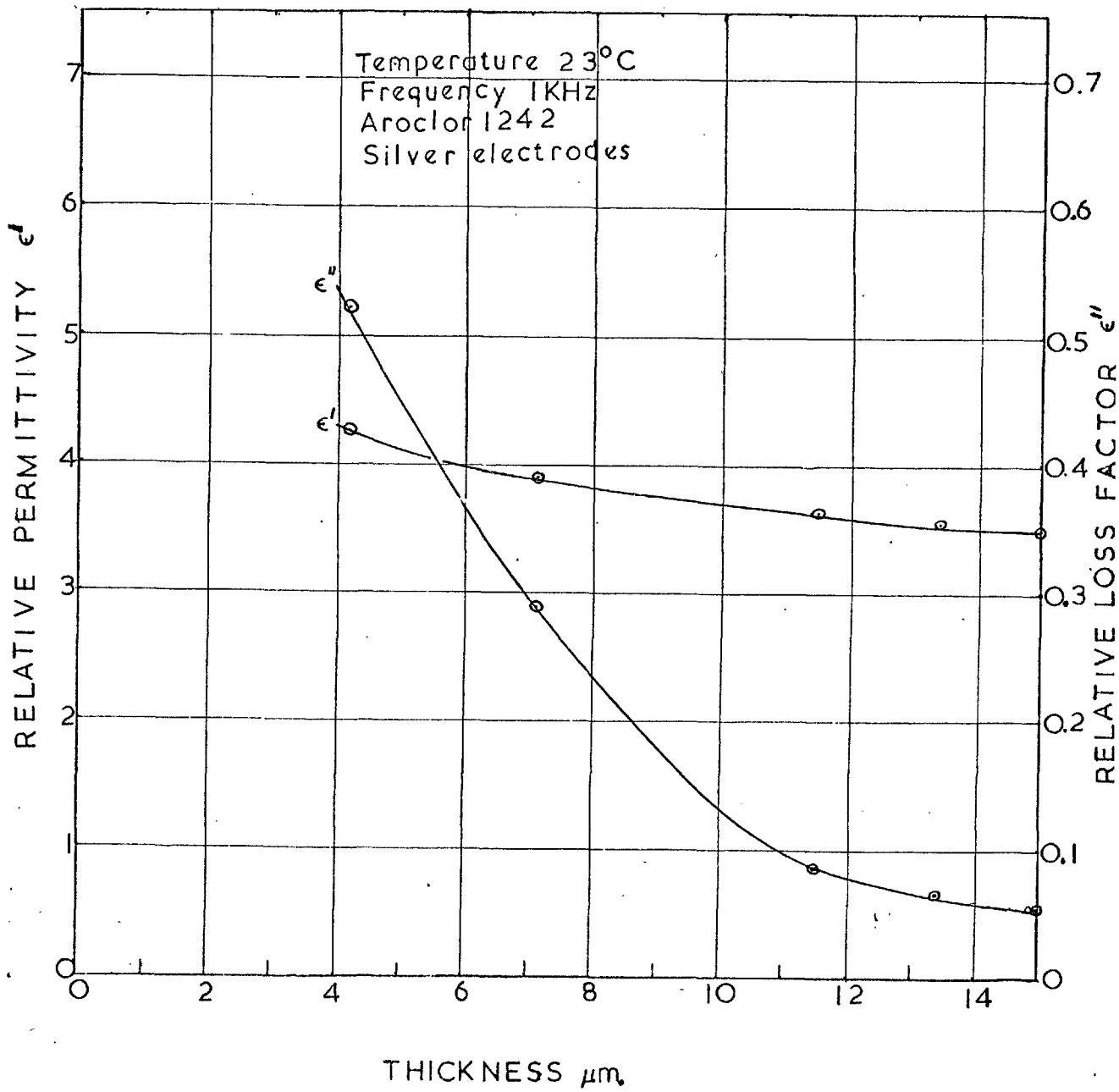


Figure 3.1. ϵ' and ϵ'' versus thickness

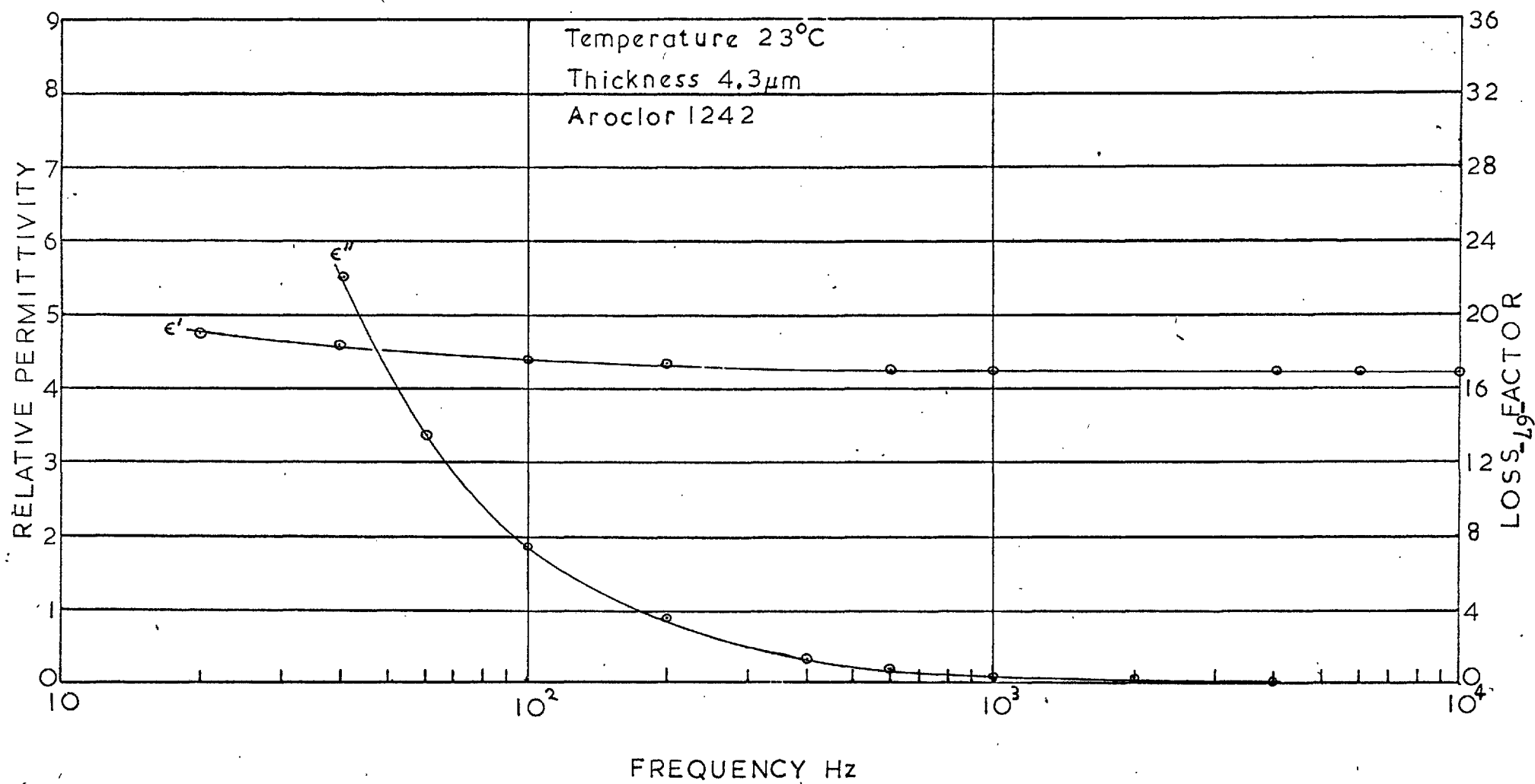


Figure 3.2. ϵ' and ϵ'' versus frequency.

should prove fruitful. I.H.Brockman¹ had noted some interesting effects in n-heptanol and it was decided to include this liquid in the study. The thickness behaviour of several liquids on gold electrodes is shown in Fig. 3.3..

It will be noted that heptane and chloroheptane show little thickness dependence of permittivity. Allowing for experimental error, the values of permittivity measured correspond with the values obtained for a large volume of liquid, for heptane and chloroheptane. As already observed, Aroclor 1242 shows a small but definite increase in permittivity with decreasing thickness, while the permittivity values obtained are below the value for a bulk specimen of the liquid.

The most interesting curve is that for n-heptanol, where the permittivity rises rapidly with decreasing thickness of film. The relative permittivity for n-heptanol, for a given thickness of liquid layer, is also strongly frequency dependent. This may be seen in Fig. 3.4., which shows the very high value to which the permittivity rose at low frequency. At higher frequencies the permittivity levels off at a value of approximately 8, which is again lower than the value of 11.4 which is obtained from measurements on bulk samples of n-heptanol. Work by J.Middelhoek and C.J.F.Bottcher² on heptanols gives a relaxation time of 1.1×10^{-9} sec. for orientation polarization. This means that the permittivity should remain constant at 11.4 for frequencies up to 100MHz or so.

The fact that a decrease, in permittivity, below the expected value is observed for frequencies higher than 5KHz is indicative of there being some constraint on the reorientation of the molecular dipoles. A marked increase in permittivity, above the bulk value, is noted as the frequency decreases. In view of the large value of permittivity obtained and the frequency at which the effect occurs,

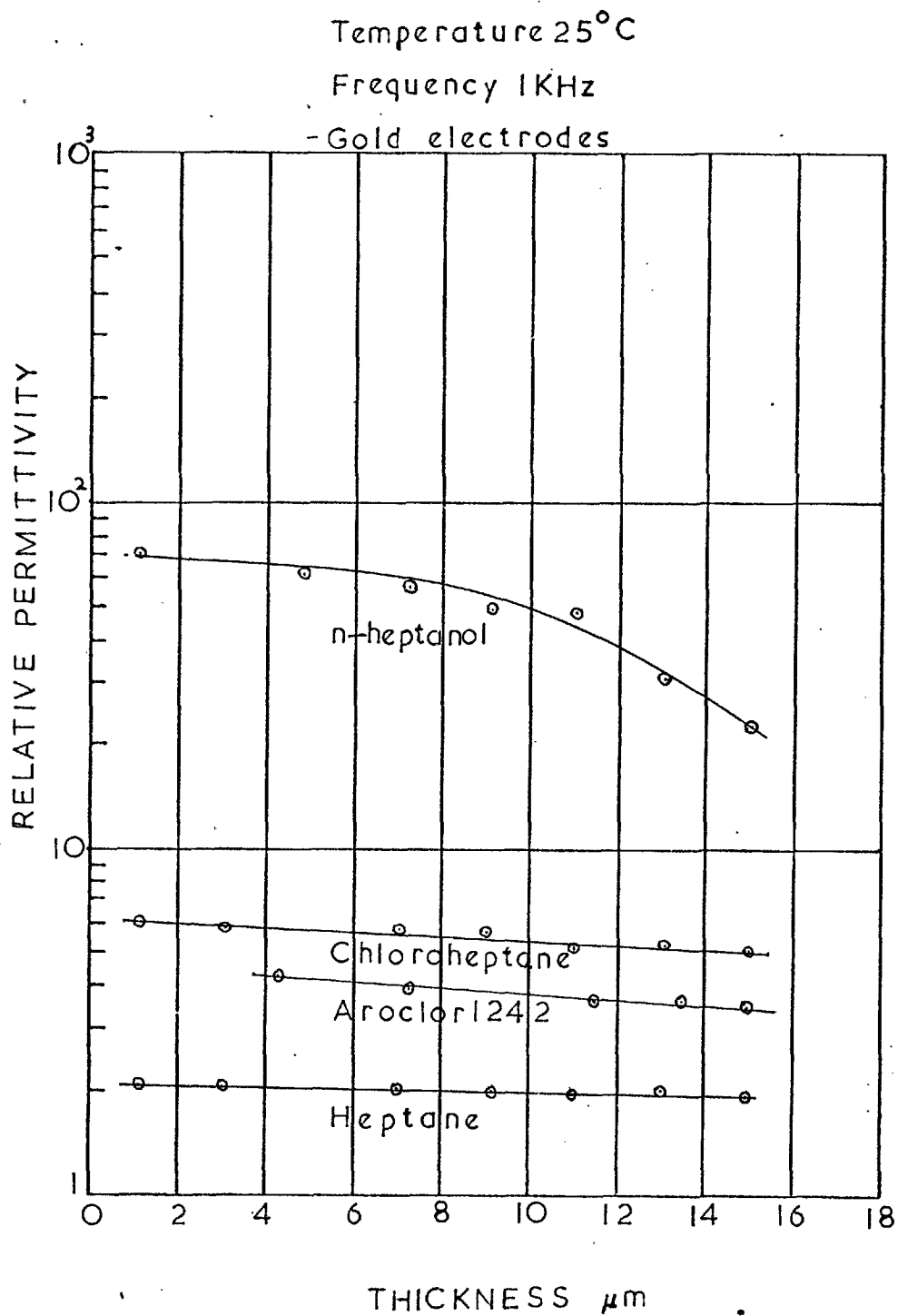


Figure 3.3 ϵ' versus thickness for various liquids

n-heptanol with gold electrodes

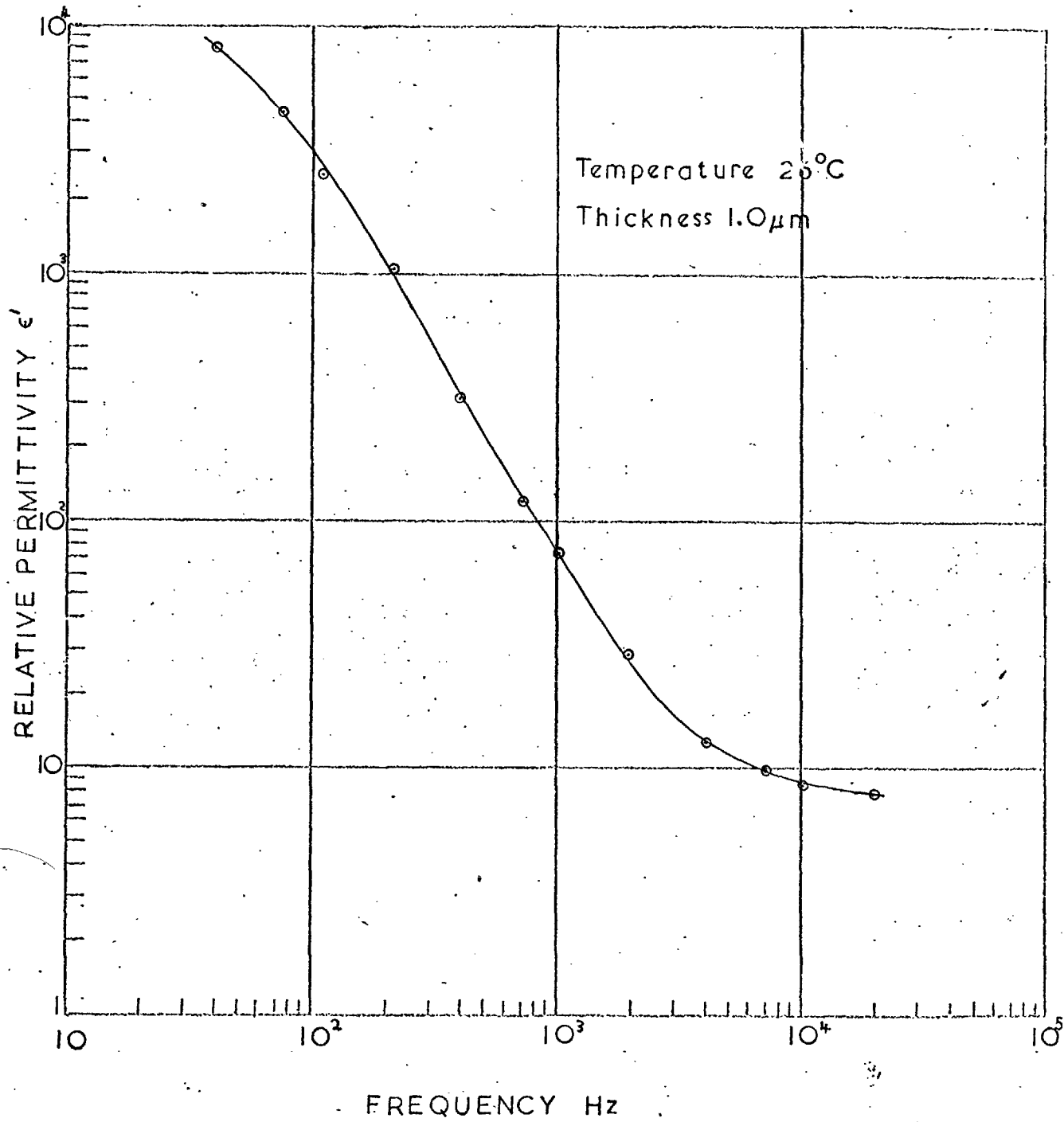


Figure 3.4 Relative permittivity versus frequency

this dispersion can be safely attributed to an interfacial polarization. Interfacial polarization arises where there are charge carriers that can migrate for some distance through a dielectric. When such carriers are impeded in their motion for any reason space charges and macroscopic field distortion results and as mentioned in chapter 1 appears to an external observer as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric permittivity. The classical example of interfacial polarization is the Maxwell-Wagner two-layer capacitor³.

It was thought, therefore, that a detailed study of the variation of the relative permittivity and loss factor with thickness, frequency and temperature should give valuable information about the relevant conduction mechanisms occurring in these thin liquid layers. Since we are dealing with liquids, any space charge build up can be reasonably expected to occur at the electrodes, where the charge carriers may not be able to discharge freely or be replaced. It therefore seems possible that the electrode material may have an effect on the conduction.

3.3. Thickness and Frequency Behaviour of n-heptanol on Gold Electrodes.

It was noticed in the initial measurements that there seemed to be an ageing process of some sort occurring. If one begins to monitor the capacitance of a specimen immediately after introducing the liquid into the cell, then the capacitance changes with time. Fig.3.5. illustrates this effect where three curves are presented showing the behaviour of permittivity with thickness after 15 minutes, 6 hours and 3 days. This ageing was observed to be virtually complete 2 to $2\frac{1}{2}$ days after the liquid was first introduced.

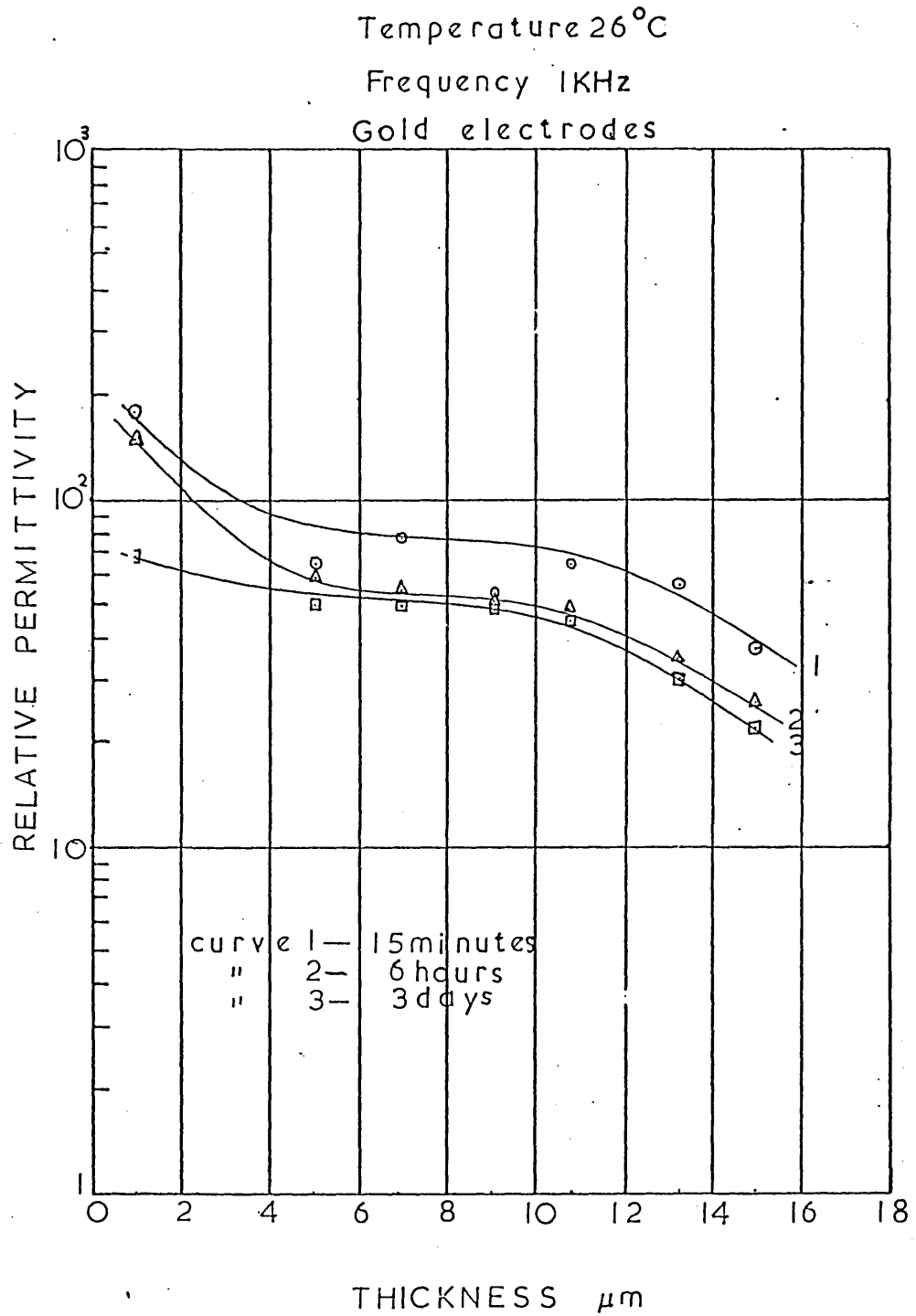


Figure 3.5. Ageing effect in n-heptanol

When ageing seemed complete measurements were made to determine the frequency dependence of the permittivity and loss factor. This enables us to see the effect of frequency on the shape of the permittivity / thickness curves (Fig. 3.6.).

For a given thickness of liquid layer we can draw curves showing the dependence of relative permittivity and relative loss factor on frequency. Figs 3.7. to 3.13. show this frequency dependence for seven different thicknesses of liquid film, from $1.0\mu\text{m}$ to $20\mu\text{m}$. A few comments of a general nature may be made concenerring these curves. In the first instance, the amplitude of the effect, causing the marked rise in permittivity, decreases with increasing thickness. Secondly the limiting value of permittivity reached at high frequencies also decreases with increasing thickness and is, for all thicknesses considered, less than the value appurtenant to a bulk sample of heptanol, viz.11.4. Finally, at the higher end of the frequency range considered, the loss factor is seen to be inversely proportional to frequency. Further comments on these results and their interpretation may be found in Chapter 4.

3.4. The Effects of Temperature on the Behaviour of the n-heptanol Gold Electrode System.

After completing the frequency measurements mentioned in 3.3. the effects of temperature on the permittivity and loss factor were investigated, and their temperature dependence is shown in Figures 3.14a and 3.14b. The magnitude of the interfacial polarization is seen to decrease with decreasing temperature. This seems consistent with the fact that decreasing temperature will result in a lowering of the mobility of any charge carriers present. The curves at thicknesses corresponding to $5.0\mu\text{m}$ and $11.0\mu\text{m}$ would seem to exhibit a maximum at a temperature between 15 and 20°C . The value of permittivity for a bulk specimen of n-heptanol is shown by the broken line

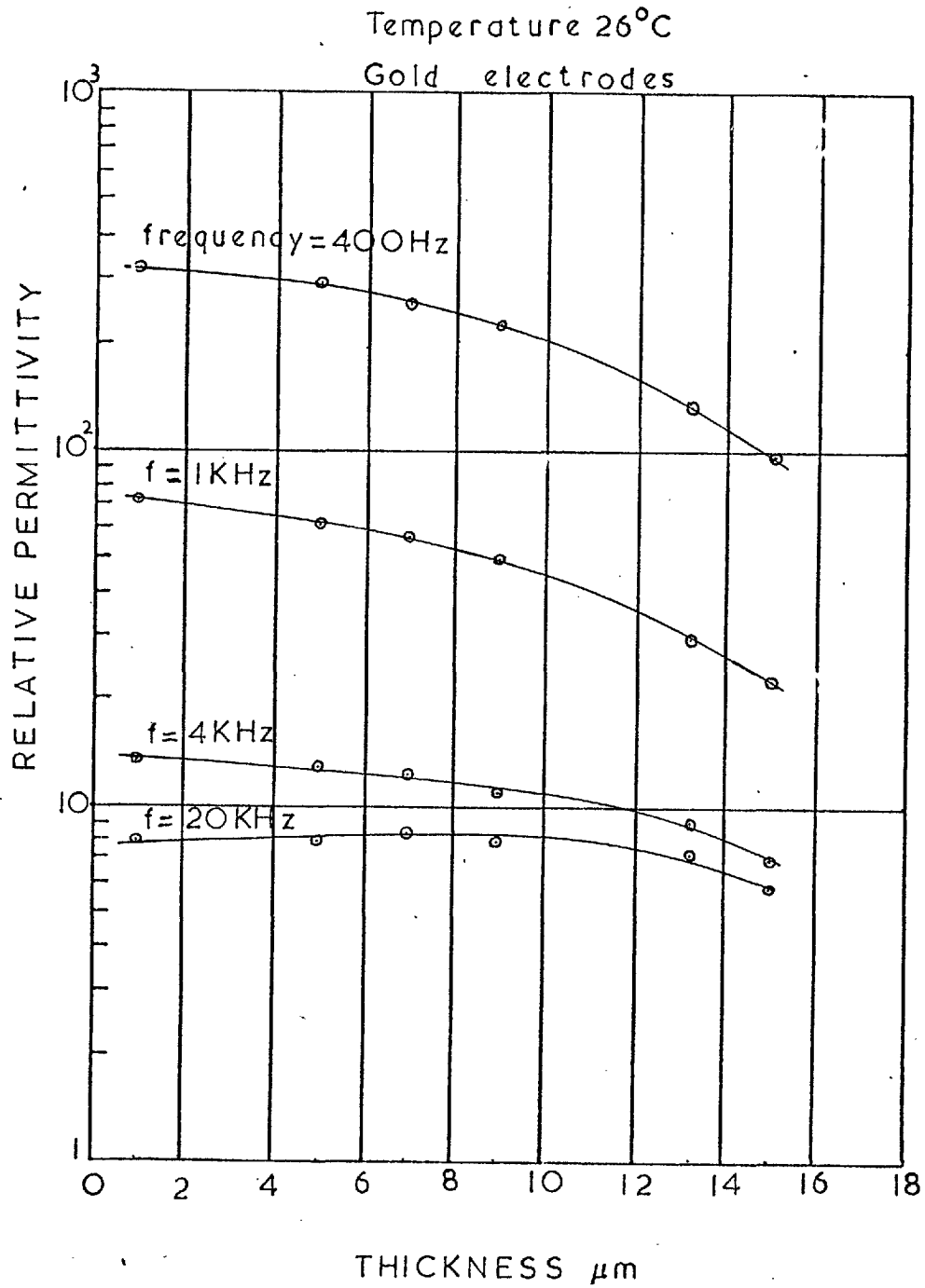


Figure 3.6a ϵ' versus thickness at various frequencies

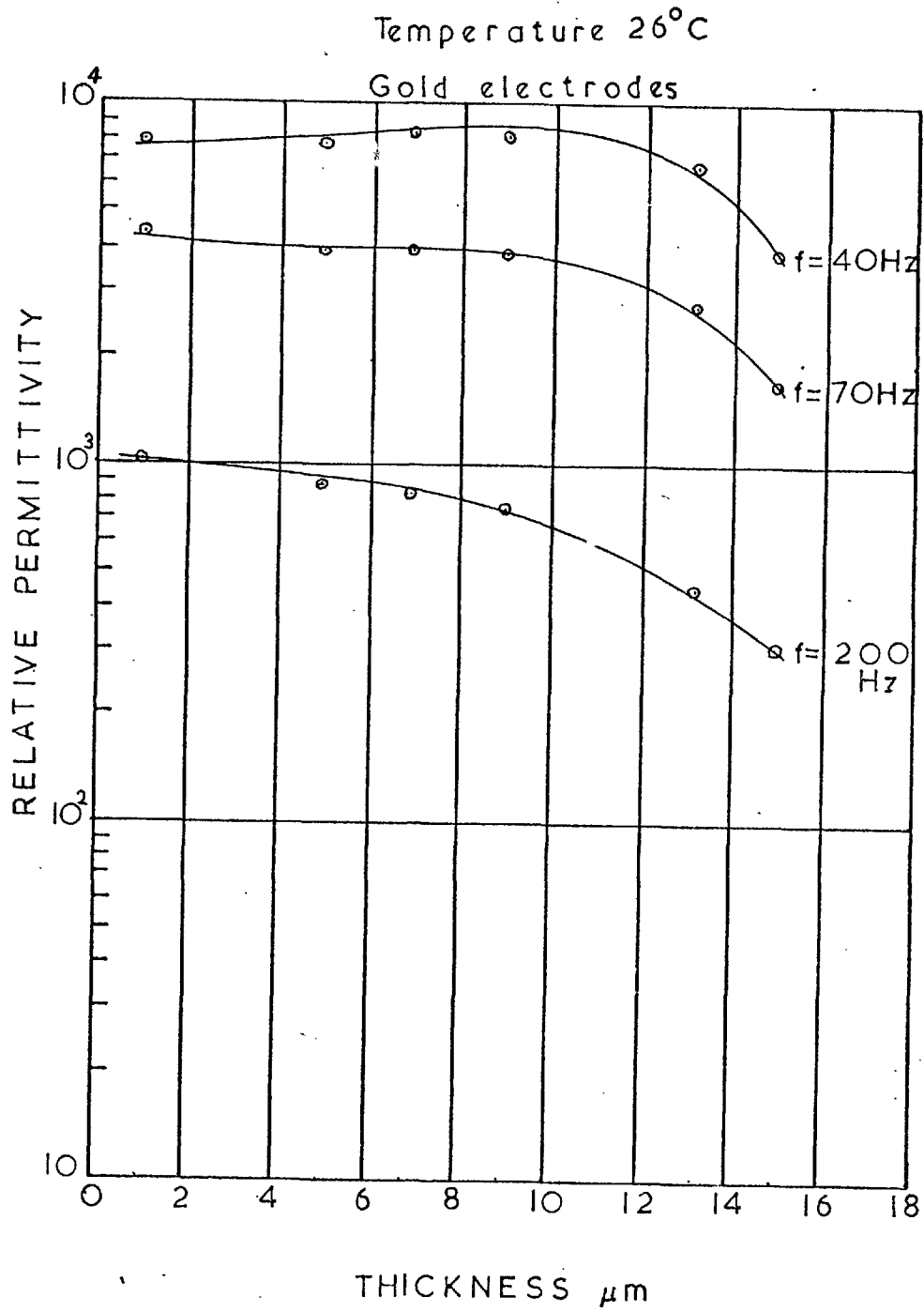


Figure 3.6b ϵ' versus thickness

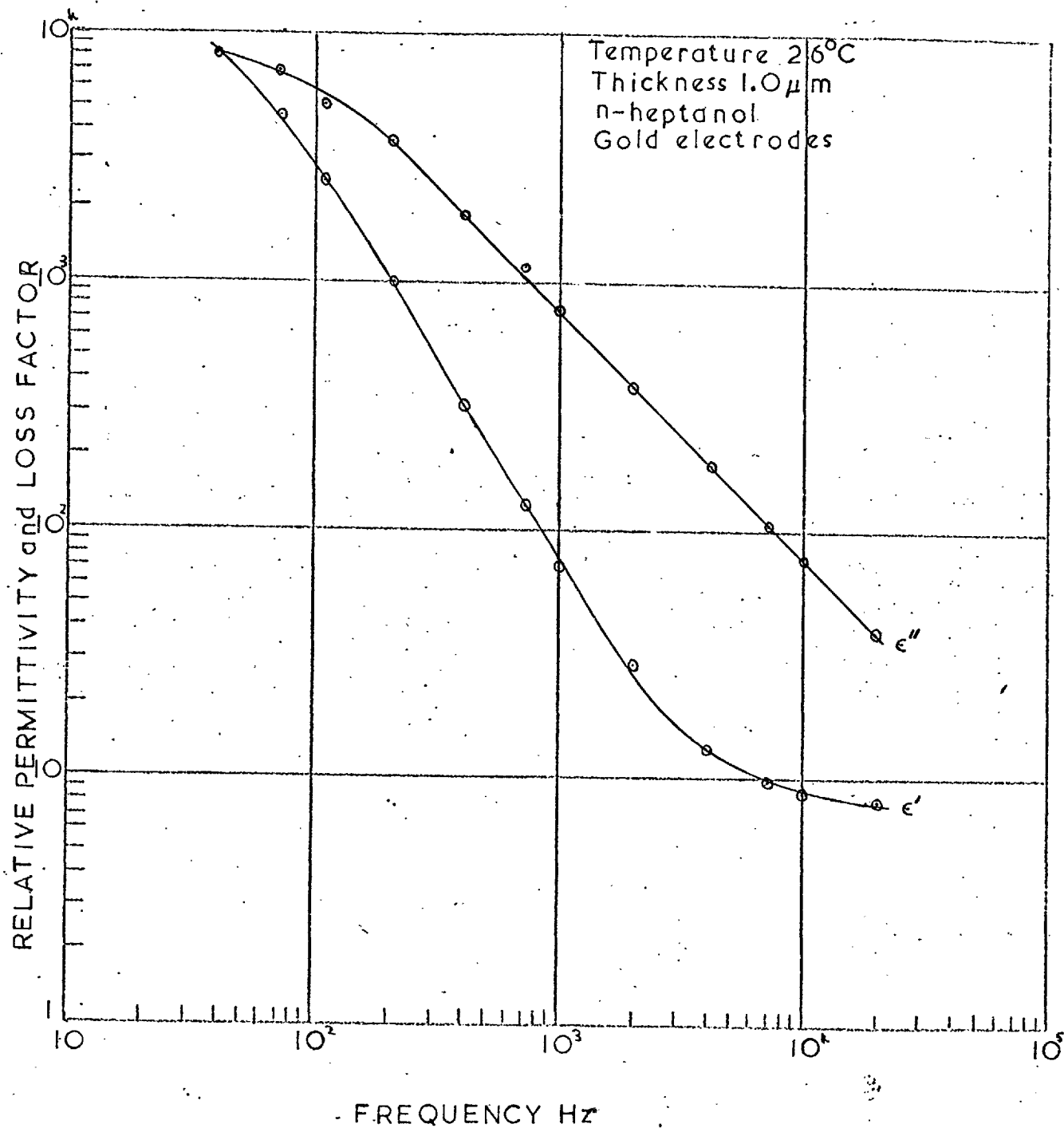


Figure 3.7 ϵ' and ϵ'' versus frequency

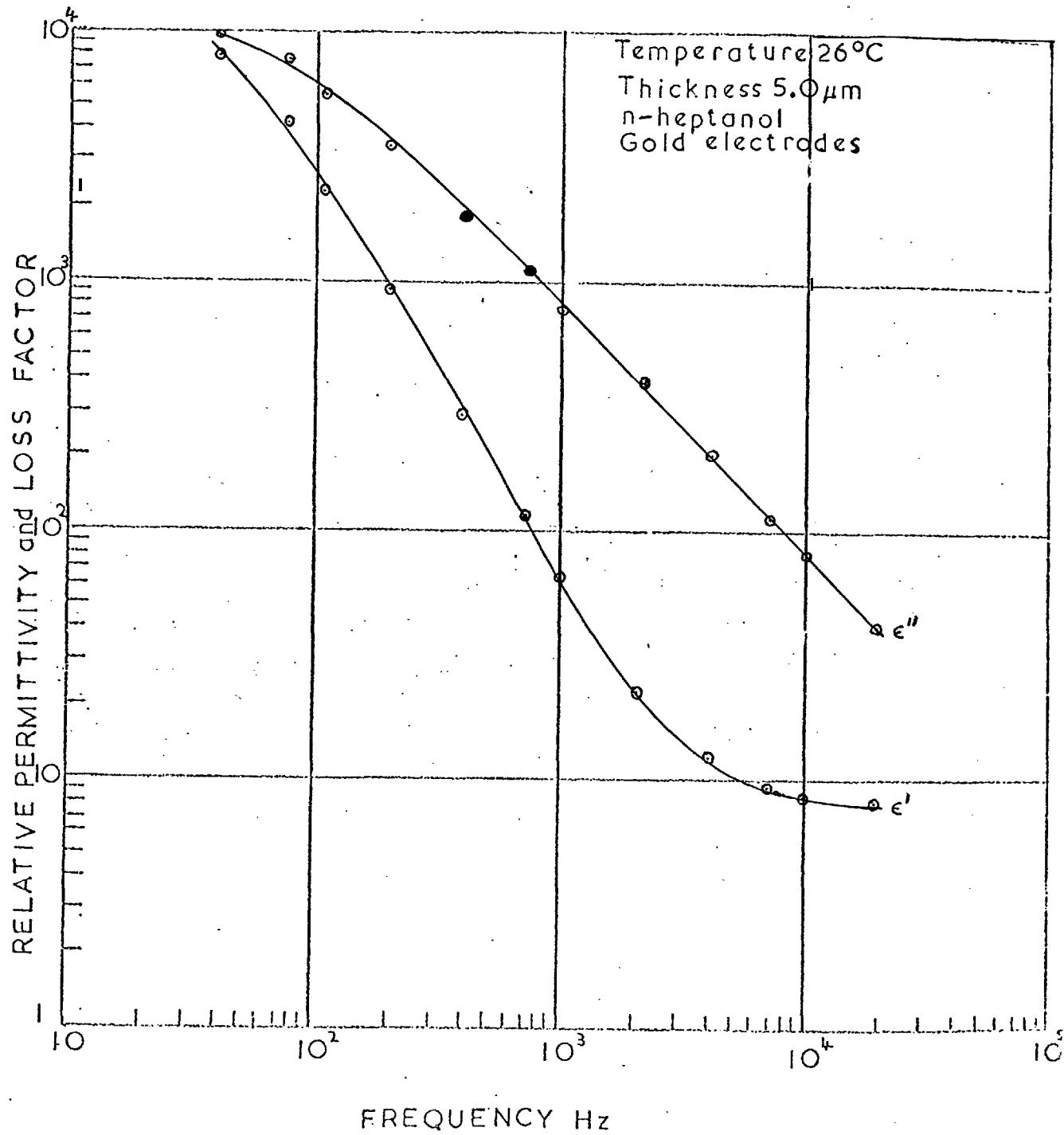


Figure 3. 8. ϵ' and ϵ'' versus frequency

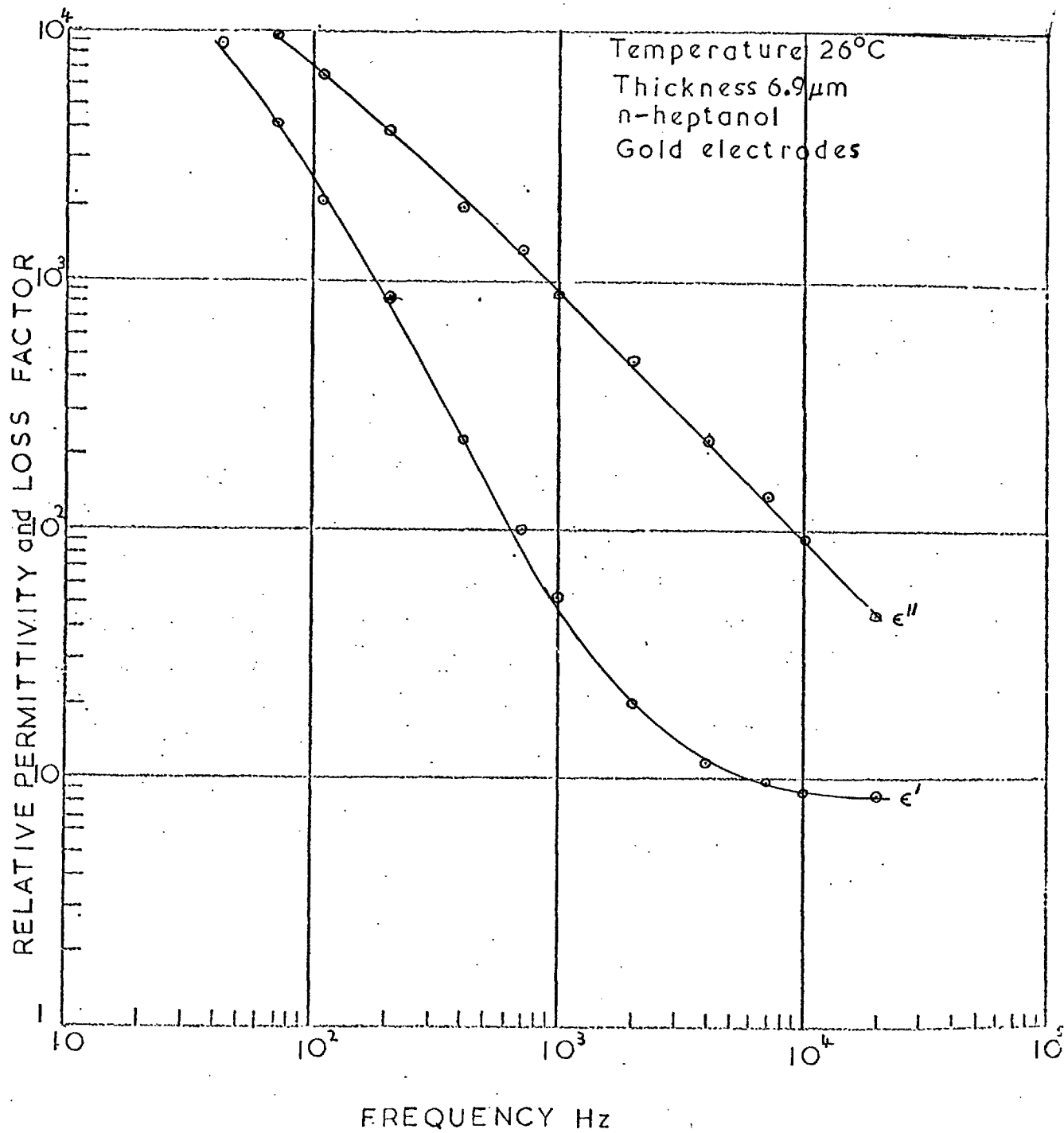


Figure 3.9 ϵ' and ϵ'' versus frequency

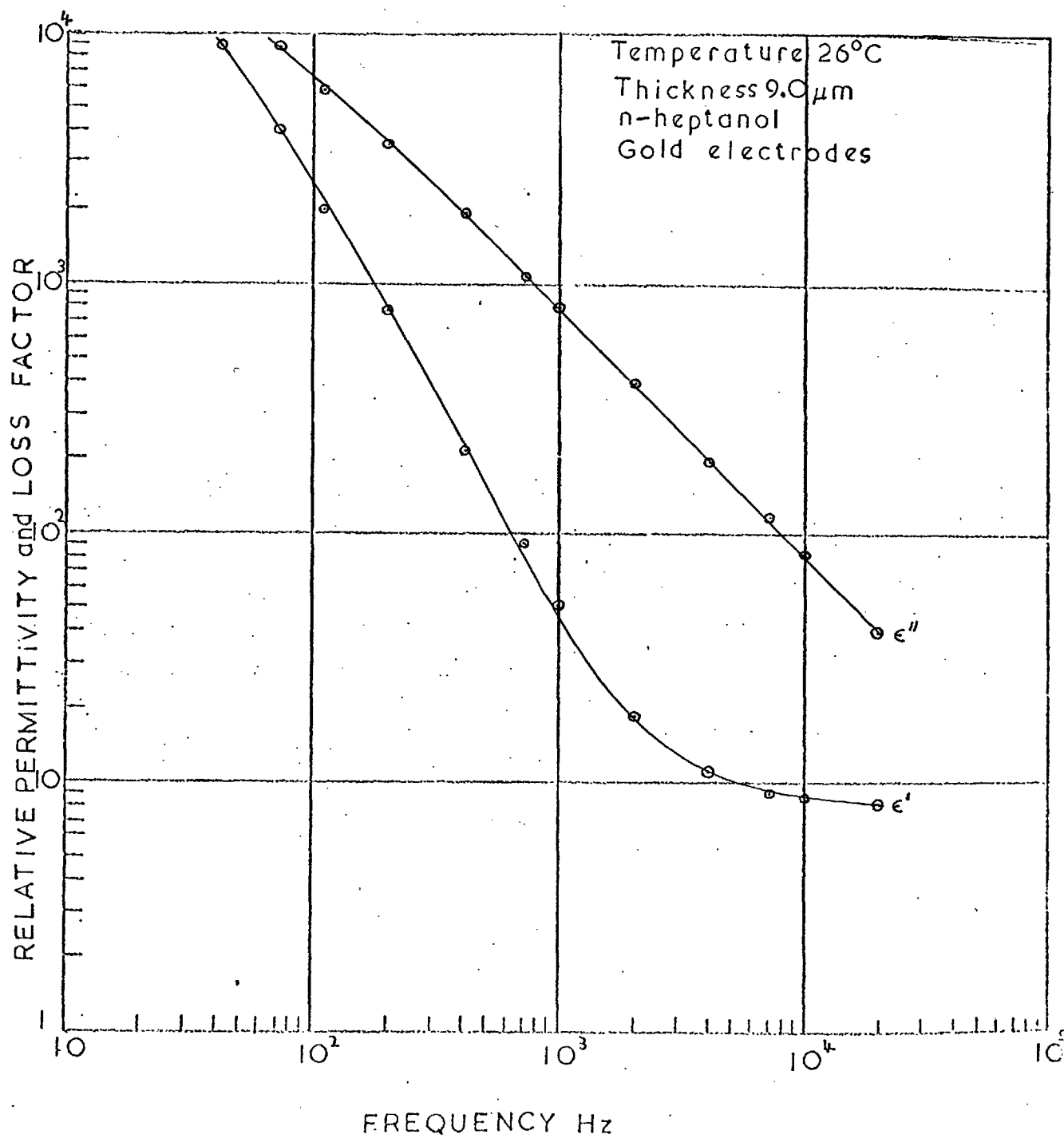


Figure 3.10. ϵ' and ϵ'' versus frequency

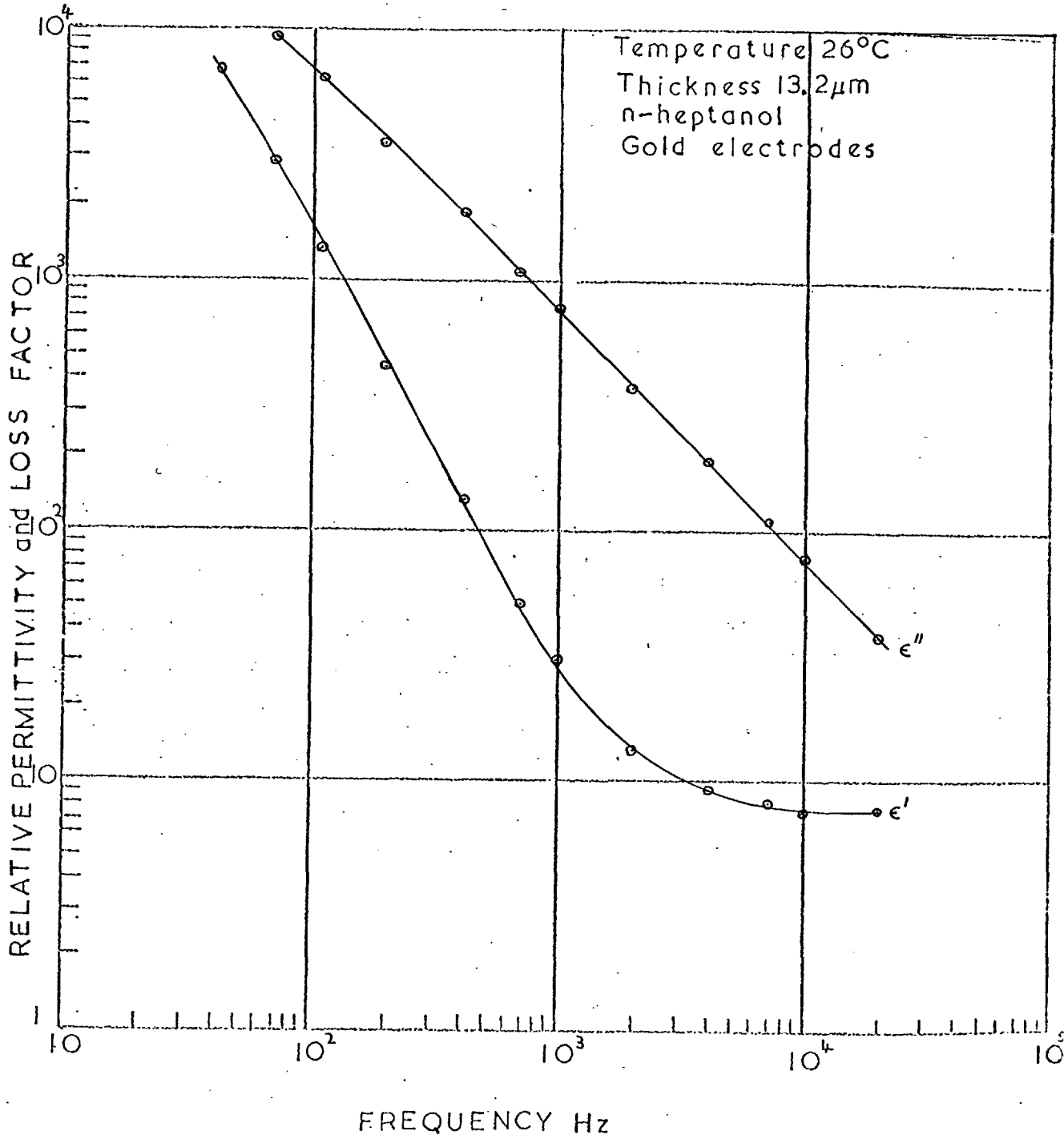


Figure 3.11. ϵ' and ϵ'' versus frequency

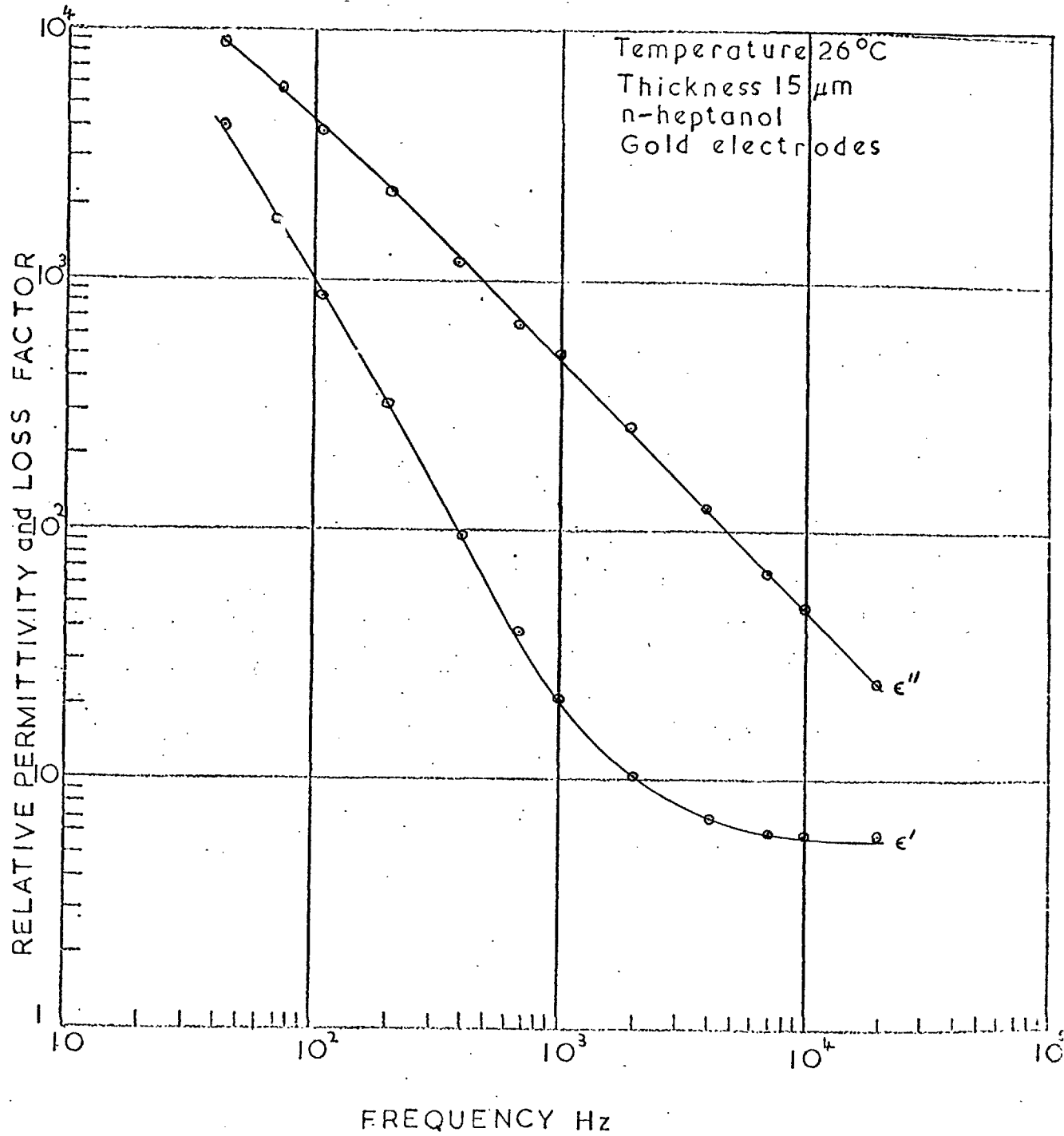


Figure 3.12. ϵ' and ϵ'' versus frequency

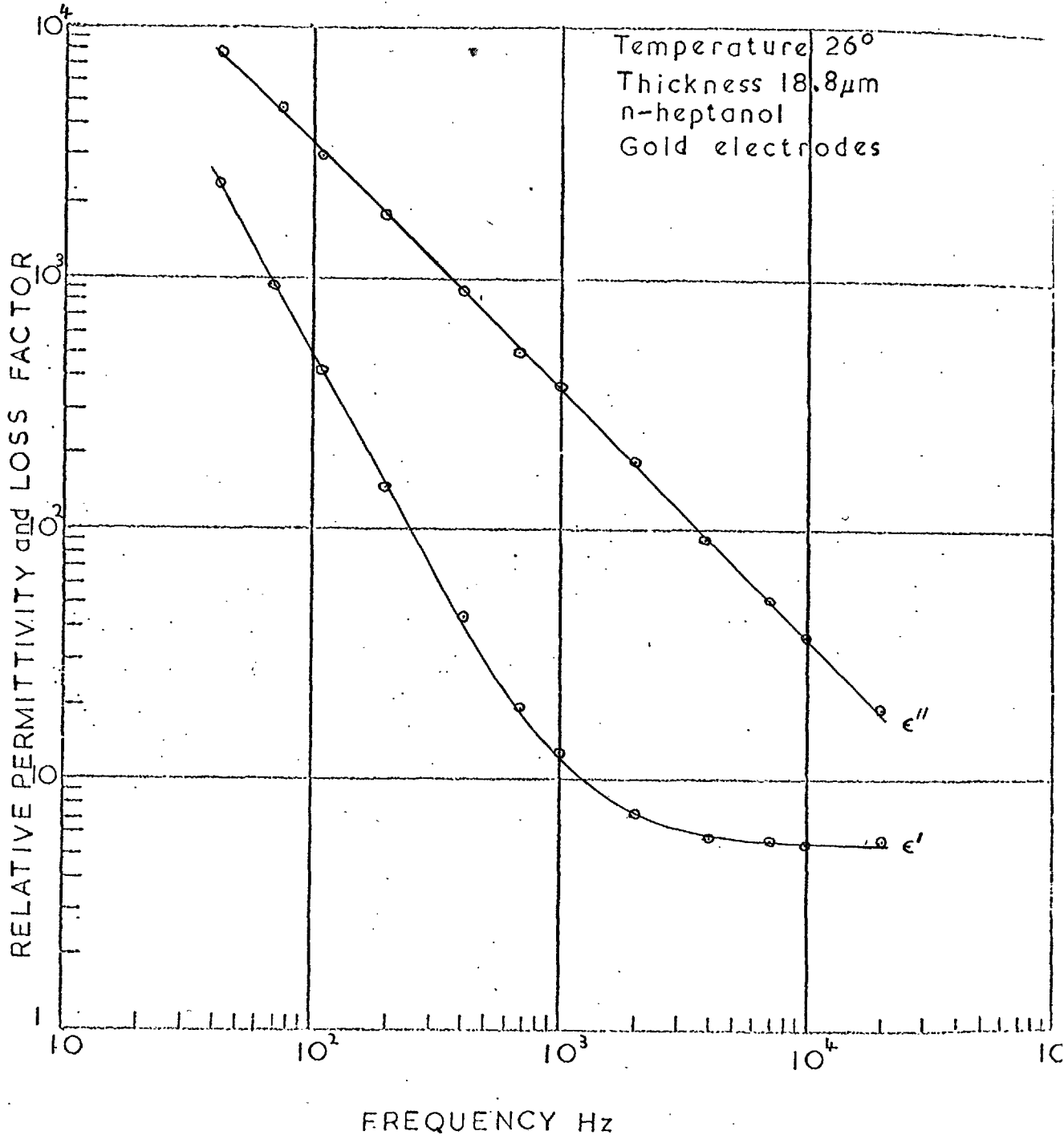


Figure 3.13. ϵ' and ϵ'' versus frequency

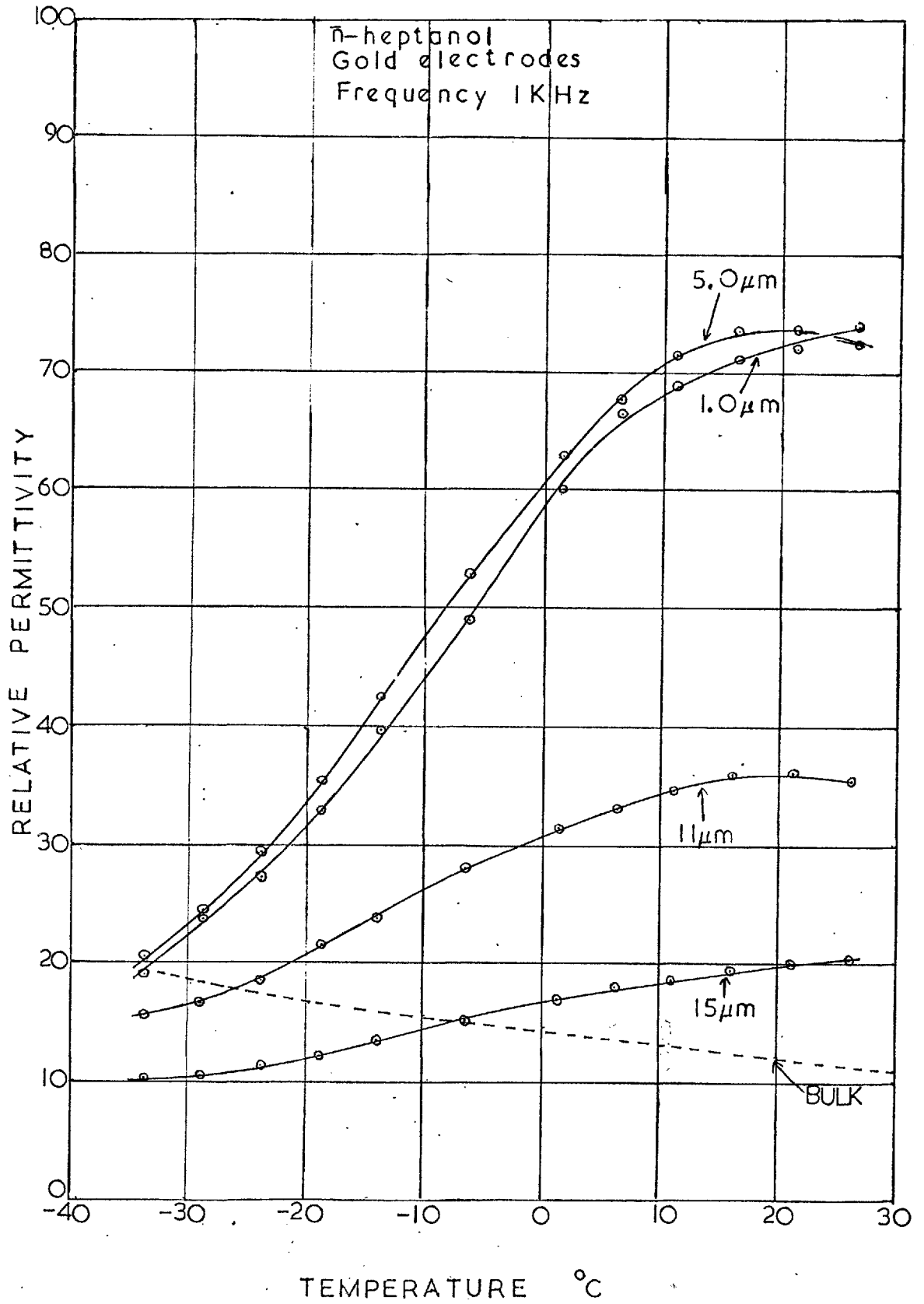


Figure 3.14.a ϵ' versus temperature

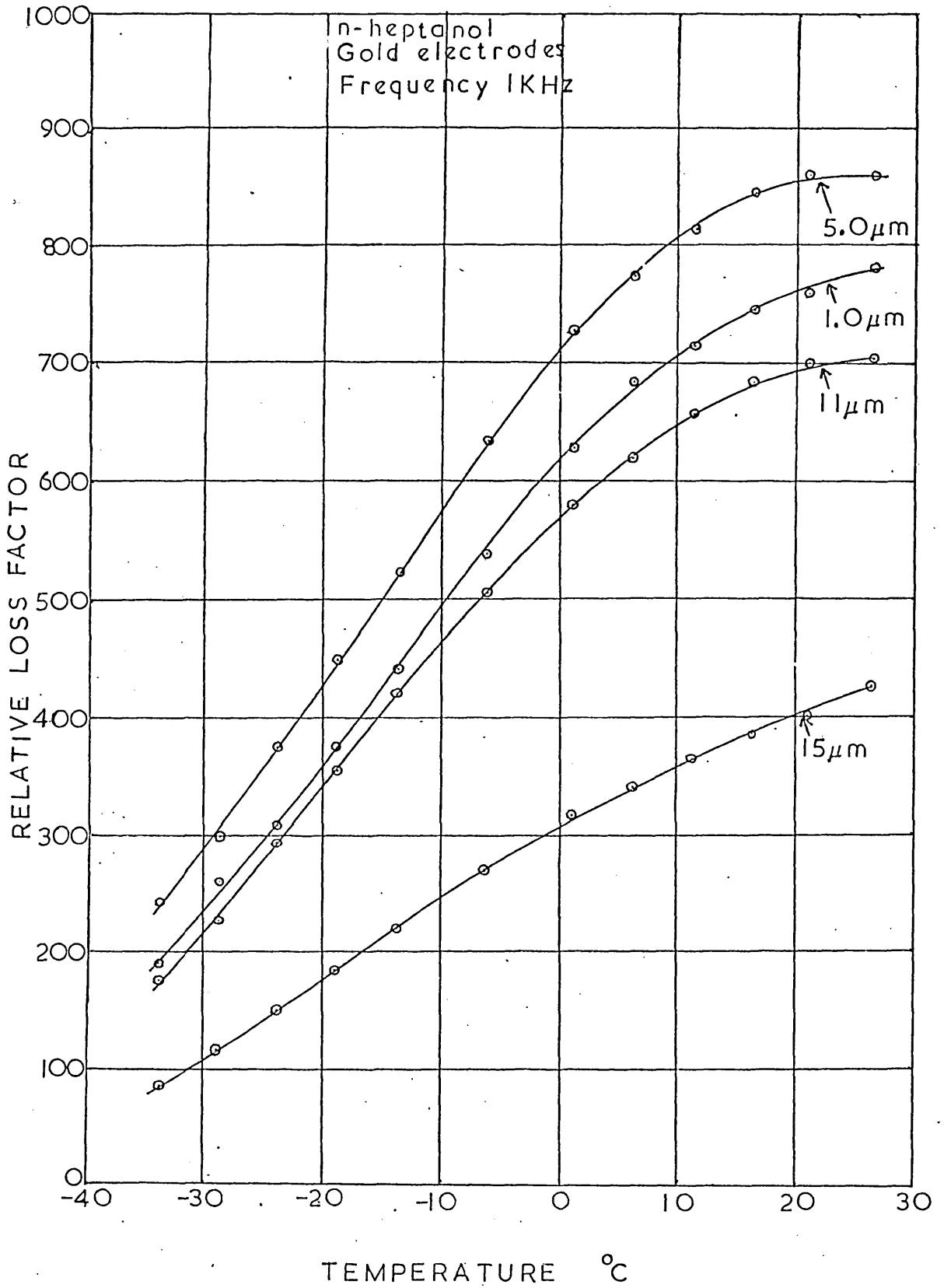


Figure 3.14b. ϵ'' versus temperature

in Figure 3.14a.

3.5. Thickness and Frequency Behaviour of n-heptanol with Silver Electrodes.

The ageing effect noted with gold electrodes was present again for the case of silver electrodes. After a period of 2 to 3 days the ageing seemed to have settled to a very slow rate (Figure 3.15).

Measurements were again made to ascertain the response of the permittivity and loss factor to variation of frequency. Curves showing the variation of permittivity with thickness, at various frequencies (Figure 3.16), are not as simple as in the case of gold electrodes. It was unfortunate that measurements could not be made at thicknesses intermediate to the ones shown. Despite all precautions some capacitors showed a short-circuit when air capacitance at each site was measured. It was doubly unfortunate that the thinner samples were usually found to be shorted-out. In all cases the cell has the potential to realize ten capacitors of differing electrode spacing. For the measurements in this section two capacitors were short-circuited after assembly of the cell. In this particular case the thinnest one at $1.6\mu\text{m}$ and the thickest at $18.1\mu\text{m}$ were affected.

Upon adding the liquid to the cell, in addition to the two capacitors already short-circuited a further capacitor, having an electrode spacing of $9.2\mu\text{m}$, was now short-circuited. At this point the system was left to age over the weekend and upon making measurements, after a period of 46 hrs. had elapsed, a further two capacitors, with electrode spacings of $15.0\mu\text{m}$ and $16.4\mu\text{m}$ respectively, were now short-circuited.

Therefore, out of a possible ten different thicknesses, two were found to be out of commission before the liquid was introduced. This is probably a result of dust particles bridging the gap between the

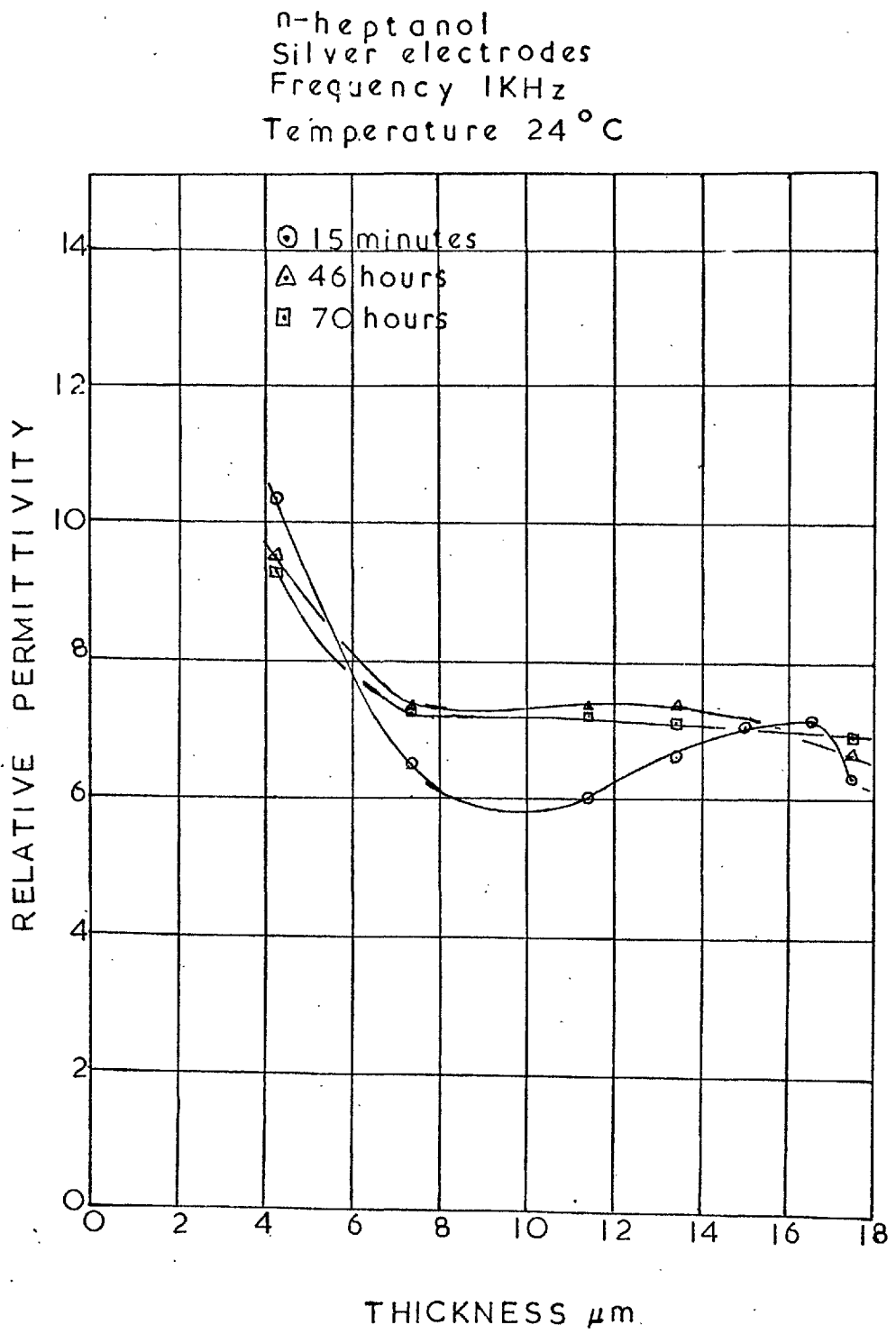


Figure 3.15 Aging effect

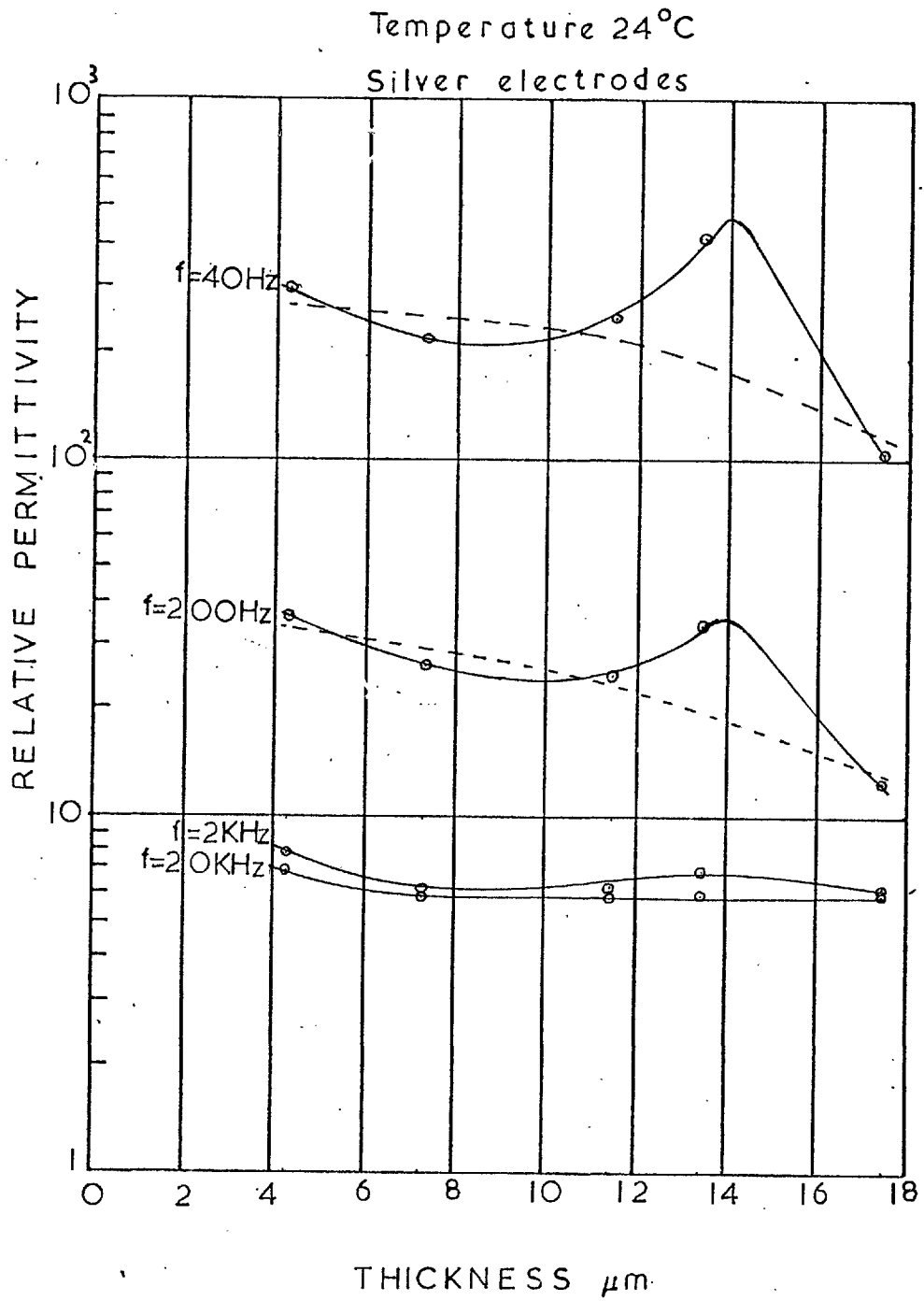


Figure 3.16. ϵ' versus thickness

electrodes and causing a short-circuit. Precautions were taken to exclude dust as far as possible but unfortunately no "clean room" facilities were easily accessible. This was not too much of a problem since one or two capacitors at the most were affected in this way providing care was exercised when assembling the cell.

The spontaneous failure of capacitors after the liquid has been added is more difficult to understand. Breakdown of the liquid is of course a possible explanation, but the voltage applied to the sample was of the order of 0.1 volts corresponding to an electric field of 1KV. cm^{-1} for a specimen $1\mu\text{m}$ in thickness, falling to 100 volt cm^{-1} for a $10\mu\text{m}$ specimen thickness. These values of electric field are not excessive and also one could reasonably expect the thinner samples to breakdown first and this is not observed to be the case.

We are therefore left with measurements relating to only five different thicknesses of liquid layer. At low frequencies there appears to be a peak in the curves at a thickness in the range $14\mu\text{m}$ to $16\mu\text{m}$ as indicated by the solid line in Figure 3.16 for the curves 200Hz and 40Hz. Of course these curves are rather arbitrary in view of the number of experimental points. One might be justified in viewing the results at $13.4\mu\text{m}$ with suspicion. If one were to ignore the results for $13.4\mu\text{m}$ a smoother curve, having the same general shape as the curves obtained for gold electrodes, can be drawn. The most likely reason for the high values of permittivity, obtained at $13.4\mu\text{m}$ would be an error in the value of the air capacitance, probably caused by some stray capacitance effect.

Figures 3.17 and 3.21 show the dependence of relative permittivity and relative loss factor on frequency at the five thicknesses at which measurements were made. These curves show the same general relaxation behaviour observed with gold electrodes. The magnitude

of the inter-facial polarization effect is not as large as that observed with gold electrodes, the maximum permittivity recorded being 302 for a thickness of $4.29\mu\text{m}$. The observations made in section 3.3 relating to the frequency response of permittivity and loss factor for gold electrodes also apply to the case of silver electrodes, noting that the variation of the limiting value of permittivity observed at high frequencies is less marked for the case of silver electrodes.

3.6. The Effects of Temperature on the Behaviour of n-heptanol with Silver Electrodes.

The temperature dependence of permittivity and loss factor is shown in Figures 3.22a and 3.22b. The effect of temperature on the permittivity and loss factor of n-heptanol on silver electrodes is similar to the effect with gold electrodes.

In this instance the frequency response was observed at six temperatures and Figure 3.23 gives the behaviour at three of these temperatures (the other three have been omitted for the sake of clarity). It would appear from the graphs that the magnitude of the space-charge polarization effect decreases with decreasing temperature. However on the basis of the data, as presented, one should proceed to this conclusion cautiously. As previously mentioned the interfacial polarization results in a relaxation type of behaviour. Associated with a relaxation there is a characteristic time, called the relaxation time and given the symbol τ . Returning to Figure 3.23, if the relaxation time for the interfacial polarization increases with decreasing frequency, then the lower temperature curves will be shifted, along the frequency axis, towards lower frequencies. If this is the case then the lower temperature curves may reach the same permittivity values observed at higher temperatures, but they will do so at lower frequencies.

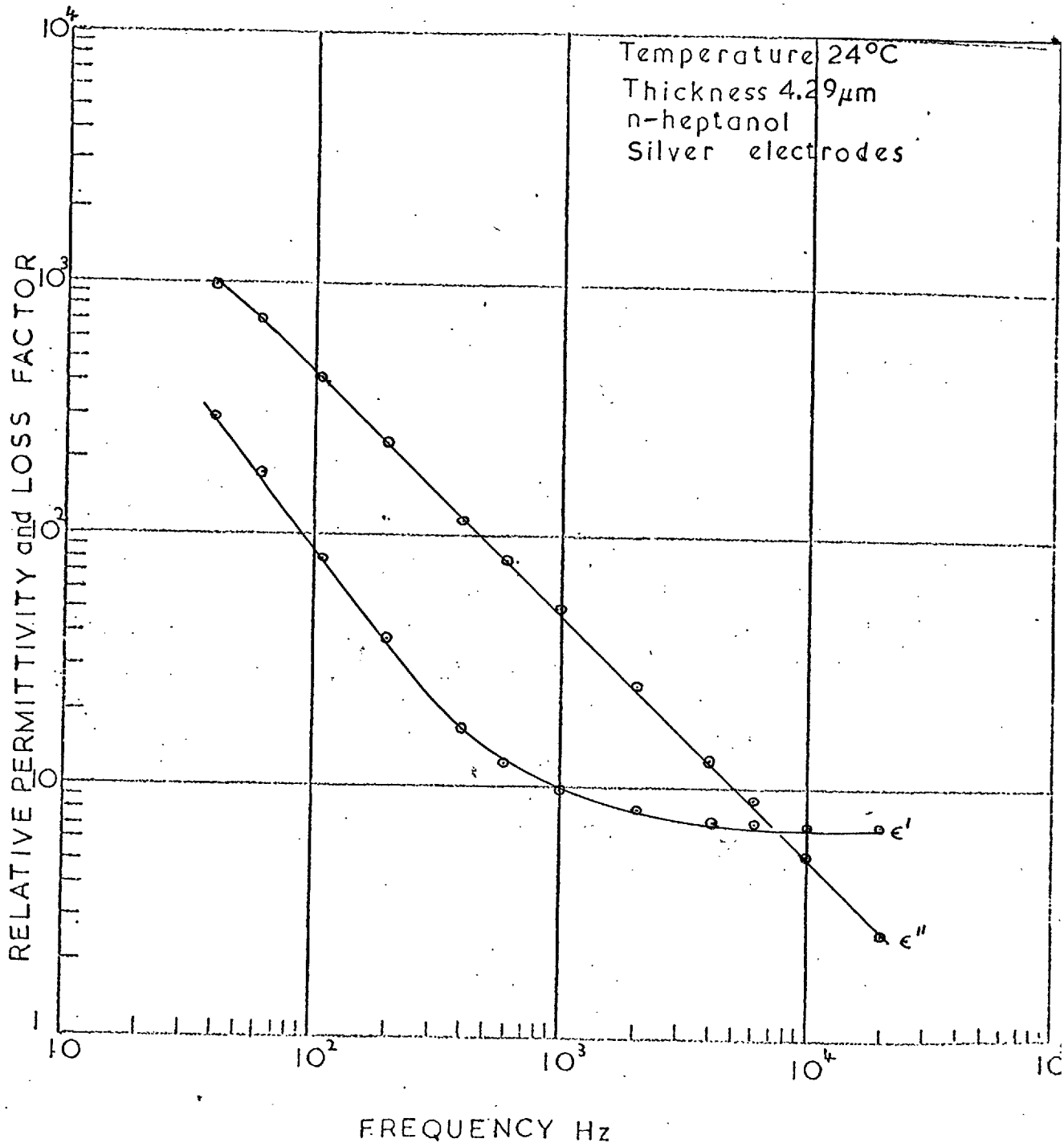


Figure 3.17 ϵ' and ϵ'' versus frequency

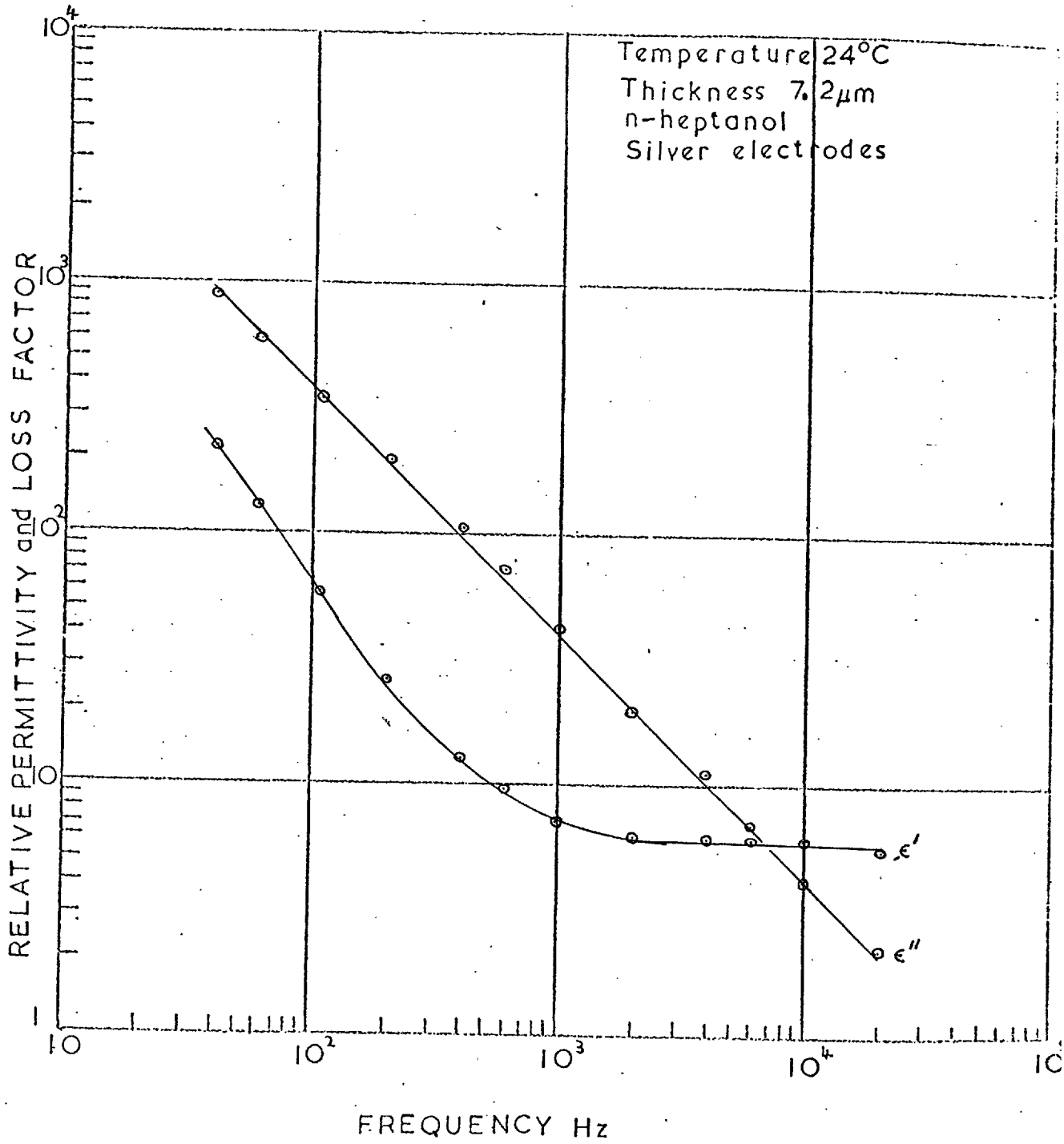


Figure 3.18. ϵ' and ϵ'' versus frequency

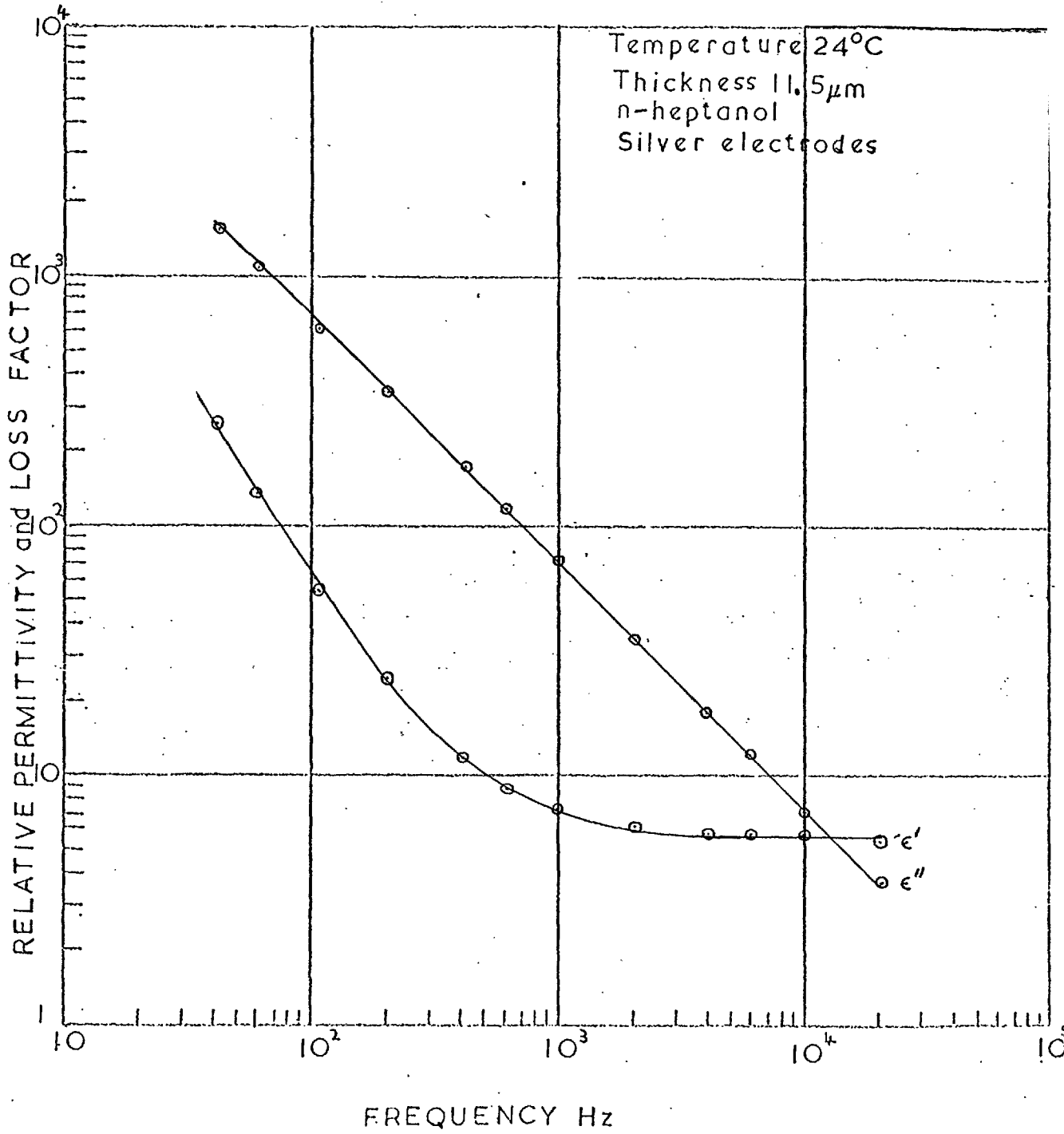


Figure 3.19. ϵ' and ϵ'' versus frequency

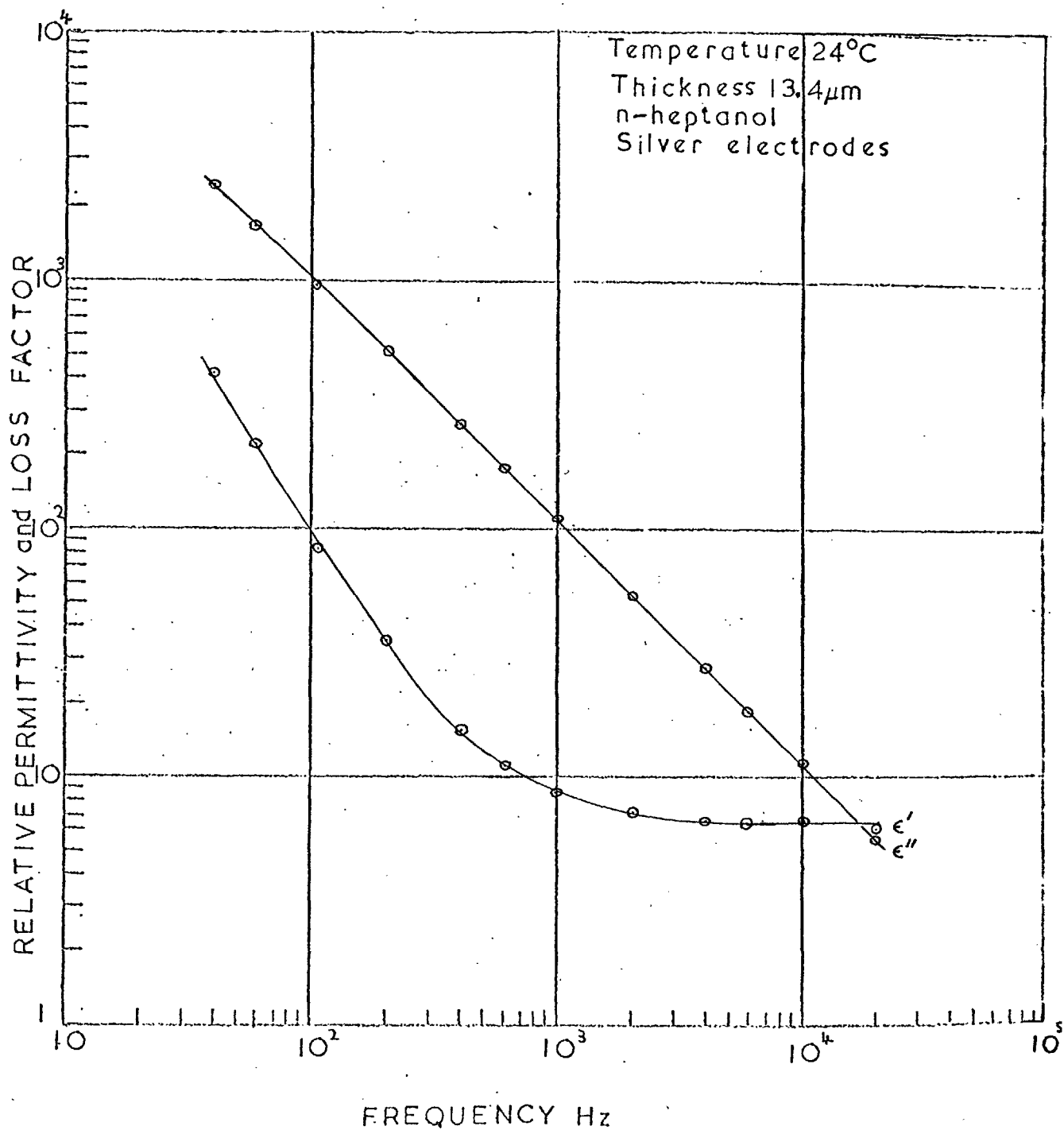


Figure 3.20. ϵ' and ϵ'' versus frequency

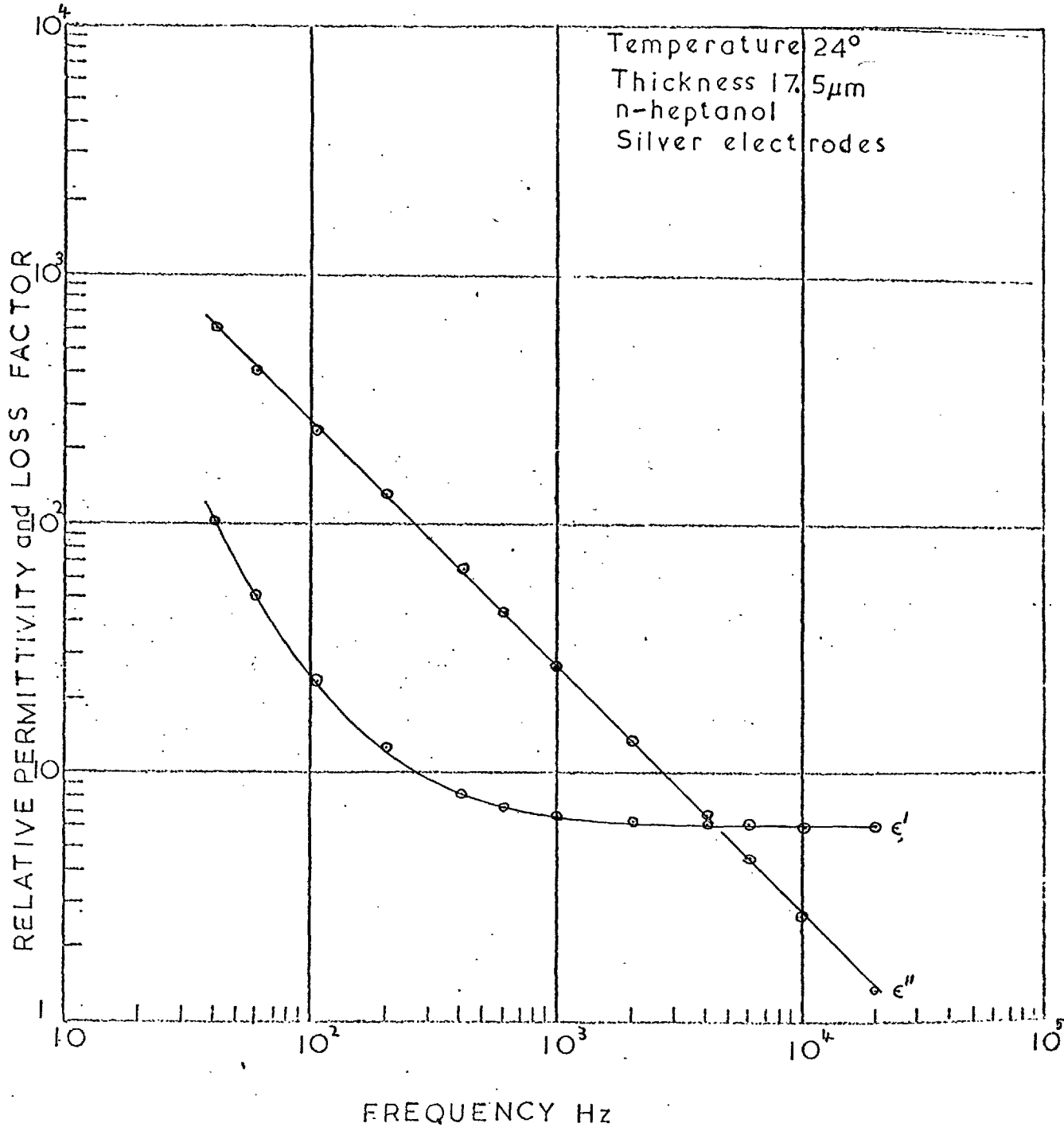


Figure 3.21. ϵ' and ϵ'' versus frequency

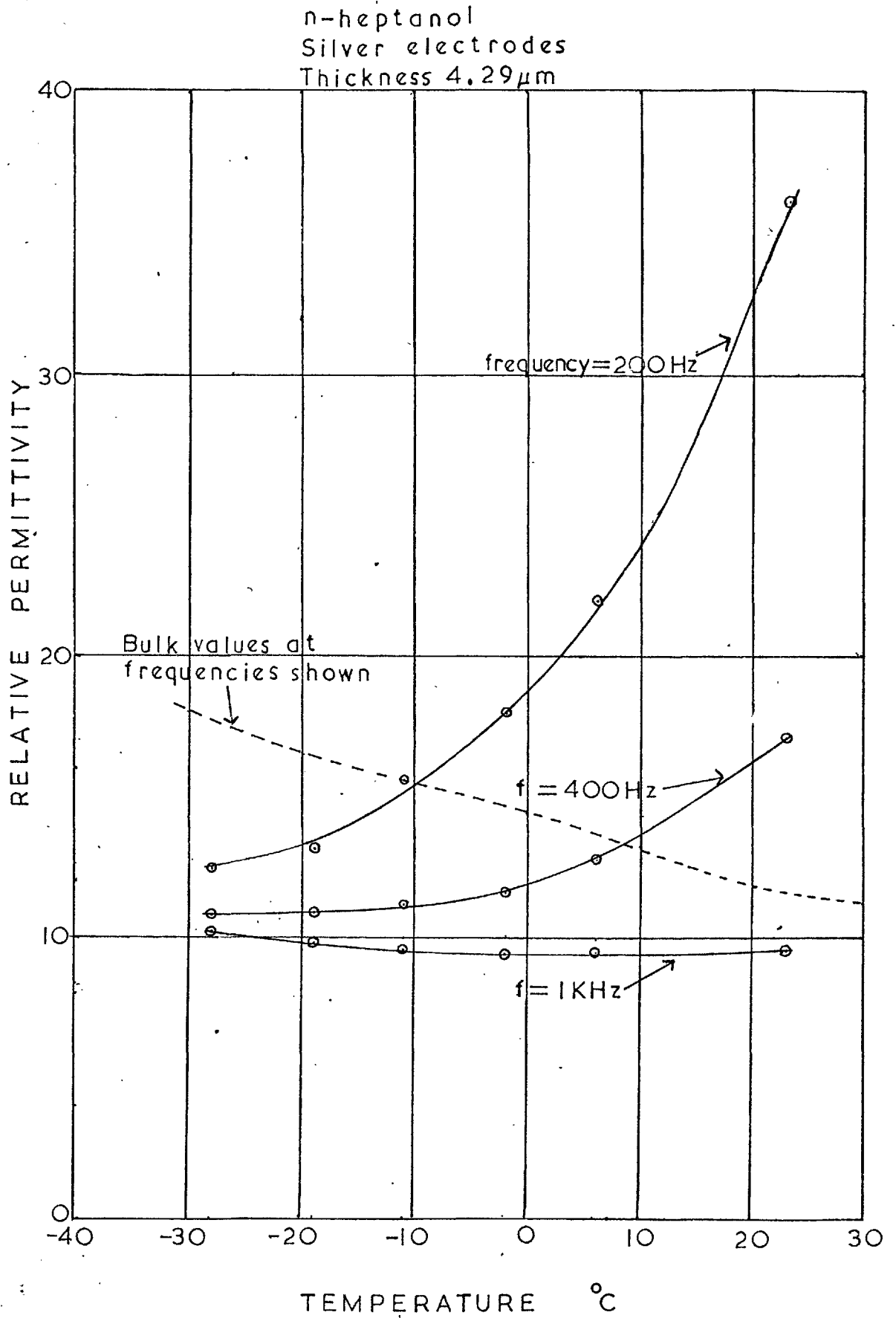


Figure 3.22a. ϵ' versus temperature

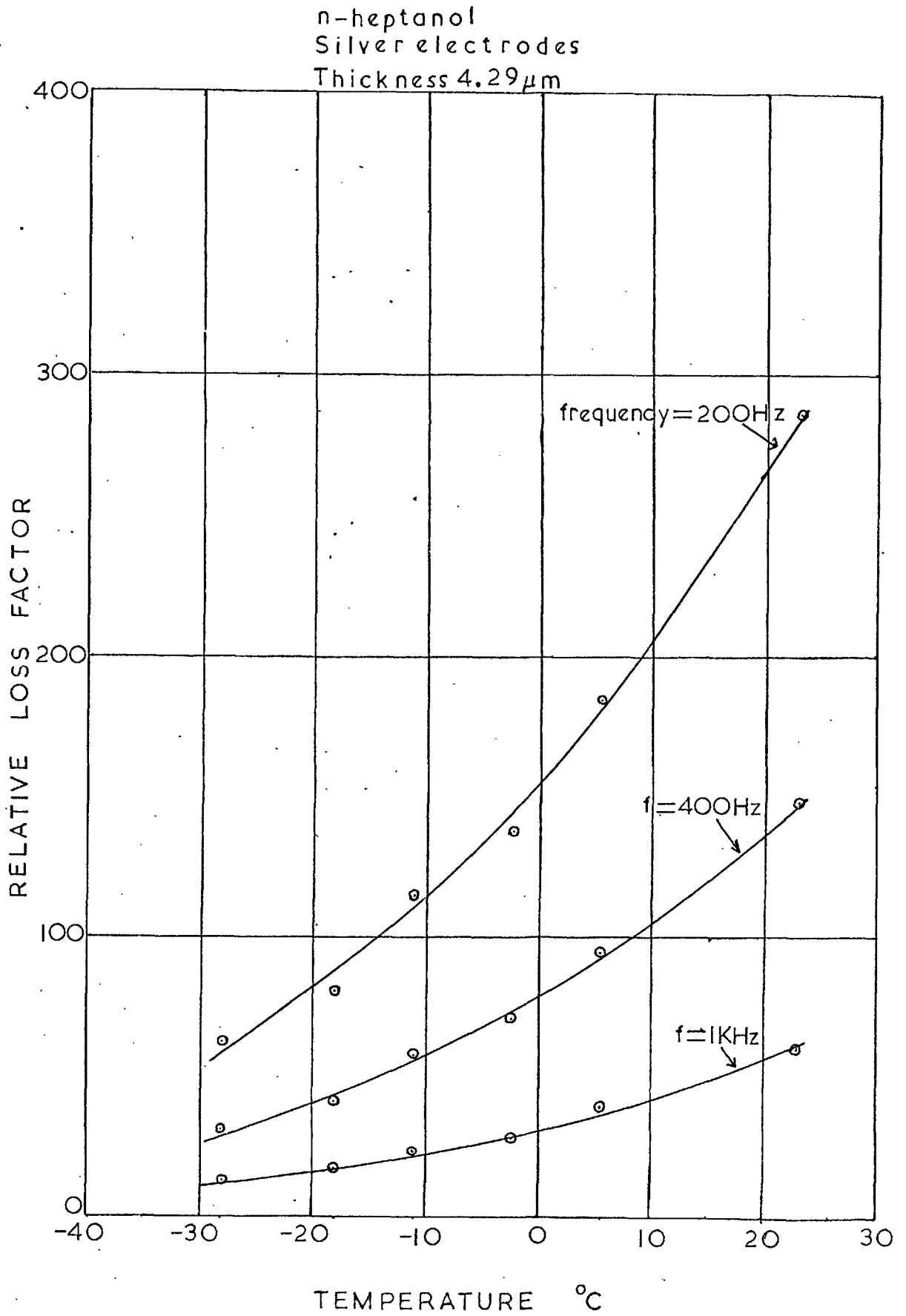


Figure 3.22b. ϵ'' versus temperature

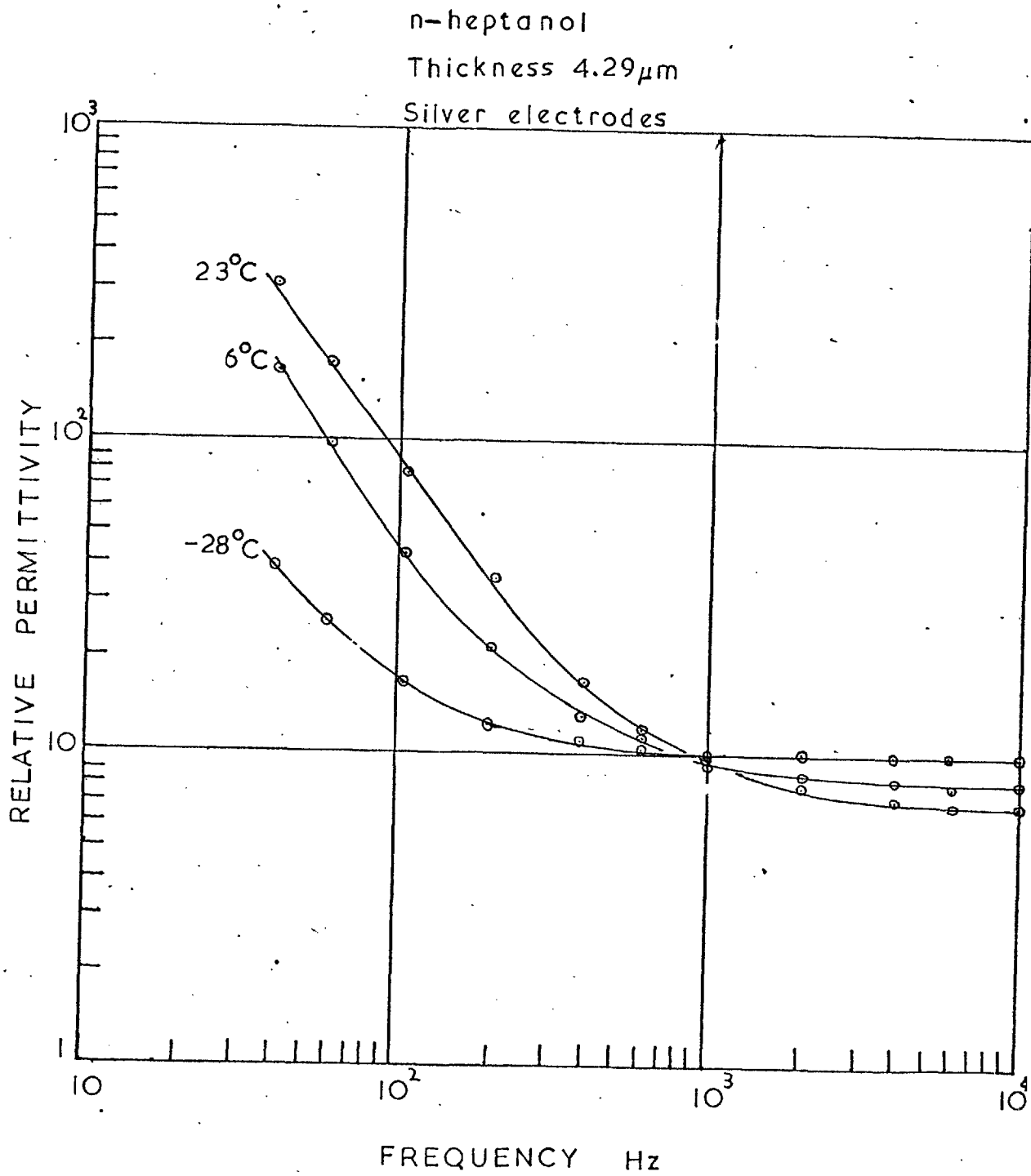


Figure 3.23. ϵ' versus frequency at various temperatures

Figure 3.23 also shows that the limiting value of permittivity, reached at higher frequency, increases with decreasing temperature. This is consistent with the observation that the bulk permittivity of n-heptanol increases with decreasing temperature.

3.7. The Behaviour of n-heptanol with Aluminium Electrodes.

The same series of experiments was made with aluminium electrodes. In order to elucidate the effects of impurity level two series of results were obtained

- 1) for a sample of n-heptanol as received from the manufacturer and
- 2) for a sample of n-heptanol purified by the method described in Chapter 2.

The usual ageing effect is found, but for aluminium electrodes the ageing time seems to be of the order of 4 to 5 days (Figure 3.24). The frequency dependence of permittivity and loss factor were determined for various thicknesses (Fig. 3.25a and Fig 3.25b compare the pure and impure samples for a thickness of about $3\mu\text{m}$). As one would expect, for comparable thickness, the loss factor, for all frequencies, is higher for the higher impurity level. At low frequencies the relative permittivity increases with increasing impurity level, while the "relaxation" frequency for the interfacial polarization decreases with increasing impurity concentration.

3.8. The Effects of Temperature on the Behaviour of n-heptanol with Aluminium Electrodes.

Once more, the general trend of decreasing interfacial polarization effect, with decreasing temperature, is noted (Fig. 3.26a and 3.26b). These particular curves exhibit a maximum for the thinnest specimen and a minimum for a specimen of intermediate thickness in the case of the purified specimen of liquid.

These curves also show the freezing point quite clearly as a

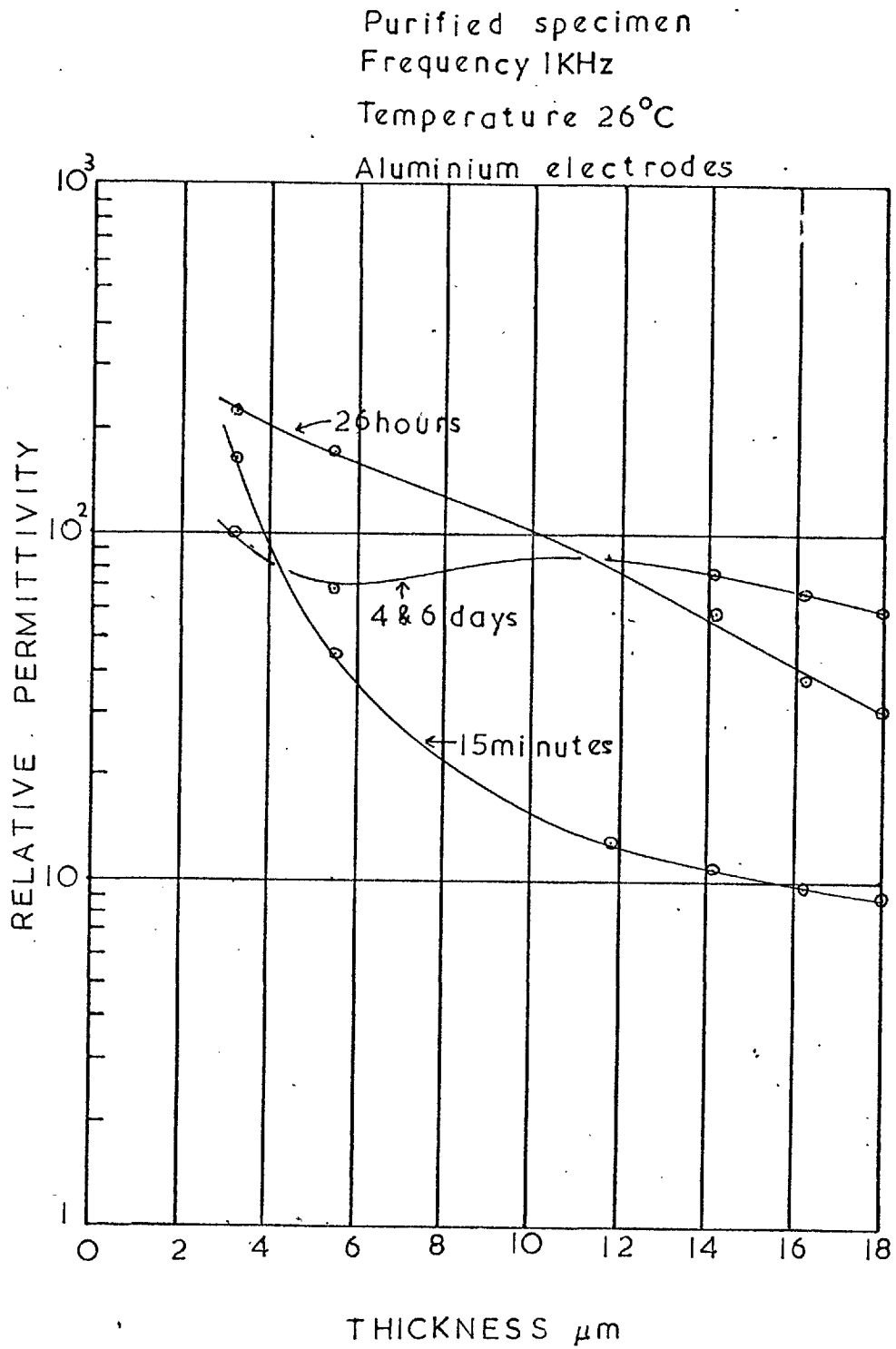


Figure 3.24. Ageing effect in n-heptanol

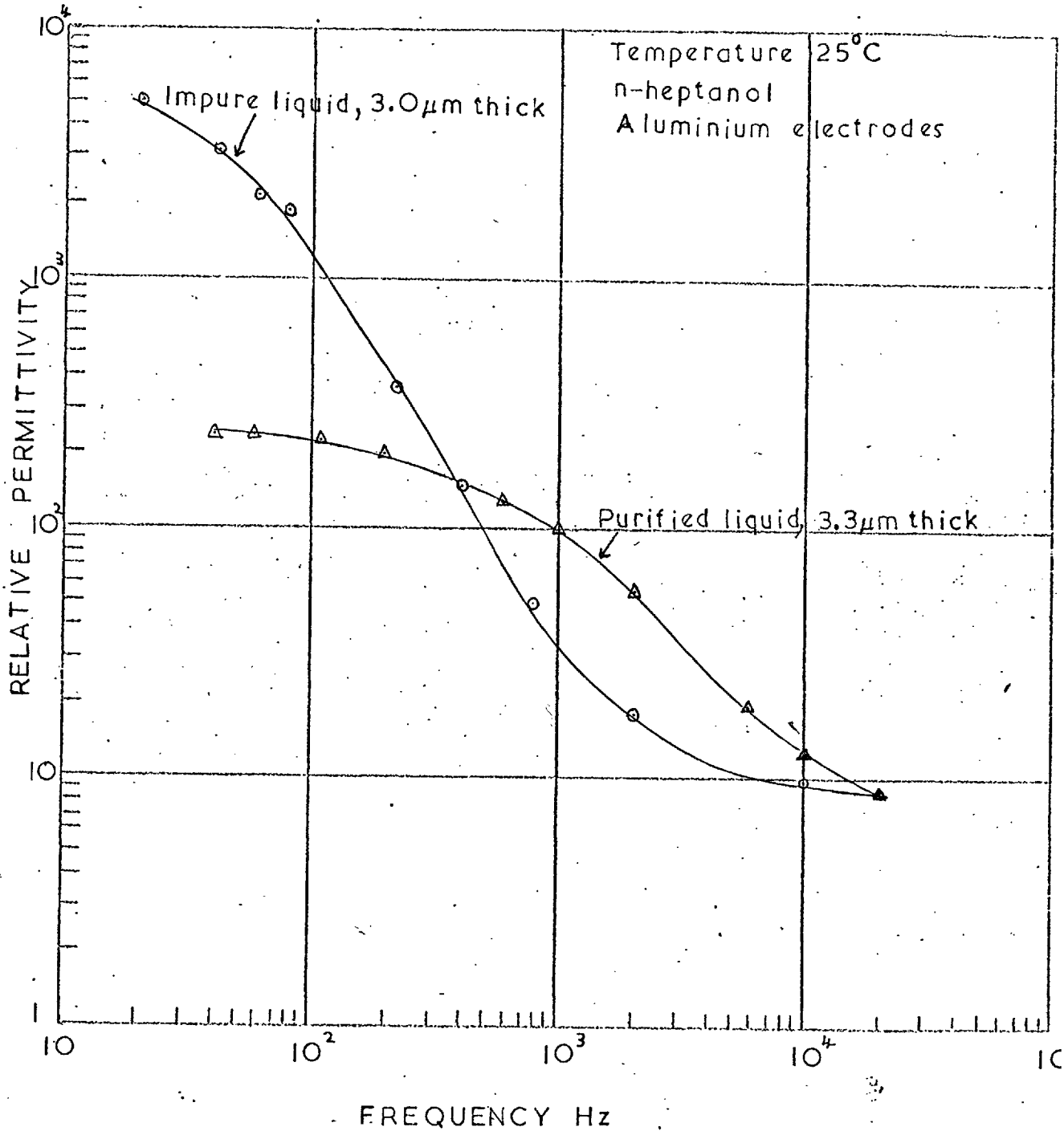


Figure 3.25a. Effects of purity of liquid sample.
Frequency dependence of permittivity

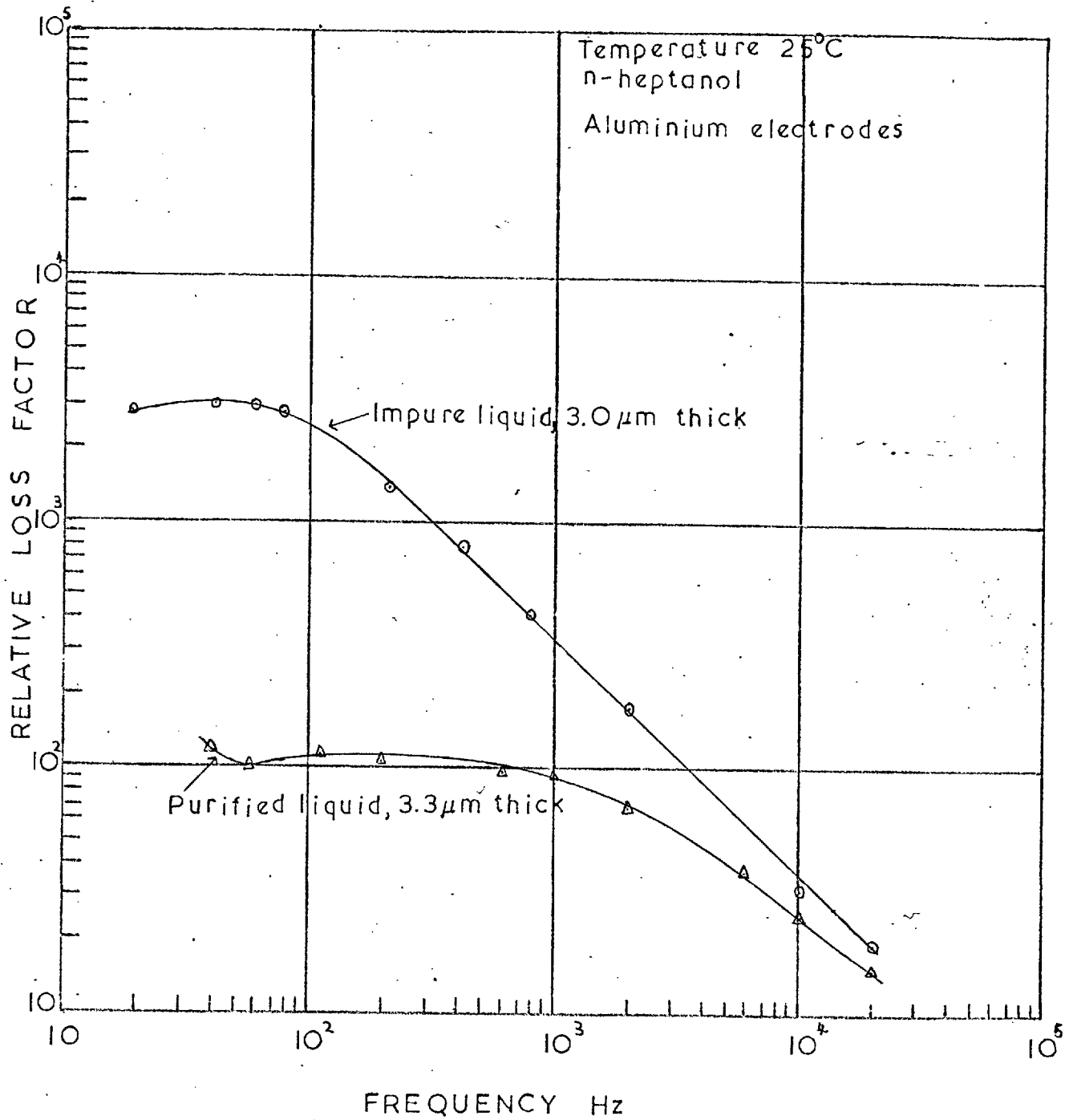


Figure 3.25b. Effects of purity of liquid sample.

Frequency dependence of loss factor

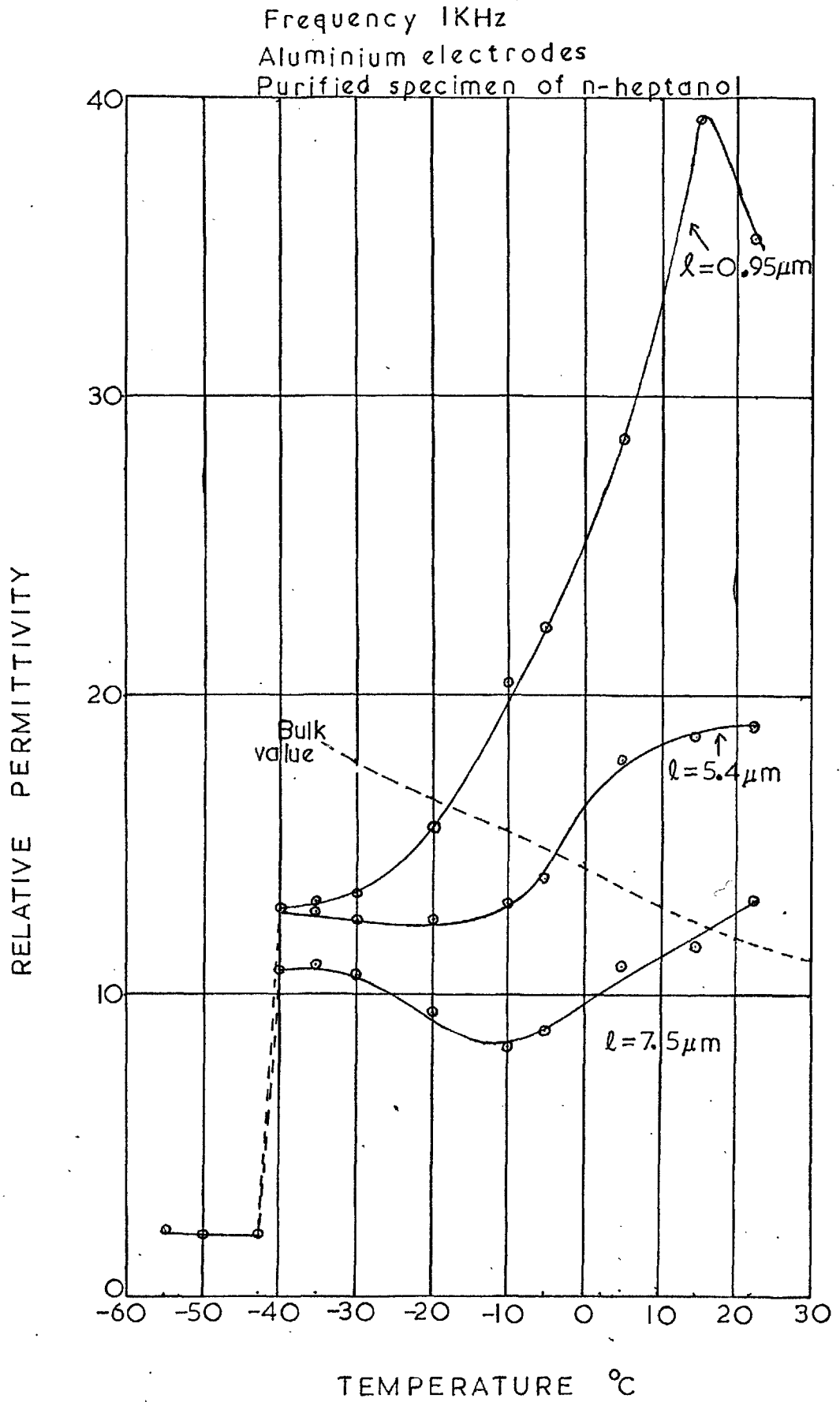


Figure 3.26a. Temperature dependence of permittivity

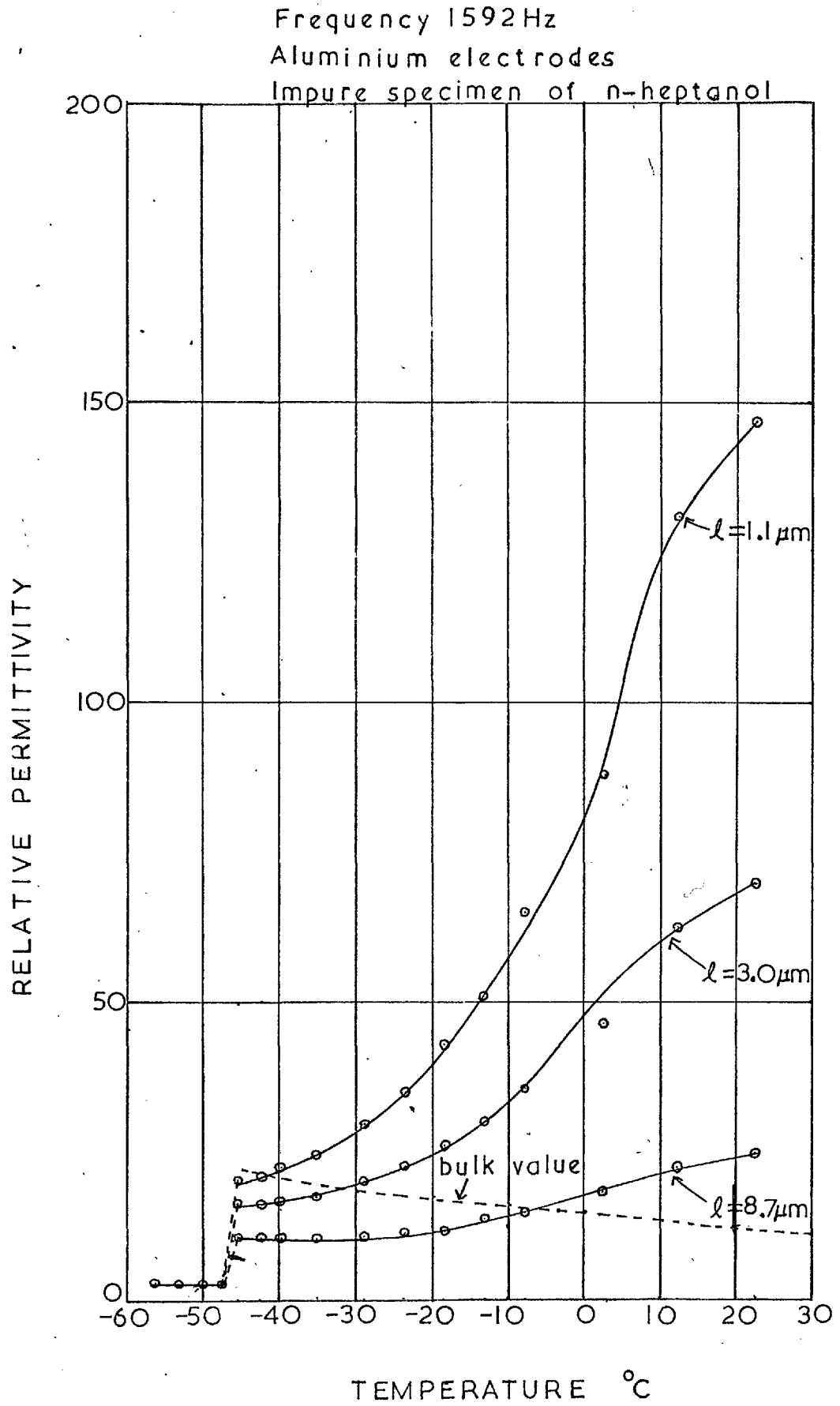


Figure 3.26b. Temperature dependence of permittivity

discontinuity in the curve. After freezing the measured permittivity was the same, to within 10%, for all thicknesses.

3.9. "Garton Effect" Measurements.

Garton⁴ has pointed out that a stress-dependent loss angle may arise in a film of liquid if the film is thin enough for the motion of ions, under the influence of an alternating field, to be limited by the boundaries of the film. In this work Garton relates the shape of the $\tan \delta$ versus stress curves to the ionic concentration, radius and mobility.

All the measurements made indicate an interfacial polarization effect taking place and so one would expect to be able to make "Garton Effect" measurements on these liquid samples, thus providing valuable information on the impurity concentrations present and the ionic mobility.

The a.c. measurements were all made using a Wayne Kerr B221 Universal Bridge, a brief description of the operation of which is given in Appendix I. In order to make "Garton Effect" measurements it is necessary to vary the voltage applied to the sample. The voltage appearing across the sample, with B221 bridge, depends on the input voltage to the bridge and the range setting. On the lowest capacitance range (Range I) the full input voltage appears across the unknown capacitor, ranges 2 and 3 give one tenth of the input voltage, ranges 4 and 5 one hundredth of the input voltage and ranges 6 and 7 one thousandth of the input voltage. The maximum allowable input voltage to the bridge is 40 volts r.m.s. (113 volts peak-to peak) and the typical capacitance values obtained made it necessary to use ranges 3 and 4 for most measurements. Thus the maximum voltage that could be applied to a sample was limited to 4 volts r.m.s. (11.3 volts p.p.).

Measurements with gold and silver electrodes showed little or no variation in loss angle with applied voltage over the voltage range available. With aluminium electrodes however a marked dependence of loss angle on stress was found, as predicted by the "Garton Effect". This is presumably related to the oxide layer present on aluminium which makes discharge of ions difficult.

"Garton Effect" measurements were made on the impure specimen of n-heptanol described in section 3.7. It was found that the clearest results were obtained if the measurements were made at a frequency of 600 Hz. Figure 3.27a shows the variation of $\tan \delta$ with stress over a range of temperature for a sample thickness of $1.8\mu\text{m}$.

In addition to the loss angle, the permittivity is stress dependent. The permittivity is constant at low values of applied field, but begins to decrease as the field strength is increased. This effect was not reported by Garton.

Figures 3.28a and 3.28b show the measurements repeated on the same sample after two days. This again illustrates the time dependence of the liquid properties.

It must be pointed out that, even with aluminium electrodes, it was not always possible to observe a variation of $\tan \delta$ with applied voltage. This must be because it was not possible to apply a sufficiently high voltage. It could be that "The Garton Effect" is present with gold or silver electrodes but no variation in $\tan \delta$ could be observed because insufficient voltage was available.

3.10. D.C. Conduction Currents.

The problem of making a satisfactory measurement of the d.c. conductivity of an insulating liquid has long been recognised. The troublesome dependence upon the magnitude and time of application of the test voltage makes it necessary to specify these variables for a

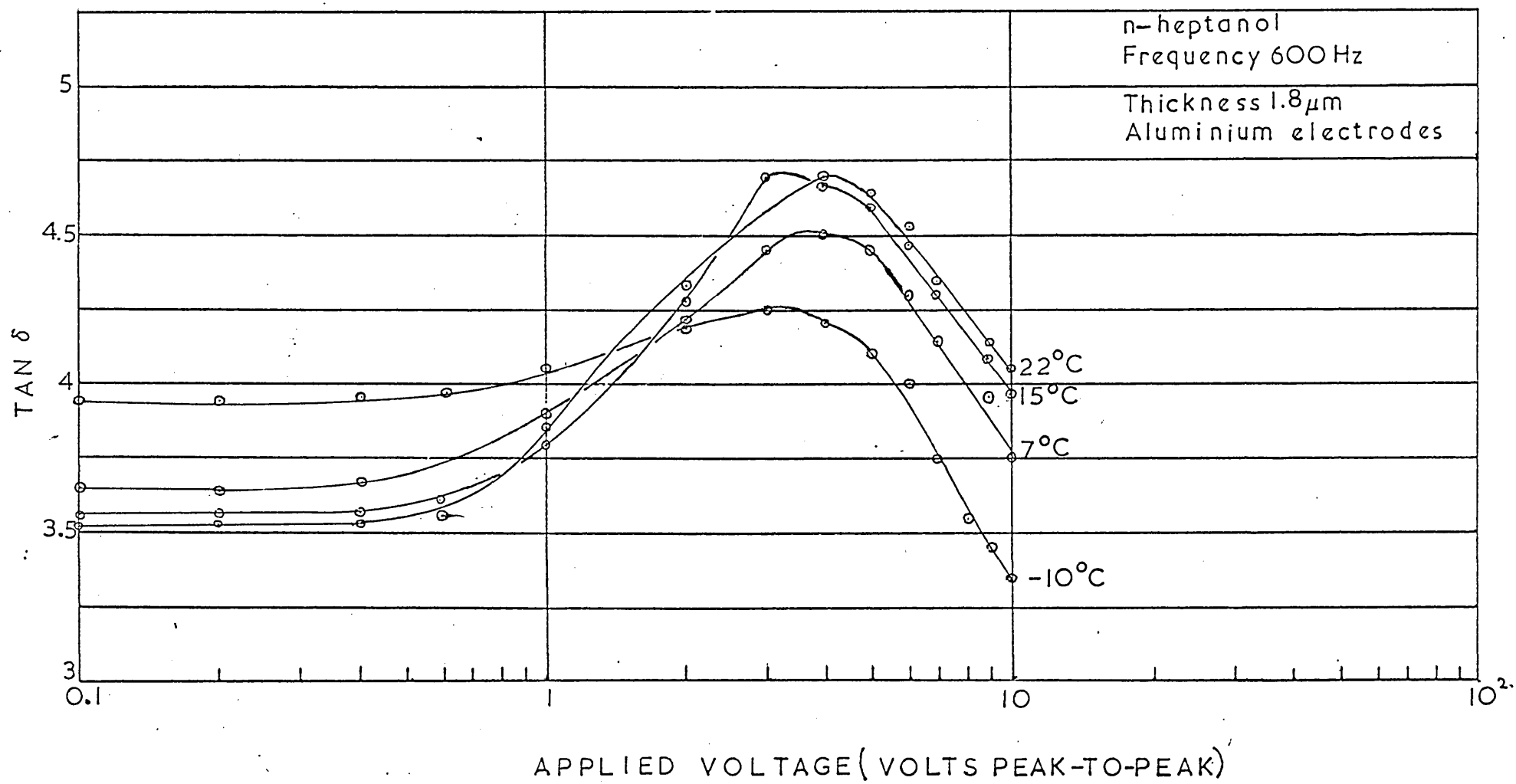


Figure 3.27a. Garton effect measurements

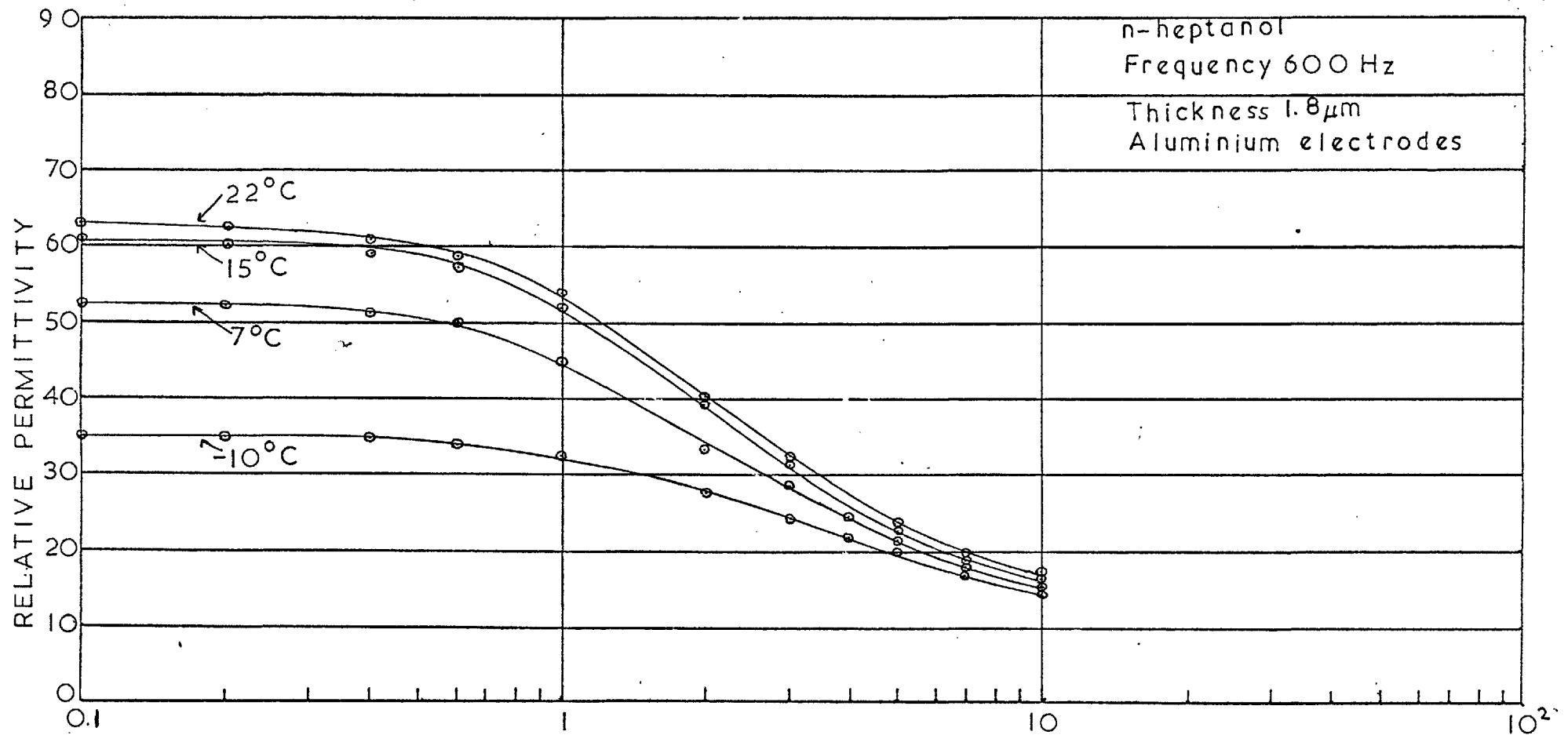


Figure 3.27b. Garton effect measurements.

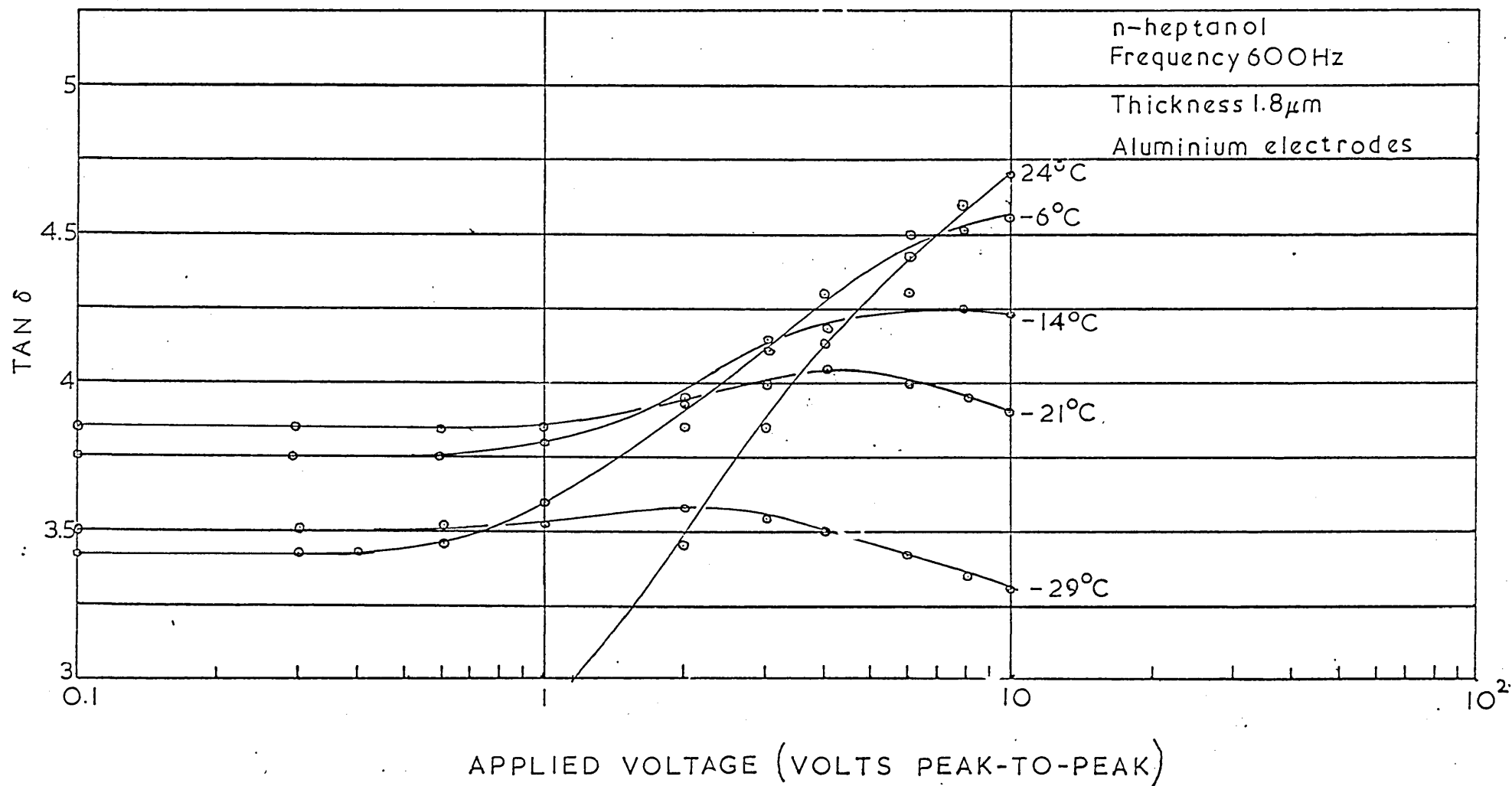


Figure 3.28a. Garton effect measurements.

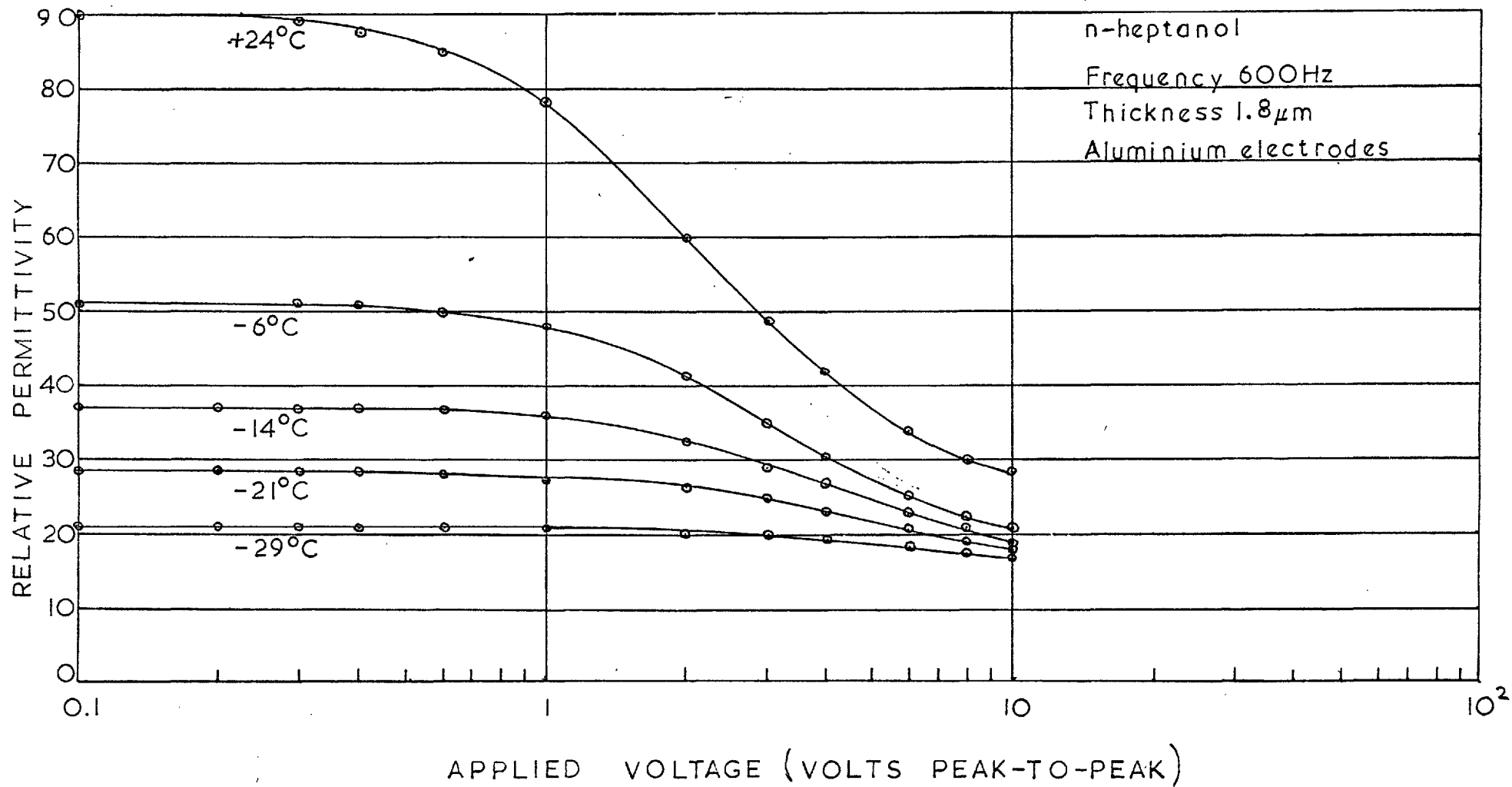


Figure 3.28b. Garton effect measurements

quoted value of conductivity. In spite of these troubles, a d.c. measurement is convenient to make and provides useful information about the purity of the liquid.

An added complication occurring in the thin layers investigated was breakdown of the film. This phenomenon was found at moderate voltages and there seemed to be no discernable pattern to the effect. Despite the difficulties some d.c. current/voltage curves were obtained. Current measurements were made using a Keithley Model 601B Electrometer, whilst the driving voltage was supplied by a Solatron variable d.c. voltage source. Current readings were taken one minute after the application of the voltage.

Figs 3.29a to 3.29e show the shape of the current voltage curves obtained, for the same impure sample of n-heptanol used in section 3.7, at several different temperature, for specimen thickness of $4.9\mu\text{m}$. Fig. 3.30 shows curves at various temperatures and at a series of times after the first addition of the liquid.

The curves illustrated in Figs 3.29 and 3.30 all exhibit three distinct regions. Within the limits of experimental error the current rises, initially, in proportion to the square root of the applied voltage. This is followed by an ohmic region, i.e. current proportional to applied voltage and finally a further change in slope results in a current proportional to the square of the applied voltage.

At greater thicknesses the picture is less clear and the current is seen to rise rapidly (at a higher rate than voltage-squared) with increasing voltage (Figs 3.31).

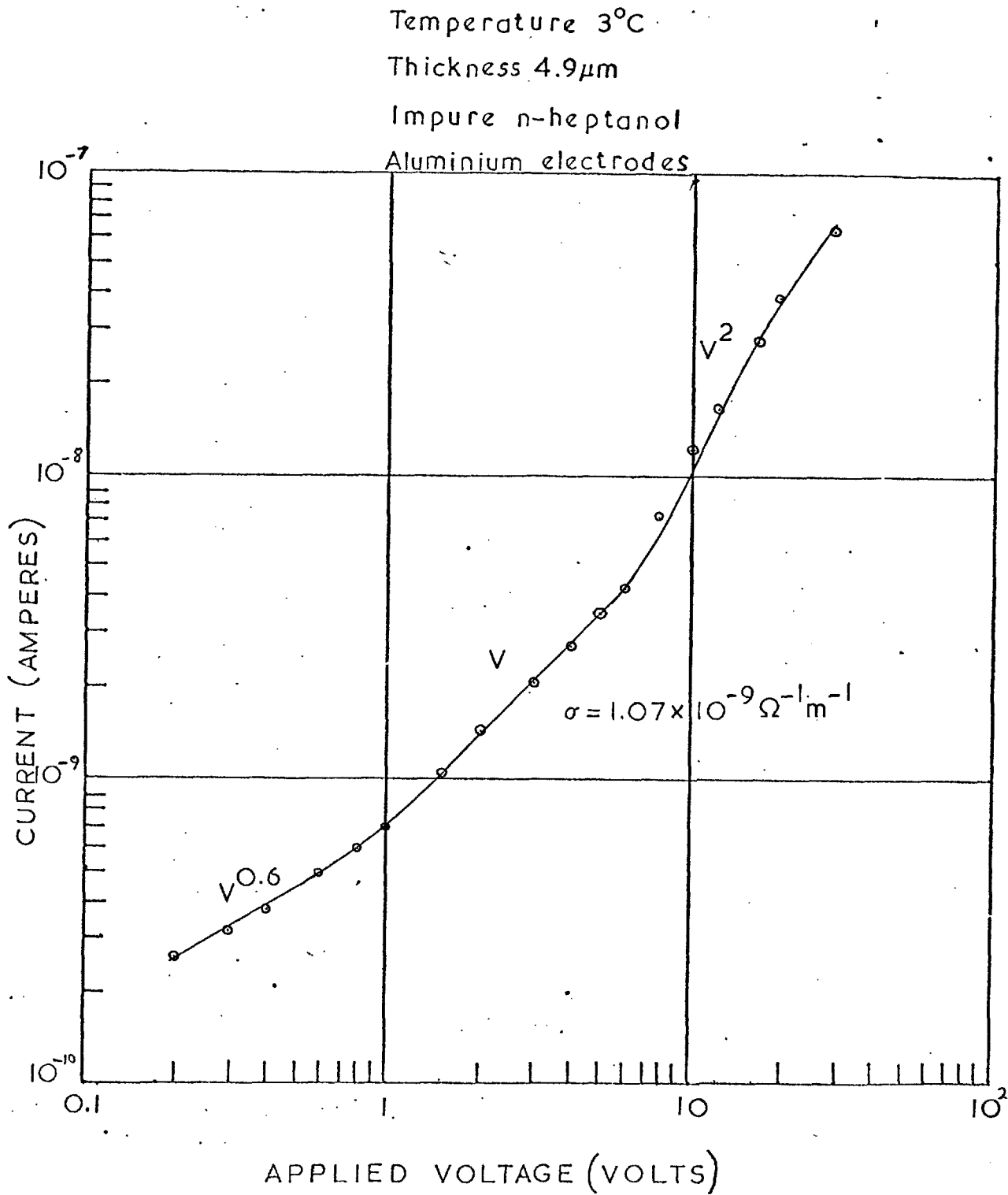


Figure 3.29a. D.c. current-voltage curves

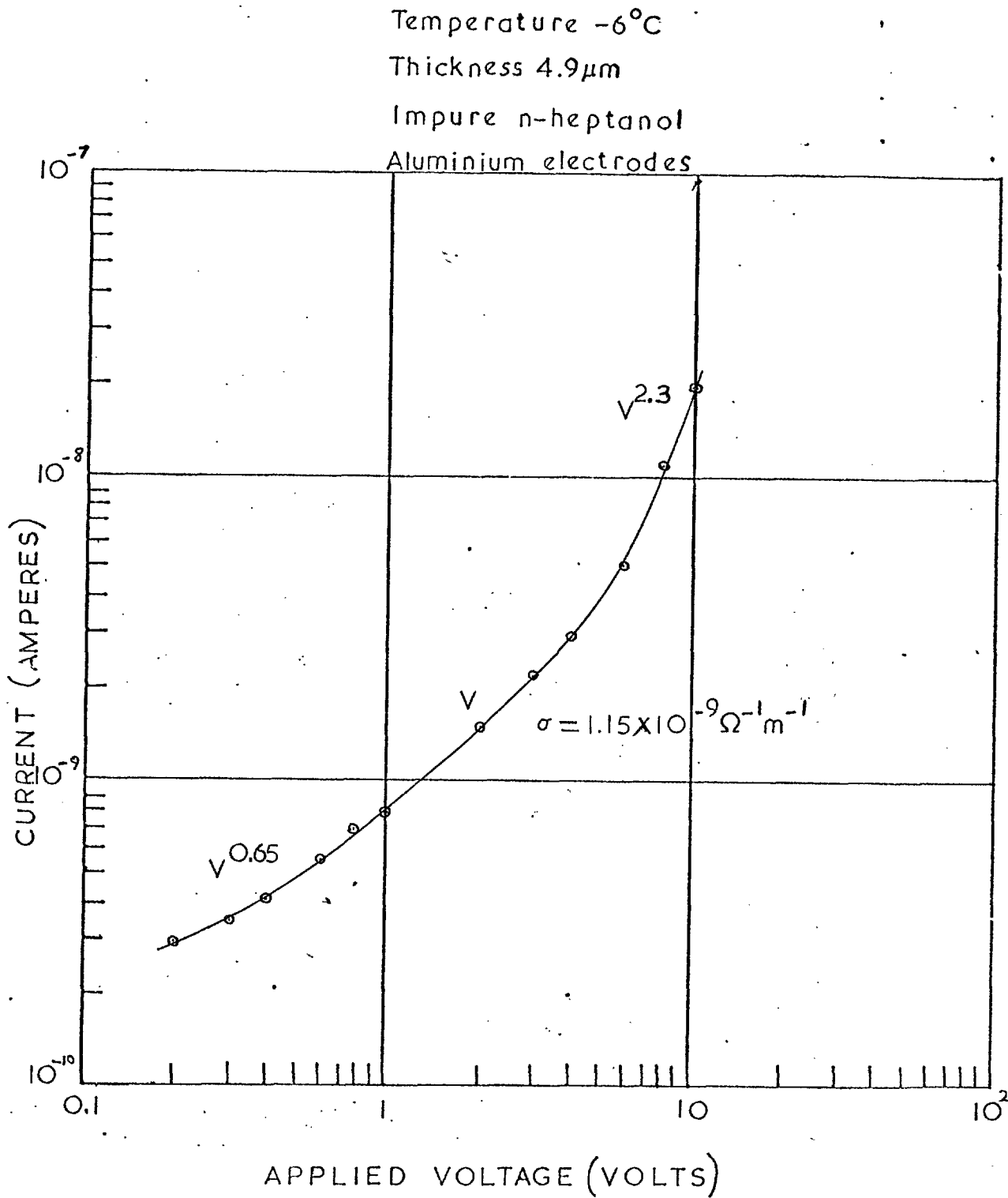


Figure 3.29b. D.c. current-voltage curves

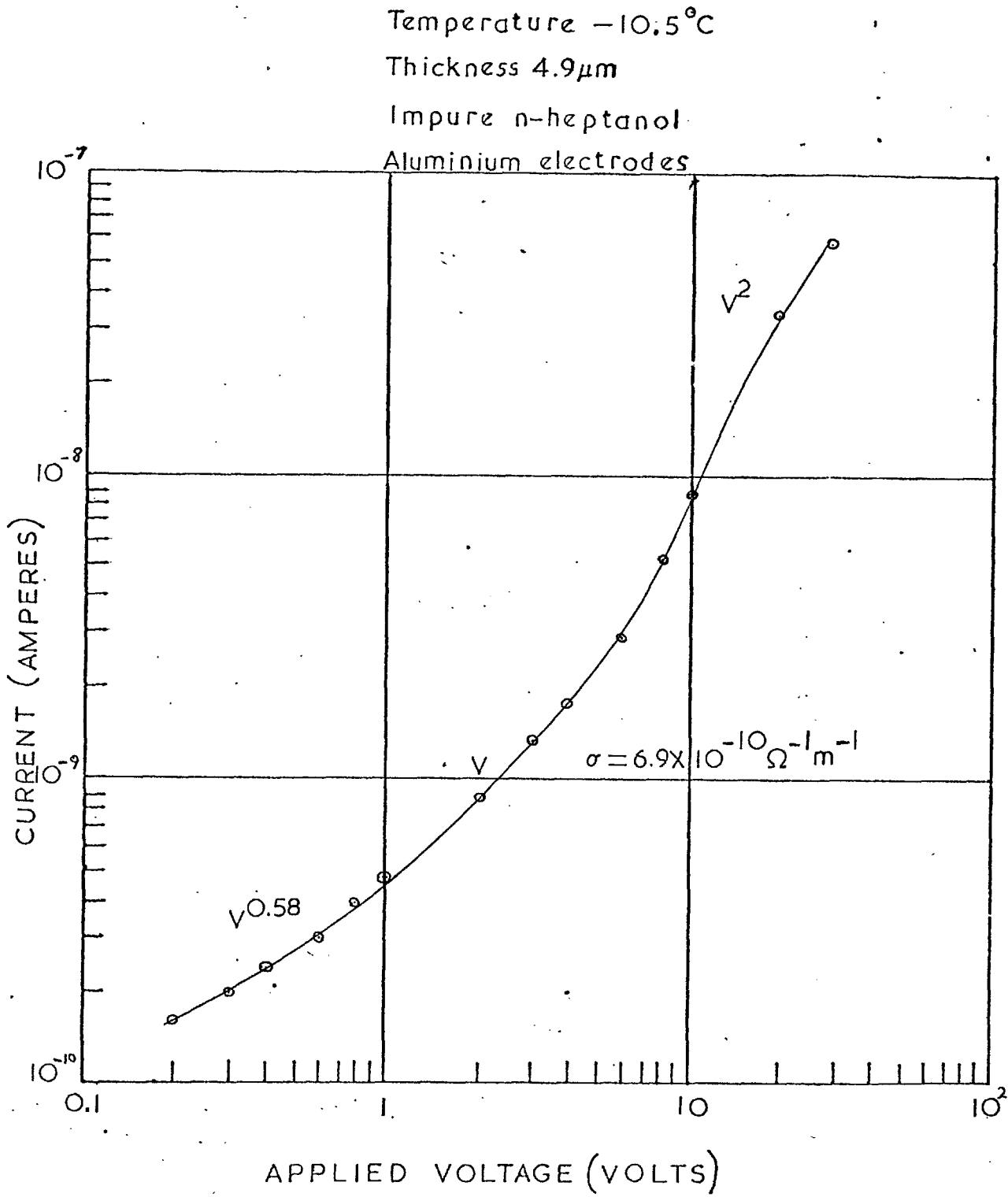


Figure 3.29c. D.c. current-voltage curves

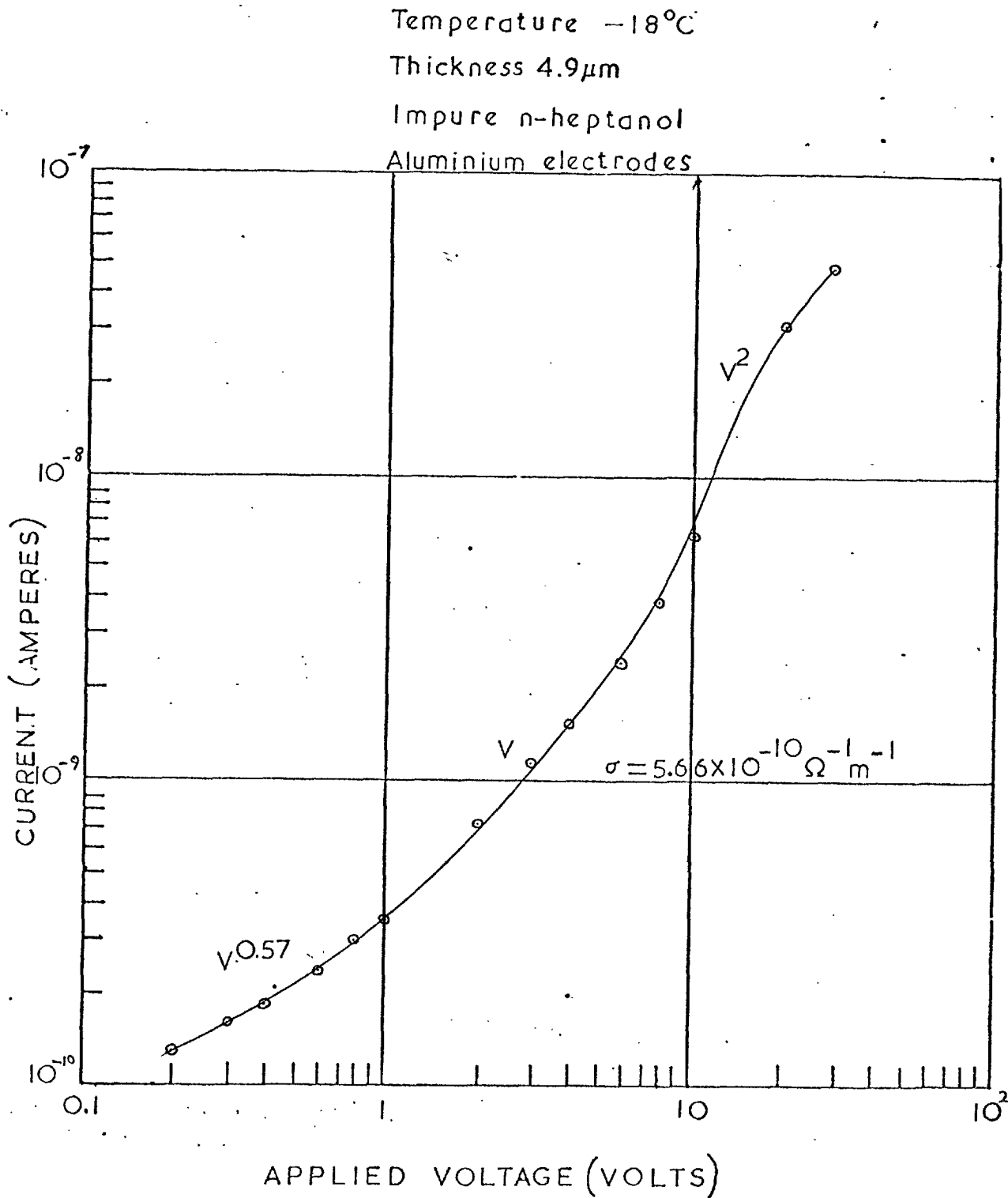


Figure 3.29d. D.c. current-voltage curves

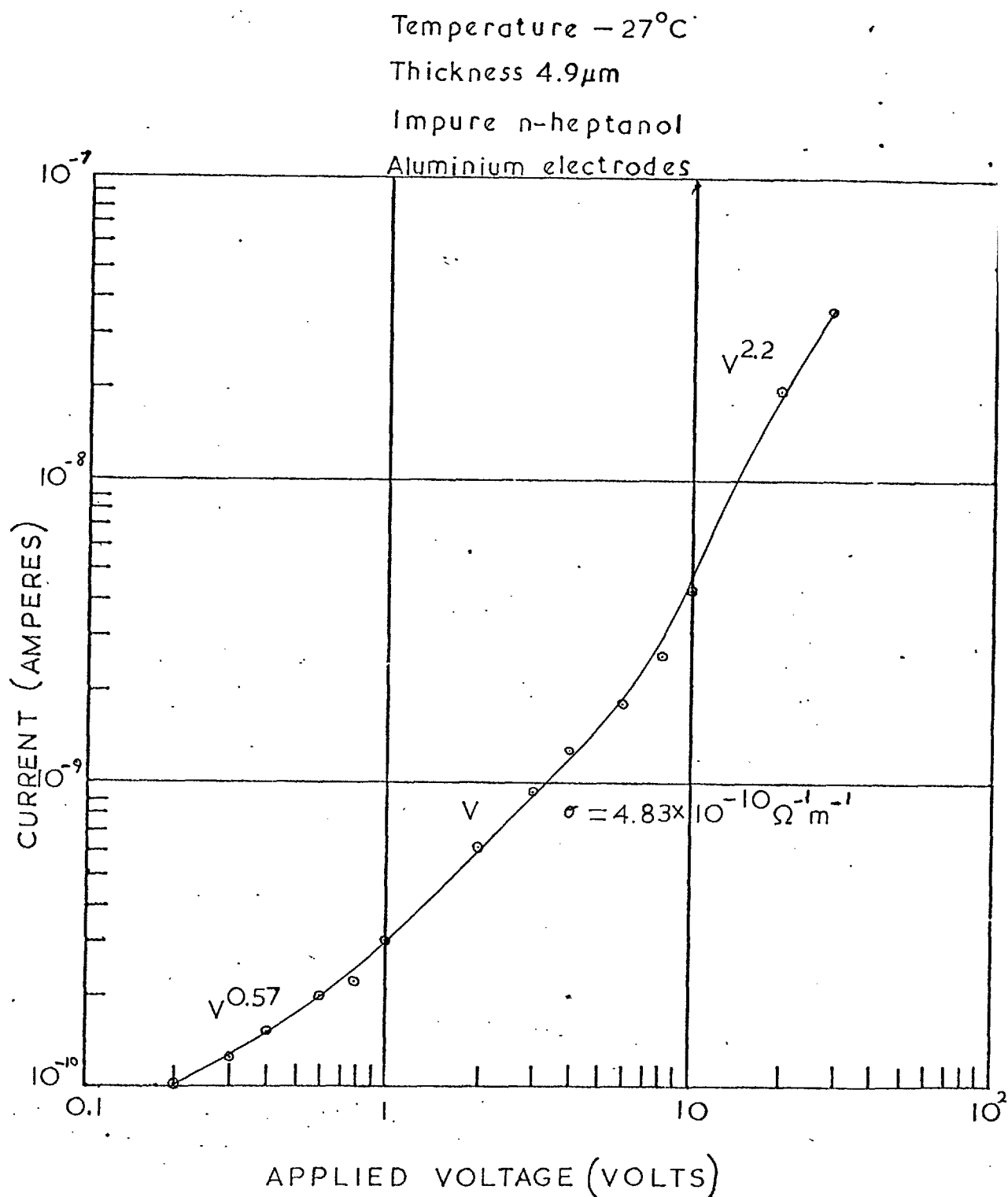


Figure 3.29e. D.c. current-voltage curves

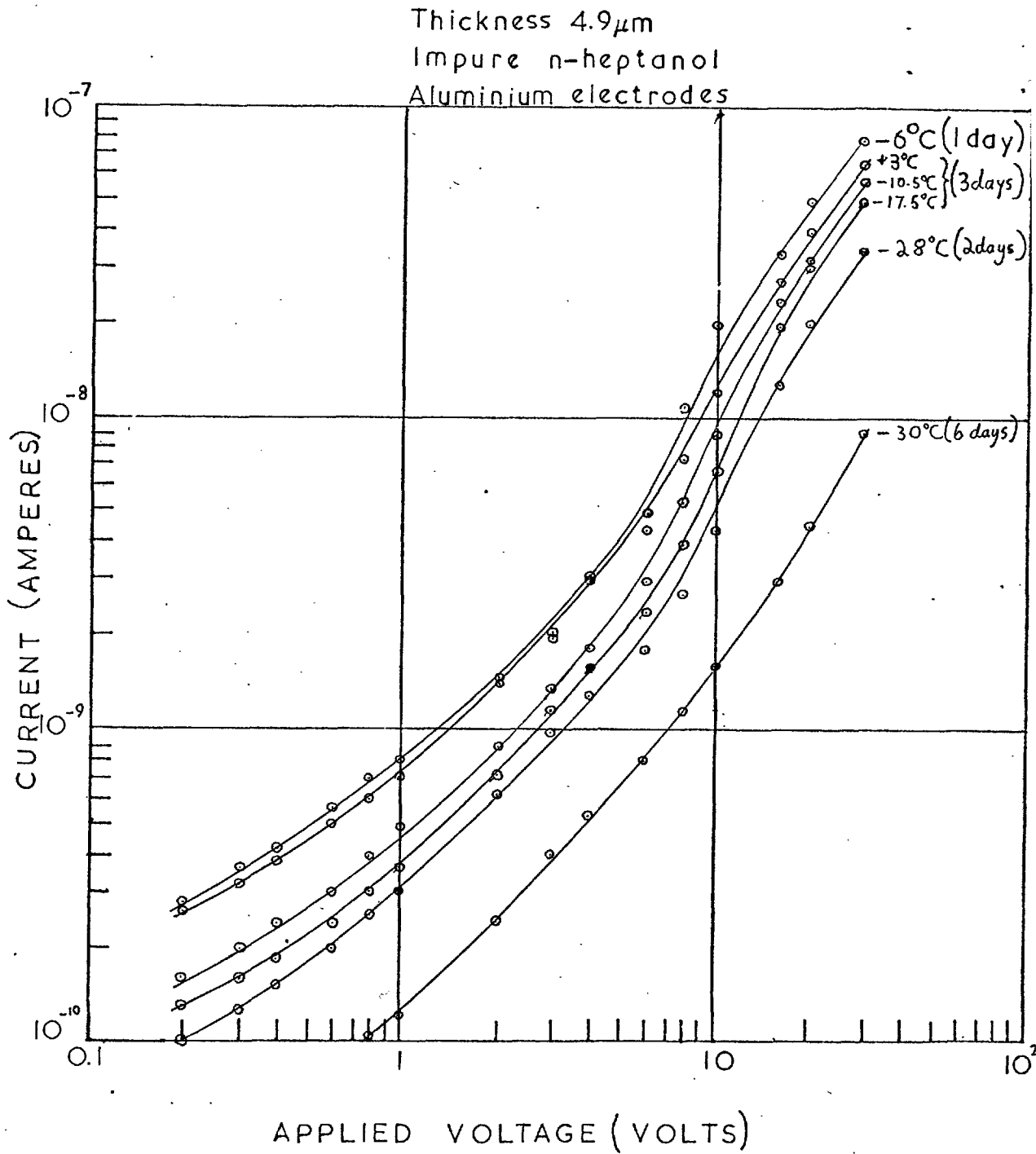


Figure 3.30. D.c. current-voltage curves

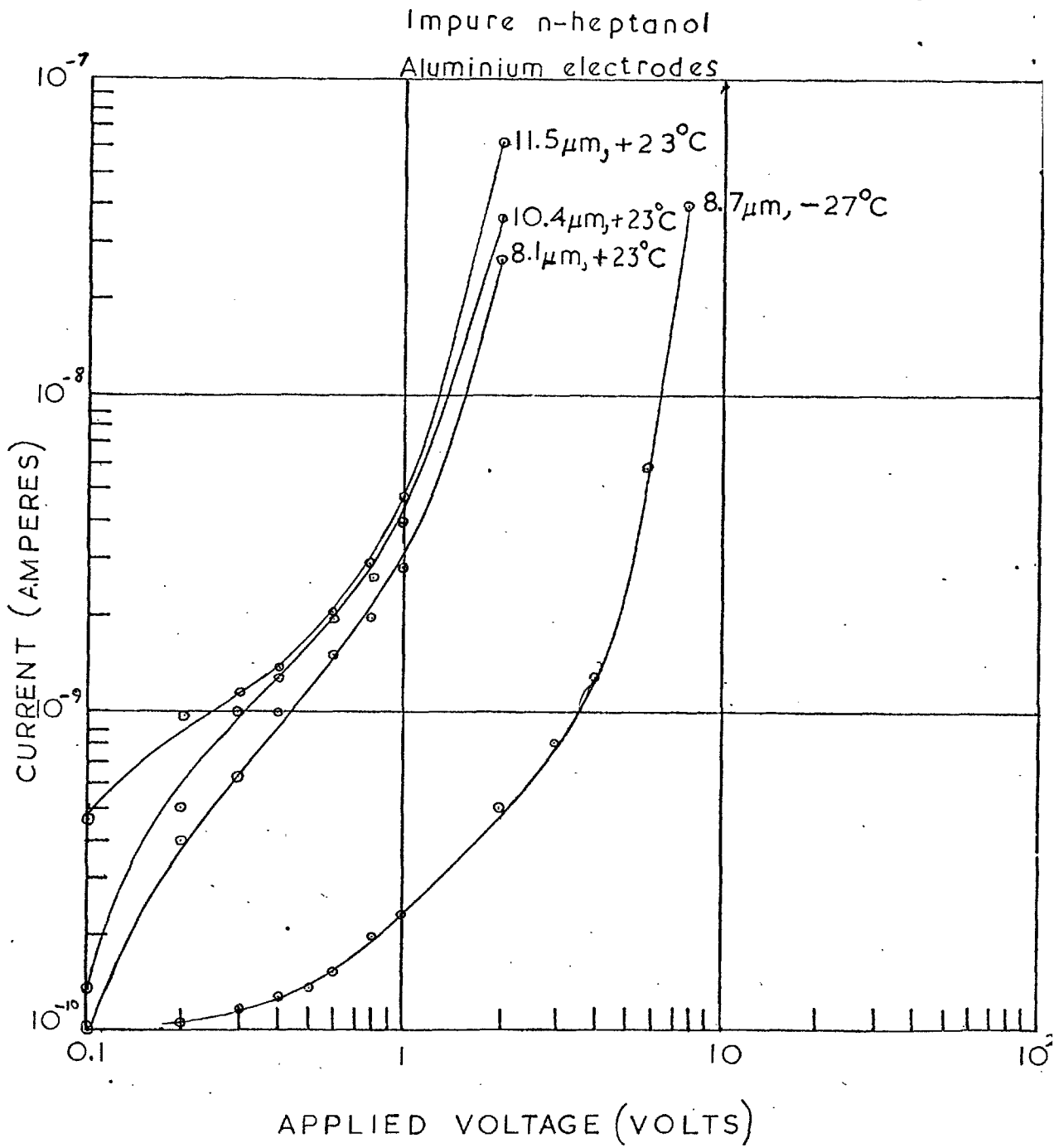


Figure 3.31 D.c. current-voltage curves

3.11. References.

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2. Middelhoek, J., and Bottcher, C.J.F., Chem. Soc. Spec. Publ. No. 20, Academic Press, London, (1966).
3. "Electricity and Magnetism, Maxwell, J.C., Clarendon Press, Oxford, Vol. 1, (1892); Wagner, K.W., Die Isolierstoffe der Elektrotechnik, Schering, H. (ed.), Springer, Berlin (1924).
4. Garton, C.G., J.I.E.E., 88, 23, (1941).

CHAPTER 4

Discussion of Results.

4.1. Introduction.

The results presented in the previous chapter show that, depending on conditions, the measured permittivity of a thin layer of liquid may either be greater or less than the relevant value for a bulk specimen.

The marked rise in permittivity found at low frequencies is indicative of an interfacial polarization effect, while the lowering of permittivity below bulk values found at higher frequencies may be attributed to some constraint on the rotation of the molecular dipoles present in the liquid. In the subsequent sections of this chapter it is hoped to present theories to account for these phenomena.

4.2. Space Charge Effects.

Numerous workers have considered space-charge distributions resulting from diffusion and conduction of charge carriers. In general, these have had to do with special cases, usually involving liquid electrolytes. Analysis of space-charge formation under the influence of diffusion forces and of electric fields involves the solution of non-linear partial differential equations. As a result, a theory permitting quantitative predictions for general cases is not available.

Theories treating the calculation of charge distribution in the diffuse double layer are given by Gouy¹, Chapman², Debye and Huckel³, Jaffe⁴, Muller⁵, Grahame⁶, Breyer and Gutmann⁷, and Macdonald and Brackman⁸.

All of these and most other similar problems are treated by assuming the material to be a continuum containing equivalent, mobile, uncombined positive and negative charges. Further, almost all such treatments involve only one electrode embedded in an infinite or semi-

infinite material.

Space-charge build up in liquids is assumed to occur at the electrodes. The large experimental values of permittivity obtained may be explained by assuming an equally large dielectric polarization to the liquid films and this is consistent with the idea of a large charge carrier concentration moving through the liquid. Sutton⁹ has developed a theory to describe the distribution of static space charge in a material having only a single mobile charge carrier and this theory seems to be of relevance to a thin layer of liquid trapped between two electrodes.

4.3. Single Mobile Charge Carrier Theory.

The problem considered is that of the conduction - diffusion differential equations that describe the motion of a charge carrier of one kind only. The charge carriers present in the liquid may be ionic or electronic in nature. Electronic conduction implies injection of charge carriers at the electrodes and this is difficult to visualize in insulating liquids since the energy ^{barrier} ~~gap~~ for electrons is so large. Charge injection in insulating liquids has been observed by many workers, notably by the group working under Felici¹⁰ at the laboratory for Electrostatics, Centre National de la Recherche Scientifique, Grenoble, but large and non-uniform electric fields are required.

The ionic content of a liquid may arise in two ways: either by dissociation of the molecules of the liquid itself, or by dissociation of less stable impurities, which are inevitably present to some extent. If the charge carriers present are electrons then the situation of a single carrier species obtains. For ionic charge carriers, whether their source be self-ionization of the liquid or ionization of impurities, it is unlikely that the mobilities of the two charge

carrying species will be the same. In this case, providing the mobility of one type of carrier is much greater than the mobility of the other type, the concept of a single charge carrier is still valid.

The assumptions made in the development of this theory are as follows:

- 1) The processes taking place are conduction, diffusion, dissociation of neutral centres, and recombination of charges of opposite sign to form neutral centres.
- 2) Plane-parallel identical electrodes, separated by a finite thickness of insulator, are assumed. The electrodes are further assumed to be infinite planes, giving the problem one-dimensional-symmetry.
- 3) The electrodes are assumed to be completely blocking (polarizable). This means that charge carriers cannot penetrate or leave the electrodes and cannot be neutralized by the electrode. This is a reasonably safe assumption to make in the case of aluminium electrodes but its validity in the case of say gold electrodes is open to question.
- 4) Electrochemical potentials due to chemical phase differences are neglected. Such potentials are equal and opposite if the electrodes are identical. They will cause some space charge, which should, in general, be considered. However, potentials of several volts were applied in most experiments and it is hoped that these effects may be ignored in practice.
- 5) Diffusion and mobility of one of the two charge carriers are considered to be zero. To the extent that they are not actually zero, the solution obtained will represent an approximation to a quasi-static state at some intermediate time, as long as the diffusion coefficient and mobility of the other carrier are relatively much larger, for d.c. potentials.
- 6) Recombination is assumed to be bimolecular and proportional

simply to the product of the positive and negative concentrations.

7) Similarly, dissociation is assumed to be proportional to the remaining undissociated charge concentration.

The symbols to be used are listed and defined as follow:

x = perpendicular distance between electrodes; $x = 0$ and $x = \ell$ at the two electrodes.

ℓ = specimen thickness measured in metres.

p = number of uncombined positive charges per unit volume.

n = number of uncombined negative charges per unit volume.

q = dissociation rate, i.e. the number created per unit volume per unit time.

a = recombination rate, i.e. the number vanishing per unit volume per unit time.

c = the number of charges of the immobile kind per unit volume; this is essentially the initial immobile charge concentration when the specimen is neutral.

D, D' = the diffusion constants for the mobile and "immobile" carriers respectively.

μ, μ' = mobilities for the mobile and "immobile" carriers respectively.

$E = E(x)$ = the electric field within the specimen.

V_0 = total potential difference applied between the electrodes.

V = electrical potential at x ($V = V_\ell = 0$ at $x = \ell$).

t = time (after the application of V_0).

α = recombination rate constant (defined by equation (4.8.)).

K = dissociation rate constant (defined by equation (4.9.)).

$P = p/c$

$N = n/c$

$R = c/K$

e = magnitude of charge on both carriers.

ϵ = bulk permittivity of the specimen material.

$y = \log_e P$ ($P = e^y$).

$v = dy/dx$

L_D = Debye length = $\left(\frac{\epsilon \epsilon_0 D}{2ce\mu}\right)^{1/2}$ (ϵ_0 = permittivity of free space).

ρ = ratio of overall average net dissociated charge density to c ,
i.e. ratio of total excess charge present to total immobile charge.

o as a subscript denotes value at $x = 0$

ℓ as a subscript denotes value at $x = \ell$

Assuming free-charge conservation in any volume element, taking into account dissociation and recombination, one can write

$$\frac{\partial \rho}{\partial t} = q - a + D \frac{\partial^2 \rho}{\partial x^2} - \mu \frac{\partial(E\rho)}{\partial x} \quad (4.1.)$$

$$\frac{\partial n}{\partial t} = q - a + D' \frac{\partial^2 n}{\partial x^2} - \mu' \frac{\partial(E n)}{\partial x} \quad (4.2.)$$

Poissons equation also may be written

$$\frac{\partial E}{\partial x} = \frac{e(\rho - n)}{\epsilon \epsilon_0} \quad (4.3.)$$

The relevant boundary conditions are

$$\int_0^\ell dV = \int_0^\ell E dx = V_0 \quad (4.4.)$$

$$\text{and current} = 0 = D \frac{d\rho}{dx} - E\mu\rho \text{ at } x = 0, \ell \quad (4.5a.)$$

$$0 = D' \frac{dn}{dx} - E\mu'n \text{ at } x = 0, \ell \quad (4.5b)$$

Equations (4.5.) arise from assumption 3) above.

Equations (4.1) to (4.5.) comprise the general case of a two carrier, time-dependent equation. Sutton then proceeds to solve these equations for the d.c. case. All time variations are assumed to vanish and one carrier, say the negative one, is chosen to be immobile

so that $D' = \mu' = 0$

Assumptions (6) and (7) are written as

$$a = \alpha np \quad (4.6.)$$

$$q = K(c - n) \quad (4.7.)$$

The analysis is then straight forward but rather involved and it is sufficient here to quote the results.

$$\int_{y_0}^y I(y) dy = x/L_0 \quad (4.8a.)$$

$$\int_{y_0}^{y_0 + \mu V_0/D} I(y) dy = \ell/L_0 \quad (4.8b.)$$

$$v_0 \rho \ell + (\rho^2 \ell^2 / 4 L_0^2) = e^{y_0} (e^{(\mu/D)V_0} - 1) + \ln \left[(e^{-y_0} e^{-(\mu/D)V_0} + R) (e^{-y_0} + R)^{-1} \right] \quad (4.8c.)$$

where $[I(y)]^2 \equiv [L_0^2 v^2]^{-1} \quad (4.9.)$

and $\rho \equiv \ell^{-1} \int_0^\ell (P - N) dx = \text{average excess charge} \quad (4.10.)$

The following two equations are also useful

$$y = y_0 + \frac{\mu(V_0 - V)}{D} \quad (4.11.)$$

$$v_\ell = v_0 + \frac{\rho \ell}{2 L_0} \quad (4.12.)$$

Equation (4.8a) is the solution giving y and hence P , p and n as a function of x . Equations (4.8b) and (4.8c) are two simultaneous equations in y_0 and v_0 which are solved to obtain these quantities for use in equation (4.8a). If $\rho = 0$, this procedure is simple since equation (4.8c) gives y_0 directly. Most situations of interest have $\rho = 0$ and this is the case that will be discussed. It turns out that I , always has a sharp maximum near the middle of the specimen. This results (see equation (4.8a)) in a point of inflection in the curve $y = f(x)$ given by

$$P_m = e^{Y_m} = [-1 + (1 + 4R)^{1/2}] / 2R \quad (4.13.)$$

or $R = \frac{P_m^{-2}}{P_m^{-1}}$

This relation is of particular interest since it is wholly independent of length of specimen or applied voltage. The y curve always has its point of inflection given by the same concentration P_m so that R is directly associated with the proportion of dissociated mobile charge. If the charge is highly dissociated, R is small; if only a little dissociation prevails, R is large. R is of the order of magnitude of P_m^{-2} .

The nonlinearity of the differential equations leads to quite unusual behaviour for various values of the parameters. For a given specimen the quantities ℓ , V_0 and R control the form of the solution and the several possible combinations of these give a wide variety of differing solutions. The simplest case is that of a linear potential drop across the specimen. This arises for ℓ small enough, V low enough, or R large enough. As ℓ , V , and R^{-1} increase, the solution exhibits both a curvature and an asymmetry in the potential and charge distributions.

One of the virtues of the present treatment over previous treatments of the two-ion case is the fact that charge concentrations are limited to reasonable values even for high potentials and large degree of dissociation. For $R = 0$ (complete dissociation) and significant voltages

$$P_\ell = (\mu/D)V_0 = 38.5V_0$$

where the $\mu/D = e/kT$ (Einstein) relationship is used. Thus $P_\ell = 122$ for $V_0 = 3.16$ compared with $P_\ell = 10^{53}$ from the two-ion theory¹¹.

N is always small since $N \leq 1$. Special approximate solutions for simplified values of the parameters have been worked out to replace the solution given by equations (4.8.)¹². In particular, thin specimens or large R (low charge concentration) give linear results.

More generally, the potential in the immediate vicinity of the electrodes can be given by $\sinh x$ and/or $\exp(-x)$ relations.

4.4. Time-dependent Solutions for the Single Mobile Carrier Theory.

A time-dependent solution of the conduction-diffusion differential equations for the motion of a single charge carrier is of more relevance to the work contained in this thesis. Solution of these nonlinear partial differential equations is a daunting task. A solution can be obtained in analytic form by considering small amplitudes of potential and charge flow and neglecting second order terms. Such a solution is obviously limited and will not describe the large charge flows that are likely to be important for say dielectric breakdown. Nevertheless, insight into some of the consequences of the single-ion model for a.c. fields is possible.

The general two-carrier, time-dependent problem is set up as described by equations (4.1.) to (4.5.). Again D' and μ' are set to zero so that one carrier is immobile. Equations (4.6.) and (4.7), which define the nature of the dissociation and recombination assumptions, are retained and a sinusoidal a.c. potential V_0 is assumed. The new symbols arising can be defined as follows.

f = frequency of potential variation

$\omega = 2\pi f$ = angular frequency

E' = amplitude of the electric field E

V' = amplitude of the applied potential V_0 ; V' is taken as real

p' = complex amplitude of the varying part of the positive charge concentration

n' = complex amplitude of the varying part of the negative charge concentration

$\delta = \omega P_m / K$

$$\Delta = 1 - P_m < 1$$

The defining equations for these symbols are

$$V_o \equiv V' e^{i\omega t}$$

$$E \equiv E' e^{i\omega t} \quad (4.14.)$$

$$p \equiv p(\omega = 0) + p' e^{i\omega t}$$

$$n \equiv n(\omega = 0) + n' e^{i\omega t}$$

Since the steady-state d.c. potential is assumed to be zero, the $\omega = 0$ charge distributions are constants and $p(\omega = 0) = n(\omega = 0) = cP_m$.

Thus we have

$$\frac{\partial p}{\partial t} = q - a + D \frac{\partial^2 p}{\partial x^2} - \mu \frac{\partial (Ep)}{\partial x} \quad (4.1.)$$

$$\frac{\partial n}{\partial t} = q - a \quad (\text{from Eqn. (4.2.)}) \quad (4.15.)$$

$$\frac{\partial E}{\partial x} = \frac{e(p-n)}{\epsilon \epsilon_0} \quad (4.3.)$$

$$\int_0^l dV = \int_0^l E dx = V_o \quad (4.4.)$$

$$D \frac{\partial p}{\partial x} = E \mu p \quad \text{at } x=0, l \quad (4.5a.)$$

$$a = \alpha n p \quad (4.6.)$$

$$q = K(c-n) \quad (4.7.)$$

Combining equation (4.15.), (4.6.) and (4.7.) gives

$$n' = \frac{-\Delta p'}{1+i\delta} = - \left[\frac{\Delta e^{-i\tau \tan^{-1} \delta}}{(1+\delta^2)^{1/2}} \right] p' \quad (4.16.)$$

so that n' and p' are always related for any frequency f . n' differs in phase from p' relative to the driving potential V_o . Further $|n'|$ is always smaller than $|p'|$ since $\Delta < 1$. For ω small $n' \sim -p'$, but n' approaches zero for high frequencies.

Using equation (4.16.) in equations (4.1.) and (4.3.) gives

$$\frac{\partial^2 p'}{\partial x^2} - A^2 p' = 0 \quad (4.17)$$

where $A^2 = \frac{1}{D\tau} \left(1 + \frac{\Delta}{1+i\delta} \right) (1+i\omega\tau)$

and $\tau = \frac{\epsilon\epsilon_0}{\mu c P_m e} \Rightarrow \frac{2(L'_0)^2}{D}$

$$L'_0 \equiv L_0 / P_m^{1/2}$$

The general solution of equation (4.17.) is of the form

$$p' = C_1 \cosh Ax + C_2 \sinh Ax \quad (4.18.)$$

Applying the boundary conditions given by equations (4.4.) and (4.5.), and assuming no excess charges in the specimen ($\rho = 0$) results in the final expression for the positive charge distribution p' .

$$p' = \frac{\mu c P_m V' B}{2D} \frac{\sinh[A(x-l/2)]}{\sinh[A\ell/2]} \left(\frac{1+i\omega\tau}{B+i\omega\tau} \right) \quad (4.19.)$$

where $B \equiv \frac{\tanh(A\ell/2)}{A\ell/2}$

It is now possible to calculate the current flowing in the external circuit for the a.c. case. The current is given by

$$\Delta I(x) = \frac{d(qp)}{dt} = i\omega p' e^{i\omega t} e$$

Writing $\Delta I = \Delta I' e^{i\omega t}$

gives $\Delta I' = i\omega e p'$

Therefore the total current is given by

$$\begin{aligned} I' &= 2i\omega e \int_0^{\ell/2} p' dx \\ &= \frac{i\omega e \mu c P_m B V'}{A D \sinh(A\ell/2)} \left(\frac{1+i\omega\tau}{B+i\omega\tau} \right) (1 - \cosh(A\ell/2)) \end{aligned} \quad (4.20.)$$

Thus the admittance is given by

$$Y = I'/V' = \frac{2i\omega\epsilon\mu c P_m}{A^2 D \ell} \left(\frac{1 + i\omega\tau}{B + i\omega\tau} \right) \quad (4.21.)$$

for $A\ell/2 \gg 1$

However if the specimen has a capacitance C per unit area we can write

$$Y \equiv i\omega C \quad (4.22.)$$

where $C = \frac{\epsilon_r \epsilon_0}{\ell} \quad (4.23.)$

Thus substituting equations (4.22.) and (4.23.) into equation (4.21.) yields

$$\epsilon_r = \frac{\epsilon}{A^2 (L'_D)^2} \left(\frac{1 + i\omega\tau}{B + i\omega\tau} \right) \quad (4.24.)$$

For $\omega\tau \ll 1$, $A^2 \sim 1/(L'_D)^2$ and so equation (4.24) becomes

$$\epsilon_r = \epsilon \left(\frac{1 + i\omega\tau}{B + i\omega\tau} \right) \quad (4.25.)$$

Now $B \rightarrow 0$ as $\omega \rightarrow \infty$ and therefore (4.25.) gives

$$\epsilon_r(\omega \rightarrow \infty) = \epsilon = \epsilon_\infty$$

This is consistent since the ϵ used throughout is that arising from other kinds of polarization and cannot involve migration charges. Equation (4.25.) also states that for $\omega \rightarrow 0$ but $\omega \neq 0$

$$\epsilon_r(\omega \rightarrow 0) = \epsilon_s = \frac{\epsilon}{B} = \frac{\epsilon A \ell}{2 \tanh(A\ell/2)} \sim \frac{\epsilon \ell}{L'_D}$$

This relation correctly indicates the observed behaviour of dielectric absorption since ℓ/L'_D may be of the order of 10^3 or 10^4 . The d.c. or low-frequency surge of space charge across the "thick" specimen results in large storage, at slow rates, of charge.

To carry this line of thought further one can define a complex permittivity in the usual way

$$\epsilon_r = \epsilon' - i\epsilon''$$

allowing equation (4.25) to be re-written

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

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_{\infty}) \omega \tau'}{1 + (\omega \tau')^2} \quad (4.26.)$$

where $\tau' \equiv \tau/B$

These expressions are identical in form to the Debye equations for the dielectric properties of a material containing molecules having a permanent electric dipole moment.

Hence the permittivity and loss factor will behave as if there were a single relaxation mechanism, characterized by a single relaxation time, as long as τ' and ϵ_s are real (and constant). However, B is in general complex and consequently the relations (4.26) display the simple Debye relaxation property only in a range of ω and ℓ where B is essentially real and reasonably constant. This is true in the region of practical interest where $\omega \tau \ll 1$ and $\delta \gg 1$.

4.5. Comparison of A.C. Theory with Data.

The a.c. theory presented in the previous section predicts a simple Debye behaviour. The general shape of the permittivity versus frequency curves presented in chapter 3 does indeed resemble a Debye curve. The shape of the loss factor versus frequency curves also suggests that, superimposed on the Debye-type loss factor, there is a "d.c." conduction term. A conductivity $\sigma \Omega^{-1} \text{m}^{-1}$ contributes a term $\sigma/\omega \epsilon_0$ to the loss factor. Consequently attempts were made to correlate the data with the following equations.

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (\omega \tau')^2} \quad (4.27.)$$

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

There are several methods of determining the parameters ϵ_s , ϵ_∞ and τ' given a set of experimental points covering the frequency region over which the dispersion occurs. Cole¹³ discusses several methods of analyzing dielectric dispersions and loss data satisfying the Debye equations.

The obvious and direct means of testing (4.27.) is to compare experimental values of ϵ' and ϵ'' as functions of frequency. Direct tests of these equations can be made by curve fitting with proper choice of the four adjustable parameters ϵ_s , ϵ_∞ , τ' and σ , but there is considerable trial and error, especially if ϵ_s and ϵ_∞ are not known from measurements made over a considerable frequency range.

The more usual approach is to employ the complex plane locus of ϵ'' versus ϵ' , which, if the Debye equations (4.26.) are valid, is a semicircle with its centre on the real axis and intercepts on this axis at ϵ_s and ϵ_∞ . This representation is often referred to as the Cole-Cole plot. The intercepts of a satisfactory fit give ϵ_s and ϵ_∞ directly, but the value of relaxation time is not accurately determined from the plot, although it can often be estimated with fair accuracy from the interpolated frequency of the mid-points of the semi-circle. When the loss factor data is distorted by a "d.c." term, as in the present case the Cole-Cole plot is no longer a viable method of determining the parameters.

An alternative graphical method results from rearrangement of the Debye equations giving

$$\begin{aligned}\epsilon' &= \epsilon_s - \tau'(\omega \epsilon'') \\ \epsilon' &= \epsilon_\infty + (1/\tau')(\epsilon''/\omega)\end{aligned}\tag{4.28.}$$

The advantage of these equations is that they are linear relations in the measured quantities ϵ' , $\omega \epsilon''$, and ϵ''/ω , and from them, if they are satisfied, the parameters ϵ_s , ϵ_∞ and τ' can be derived

as intercepts and slopes without using assumed values.

The inclusion of the "d.c." conduction term modifies equations (4.28.) as follows

$$\epsilon' = -\tau'\omega\epsilon'' + \epsilon_s + \sigma\tau'/\epsilon_0 \quad (4.29a.)$$

$$\epsilon' = (1/\tau')(\epsilon''/\omega) - (\sigma/\tau'\epsilon_0)(1/\omega^2) + \epsilon_\infty \quad (4.29b.)$$

and the data was analyzed in terms of these equations. A simple computer programme was written to perform a regression analysis on the data according to equations (4.29a) and (4.29b). The relaxation times, τ' , were obtained from the slope of the line ϵ' versus $\omega\epsilon''$ (equ. 4.29a) and the coefficient of ϵ''/ω from equation (4.29b). Close agreement was found between the two values obtained and the mean value was taken to be the relaxation time. The coefficient of the $1/\omega^2$ term in equation (4.29b) then allows the calculation of σ . In all the curves analysed the correlation coefficient was never found to be less than 0.95, and 12 or more pairs of experimental observations were used in the regression analysis, giving 10 degrees of freedom. The expected value of correlation coefficient for 10 degrees of freedom is 0.823 for a significance level of 0.1%. Thus it may be seen that the correlation between the data and the theoretical curves is highly significant. In fact correlation coefficients as high as 0.999 were obtained in some cases. Despite the very good fit, the values of ϵ_∞ obtained from equation (4.29b) tended to be rather high in most cases. This stems from the high values of the ratio $\epsilon_s/\epsilon_\infty$. Thus quite small changes in the values of $1/\tau'$ and $\sigma/\tau'\epsilon_0$ results in large variations in the values of ϵ_∞ obtained. Consequently the values of ϵ_∞ were estimated from the experimental data. Finally ϵ_s may be determined from the intercept in equation (4.29a) since τ' and σ are known.

Tables 1,2 and 3 contain the results of the above analysis

performed on the data presented in chapter 3. To illustrate the fit of the data to the theoretical curves, the parameters contained in Tables 1, 2 and 3 were used to compute the curves shown in Figs. 4.1 to 4.6.

It is obvious that the fit is not perfect, but then several assumptions and approximations were made in the analysis, resulting in the prediction of a Debye type relaxation. However, the fit is sufficient to allow a reasonable degree of confidence to be placed on the values of carrier concentration and mobility calculated from the parameters of the relaxation.

4.6 Calculation of Impurity Concentration and Mobility from Single Mobile Carrier Theory.

The behaviour of the permittivity and loss factor with frequency can be represented by the Debye equations for a single relaxation time as predicted by the theory presented in section 4.4. The static permittivity, ϵ_s , relaxation time, τ' and ϵ_∞ may be used to calculate the impurity concentration and mobility as follows.

Equations (4.25) leads to the expression $\epsilon_s = \epsilon_\infty/B$, for $\omega \rightarrow 0$.

Therefore

$$B = \epsilon_\infty / \epsilon_s \quad (4.30.)$$

The definition of τ' is $\tau' = \tau/B$ and so

$$\tau = \tau' B \quad (4.31.)$$

One of the necessary conditions for a Debye type behaviour is that $\omega\tau \ll 1$. The values of B (i.e. of $\epsilon_\infty / \epsilon_s$) obtained varied from approximately 4×10^{-4} to 3×10^{-2} . Thus, the description of the behaviour of permittivity with frequency by a Debye relaxation remains valid for frequencies well above $1/\tau'$. Equation (4.19) defines B as follows

$$B = \frac{\tanh(AQ/2)}{AQ/2}$$

performed on the data presented in chapter 3. To illustrate the fit of the data to the theoretical curves, the parameters contained in Tables 1, 2 and 3 were used to compute the curves shown in Figs. 4.1 to 4.6.

It should be noted that, of necessity, the results in each table refer to different samples of liquid. Thus the values quoted for similar thicknesses and temperatures in each table are not necessarily the same. The important result is that the curves always conform to the predicted Debye shape.

4.6 Calculation of Impurity Concentration and Mobility from Single Mobile Carrier Theory.

The behaviour of the permittivity and loss factor with frequency can be represented by the Debye equations for a single relaxation time as predicted by the theory presented in section 4.4. The static permittivity, ϵ_s , relaxation time, τ' and ϵ_∞ may be used to calculate the impurity concentration and mobility as follows.

Equation (4.25) leads to the expression $\epsilon_s = \epsilon_\infty/B$, for $\omega \rightarrow 0$.

Therefore

$$B = \epsilon_\infty / \epsilon_s \quad (4.30.)$$

The definition of τ' is $\tau' = \tau/B$ and so

$$\tau = \tau' B \quad (4.31.)$$

One of the necessary conditions for a Debye type behaviour is that $\omega\tau \ll 1$. The values of B (i.e. of $\epsilon_\infty / \epsilon_s$) obtained varied from approximately 4×10^{-4} to 3×10^{-2} . Thus, the description of the behaviour of permittivity with frequency by a Debye relaxation remains valid for frequencies well above $1/\tau'$. Equation (4.19) defines B as follows

$$B = \frac{\tanh(A\ell/2)}{A\ell/2}$$

TABLE I.

Debye Parameters for n-Heptanol with Silver Electrodes.

Temperature = 24°C

Specimen thickness l (μm)	ϵ_{∞}	ϵ_s	τ' (secs.)	Conductivity σ ($\Omega^{-1}\text{m}^{-1}$)
4.29	7	394	2.50×10^{-3}	1.53×10^{-6}
7.20	6	293	3.10×10^{-3}	1.70×10^{-6}
11.5	6	491	3.33×10^{-3}	3.11×10^{-6}
13.4	6	470	3.40×10^{-3}	4.90×10^{-6}
17.5	6	520	7.35×10^{-3}	8.55×10^{-6}

Specimen Thickness = 4.29 μm .

Temperature (°C)	ϵ_{∞}	ϵ_s	τ' (secs.)	Conductivity σ ($\Omega^{-1}\text{m}^{-1}$)
23	7.00	385	3.09×10^{-3}	2.30×10^{-6}
6	8.25	245	3.05×10^{-3}	1.59×10^{-6}
-11	9.11	256	5.50×10^{-3}	1.12×10^{-6}
-18	9.80	84.3	3.05×10^{-3}	7.55×10^{-7}
-28	10.0	103	5.87×10^{-3}	4.85×10^{-7}

TABLE 2.

Debye Parameters for n-Heptanol with Gold Electrodes.

Temperature = 26°C

Specimen thickness l (μm)	ϵ_{∞}	ϵ_s	τ' (sec)	Conductivity σ ($\Omega^{-1}\text{m}^{-1}$)
1.0	8.0	11,100	2.59×10^{-3}	5.03×10^{-6}
5.0	8.0	11,700	3.02×10^{-3}	8.26×10^{-6}
6.9	8.0	14,000	3.37×10^{-3}	1.11×10^{-5}
9.0	8.0	14,800	3.92×10^{-3}	1.32×10^{-5}
13.2	7.4	16,000	4.97×10^{-3}	1.66×10^{-5}
15.0	5.9	7,600	4.15×10^{-3}	1.41×10^{-5}
18.8	5.5	7,660	6.15×10^{-3}	8.81×10^{-6}

TABLE 3.

Debye Parameters for n-Heptanol with Aluminium Electrodes.

Purified specimen, temperature = 25°C.

Specimen thickness $l(\mu\text{m})$	ϵ_{∞}	ϵ_s	τ' (sec.)	Conductivity $\sigma(\Omega^{-1}\text{m}^{-1})$
3.3	7.0	214	1.35×10^{-4}	2.34×10^{-7}
5.5	7.0	259	2.55×10^{-4}	3.00×10^{-7}
11.8	6.5	380	3.09×10^{-4}	1.70×10^{-7}
16.2	6.0	403	3.56×10^{-4}	3.50×10^{-7}
18.3	6.0	542	5.07×10^{-4}	1.84×10^{-7}

Impure specimen, temperature = 20°C.

Specimen thickness $l(\mu\text{m})$	ϵ_{∞}	ϵ_s	τ' (sec.)	Conductivity $\sigma(\Omega^{-1}\text{m}^{-1})$
1.1	9.3	2580	1.66×10^{-3}	5.44×10^{-7}
3.0	9.2	4960	2.79×10^{-3}	1.10×10^{-6}
4.9	8.4	5940	3.84×10^{-3}	1.22×10^{-6}
6.8	7.5	6830	4.73×10^{-3}	1.53×10^{-6}
8.7	6.3	2210	4.40×10^{-3}	2.95×10^{-6}

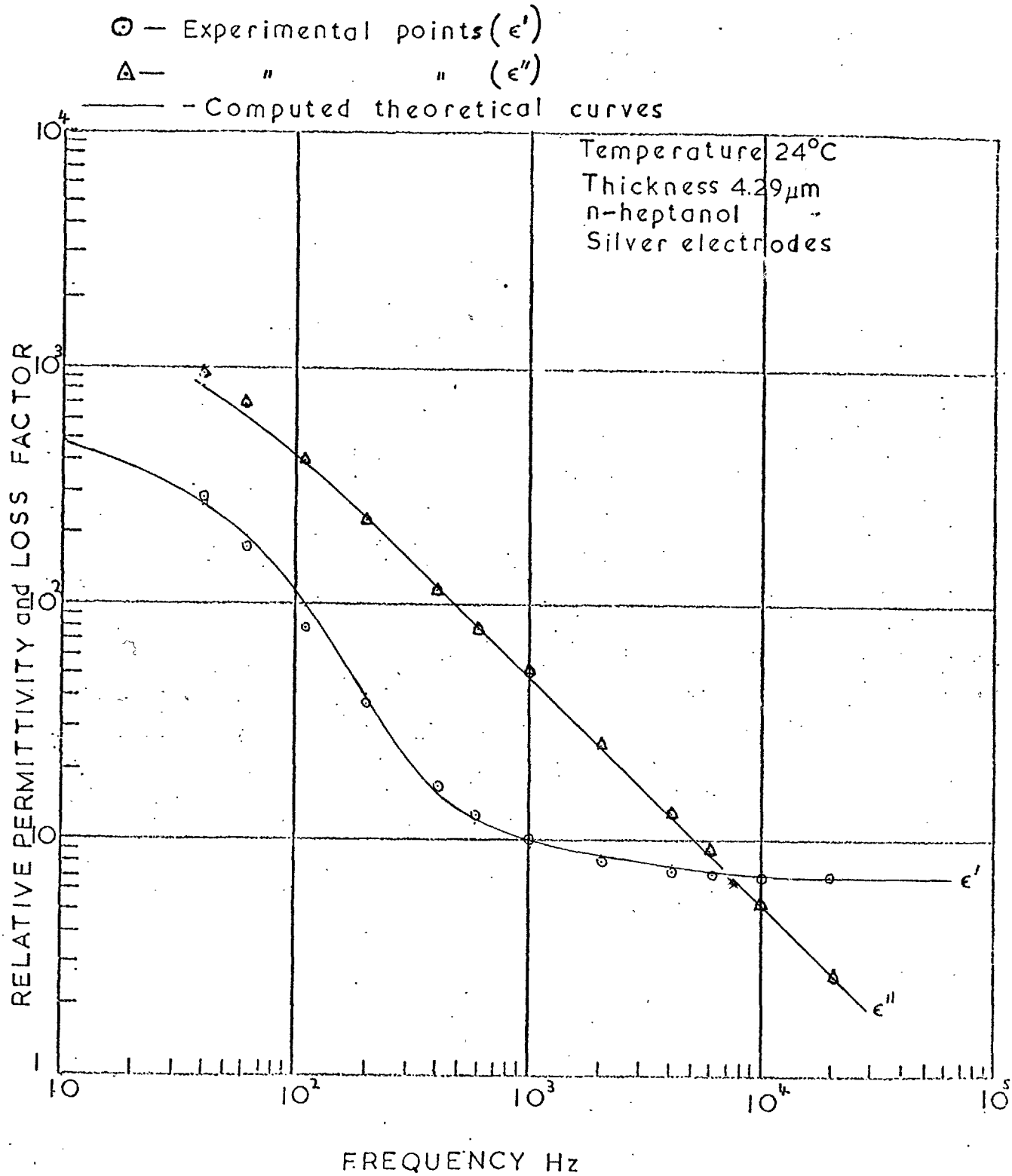


Figure 4.1 ϵ' and ϵ'' versus frequency

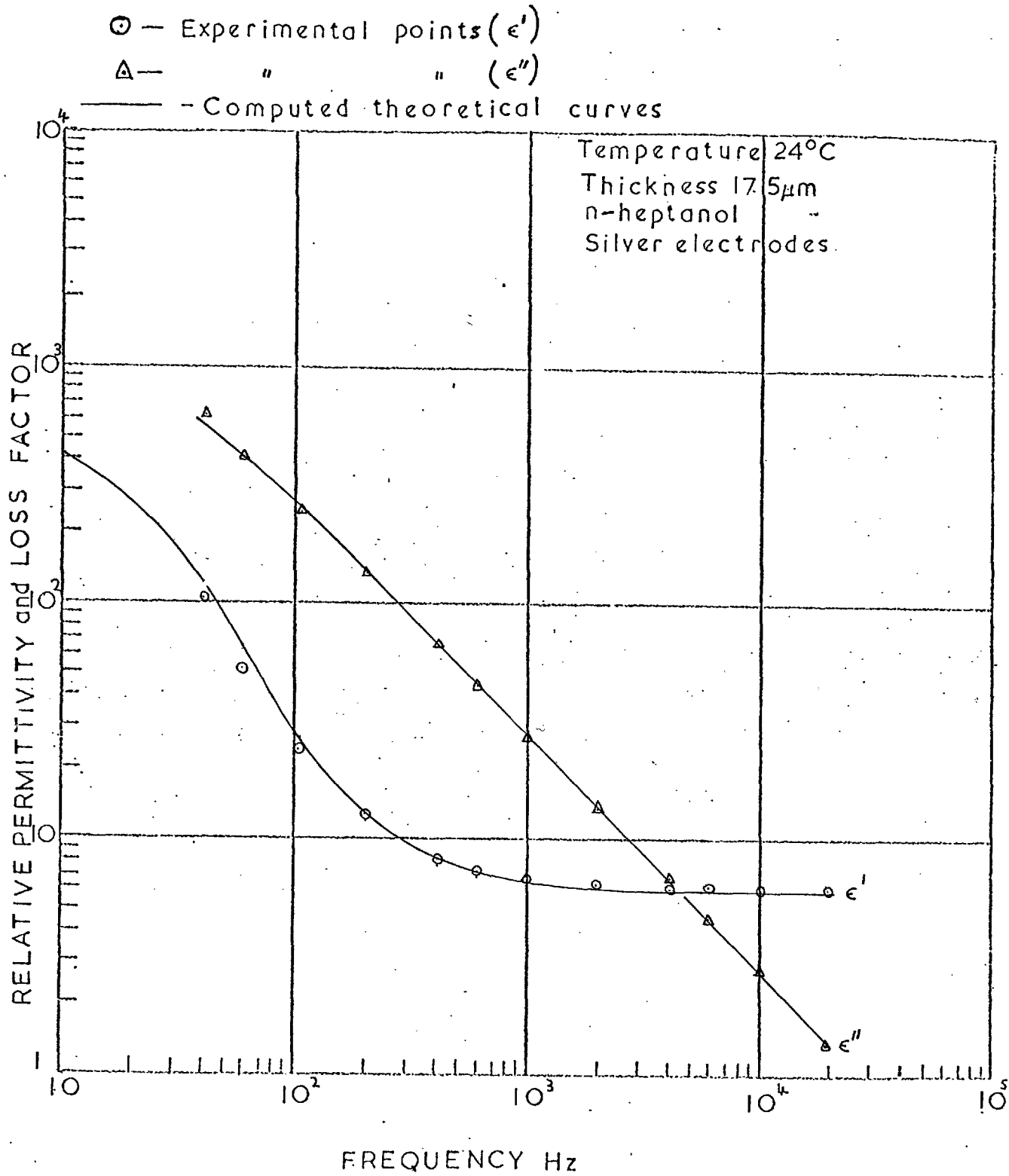


Figure 4.2. ϵ' and ϵ'' versus frequency

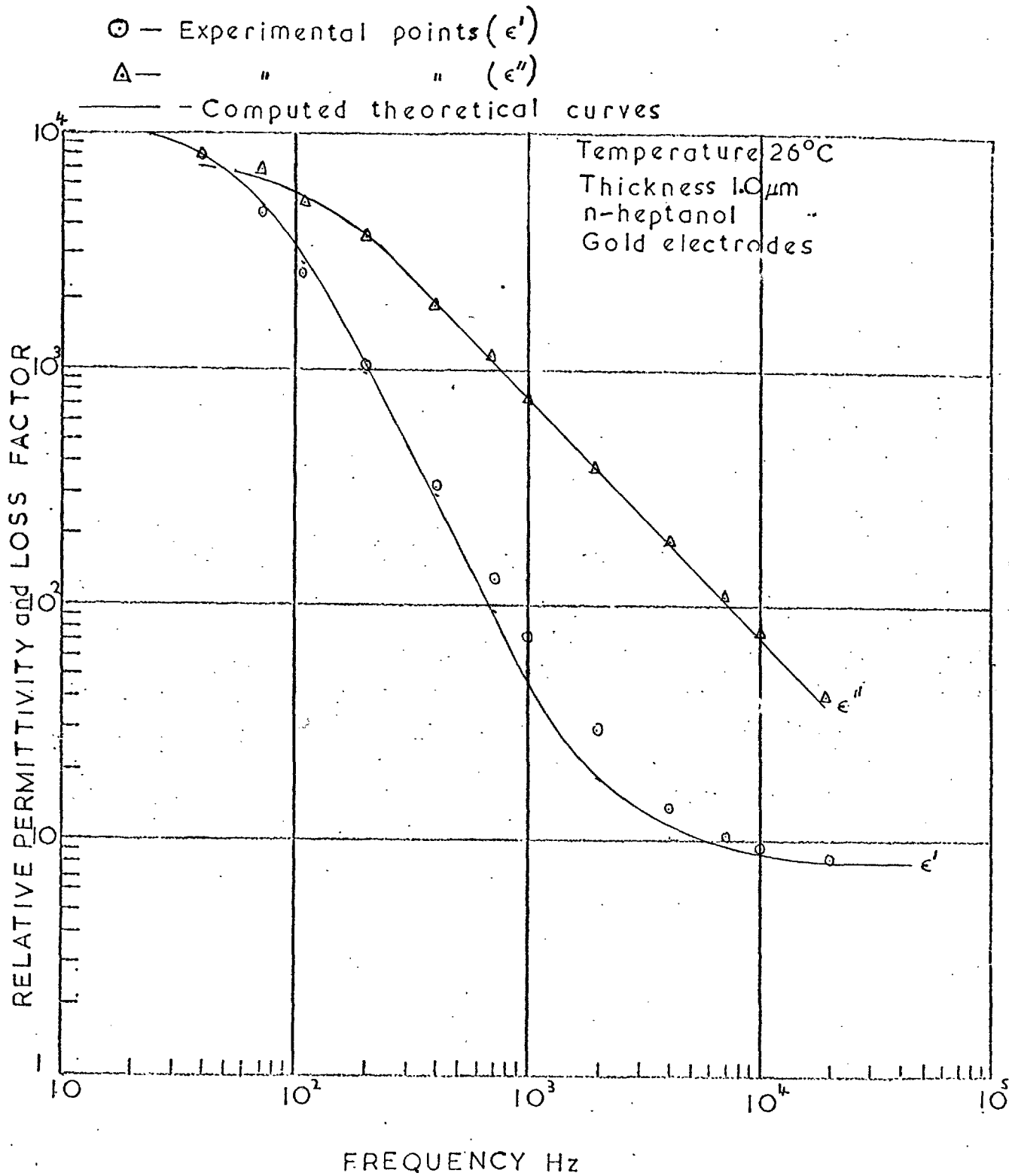


Figure 4.3. ϵ' and ϵ'' versus frequency

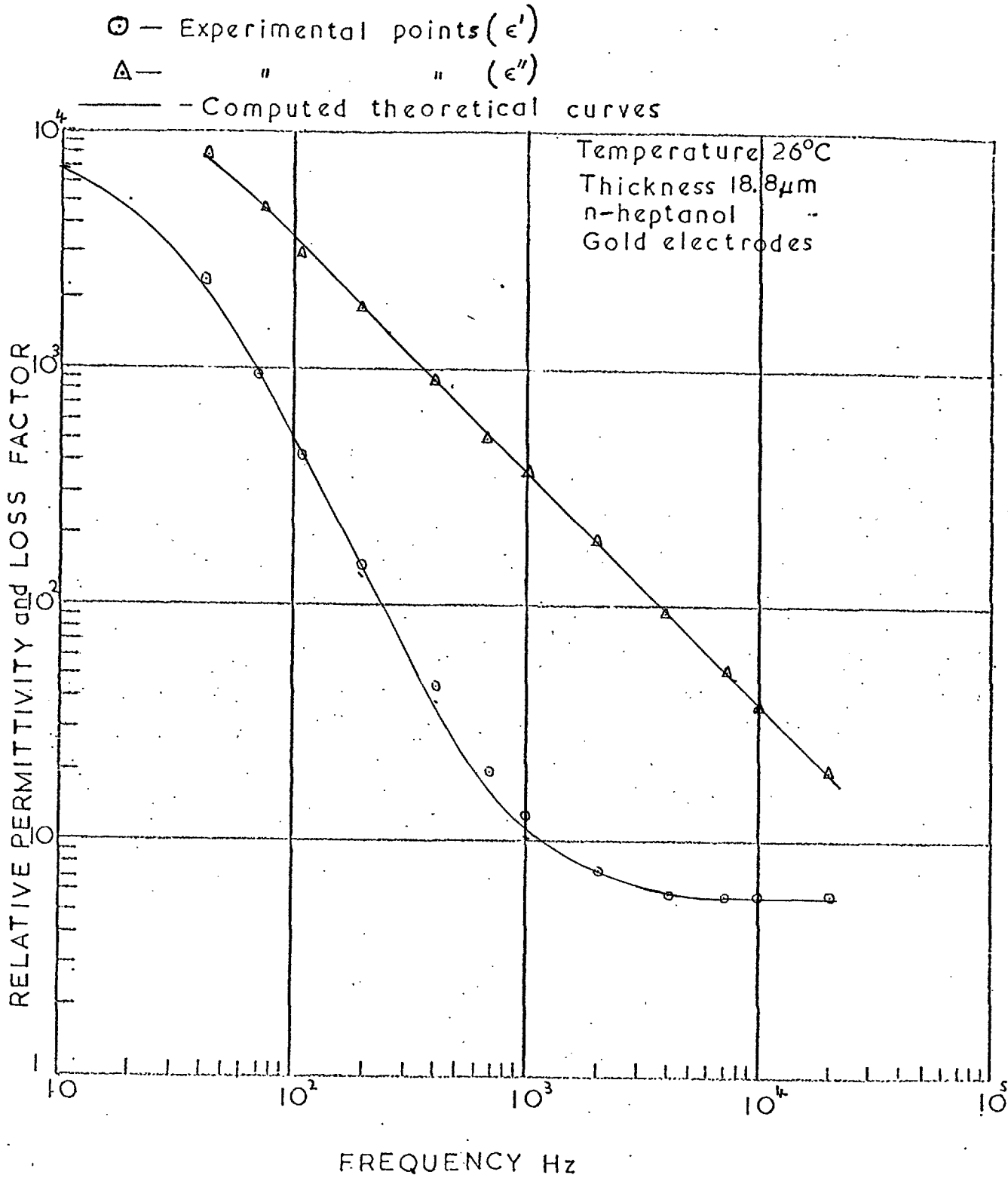


Figure 4.4. ϵ' and ϵ'' versus frequency

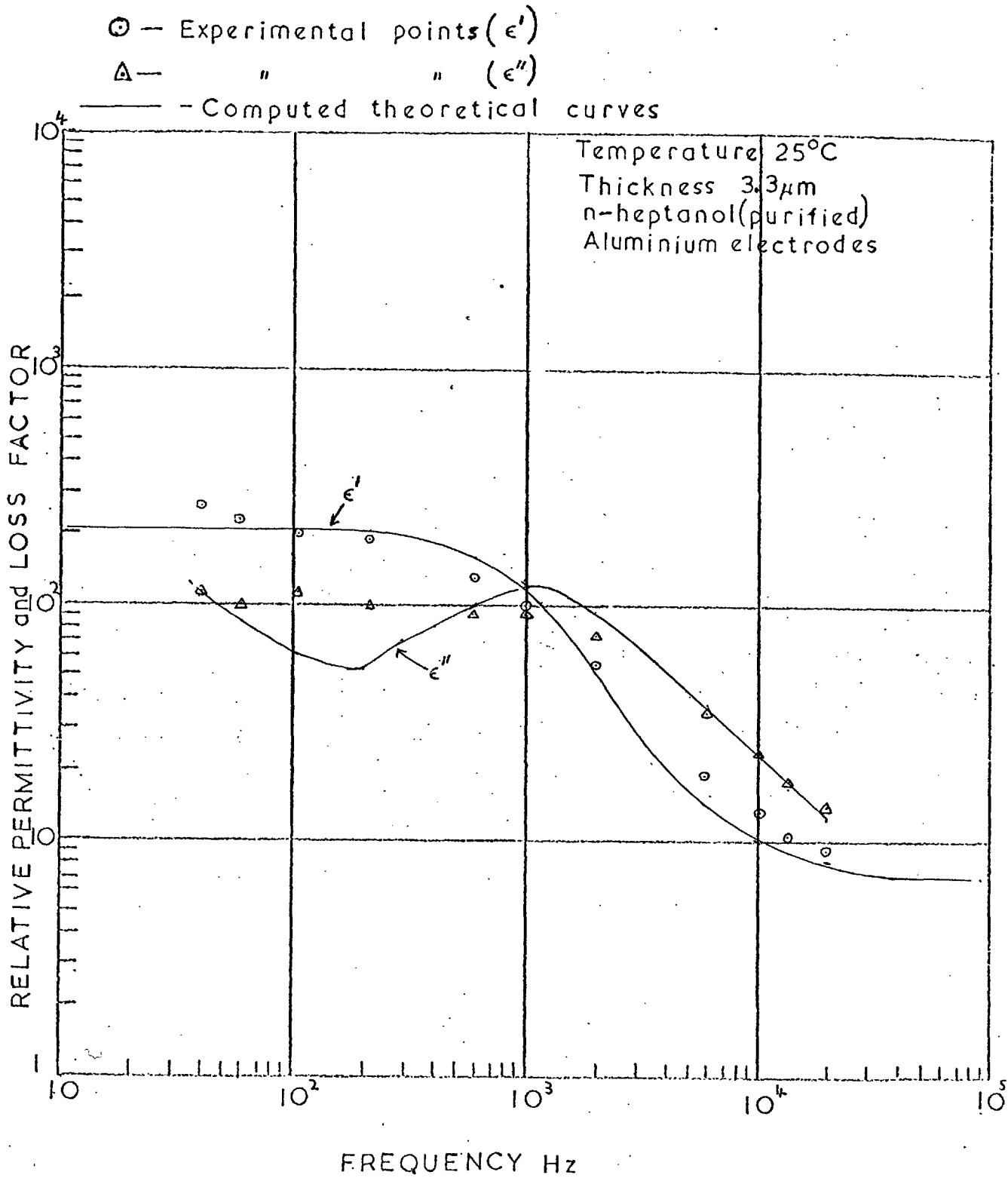


Figure 4.5. ϵ' and ϵ'' versus frequency

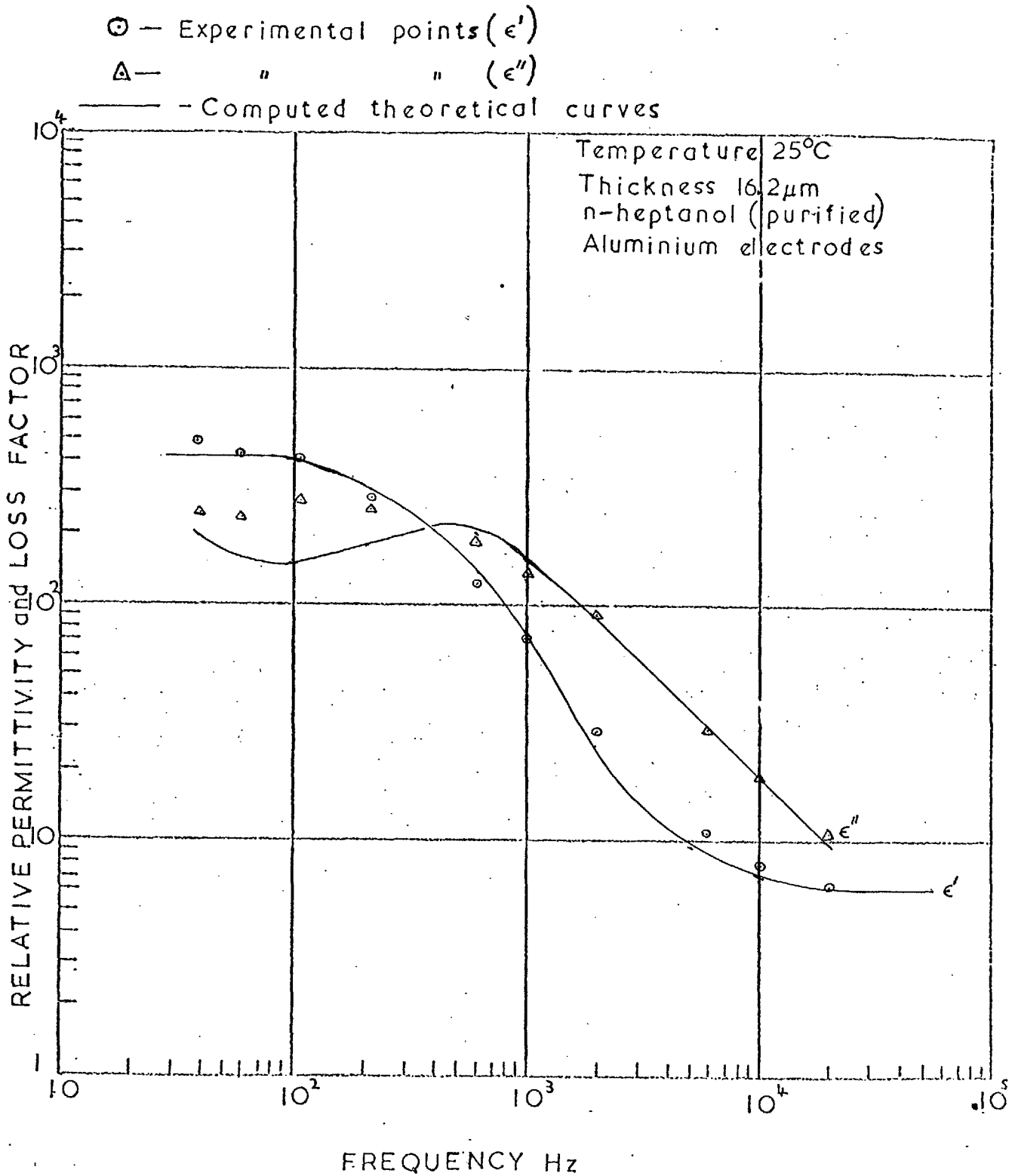


Figure 4.6. ϵ' and ϵ'' versus frequency

Now $\tanh (A\ell/2) = 1$ for $|A|\ell/2 \gg 1$ and in fact $\tanh (A\ell/2) \sim 1$ for $|A|\ell/2 \geq 5$. Providing this condition holds we have

$$B = (A\ell/2)^{-1} \quad (4.32.)$$

The value of A is given by equation (4.17) and for $\omega\tau \ll 1$ reduces to

$$|A| = (2)^{-\frac{1}{2}} (L_D')^{-1} \quad (4.33.)$$

Combining equations (4.32) and (4.33) gives

$$L_D' = B\ell/2\sqrt{2} = 0.35B\ell \quad (4.34.)$$

The diffusion constant, D, is related to the "Debye" length and relaxation time (see equation 4.17) by

$$D = 2(L_D')^2 / \tau \quad (4.35.)$$

The mobility of the charge carriers can then be obtained using the Einstein relationship

$$\mu = eD / kT \quad (4.36.)$$

Finally, the definition of τ in equation (4.17) allows us to write

$$cP_m = \epsilon_s \epsilon_0 / e\mu \tau' \quad (4.37.)$$

Putting the experimental values of ϵ_s , ϵ_∞ , and τ' into equations (4.30), (4.31), (4.34), (4.35), (4.36) and (4.37) permits the calculation of μ and cP_m , where cP_m is the number of charge carriers per unit volume. The results of these calculations, for the experimental data found in Chapter 3, may be found in Tables 4, 5 and 6.

4.7 Interpretation of Carrier Concentration and Mobility Values.

It is apparent from Tables 4, 5 and 6 that, for a given sample of liquid, the impurity concentration varies with thickness. This is not a systematic effect and the most probable cause would seem to be contamination from the material of the measuring cell. Despite rigorous cleaning of the cell it is not possible to remove all contamination, and glass itself contains ionic impurities which could migrate into the liquid. Thus one would not expect to find exactly the same impurity concentration at each electrode site. Table 6 clearly

TABLE 4.

Results of Application of Single Mobile Carrier Theory to Data for
n-Heptanol with Silver Electrodes.

Temperature = 24°C.

Specimen Thickness ℓ (μm)	"Debye" Length L_D (m)	Mobility μ ($\text{m}^2 \text{volt}^{-1} \text{sec}^{-1}$)	Charge Concentration c_{Pm} (m^{-3})	Calculated Conductivity $c_{Pme}\mu$ ($\Omega^{-1} \text{m}^{-1}$)
4.29	2.7×10^{-8}	1.3×10^{-9}	6.8×10^{21}	1.4×10^{-6}
7.20	5.2×10^{-8}	3.3×10^{-9}	1.6×10^{21}	8.4×10^{-7}
11.5	4.9×10^{-8}	4.5×10^{-9}	1.8×10^{21}	1.3×10^{-6}
13.4	6.0×10^{-8}	6.5×10^{-9}	1.2×10^{21}	1.2×10^{-6}
17.5	7.1×10^{-8}	4.6×10^{-9}	8.4×10^{20}	6.3×10^{-7}

Specimen Thickness = 4.29 μm .

Specimen Temperature (°C)	"Debye" Length L_D (m)	Mobility μ ($\text{m}^2 \text{volt}^{-1} \text{sec}^{-1}$)	Charge Concentration c_{Pm} (m^{-3})	Calculated Conductivity $c_{Pme}\mu$ ($\Omega^{-1} \text{m}^{-1}$)
+23	2.7×10^{-8}	1.0×10^{-9}	6.5×10^{21}	1.1×10^{-6}
+ 6	5.1×10^{-8}	2.1×10^{-9}	2.1×10^{21}	7.1×10^{-7}
-11	5.4×10^{-8}	1.3×10^{-9}	2.0×10^{21}	4.1×10^{-7}
-18	1.7×10^{-7}	7.8×10^{-9}	2.7×10^{20}	3.4×10^{-7}
-28	1.5×10^{-7}	3.5×10^{-9}	2.7×10^{20}	1.6×10^{-7}

TABLE 5.

Results of Application of Single Mobile Carrier Theory to Data for
n-Heptanol with Gold Electrodes.

Temperature = 26°C

Specimen Thickness l (μm)	"Debye" Length L_D (m)	Mobility μ ($\text{m}^2 \text{volt}^{-1} \text{sec}^{-1}$)	Charge Concentration c_{P_m} (m^{-3})	Calculated Conductivity $c_{P_m} e \mu$ ($\Omega^{-1} \text{m}^{-1}$)
1.0	2.5×10^{-10}	2.6×10^{-10}	8.9×10^{23}	3.8×10^{-5}
5.0	1.2×10^{-9}	5.4×10^{-11}	3.9×10^{24}	3.4×10^{-5}
6.9	1.4×10^{-9}	7.7×10^{-11}	2.9×10^{24}	3.7×10^{-5}
9.0	1.7×10^{-9}	1.1×10^{-10}	1.9×10^{24}	3.3×10^{-5}
13.2	2.1×10^{-9}	1.5×10^{-10}	1.1×10^{24}	2.9×10^{-5}
15.0	4.1×10^{-9}	4.0×10^{-10}	2.8×10^{23}	1.5×10^{-5}
18.0	4.7×10^{-9}	3.9×10^{-10}	1.7×10^{23}	1.1×10^{-5}

TABLE 6.

Results of Application of Single Mobile Carrier Theory to Data for
n-Heptanol with Aluminium Electrodes.

Purified Specimen, Temperature = 25°C.

Specimen Thickness ℓ (μm)	"Debye" Length L_D (m)	Mobility μ ($\text{m}^2 \text{volt}^{-1} \text{sec}^{-1}$)	Charge Concentration cP_m (m^{-3})	Calculated Conductivity $cP_m e \mu$ ($\Omega^{-1} \text{m}^{-1}$)
3.3	3.8×10^{-8}	2.5×10^{-8}	3.4×10^{21}	1.4×10^{-5}
5.5	5.2×10^{-8}	3.1×10^{-8}	1.8×10^{21}	9.0×10^{-6}
11.8	7.1×10^{-8}	7.3×10^{-8}	9.2×10^{20}	1.1×10^{-5}
16.2	8.5×10^{-8}	1.0×10^{-7}	5.9×10^{20}	1.0×10^{-5}
18.3	7.1×10^{-8}	7.0×10^{-8}	8.3×10^{20}	9.5×10^{-6}

Impure Specimen, Temperature = 20°C.

Specimen Thickness ℓ (μm)	"Debye" Length L_D (m)	Mobility μ ($\text{m}^2 \text{volt}^{-1} \text{sec}^{-1}$)	Charge Concentration cP_m (m^{-3})	Calculated Conductivity $cP_m e \mu$ ($\Omega^{-1} \text{m}^{-1}$)
1.1	1.4×10^{-9}	2.5×10^{-11}	3.3×10^{24}	1.4×10^{-5}
3.0	2.0×10^{-9}	5.7×10^{-11}	1.7×10^{24}	1.6×10^{-5}
4.9	2.4×10^{-9}	2.9×10^{-11}	2.9×10^{24}	1.4×10^{-5}
6.8	2.6×10^{-9}	1.0×10^{-10}	7.6×10^{23}	1.3×10^{-5}
8.7	8.7×10^{-9}	4.8×10^{-10}	5.8×10^{22}	4.5×10^{-6}

shows that the method of analysis can distinguish between a purified sample of liquid and one which has received no treatment. Allowing for the spread of results, the impurity concentration for aluminium and silver electrodes with purified heptanol agree with one another closely. However, the values of impurity concentration for purified heptanol with gold electrodes is several orders of magnitude higher than for aluminium or silver electrodes (see Table 5). This is rather more difficult to understand but a possible explanation would be the generation of extra charge carriers in the case of gold electrodes.

The mobility values, for a given sample of liquid, also vary with thickness. There is a general trend for lower values of mobility to be associated with thinner specimens. The work by Smith¹⁴ has shown that the viscosity of a dilute solution of stearic acid in cetane is of the order of 1,000 times the bulk viscosity of cetane over the thickness range $3.5\mu\text{m}$ to $0.85\mu\text{m}$. This anomalously high value of viscosity is attributed to the presence of a solid or semi-solid boundary layer chemi-sorbed on the electrodes. Heptanol is an associated liquid, in which the molecules form chain structures by hydrogen bonding.

This "structure" allows the possibility of an oriented structure being adsorbed on the electrodes with the orientation extending into the liquid for many molecular layers, and it is hoped to invoke this sort of structure to explain the reduction in permittivity, below bulk values, which occurs at high frequencies. Thus the possibility exists, if not of a solid or semi-solid layer then of a region of high viscosity near the electrodes. There are several formulae relating the mobility of ions to the viscosity of the liquid in which they move for example;

- 1) Walden's law $\mu = A\eta^{-1}$, which is valid for electrolytic ions,

- 2) Stokes law $\mu = e/6\pi r\eta$ derived for spherical particles,
- 3) the relation $\mu = C \eta^{-3/2}$ for the mobility of ions in saturated hydrocarbons found by Adamczewski^{15,16},
- 4) The relation $\mu = B \eta^{-x}$ where x is the ratio of the activation energy for the mobility of ions to the activation energy for viscosity¹⁷.

If a region of high viscosity does exist, adjacent to the electrodes, then the mobility of the ions will be lower in this region than in the rest of the liquid, and the mobility figure obtained would be intermediate between the values relevant to the two regions. This is consistent with the observed data since the effects of an adsorbed layer would be greater at lower thicknesses. This could also explain the small departures from the simple Debye type behaviour predicted, since the analysis assumes the mobility of the mobile charge carrier to be constant.

A second possible reason for this variation in mobility could be the fact that the second charge carrier may not be truly immobile. It has not been possible in the present work to investigate the effects of allowing the second charge carrier to be mobile and therefore little can be said about the effects of so doing.

Finally there seems to be some relationship between impurity concentration and mobility. Samples of liquid found to have large values of impurity concentration are, in general, accompanied by low mobility values. The migration of the charge carriers, under the influence of an applied field, results in space charge accumulation in the region of the electrodes and the tentative idea that this would cause some resistance to the motion of the carriers seems plausible.

It is also of interest to compare the experimental values of conductivity, obtained from the loss factor versus frequency curves,

with those calculated from the values of impurity concentration and mobility. For the case of gold and silver electrodes there is reasonable agreement between the two values. For aluminium, however, the values differ significantly, the calculated values being approximately two orders of magnitude higher than the measured values. This is consistent with the fact that aluminium is a blocking electrode, while gold and silver electrodes can be expected to allow some ions to discharge. It is also significant that the values of calculated and measured conductivity are of the same order for the pure and 'impure' samples, suggesting that, for a thin layer of liquid, a measurement of conductivity is not a reliable means of estimating purity.

From the data in Table 4 we may plot impurity concentration and mobility as a function of temperature as in Fig. 4.7. The linearity suggests that these follow expressions of the form, $N = N_0 \exp(E_N/kT)$ and $\mu = \mu_0 \exp(-E_\mu/kT)$ where E_N is a kind of ionization energy and E_μ is a characteristic energy for the transport process. The values of E_N and E_μ are 0.4eV and 0.2eV respectively.

4.8. An Electron Injection Theory.

I.H.Brockman¹⁸ has done some similar work to that presented here and has also noticed the interfacial polarization effect in Heptanol. However, he invokes a model based on injection of electrons from the electrodes for the following reasons. Firstly, he argues that the small d.c. conductivity measured for his liquid layers implies a small ionic conduction. It has already been pointed out, in section 4.7, that, based on the single mobile carrier theory, conductivity measurements may not be a reliable measure of purity. Brockman assumes that a monolayer of liquid molecules establishes itself with some preferential orientation on the electrodes, subsequent layers form, maintaining the orientation to a certain depth, in the liquid, which depends on

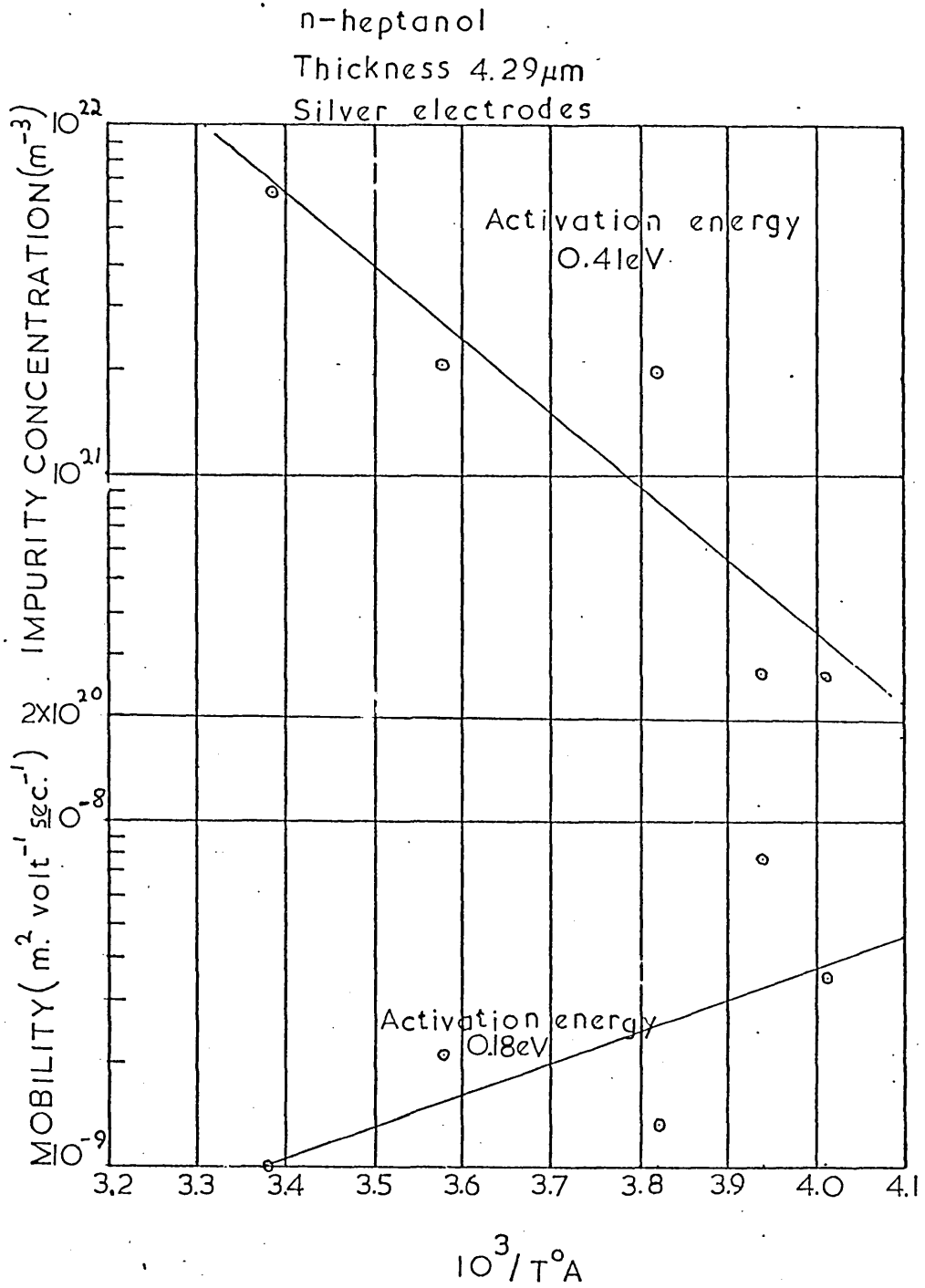


Figure 4.7. Variation of impurity concentration and mobility with temperature.

factors such as organic structure, temperature, electrode material and injected space charge. Thus, a negative space charge is assumed to establish itself in a thin layer near the electrode surfaces in a region where the electrons have relative freedom to move because of the molecular orientation.

The analysis continues by assuming the film to be made up of a series of elemental parallel plate capacitors, with electrode spacing $\Delta \ell$.

$$\text{Thus} \quad \Delta Z = \Delta R / (1 + i\omega \Delta C \Delta R) \quad (4.39.)$$

$$\text{where} \quad \Delta C = \frac{\epsilon_r \epsilon_0}{\Delta \ell} \quad \text{and} \quad \Delta R = \rho \Delta \ell \quad (\text{assuming unit electrode area}).$$

The resistivity is given by $\rho = 1/(Ne\mu)$ and the charge density is assumed to be given by an expression developed by Mott and Gurney¹⁹

$$N = \frac{N_0 x_0^2}{(x_0^2 + \ell^2)} \quad (4.40.)$$

$$\text{where} \quad x_0^2 = \frac{\epsilon_r \epsilon_0 kT}{2\pi N_0 e^2}$$

Substituting this in equation (4.39) and integrating over the thickness of the film one arrives at the rather formidable expression

$$Z = \frac{Q}{\omega \epsilon_r \sqrt{2}} \left[\begin{aligned} & \frac{1}{2} \ln \left(\frac{x_0^2 + \sqrt{2} Q x_0 + Q^2}{x_0^2 - \sqrt{2} Q x_0 + Q^2} \right) \\ & - \frac{1}{2} \ln \left(\frac{(\ell/2 + x_0)^2 + Q \sqrt{2} (\ell/2 + x_0) + Q^2}{(\ell/2 + x_0)^2 - Q \sqrt{2} (\ell/2 + x_0) + Q^2} \right) \\ & + \tan^{-1} \left(\frac{\sqrt{2} Q (\ell/2 + x_0)}{Q^2 - (\ell/2 + x_0)^2} \right) - \tan^{-1} \left(\frac{\sqrt{2} Q x_0}{Q^2 - x_0^2} \right) \end{aligned} \right] \quad (4.41.)$$

$$+ \frac{i2}{\omega \epsilon_r} \left[\frac{\ell}{2} - \frac{Q}{2\sqrt{2}} \left\{ \begin{aligned} & \frac{1}{2} \ln \left(\frac{(\ell/2 + x_0)^2 + \sqrt{2} Q (\ell/2 + x_0) + Q^2}{(\ell/2 + x_0)^2 - \sqrt{2} Q (\ell/2 + x_0) + Q^2} \right) \\ & - \frac{1}{2} \ln \left(\frac{x_0^2 + \sqrt{2} Q x_0 + Q^2}{x_0^2 - \sqrt{2} Q x_0 + Q^2} \right) \\ & + \tan^{-1} \left(\frac{\sqrt{2} Q (\ell/2 + x_0)}{Q^2 - (\ell/2 + x_0)^2} \right) - \tan^{-1} \left(\frac{\sqrt{2} Q x_0}{Q^2 - x_0^2} \right) \end{aligned} \right\} \right]$$

where $Q^2 = N_0 x_0^2 e \mu / \omega \epsilon_r \epsilon_0$

Fig. 4.8. shows one of Brockman's curves for heptanol where he states that a value of $4 \times 10^{-4} \text{ m}^2 \text{ volt}^{-1} \text{ sec}^{-1}$ for mobility and a surface charge density N_0 of 10^{19} m^{-3} gives a good fit to the experimental curve. No mention is made of the temperature so for the purposes of checking equation 4.41 room temperature (20°C) is assumed. Similarly there is the question of the choice of ϵ_r . Brockman nowhere indicates that values of permittivity less than bulk values were obtained. In the present work values of ϵ_r ranging from 5.5, for a thickness of $18.8 \mu\text{m}$, to 8.0, for a thickness of $1 \mu\text{m}$, were obtained with gold electrodes. For the purpose of illustration a value $\epsilon_r = 8$ was chosen. A further complication arises from the fact that the present work indicates that the mobility varies with thickness. However, assuming a constant mobility the theoretical curve shown in Fig. 4.8. may be calculated on the basis of the equations presented in section 4.4 of this chapter. The values of carrier density and mobility, obtained for the single mobile charge carrier theory, differ from those claimed by Brockman and despite the assumption of a constant mobility the agreement with the experimental curve is very good.

4.9 The relative Merits of the Electron Injection and Single Mobile Carrier Theories.

It is generally accepted that conduction in dielectric liquids is due to ionized impurities and very exhaustive purification techniques²⁰ must be employed in order to reduce these to very low levels. Ion-exchange treatment may be expected to remove large amounts of impurities. However, even after ion exchange much further improvement can be effected by the use of dialysing membranes²¹.

This would seem to indicate that the liquids investigated in

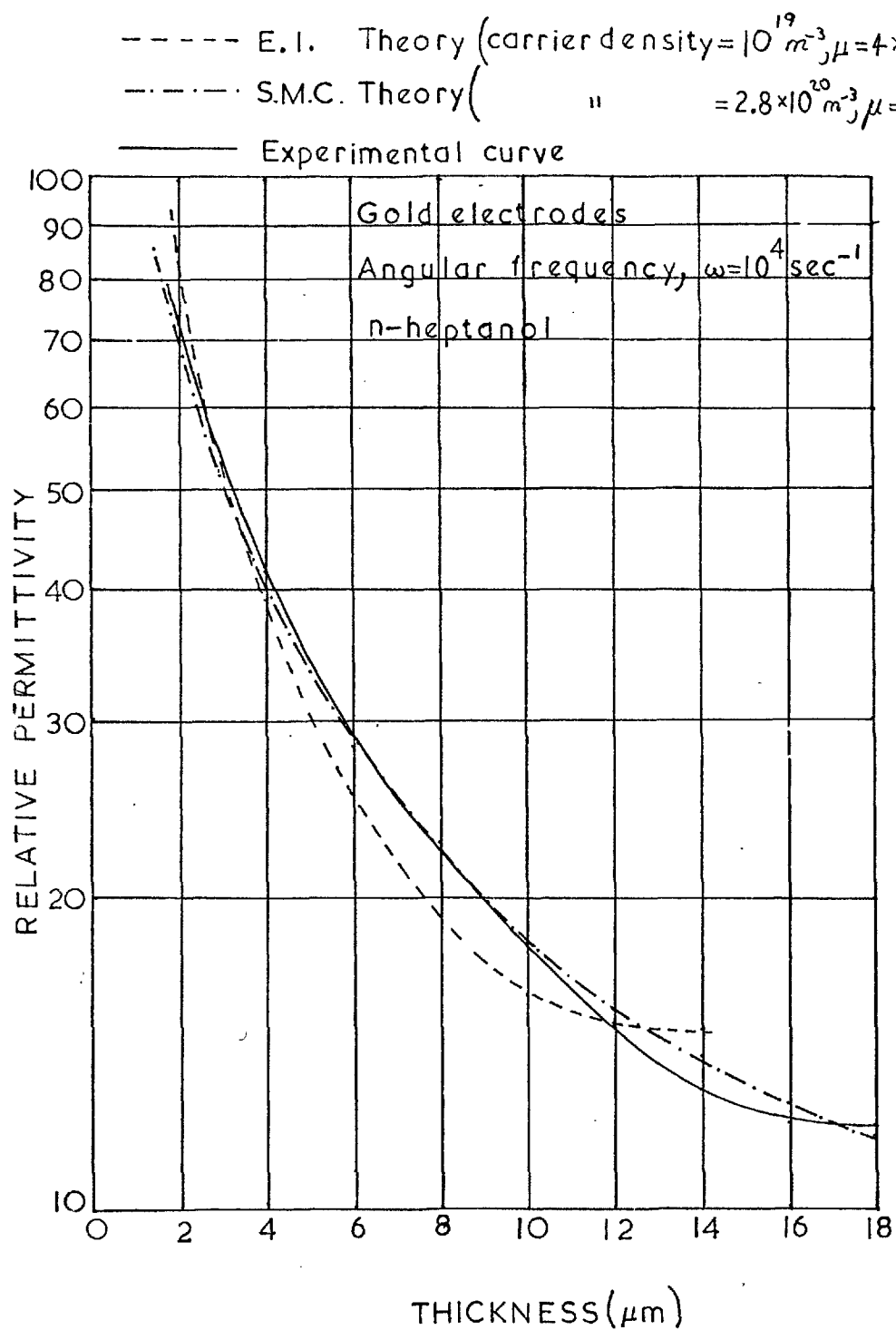


Figure 4.8. Comparison of Single Mobile Carrier and Electron Injection Theories.

the present work still contain significant amounts of ionic impurities.

Brockman assumes field-assisted emission of electrons over the potential barrier at the metal-insulator interface (i.e. Schottky emission). Hill²² has shown that Schottky emission at low fields ($<10^3 \text{ Vcm}^{-1}$) is insufficient to explain most cases of conduction in insulators. The results in Chapter 3 were obtained using a measuring voltage of less than 0.1 volt p.p. in most cases (i.e. a field of $10^3 \text{ volt cm}^{-1}$ for a film thickness of $1\mu\text{m}$).

The d.c. curves presented in Chapter 3 (Fig. 3.29) for aluminium electrodes exhibit a $V^{\frac{1}{2}}$ law at low stresses. Schottky emission could account for a $V^{\frac{1}{2}}$ law but the fields applied were much too low for significant current to be injected. An alternative explanation invoking the Poole effect is possible. In this we assume a distribution of positive ions throughout the liquid. These could act as coulombic centres trapping electrons. In the presence of a field electrons may hop or tunnel between these centres giving rise to a $V^{\frac{1}{2}}$ law²². It is assumed in this model that the ionic mobility is very small compared with that of the electrons and therefore that the ions do not move significantly in the applied field during the time in which the electrons are transported through the film.

With aluminium electrodes the liquid layers also exhibit the "Garton" effect i.e. the loss factor is stress dependent and $\tan \delta$ versus applied voltage curves exhibit maximum. This effect is explained by the movement of ions in the liquid as follows (see section 4.11 for a more detailed description). If a liquid exists between closely adjacent electrodes, provided that the ions do not discharge, or recombine on the surface of these, two main effects of an applied alternating field should be expected ; a) A decrease of loss angle with voltage, above a certain voltage depending upon the spacing between the electrodes, because the ions are not free to perform oscillations larger than the electrode spacing, b) An increase in the number of free ions with increasing voltage, because

the field, by segregating the ions of opposite sign, will lower the rate of recombination while leaving the rate of creation of new ions unaltered. It will be seen that these two effects suffice to explain the existence of a maximum value of loss angle, followed by a decrease, and is entirely consistent with the single mobile carrier theory. The approximations made in the single mobile carrier theory include restrictions on the amplitude of potential and charge flow, thus the theory cannot be expected to account for the "Garton" effect. However, it is possible that a complete solution for the conduction-diffusion differential equations for time-varying potentials would result in stress dependent losses at high fields.

Thus the weight of evidence is in favour of an explanation based on the movement of ionized impurities in the liquid. The single mobile carrier theory accounts for the observed phenomena, predicting the Debye behaviour observed in practice. Despite the fact that blocking electrodes are required by the theory, the results for silver and gold electrodes also exhibit the predicted behaviour, indicating that a space charge can still develop in the case of these electrodes. The "Garton" effect observed, for the case of aluminium electrodes, is further evidence of an ionic effect.

P155
Brockman's theory requires Schottky emission of electrons from the electrode material and this has been shown to be unlikely. Therefore, the treatment presented by Brockman seems an unlikely explanation of the effect. The value of carrier concentration, for the electron emission theory, is given by ¹⁹

$$N_0 \sim 10^{19} e^{-(\phi - \chi)/kT} \quad (4.42.)$$

where ϕ = the work function of the metal

χ = the electron affinity of the liquid

at room temperature. Typical values of carrier concentration quoted

by Brockman are of the order of 10^{19} m^{-3} , resulting in a value of $\chi \sim \phi$. For most insulators $\phi > \chi$ and thus the expected values of N_0 would be much lower than those required by Brockman's theory.

4.10. D.C. Current-Voltage Curves.

The curves shown in Figs. 3.29 and 3.30 all exhibit three distinct regions. The current rises, at low voltages, in proportion to the square root of the applied voltage. This is followed by an ohmic region and finally a further change in slope results in a current proportional to the square of the applied voltage. This suggests the following sequence, Schottky emission, followed by ohmic conduction, and finally a space charge limited current region. The values of conductivity, measured in the ohmic region of these curves, is some three orders of magnitude lower than those found for the a.c. case. The values τ' , the relaxation time characterizing the relaxation process in the single mobile carrier theory, range from 10^{-4} to 10^{-2} sec. The d.c. current measurements were made one minute after the application of the voltage, and in view of these values of τ' it is reasonable to assume that a large fraction of the ionic charge movement has taken place in this time. Thus the d.c. curves and conductivity may be explained by assuming electron emission from the electrodes resulting in the $V^{\frac{1}{2}}$ law. The values of d.c. conductivity obtained indicate that the number of carriers generated in this way is lower, by several orders of magnitude, than the ionic impurity concentration. In the a.c. case, therefore, the effects of the movement of the ionized impurities may be assumed to dominate the conduction process as indicated by the close agreement of the single mobile charge carrier theory to the observed phenomena. Fig. 4.9. shows the d.c. conductivity plotted as a function of $10^3 / T^\circ \text{A}$ and the activation energy calculated from this curve gives a value $\sim 0.2 \text{ eV}$. This value is consistent with an electronic conduction process²⁵.

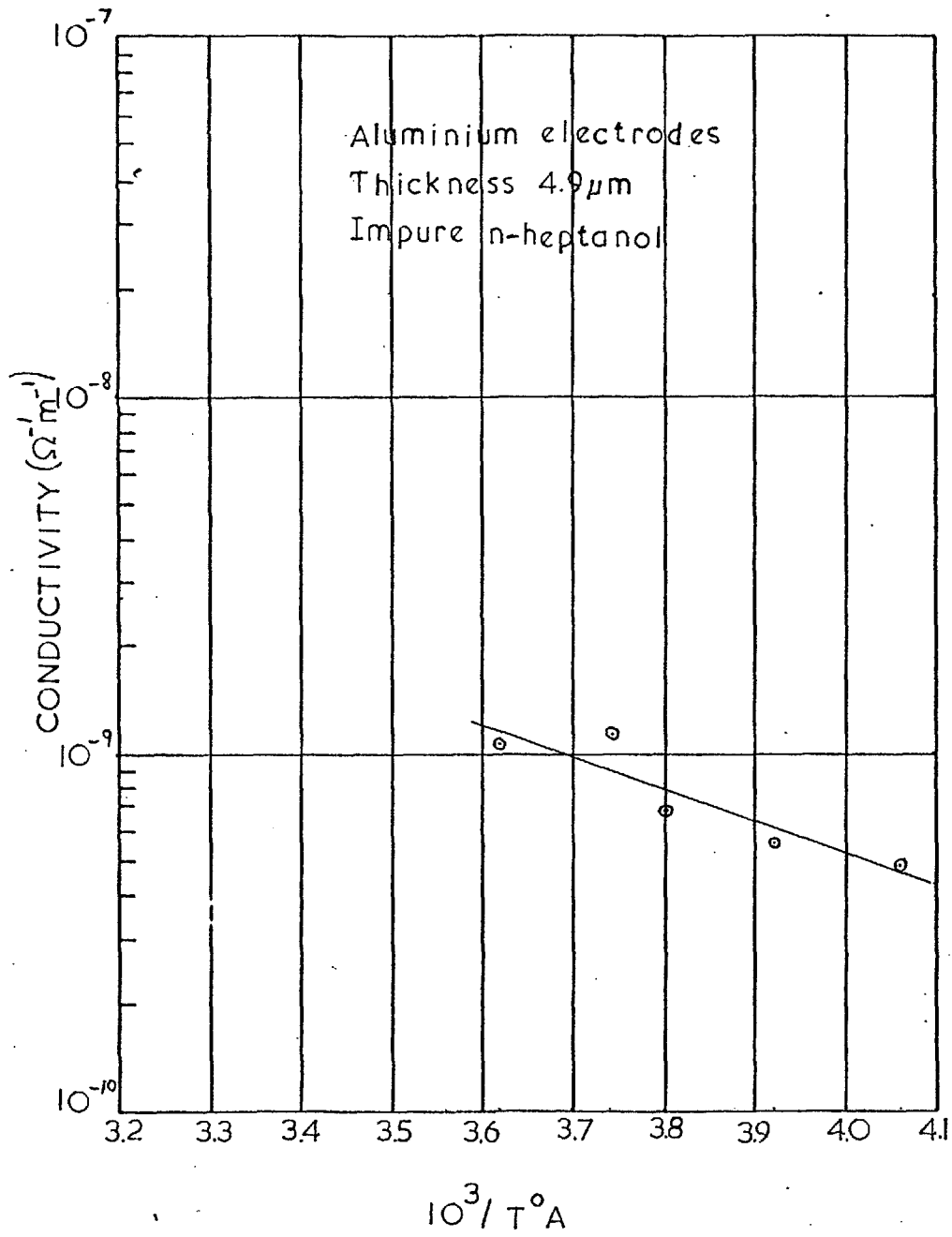


Figure 4.9. D.c. conductivity as a function of temperature

Fig 3.31 exhibits a region where the current obeys a higher than square law at high voltage. These sort of curves were generally obtained for the thicker specimens and here electrode effects are not so dominant and this is more of a bulk effect.

Breakdown of the liquid layer often occurred, in this region of higher than square law, and a possible explanation is the generation of extra charge carriers in the bulk, probably as a result of collision ionization.

4.11 Stress-dependent Loss Factor: The "Garton Effect."

Figs. 3.27 and 3.28 show clearly the dependence of $\tan \delta$ on applied voltage at high voltages. This effect is generally known as the "Garton " effect, after C.G.Garton²³ who first developed a theoretical treatment to account for this behaviour. "Garton" effect measurements are often used to determine whether impregnated paper capacitors are suffering from ionic contamination.

A number of assumptions are made in the development of the theory and these are listed as follows:

- a) The liquid exists between two plane parallel electrodes, through which the ions present cannot penetrate, and on the surface of which they are not held by any adsorption forces.
- b) The number of ions present is insufficient to create any space-charge gradients comparable with the applied field. That is, the motion of the ions is controlled solely by the applied field and the viscosity of the liquid.
- c) The life of an ion is assumed to be long compared with the time cycle of the applied field, so that changes in the number of ions present during any one cycle may be neglected.
- d) To make analysis possible, the positive and negative ions are assumed to have equal mobilities.

e) For the sake of simplicity inter-ionic, contact-potential and image forces are neglected.

Apart from d), these assumptions are consistent with the single mobile carrier theory.

Two distinct cases can be immediately distinguished, $E < E_0$ and $E > E_0$, where E is amplitude of the applied field, and E_0 is the amplitude of the field required to give the ions a double amplitude equal to the electrode spacing ℓ . For $E < E_0$, the ions of each sign will be gathered, after one cycle of the applied field, into a layer of thickness $\ell(1-m)$, where m is given by the ratio E/E_0 . This arises from the assumption that space charge is negligible. This ionic layer will oscillate, between the electrodes, every ion having the full amplitude corresponding to the applied field. In this, region, therefore, the amplitude of motion is not limited by the electrode spacing, and $\tan \delta$ will remain constant and equal to $\tan \delta_0$ over the range $0 < E < E_0$, where $\tan \delta_0$ is the value of $\tan \delta$ at the stress E_0 , assuming the number of ions to be constant. There will be two such ionic layers, one of positive and the other of negative ions. When $E = E_0$, the ions will be gathered into a layer of "negligible" thickness, and this ionic layer will oscillate from side to side, just reaching each electrode at every reversal of the applied field.

When $E > E_0$, the ionic layer will reach an electrode before the reversal of the field, and will remain stationary there until reversal occurs. During this stationary period, there will be no loss of energy, and the value of $\tan \delta$ will therefore fall with further increase of voltage.

Consideration of the motion of ions for $E > E_0$ results in the expression

$$\tan \delta = (1/\pi)(\theta - \sin \theta \cos \theta) \tan \delta_0 \quad (4.43.)$$

where θ is given by

$$\cos \theta = 1 - 2E_0/E = 1 - 2/m \quad (4.44.)$$

Eqn.(4.43) predicts a sharp fall in loss angle with increasing stress, as observed experimentally.

Experimentally a maximum is observed in the value of $\tan \delta$ and this is not predicted by eqn. 4.43. It is reasonable to expect that the segregation of the positive and negative ions into separate layers will lower their rate of recombination and thus cause an increase in the number of ions during the time the field is applied.

To find an expression for the number of ions dissociated at any instant, as a function of the applied field, the following assumptions are made.

- a) Recombination of the ions occurs only during the time when the two ionic layers interpenetrate; the rate of creation of new ions being slow enough to justify neglect of that fraction which comes into existence during any one cycle of the field.
- b) Ions of both signs have equal mobilities.
- c) There exists a limited number, P , of molecules capable of being dissociated, per m^3 .
- d) A fraction β of the undissociated ions dissociates every second. β may be a function of temperature, but is independent of the applied field. Then the number of ions of one sign dissociating per second is

$$n = \beta (P - N) \quad (4.45.)$$

where N is the number of ions of one sign per m^3 .

- e) The number (N) of ions of one sign per m^3 is the product of the number dissociating per second and the mean life of an ion.

That is

$$N = n\tau \quad (4.46.)$$

where τ is the mean life of an ion.

- f) The mean life of an ion, τ , is inversely proportional to the concentration, K , of ions of opposite polarity and to the fraction of its life which the ion spends in that concentration.

That is

$$\tau \propto 1/(K\gamma) \quad (4.47.)$$

where γ is defined as the ratio

$$\frac{\text{Time which ion spends in the concentration during one half-cycle}}{\text{Duration of one half-cycle}}$$

When the applied voltage is zero, $\gamma = 1$, since the ion is in a constant concentration of opposite ions.

Using these assumptions, combined with eqn. 4.43 the following result is obtained

$$\tan \delta = \left(\frac{-Q + (Q^2 + 4(s-1)sQ)^{\frac{1}{2}}}{2\pi(s-1)} \right) (\theta - \sin \theta \cos \theta) \tan \delta_0 \quad (4.48.)$$

θ is defined by eqn. 4.44, while the expression for Q depends on m as follows

$$Q = \ell_1 / (\gamma_1 \ell) = \pi \sqrt{2m-1} \quad \text{for } m > 1 \quad (4.49.)$$

where ℓ_1 is the thickness of the ionic layer, and γ_1 is the value of γ in the presence of an applied field.

$$Q = (1-m)^2 / (1-1.636m), \quad \text{for } 0 < m < 0.5 \quad (4.50.)$$

$$Q = \frac{\pi(1-m)\sin \phi}{2(\phi \sin \phi + \cos \phi - 1)} \quad \text{for } 0.5 < m < 1 \quad (4.51.)$$

where $\sin \phi = (1-m)/m$

The value of the quantity $s = P/N$ depends upon the nature of the ionizable impurity. A relatively large quantity of impurity, of which only a small fraction is ionized at any instant, results in large values of s . For all values above $s \sim 10$, equation (4.48) may be written with sufficient accuracy in the simpler form,

$$\tan \delta = (\sqrt{Q}/\pi)(\theta - \sin\theta\cos\theta)\tan\delta_0 \quad (4.52.)$$

On the other hand, if the impurity is completely ionized, s becomes unity, the quadratic term vanishes, and $\tan \delta$ is given by equation 4.43. It is found that the maximum loss angle always occurs when $m = 1$ (i.e. $E = E_0$), and when, therefore, $\theta = \pi$. Equation 4.43 reduces, for these conditions to

$$\tan\delta_{\max} = \tan\delta_0 \quad (4.53.)$$

and $\tan\delta_0$ is given by

$$\tan\delta_0 = \frac{N_1 e^2}{2\pi^2 f \rho \epsilon_r \epsilon_0} = \frac{N_1 e \ell}{2\pi \epsilon_r \epsilon_0 E_0}$$

or

$$N_1 = \frac{2\pi \epsilon_r \epsilon_0 E_0 \tan\delta_{\max}}{e \ell} \quad (4.54.)$$

where N_1 is the number of ions (of one sign) present per m^3 at the stress E_0 . The number N in the unstressed liquid may be somewhat smaller, down to about $0.5N_1$, according to the value of s .

The mobility of the ions may be calculated as follows. When $m = 1$ the average potential gradient during one half-cycle is $2E_0/\pi$. During the half-cycle, the ions move a distance ℓ , and their average velocity is therefore $2\ell f$. It follows that the mobility, μ , is given by

$$\mu = \omega \ell / 2E_0 \quad (4.55.)$$

The ionic radius may also be estimated as follows. If it is assumed that the motion of an ion is governed by Stokes's law, then the value of the constant ρ in equation 4.54 is given by

$$\rho = 6\pi \eta r \quad (4.56.)$$

where r is the ionic radius. Thus we can write

$$r = \frac{E_0 e}{3\pi \omega \eta \ell} \quad (4.57.)$$

The results of this analysis, applied to the data shown in Figs. 3.27 and 3.28, is shown in Table 7. These values may be compared with the values, in Table 6, of mobility and carrier

TABLE 7.

Mobility and Charge Carrier Density Calculated from
"Garton" Effect Measurements.

Specimen Thickness $1.8\mu\text{m}$.

Impure specimen of heptanol.

Measurements made at a frequency of 600 Hz.

Temperature ($^{\circ}\text{C}$)	Carrier Density (m^{-3})	$\mu(\text{m}^2\text{volt}^{-1}\text{sec}^{-1})$
22	9.5×10^{21}	2.98×10^{-9}
15	8.66×10^{21}	3.49×10^{-9}
7	9.15×10^{21}	3.40×10^{-9}
-10	7.36×10^{21}	4.53×10^{-9}
-14	1.50×10^{22}	2.31×10^{-9}
-21	1.26×10^{21}	2.72×10^{-9}
-29	4.66×10^{21}	6.80×10^{-9}

N.B. The results for -14, -21 and -29 $^{\circ}\text{C}$ refer to a different sample of liquid than the previous four measurements..

There is no such layer present in the case of gold or silver but these electrodes are still blocking and so it seems reasonable to assume that some agency prevents the ions from contact with the electrode surface. If we assume an adsorbed layer of liquid molecules on the surface of the electrodes then this provides the necessary barrier between the ions and the electrodes. The force between an ion and its image in the electrode is inversely proportional to the square of the distance between the ion and the electrode surface. Assuming a thickness of $10 \text{ \AA}$ for the adsorbed liquid layer and $40 \text{ \AA}$ for the oxide layer on aluminium means that the maximum force developed between an ion and its image in the electrode is twenty-five times greater for gold and silver than for aluminium. Thus larger fields will be required to observe the Garton effect in the case of gold and silver electrodes. Compensating this effect to some extent is the voltage dropped across the oxide layer in the aluminium system. This voltage can be calculated knowing the permittivity and thickness of the oxide layer and turns out to be approximately 1% of the total applied voltage. Thus the field across the liquid, for a given applied voltage, will be approximately the same for gold, silver and aluminium electrodes.

P164
concentration calculated for the same sample of purified heptanol. The values for carrier concentration are of the same order of magnitude while the mobility given by the "Garton" effect is a factor of 10 lower than that given by the single mobile charge carrier theory. Allowing for the approximate nature of both theories the agreement is quite good. It is difficult to understand why the Garton effect was not observed in the case of gold and silver electrodes. The Suttor theory indicates that both gold and silver electrodes, as well as aluminium, are blocking, therefore we cannot say that the Garton effect should be absent with gold and silver electrodes. A possible explanation of this can be found in terms of image forces at the electrodes. In the development of the Garton theory, image forces are neglected (see assumption e), page 159).

Aluminium will have a layer of oxide on its surface which will be typically 40 Å deep. SEE INSERT.

higher, i.e. $\sim 0.4\text{eV}$ for both mobility and carrier concentration.

Figs. 3.27 and 3.28 also show that the permittivity is stress dependent, above a certain value of applied field the permittivity falls with increasing stress. This is also a consequence of the limited ionic motion. The interfacial polarization results from the relative movement of the charge carriers. For values of applied field greater than E_0 , the ions are stationary for a time which increases with increasing stress. Since there is no relative motion between ions of opposite sign while they are stationary the interfacial polarization, and therefore the permittivity, falls as the stress is increased above E_0 .

4.12. Hindered Dipolar Rotation.

The value of ϵ_∞ obtained for the thin layers was found in general to be less than the relevant value for a bulk specimen. The majority

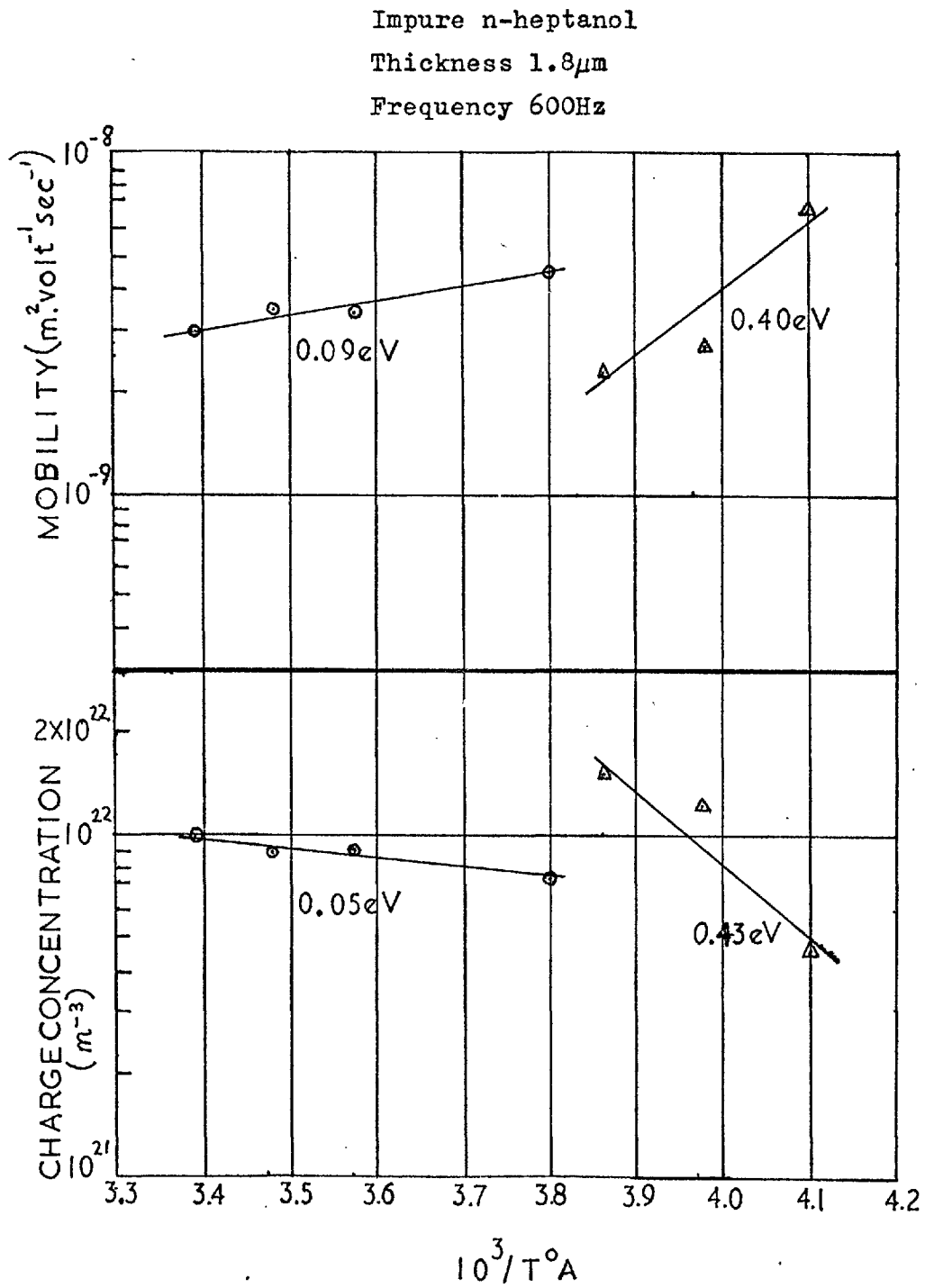


Figure 4.10. Temperature dependence of mobility and charge concentration from "Garton" effect measurements.

of the measurements were made using n-heptanol (heptan-1-ol). At room temperature the bulk static permittivity (for the orientation polarization) is approximately 12 (see Fig. 4.11) and the relaxation time is approximately 1.4×10^{-9} sec²⁴. The upper frequency limit in the present investigation was 20 KHz and thus we may expect the permittivity of a large specimen to be constant and equal to this static permittivity over the frequency range covered. The only reasonable explanation of this lowering of permittivity is that the heptanol molecules are not completely free to rotate near the electrodes and thus the orientation polarization is reduced, resulting in a lower value of permittivity than expected.

A crude theory to explain the observed values of ϵ_{∞} for the interfacial polarization effect has been developed as follows. Heptanol, in common with other alcohols, is an associated liquid. The hydroxyl groups of different molecules interact with one another, forming a hydrogen-bond, which links the molecules together. As mentioned in section 1.7. of chapter 1, this hydrogen-bond develops essentially between the hydrogen atom of one hydroxyl group and the ($2p^2z$) lone-pair electrons of another hydroxyl oxygen: its energy, of the order of 0.25eV, restricts the mobility of the hydroxyl groups, and as the bonding can continue through a chain of such groups (Fig. 1.1b) considerable "structure" is produced in the liquid. The equilibrium in the association of alcohol molecules, $nROH \rightleftharpoons (ROH)_n$, is a dynamic one, and a range of values of n , i.e., in the complexity of the multimer $(ROH)_n$ is usually encountered. It may be assumed that the formation of a hydrogen-bond does not influence the dipole moment on the monomers. Thus heptanol, in the liquid state consists of a distribution of chain-like multimers of different sizes. The terminal OH group of a heptanol multimer may be bound to the surface of the electrodes by virtue of its polar nature. Thus an oriented

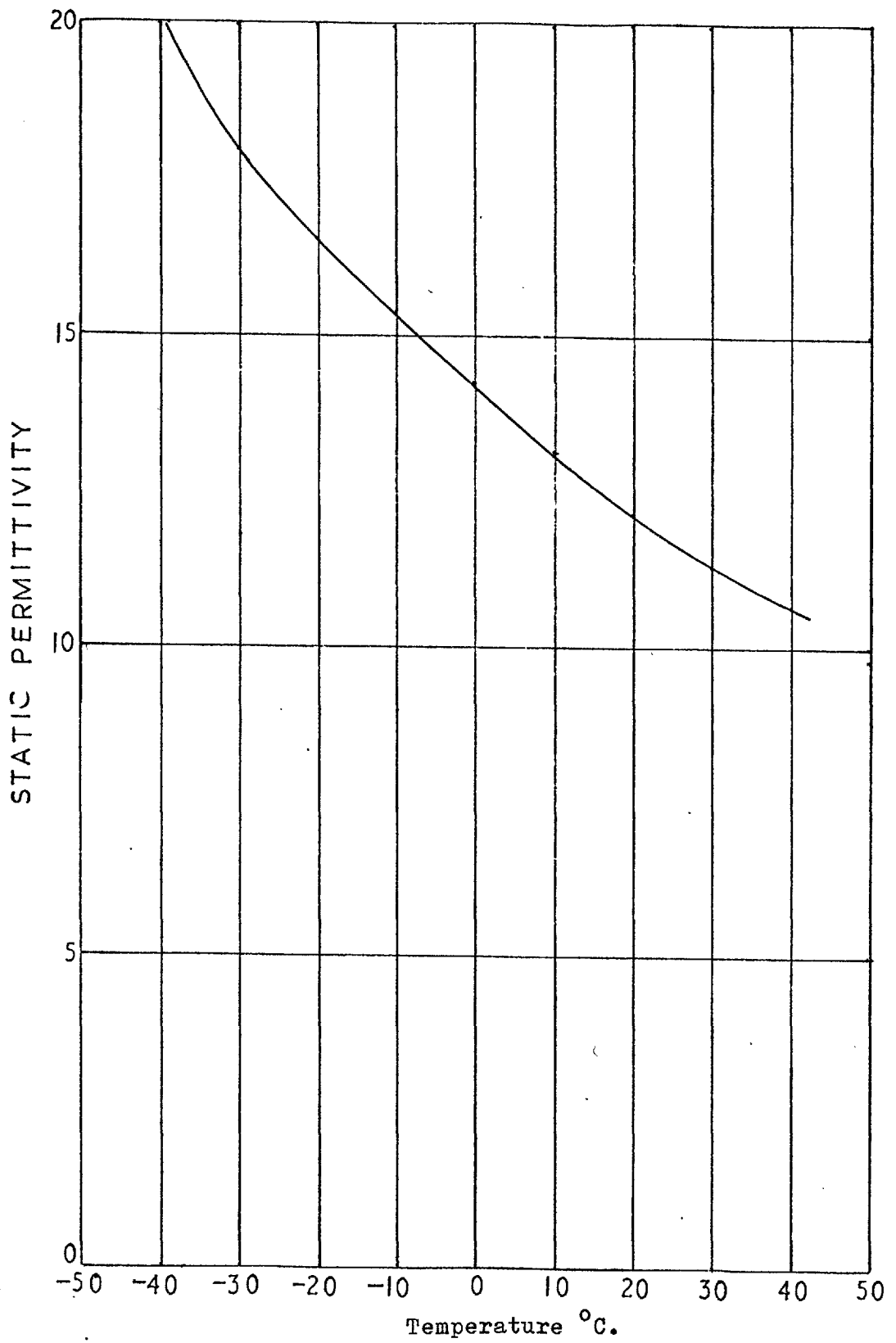


Figure 4.11. Static permittivity of (bulk) heptan-1-ol
as a function of temperature.

layer of molecules can exist at the electrode and this orientation will be maintained to a distance, into the liquid, depending on the size of the multimers.

This adsorption of the multimers onto the surface of the electrodes restricts their ability to rotate and if it is assumed that all rotation is prevented, then the orientation polarization disappears for these molecules. The permittivity for this adsorbed layer would then be given by the value of ϵ_{∞} for the orientation polarization and this is given as approximately 3.3, at room temperature, by Middlehoek and Bottcher²⁴. So the liquid layer is assumed to comprise of three regions as illustrated in Fig. 4.12. Two regions, one at each electrode, each of thickness $\ell_1/2$ metres, where the permittivity is equal to 3.3 and the bulk of the liquid, thickness $\ell_2 = \ell - \ell_1$ (ℓ = total thickness of liquid layer), where the permittivity is equal to 12, at 20°C. The liquid layer may then be treated as two capacitors in series, C_1 due to the two oriented layers with permittivity ϵ_1 (= 3.3), and C_2 due to the bulk of the liquid with permittivity ϵ_2 (= 12). The observed capacitance will be given by

$$C = \frac{C_1 C_2}{C_1 + C_2} \quad (4.58.)$$

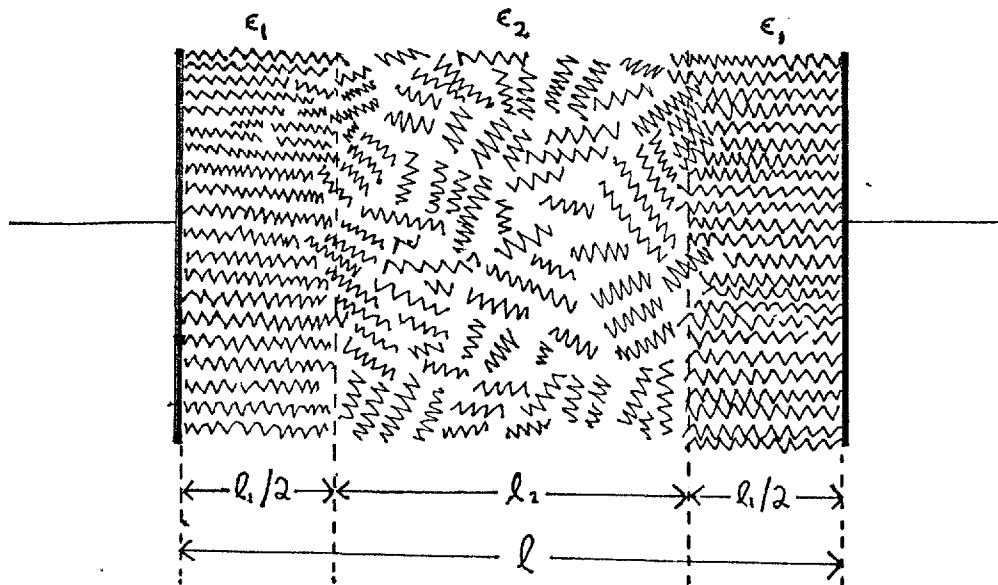
$$\text{or} \quad \epsilon = \frac{\epsilon_1 \epsilon_2 \ell}{\epsilon_2 \ell_1 + \epsilon_1 \ell_2} \quad (4.59.)$$

where $\ell = \ell_1 + \ell_2$

Rearranging (4.59) gives

$$\ell_1 = (\epsilon_1 / \epsilon) \left(\frac{\epsilon_2 - \epsilon}{\epsilon_2 - \epsilon_1} \right) \ell \quad (4.60.)$$

using eqn. (4.60) the effective depth of penetration of the oriented surface layer, $\ell_1/2$, can be calculated from the assumed values of



$$C = \frac{C_1 C_2}{C_1 + C_2}$$

$$\epsilon_r = \frac{\epsilon_1 \epsilon_2 l}{\epsilon_1 l_2 + \epsilon_2 l_1}$$

Figure 4.12. Model of hindered dipole rotation effect.

70 In view of the improbably large values of thickness of the oriented layers (up to $4\mu\text{m}$) it is unfortunate that measurements of permittivity were not made at greater thicknesses using the optical wedge cell, to check whether the measured values approach the accepted bulk values at higher thicknesses. The values of permittivity measured for non-polar liquids such as heptane agree with bulk values, however the presence of hindered rotation must remain speculative.

ϵ_1 and ϵ_2 , and the observed values of ϵ . The results of this calculation are given in Table 8. The predicted values of the effective length over which orientation is maintained are rather large, but it must be borne in mind that the model used is extremely simple. One can also calculate the percentage of oriented material in the liquid layer, and this is plotted as a function of thickness in Fig.4.13. In the cases of aluminium and silver electrodes the percentage of oriented material is reasonably constant for thicknesses greater than $10\mu\text{m}$, but shows a marked change between 5 and $10\mu\text{m}$. For gold electrodes the change in the percentage of oriented liquid occurs between 10 and $15\mu\text{m}$, while for thicknesses greater than $15\mu\text{m}$ the curve seems to be levelling off at a value comparable with that obtained in the case of aluminium and silver.

A more realistic qualitative description may be given as follows. An oriented layer is again assumed to exist on the electrodes with a value of permittivity approximately equal to ϵ_∞ (≈ 3.3 at room temp.) for the orientation relaxation. However, a more realistic size for the layer is assumed to be, say, some tens of Angstrom units. A second layer of molecules can then form on the first, but the molecules in this layer can rotate a little, and therefore have a higher permittivity than the first layer. This can be envisaged as repeating until the bulk permittivity is reached. For such a model there will be a smooth transition from the lowest value of permittivity up to bulk values and the overall permittivity of such a system would be still less than the bulk value.

4.13. Summary.

Despite the approximations made in the a.c. single mobile carrier theory it accounts very well for the observed phenomena. The experimental curves of permittivity and loss factor versus

TABLE 8.

Effective Length of Adsorbed, Oriented Layer in n - Heptanol.

a) Aluminium electrodes, temperature 25°C, purified liquid.

Specimen Thickness l (μm)	ϵ_{∞}	$l_1/2$ (μm)
3.3	7	0.45
5.5	7	0.75
11.8	6.5	1.9
16.2	6	3.1
18.3	6	3.5

b) Aluminium electrodes, temperature 20°C, impure liquid.

Specimen Thickness l (μm)	ϵ_{∞}	$l_1/2$ (μm)
1.1	9.3	0.061
3.0	9.2	0.17
4.9	8.4	0.40
6.8	7.5	0.78
8.7	6.3	1.5

c) Silver electrodes, temperature 24°C.

Specimen Thickness l (μm)	ϵ_{∞}	$l_1/2$ (μm)
4.29	7	0.58
7.20	6	1.4
11.5	6	2.2
13.4	6	2.5
17.5	6	3.3

TABLE 8 (continued)

d) Silver electrodes, specimen thickness $4.29\mu\text{m}$.

Temperature $^{\circ}\text{C}$	ϵ_{∞}	$l_1/2$ (μm)
+23	7	0.56
+ 6	8.25	0.42
-11	9.11	0.36
-18	9.8	0.32
-28	10.0	0.32

e) Gold electrodes, temperature 26°C .

Specimen Thickness $l(\mu\text{m})$	ϵ_{∞}	$l_1/2$ (μm)
1.0	8	0.095
5.0	8	0.48
6.9	8	0.66
9.0	8	0.86
13.2	7.4	1.6
15.0	5.9	3.0
18.8	5.5	4.2

Curve (1) - Aluminium electrodes, purified liquid.

Curve (2) - Aluminium electrodes, impure liquid.

Curve (3) - Silver electrodes, purified liquid.

Curve (4) - Gold electrodes, purified liquid.

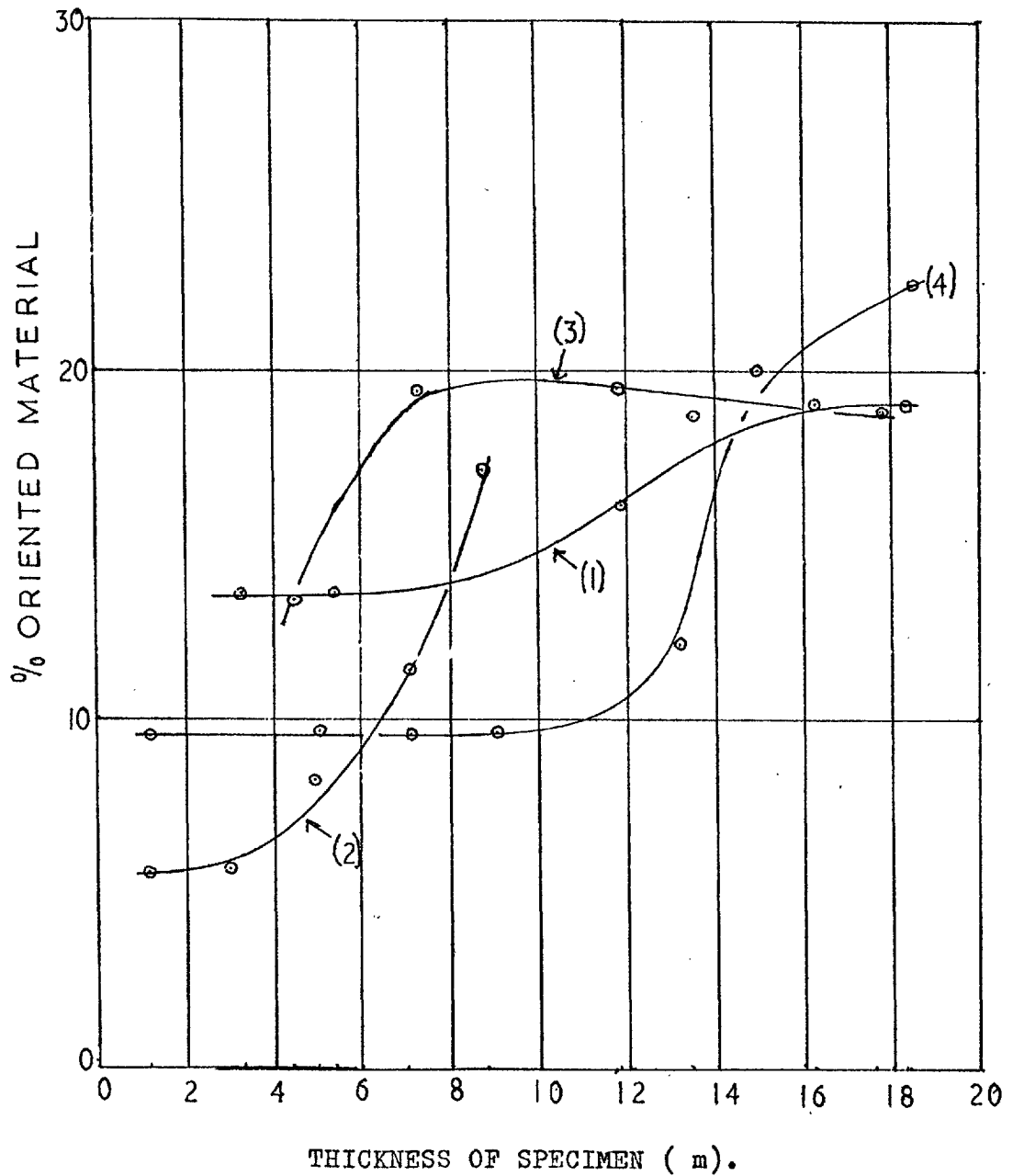


Figure 4.13. % of oriented material as a function of specimen thickness.

thickness can be described, with a high degree of accuracy, by a Debye relaxation as predicted by equations (4.26). The parameters describing the relaxation, $\epsilon_s, \epsilon_\infty$ and τ' may be used to calculate the impurity concentration and mobility. "Garton" effect measurements for specimens with aluminium electrodes also give values of carrier concentration and mobility which are in approximate agreement with those obtained from the single mobile carrier theory. The mobilities and carrier concentrations calculated from the single mobile carrier theory are different for different thicknesses. The variations in carrier concentration probably result from contamination of the liquid by the material of the measuring cell (notably the glass optical flats). The likely explanation of mobility variations arises from the existence of an oriented layer adsorbed on the electrodes.

An electron injection theory, due to I.H. Brockman¹⁸, is also presented. However it has been shown in earlier sections of this chapter that electron emission from the electrodes is insufficient to explain the conduction currents obtained with the fields used. The d.c. curves indicate that electronic conduction^c is possible but in the a.c. case this will be swamped by the ionic conduction. Also Brockman's equations are cumbersome and calculation of mobility and carrier concentration involves curve fitting with these as arbitrary constants. Furthermore for this electron injection theory, as presented, it is necessary to have a liquid which forms an oriented layer on the surface of the electrodes, while the single mobile carrier theory is applicable to any liquid containing ionized impurities, as all liquids inevitably do to some extent. The fact that little variation of permittivity with thickness is observed for liquids such as Aroclor, heptane and chloroheptane (Fig.3.3) means, in terms of the single mobile carrier theory, that the mobility and carrier concentration were such that

the relaxation was simply not observed. If one plots permittivity against thickness for heptanol at high enough frequency, then little variation is observed.

The lowering of permittivity below bulk values, observed at high frequencies is qualitatively explained in terms of hindered dipole rotation. The existence of hydrogen-bonding in heptanol results in the possibility of an adsorbed layer of molecules in which the orientation polarization is suppressed, i.e. the permittivity is lowered with respect to the bulk of the liquid layer.

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CHAPTER 5.

Conclusions.

5.1. Conclusions.

The main conclusions to be drawn from this research are that the values of permittivity of a thin layer of liquid may either be greater than or less than the value appurtenant to a bulk specimen, depending on conditions.

The enhanced permittivity at low frequencies is attributable to the motion of ionized impurities, whose concentration and mobility determine the dielectric response of the liquid. A complete solution of the conduction-diffusion differential equations is probably not possible in analytical form and the theory presented is a first order approximation. However, the predictions of the approximate solution fit the observed phenomena well. The interpretation of the calculated mobility values is difficult since they appear to be dependent upon thickness. Several ideas are put forward to explain this effect, but on the basis of the evidence available it is not possible to distinguish between them. However, the carrier concentration and mobility, the a.c. conductivity and the Garton effect measurements are all roughly in agreement with one another, indicating that the single mobile carrier theory is a fruitful approach to the problem of conduction in thin layers of insulating liquids.

One of the original aims of this research was to see if measurements of the electrical properties of thin layers of liquids could be used to easily and positively identify various types of contamination. This has not proved possible, but it is encouraging that the single mobile carrier theory, despite its approximate nature, can distinguish easily between liquids containing different levels of impurities.

It has also been shown that care must be taken in interpreting the result of a d.c. conductivity measurement. The relaxation time, τ' , which characterizes the interfacial polarization, may have a value such that a large part of the ion movement has taken place before the current is measured. As a consequence erroneously low values of conductivity can result.

Values of permittivity, less than those appropriate to bulk specimens, have been observed in two of the liquids investigated, namely Aroclor 1242 and n-heptanol. Both of these liquids form hydrogen bonds and a qualitative interpretation of the permittivity values has been advanced, based on the assumption that such molecules can form an adsorbed layer on the surface of the electrodes, in which the permittivity has a lower value than in the bulk of the liquid.

Finally the validity of the electron injection theory, put forward by Brockman, may be commented upon. While not questioning the fact that the analysis is correct, the validity of the theory for the case of a liquid dielectric existing in a thin layer is believed not to be proved. The assumptions made in this theory limit its applicability and although injection of charge carriers has been shown to be possible, the weight of evidence is in favour of a description based on the behaviour of ionizable impurities within the liquid.

5.2. Areas for Further Research.

The a.c. measurements made in this study covered a limited frequency range and the complete relaxation behaviour, which has been attributed to the movement of ionized impurities, has only been resolved for the case of heptanol. In order to test the assertion that any liquid which contains ionic impurities shows this interfacial polarization, the frequency range needs to be

extended to much lower frequencies and thinner films investigated. Very low frequency measurements can give information about the structure of amorphous films.

Further investigation of the Garton effect would be very useful in view of the fact that gold and silver electrodes do not show the effect. As pointed out in Chapter 4, section 11, there is some reason for believing that higher fields are needed for gold and silver electrodes before the peak in the loss tangent curve will be observed. Experiments with gold and silver electrodes need to be performed at higher stresses than those possible in this work. The effects of thickness, frequency and temperature on the stress-dependence of the loss factor should also help to resolve the problem.

There is also the question of reproducibility of the results with different liquid samples. Experiments where the measuring cell is incorporated within a purification system should improve reproducibility since this would give better control over the impurity levels present.

Various experiments could be performed to determine the nature of the carriers responsible for the observed relaxation effect. The weight of evidence is in favour of ionic conduction and there are three experimental methods of distinguishing ionic and electronic charge carriers when activation energy measurements are indeterminate. If the carrier is ionic, the application of a d.c. voltage for a sufficiently long period of time will cause the carriers to accumulate at the electrodes where their presence may be detected by physical methods. Secondly, the large transit time involved in the transport of ions can be detected by applying rectangular voltage pulses and observing the decay in current response. The third method involves observing whether or not the current decays to a steady d.c. level,

after applying a d.c. voltage.

Finally, it would be instructive to investigate the hindered rotation effect more carefully to determine whether or not the effect is a real property of these thin liquid films.

APPENDIX I.

The Wayne-Kerr B221 Universal Bridge.

The Universal Bridge operates on the transformer ratio-arm principle (see Wayne-Kerr Monograph No. 1, The Transformer Ratio-Arm Bridge, Wayne-Kerr Ltd., New Malden, Surrey.) and a brief description of the principle of operation is given here.

With reference to Fig.1 the bridge consists essentially of two transformers T1 and T2 and a set of shunt connected conductance and capacitance standards G_s and B_s . The operation of the bridge is as follows. The primary of T1 is energised by an oscillator at any frequency within the range 50 Hz to 20 KHz and voltages (V_s , V_x) are induced in the secondary windings. These voltages are applied to the standard admittance Y_s ($= G_s + jB_s$) and the unknown admittance Y_x respectively. Currents proportional to the product of these respective voltages and admittance flow into the two primaries of T2.

These currents are given by the equations

$$i_x = V_x Y_x \quad (1)$$

$$i_s = V_s Y_s \quad (2)$$

and flow through the windings of T2 in such directions that the magnetic fields which they induce in its core are in opposition. A voltage proportional to the difference between i_s and i_x is then induced in the secondary of T2 and this voltage is amplified and detected. When the bridge is in balance $i_s = i_x$ and the detector indicates zero voltage. Then from equations (1) and (2)

$$Y_x = Y_s V_s / V_x \quad (3)$$

Tappings on the secondary winding of T1 enable V_s / V_x to be varied, thereby enabling a wide range of values of Y_x to be measured with a single set of standard capacitors and conductors.

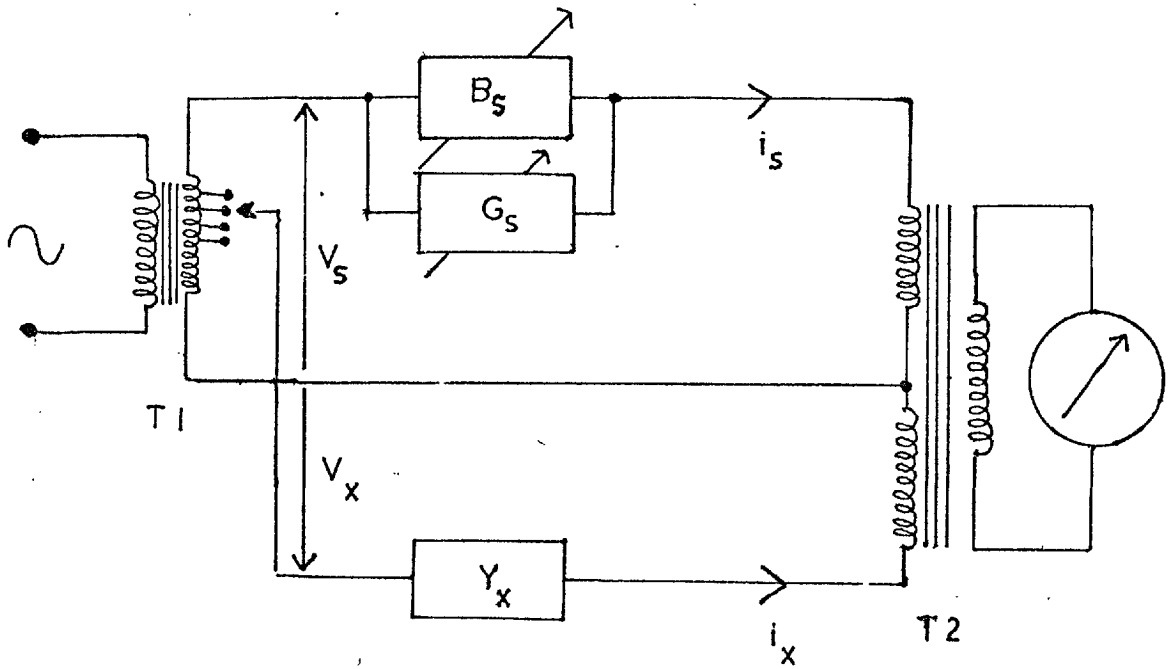


Figure 1. The transformer ratio-arm bridge.

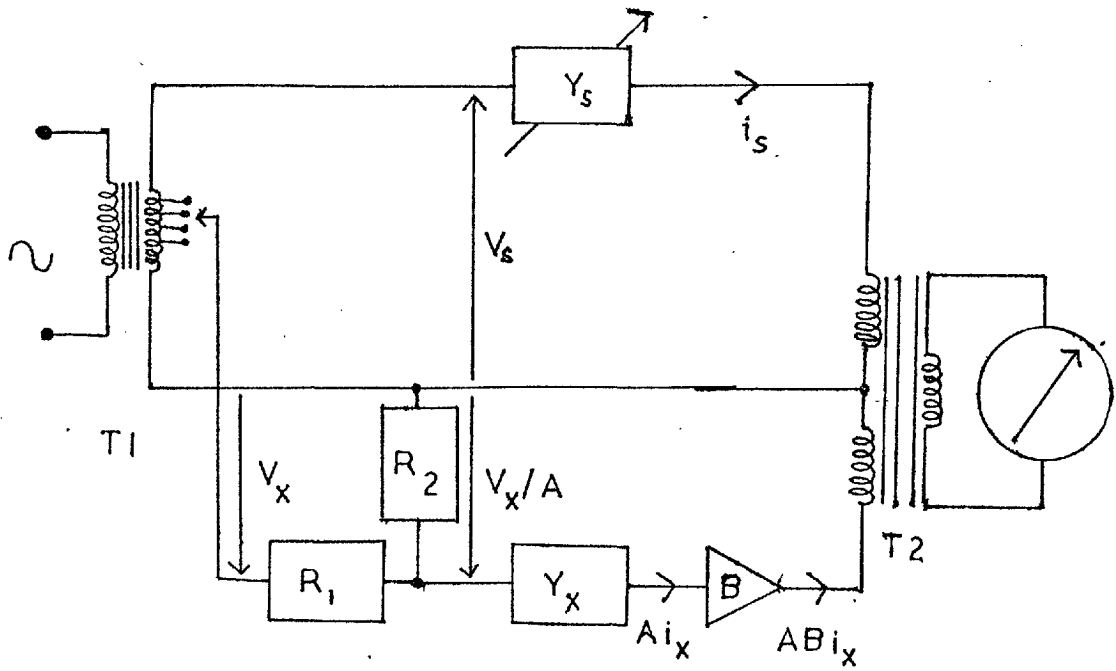


Figure 2. Modified bridge circuit.

In order to avoid problems of breakdown due to too high a value of the voltage (V_x) applied to the sample an attenuator can be inserted between T1 and the unknown admittance (Y_x). The reduced voltage results in a correspondingly reduced current (i_x) flowing through the unknown, and this arrangement alone would result in a false value for the unknown being obtained when balance was achieved. The situation was corrected by inserting a current amplifier between the unknown (Y_x) and T2 which magnified the current (i_x) by the same factor as that by which V_x was reduced. A simplified diagram of the modification is given in Fig.2.

The network R_1, R_2 reduces the voltage across the unknown by a factor $A = (R_2 / (R_1 + R_2))$. This reduced voltage drives a current through the unknown which, if the input impedance of the amplifier is small is $i_x A$

$$\text{i.e. } i_x A = Y_x V_x A \quad (4)$$

The amplifier boosts the input current by a factor B to give the current $i_x AB$ which is fed to one of the Primaries of T2. If A is adjusted to be equal to $1/B$ this current will then become i_x , as in the unmodified case. The modified bridge can then be used in exactly the same manner as the unmodified one, and the unknown admittance can then be measured directly as above.

APPENDIX II.

The Measurement of Film Thickness by Optical Interferometry.

The law governing the formation of interference fringes produced by division of amplitude is usually called the "cosine law". With interference between plane surfaces the effects produced depend upon whether the reflections (or transmissions) arise from a parallel-sided reflecting film of transparent material, or from a film in which the faces are inclined to each other, the latter case usually being called a wedge. In the former case the fringes occur at infinity, but the wedge-fringes are localised.

The cosine law is most easily deduced from the interference effect in the parallel-sided film. Consider parallel rays (Fig.1), A_1 , A meeting the surface B_1 , B of a plane parallel sheet of material of thickness t and refractive index μ . The ray A_1B_1 refracts to C_1 where it reflects to B. At B it meets the ray AB and both travel towards C. The two rays are in a condition to interfere.

From B_1 and B drop respective perpendiculars B_1D and BD_1 . The path difference in the air is BD. In the medium the path length is B_1C_1 plus C_1B . The time taken for B_1 to reach D_1 in the medium is the same as that for D to reach B in air. Thus the path difference Δ is $B_1C_1 + C_1B - B_1D_1$ in the medium. Now produce B_1C_1 its own length to E and join BE. The path difference Δ equals D_1E . As $BE = 2t$ then $D_1E = 2t \cos \theta$ in which θ is the angle of refraction in the medium. In air the equivalent path difference is then $2\mu t \cos \theta$.

Reflection at B will introduce a phase change of π which is equivalent to altering the path length by $\lambda/2$. Since the beams would have reinforced when the retardation is an integral number of waves (if not for the phase change), it follows that when $n\lambda = 2\mu t \cos \theta$ we get interference producing a dark fringe. This is the cosine law.

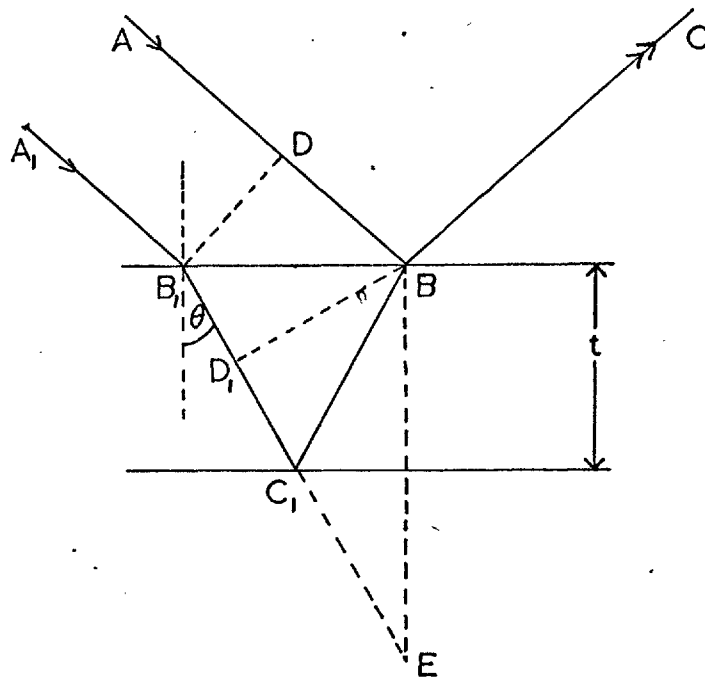


Figure 1.

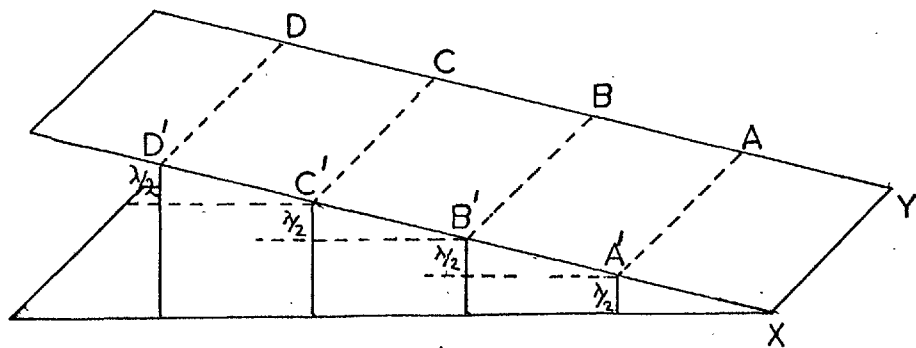


Figure 2.

Bright fringes form for $(n + \frac{1}{2})\lambda = 2\mu t \cos \theta$.

The basic formula $n\lambda = 2\mu t \cos \theta$ contains the possible variables μ, λ, t and θ which determine n , the order of interference. In general, μ cannot easily be varied and in very many experiments it is constant; often it can be taken as unity. This leaves λ, t and θ as the frequent variables, and on this basis a classification of fringes can be made as follows:

Nature of light	Constant quality	Fringe type	Name
Monochromatic i.e. λ constant	t	Equal inclination	Fabry-Perot
	θ	Equal thickness	Multiple-beam Fizeau
White light i.e. λ variable	θ	Equal t/λ	Equal chromatic order
	t	Equal $(t \cos \theta)/\lambda$	White-light Fabry-Perot

For the work contained in this thesis fringes of equal chromatic order were used to measure the electrode spacing in the mercury squeeze film cell, the micrometer cell and the cells using optically flat discs. All the experimental data was obtained using the optical-wedge form of cell and fringes of equal thickness of the Fizeau type were used to determine the inter-electrode spacings in this cell.

If a wedge of quite small angle is considered, then the basic formula $n\lambda = 2\mu t \cos \theta$ derived for a parallel sided film will still hold closely enough. With such a system the fringes will appear as in Fig. 2, at those positions A,B,C,... on the upper surface at which the wedge thicknesses t are $\lambda/2, 2\lambda/2, 3\lambda/2...$, etc., if for convenience it is assumed that the incidence is normal and μ is unity.

A line such as AA' is the locus of points for which n is constant, since, for such a line parallel to the edge of the wedge XY, t is constant. Thus straight-line fringes are formed and these are called "fringes of equal thickness", for although t varies on moving from Y to D, yet each fringe is a traverse of points for which the wedge thickness is constant. The fringes can be considered as height-contour lines exactly as on a geographical contour map. If either of the two surfaces is irregular, then the fringes will contour the irregularity, each following a path of constant optical thickness of the air film.