THE DIELECTRIC RELAXATION OF POLAR MOLECULES IN SOLUTION, AND ITS RELATION TO MUTUAL VISCOSITY.

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by

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ABSTRACT

A new theory of dielectric relaxation is developed, which relates the relaxation time of a polar solute in a non-polar solvent to the "mutual viscosity" of the polar- non-polar combination. The theory is based on Andrade's theory of viscosity and the "mutual viscosity" η_{AB}, which appears when this theory is extended to the case of a mixture, can be calculated from the relation

$$\eta\sigma = f_A^2\eta_A\sigma_A + f_B^2\eta_B\sigma_B + 2f_Af_B\eta_{AB}\sigma_{AB}$$

where η_A, η_B, η are the viscosities of the pure components, A and B, and the mixture respectively, the σ's are intermolecular distances, and the f's are mole fractions.

This mixture law is tested against experimental results for seven pairs of substances, and is found to represent the variation of viscosity with concentration well, the mean error being 2%, and the maximum error 9%.

The relation between the relaxation time and mutual viscosity is

$$\tau = \frac{1}{2kT}\left\{f_A \cdot 6\,\frac{I_{AB}I_B}{I_{AB}+I_B}\cdot\frac{m_A+m_B}{m_A m_B}\,\eta_{AB}\sigma_{AB} + f_B\,3(3-\sqrt{2})\,\frac{c_B'}{c_B}\,\frac{I_B}{m_B}\,\eta_B\sigma_B\right\}$$

where the I's are moments of inertia, the m's are molecular masses, and $\frac{c_B'}{c_B}$ is independent of concentration and does not differ much from unity. This relation is tested against existing results, and further measurements made to supply the deficiencies in these, and is found to be in closer agreement with experiment than the Debye relation, both for pure polar liquids and for polar molecules in solution.

CONTENTS

1. INTRODUCTION

When a non-conductor is placed between the plates of a charged condenser, it reduces the potential difference between them. This effect is characterized by the dielectric constant of the substance and is attributed to the re-distribution of the charges in the substance (polarisation) by the action of the electric field between the plates. This commonly occurs in two ways; firstly by the redistribution of electric charges within the molecules or atoms, producing an electric moment in the direction of the external field (distortion polarisation), secondly by the orientation of permanent molecular moments, which in the absence of the external field have a random orientation and so produce no resultant moment (orientation polarisation) (Debye "Polar Molecules"). If the external field does not alternate with too high a frequency, the first effect is always present. Substances whose molecules possess permanent electric moments also exhibit the second effect, again provided the frequency is not too high. Such substances are characterised by high dielectric constants (e.g., chloroform 4.7, water 79.5, compared with the non-polar substance benzene 2.27). As the frequency of the external field is increased, a point is reached beyond which it is not possible for the polar molecules to alternate in phase with the field owing to the resistance to their motion produced by the surrounding molecules. The molecular moments lag behind the field with a consequent absorption of energy and reduction of the dielectric constant. At sufficiently high frequencies, the orientation polarisation vanishes, and when optical frequencies are reached only the distortion polarisation remains. For this reason the distortion polarisation is also called the "optical polarisation".

The polarisability (α) of a molecule is defined as the average over a sufficient length of time of the electric moment acquired per unit applied field. In the case of a polar molecule this is made up of two parts; the polarisability due to distortion (α_0), and that due to orientation. Debye has shown that the average moment in the direction of the field, due to the orientation of the permanent moment (μ) of a molecule is

$$\overline{m} = \mu^2 \overline{F} / 3kT$$

in a steady orientating field F which is small so that $\mu F / kT < 1$, k being Boltzmann's constant, and T the absolute temperature. The total polarisability is then

$$\alpha = \alpha_0 + \mu^2 / 3kT.$$

Debye also calculated (following the method of Einstein's theory of the Brownian movement) the average moment in the direction of the field produced by the orientation of a polar molecule in an alternating field, $F = F_0 e^{j\omega t}$,

$$\overline{m} = \frac{1}{1+j\omega\tau} \cdot \mu^2 / 3kT \cdot \overline{F}$$

$$\alpha = \alpha_0 + \frac{1}{1+j\omega\tau} \, \mu^2 / 3kT$$

where τ is the relaxation time of the molecule, that is, the time taken for the average moment to fall by a factor of $\frac{1}{e}$ when the orienting field is removed. The calculation is based on the assumption that a molecule rotating with an angular velocity $\frac{d\theta}{dt}$ experiences a torque

$$M = \zeta \frac{d\theta}{dt}$$

due to the surrounding molecules, where ζ is a constant measuring the "inner friction", and

$$\tau = \frac{\zeta}{2kT}$$

An investigation of the behaviour of polar substances at frequencies at which the dielectric constant is falling from its static value to its optical value will yield information about the forces which are exerted on a rotating molecule by its neighbours. Conversely, knowledge of the forces of inner friction will allow the calculation of the relaxation time and therefore of the range of frequencies in which anomalous dispersion will occur. Debye calculated the order of magnitude of the relaxation time by assuming that the rotating molecule may be regarded as a sphere of molecular dimensions, (radius a) rotating in a viscous medium which has the viscosity of the substance in bulk; that is

$$\zeta = 8\pi\eta a^3$$

From this he calculated that for water

$$\tau = 0.25 . 10^{-10} \text{ sec.}$$

so that anomalous dispersion is to be expected at frequencies in the neighbourhood of

$$\omega_0 = \frac{1}{0.25} . 10^{10} \text{ sec.}^{-1}$$

i.e., at centimetre wave-lengths.

It is thus to be expected that many liquids will show anomalous dispersion in the micro-wave region of the spectrum.

RELATION BETWEEN THE DIELECTRIC CONSTANT AND THE POLARISABILITY.

Actual measurements do not yield the polarisability directly. The quantities measured are related to the real and imaginary parts of the dielectric constant (which is complex in the region of anomalous dispersion because the polarisation is out of phase with the field). To find the polarisability in terms of the dielectric constant it is necessary to make some simplifying assumption which will allow the field experienced by a molecule to be calculated in terms of the external field and the bulk properties of the dielectric.

Debye's method was to imagine a sphere drawn in the substance about a particular molecule, the radius of the sphere being small compared with macroscopic measurements but large compared with molecular dimensions. The field acting on the molecule was considered to consist of three components; the external field, the additional field due to the presence of the material outside the small sphere, and the field due to the presence of the material in the sphere. He then made the further assumption that the third component is zero, and so found that

$$F = E + \frac{4\pi I}{3}$$

F being the field acting on the molecule, E the external field and I the polarisation of the medium. The polarisation is the electric moment per unit volume produced by the field. If there are n molecules per unit volume

$$I = n\alpha F$$

Since the dielectric constant is

$$\epsilon = 1 + 4\pi \frac{I}{E},$$

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi n\alpha}{3}$$

$$\frac{\epsilon - 1}{\epsilon + 2}\,\frac{M}{\rho} = \frac{4\pi N\alpha}{3}$$

where M is the molecular weight and ρ the density of the substance, and N is Avogadro's number.

This argument does not take into account the effect of the dipole under consideration on the surrounding medium, except in so far as the bulk properties of the medium are determined by the averaged effect of all such dipoles.

Onsager[2] has calculated the relation between the bulk properties and the polarisability in a slightly different way. He considers the central dipole as being in a spherical hole of molecular radius in a medium which has the bulk properties of the substance, and calculates the field at the dipole in two parts; firstly the field in the cavity due to an external field, in the absence of the central dipole, and secondly the field due to the polarisation of the walls of the cavity by the central dipole. The moment of the dipole is determined by its permanent moment and the moment induced in it by the field in the cavity.

In this way, Onsager finds for the polarisation

$$\bar{I} = N\left\{\frac{\mu_0^2}{3kT}\,\frac{(n^2+2)^2(2\epsilon+1)}{3(2\epsilon+n^2)^2}\,\epsilon + \frac{\epsilon(n^2+2)\alpha}{2\epsilon+n^2}\right\}\bar{E}$$

where ϵ is the dielectric constant of the bulk material and n is the "internal refractive index" of the polar molecule, defined in terms of the optical polarisability α_0 by

$$\alpha_0 = \frac{n^2-1}{n^2+2}\,a^3$$

a being the radius of the molecule.

As Fröhlich[3] has pointed out, Debye's theory, which neglects the effect of the central molecule on the surrounding medium, is equivalent to supposing that the thermal motion of the central molecule is so rapid that the polarisation of the surrounding medium cannot follow it, while Onsager's is equivalent to assuming that the motion is sufficiently slow that the polarisation can always follow. This is interesting because it will be shown subsequently (Chap. 3) that the relaxation time of a polar molecule is intimately related to the frequency with which it collides with its neighbours, that is, the frequency with which it changes its direction due to thermal motion. In fact

$$\tau = \frac{A\nu}{kT}$$

where ν is the frequency of vibration of the molecule about its mean position and A has the dimensions of a moment of inertia and is of the order of magnitude of the product of the molecular mass and the square of the molecular radius, i.e. $10^{-22} \times 10^{-16}$ gm. cm.^2

$$\tau \sim 10^{-24}\nu$$

The relaxation time increases as the frequency of vibration increases, so that Debye's theory should give the best representation for substances with high relaxation times (that is, high viscosity) for which the heat motion is rapid and the relaxation time long, while Onsager's should give the best representation for substances with low viscosity. The dividing line between the two cases may be drawn where

$$\nu = \frac{1}{\tau} = 10^{12}\ \text{sec.}^{-1}$$

The viscosity of such a substance is

$$\eta \sim 10^{-2}\ \text{poise.}$$

Thus water, with a viscosity of about one centipoise at room temperature, is an intermediate case between the two extremes represented by the theories of Debye and Onsager. (This argument does not apply to substances consisting of long chain molecules since these cannot be represented by the simple model on which the theory is based).

DIELECTRIC CONSTANT OF A SOLUTION OF A POLAR SUBSTANCE IN A NON POLAR SOLVENT.

The assumption made in Debye's theory, that the field due to the material in a small sphere round the central molecule is zero, is more likely to be justified in a dilute solution of a polar substance in a non-polar solvent, than in a pure polar liquid. The same is true of Onsager's assumption that the dielectric outside the small sphere can be regarded as homogeneous. If f_A and f_B are the mole fractions of the non-polar and polar components in such a solution Debye's theory shows that

$$\frac{\epsilon-1}{\epsilon+2}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left\{f_A\alpha_A + f_B\left(\alpha_B + \frac{1}{1+j\omega\tau_B}\,\frac{\mu_B^2}{3kT}\right)\right\}$$

where the symbols without suffix refer to the solution and

$$M = f_A M_A + f_B M_B$$

Onsager's theory gives

$$\frac{M}{\rho}(\epsilon-1) = \frac{4\pi N}{3}\left\{\frac{f_A\epsilon(n_A^2+2)\alpha_A}{2\epsilon+n_A^2} + \frac{f_B\epsilon(n_B^2+2)\alpha_B}{2\epsilon+n_B^2} + \frac{f_B^2(n_B^2+2)(2\epsilon+1)\epsilon}{3(2\epsilon+n_B^2)}\,\frac{1}{1+j\omega\tau}\,\frac{\mu_B^2}{3kT}\right\}$$

If $f_B \ll f_A$, and $\epsilon_A \gg \epsilon-\epsilon_A$, so that $n_A^2 = \epsilon$ this reduces to

$$\frac{\epsilon-1}{\epsilon-2}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left\{f_A\alpha_A + f_B\alpha_B + f_B\left[\frac{(2\epsilon+1)(\epsilon+2)}{9\epsilon}\right]\frac{1}{1+j\omega\tau}\,\frac{\mu_B^2}{3kT}\right\}$$
$$(n_A = n_B)$$

If ϵ is about 2, the term in square brackets is $\frac{20}{18}$, so that for dilute solutions the two theories lead to very similar results. In the present case Debye's theory has been used because of its greater simplicity. Other theories[4] which have been put forward in an attempt to produce a more rigorous argument, necessarily contain terms which depend on the structure of the liquid, and cannot be applied without making some further assumptions.

In the region of anomalous dispersion the dielectric constant of a solution containing polar molecules is complex. If

$$\epsilon = \epsilon' - j\epsilon''$$

and ϵ''^2 can be neglected compared with ϵ'^2, Debye's theory gives

$$\frac{\epsilon'-1}{\epsilon'+2}\frac{M}{\rho} = \frac{4\pi N}{3}\left\{f_A\alpha_A + f_B\left(\alpha_B + \frac{\mu_B^2}{3kT}\frac{1}{1+\omega^2\tau^2}\right)\right\}$$

and

$$\frac{3\epsilon''}{(\epsilon'+2)^2}\frac{M}{\rho} = \frac{4\pi N}{3} f_B \frac{\omega\tau}{1+\omega^2\tau^2}\frac{\mu^2}{3kT}$$

THE INTERPRETATION OF τ.

Debye[1] suggested that the relaxation of a pure polar liquid might be estimated by regarding the polar molecule as a sphere rotating in a viscous medium, so that

$$\tau = \frac{4\pi\eta a^3}{kT}$$

where η is the macroscopic viscosity of the liquid, and a is the radius of the molecule. This has been generalised by Girard and Abadie[5] to the case of an ellipsoidal molecule, for which more than one relaxation time is possible.

Experimental results of Conner and Smyth,[6] and Hennelly, Heston Jr. and Smyth[7] show that for approximately spherical molecules, the electrical properties of a liquid can be interpreted in terms of a single relaxation time, and that the relaxation time and macroscopic viscosity vary in a similar manner with temperature and molecular size. There is also a close similarity in the behaviour of the activation energies, free energies and entropies of dielectric relaxation and viscosity regarded as rate processes. The quantitative agreement between theory and experiment is not so close, for the molar volume calculated from

$$V_D = \frac{4\pi}{3}Na^3 = \frac{\tau RT}{3\eta}$$

is only about 10-20% of the molar volume calculated from the molecular weight and density; that is, the measured relaxation time is lower by a factor of 5-10 than that predicted by the theory.

Zienau[8] (1950) suggested that the observed relaxation times might be produced by the simultaneous operation of two relaxation processes - the Debye process described above, and the process described by Frölich and Sack,[9] in which the dipole jumps from one equilibrium position to another. The experimentally observed relaxation time (τ) is then given by

$$\frac{1}{\tau} = \frac{1}{\tau_D} + 2\omega_0$$

where τ_D is the Debye relaxation time, and $2\omega_0$ represents the contribution of Frölich and Sack's process, and has to account for 80% of $\frac{1}{\tau}$.

This argument is unsatisfactory because it combines two distinct and independent models. Also Frölich and Sack's model is only applicable to liquids with high viscosity, whereas the discrepancy between τ and τ_D occurs also in low-viscosity liquids.

The assumptions upon which the Debye equations of anomalous dispersion are based are not really justified in a pure polar liquid. For this reason many authors (10-13) have studied the behaviour of polar molecules in dilute solution in non-polar solvents. To interpret the results they have used the Debye relation, replacing the viscosity of the pure polar liquid by that of the solution or solvent. The experimental results again show a general agreement with theory. When low viscosity solvents are used, approximately spherical molecules show single relaxation times which vary in the expected manner with the size of the solute molecule. The variations of relaxation time and viscosity with temperature again show similar forms, and the activation energies are similar, that for dielectric relaxation being in general slightly smaller than that for viscous flow. As in the pure liquid the molar volume calculated from the relaxation time is generally too small by a factor of about 10.

The relaxation time in the solution is nearly always lower than that in the pure polar liquid. Observations on one solute in different solvents show that the relaxation time is certainly not determined by the viscosity of the solvent alone. The table below shows values obtained by Curtis, McGreer, Rathmann and Smyth[13] for the relaxation times of various solutes in carbon tetrachloride and in cyclohexane, which has practically the same viscosity.

Solute	Critical wavelength (cm.)		Relaxation time $\times 10^{12}$ sec.	
	in C_6H_{12} $\eta=0.97$	in CCl_4 $\eta=0.97$	in C_6H_{12}	in CCl_4
C_4H_9Cl	0.3	0.65	1.59	3.44
$CHCl_3$	0.6	0.94	3.18	4.97
$C_6H_5NO_2$	1.8	2.9	9.55	15.35

(Temperature 20°C)

The relaxation times are in all cases higher in the carbon tetrachloride. Hall, Halliday, Johnson and Walker,[12] using nitrobenzene in mixtures of carbon tetrachloride, benzene, carbon disulphide and hexane with medicinal paraffin, observed a similar effect, the maximum absorption occurring at different points of the viscosity scale for each pair of solvents.

Both authors suggest that a modification of the theory which takes into account the polarisability of the solvent molecule is necessary.

When highly viscous solvents are used, the discrepancy between theory and experiment becomes more marked. Increases in the viscosity by factors of several hundred being accompanied by increases of only three to twenty in the relaxation times.(10,11,13)

If one regards the process of relaxation from a microscopic point of view, the origin of these discrepancies appears, for the use of the viscosity to calculate the relaxation time in the case of a solution is open to an objection which cannot be raised against Debye's calculation for a pure polar liquid. In a pure liquid every molecule is surrounded by molecules of the same kind, and the interaction between these molecules determines both the viscosity and the relaxation time, so that, regardless of the particular argument by which a relation between the two quantities is found, it is to be expected that they will vary in a similar manner from one substance to another. But in the case of a polar solute in a non-polar solvent, the relaxation time is determined by the interaction between solvent and solute molecules, while the viscosity of the solution is determined almost entirely by the interactions between the solvent molecules. If the solvent is a mixture of two non-polar liquids a similar argument applies, the interactions which determine the viscosity being distinct from those which determine the relaxation time.

The interaction between solvent and solute molecules which determines the relaxation time does influence the viscosity of the solution as the concentration of the solute is increased, and the object of the present work is to find the connection between the variation of viscosity of a non-polar polar mixture with concentration, and the relaxation time of the polar substance when in dilute solution in the non-polar solvent.

2. THE VISCOSITY OF A MIXTURE

In order to obtain a more accurate relation between dielectric relaxation and viscous flow, it is necessary to consider more closely the interactions which determine the viscous and "inner friction" forces in a liquid, particularly in a mixture.

Theories of the viscosity of a liquid fall into two main classes: those based on simple transfer of momentum by collision e.g., van der Waals Jr.[14] (1918), Andrade[15] (1934), and van Wijk and Seeders[16] (1937); and those based on the change in the inter-molecular forces caused by the relative motion of two layers, e.g., Burgers[17] (1938), based on Prandtl's model of a liquid, and Born and Green[18] (1947). Of the two approaches, the first lends itself more readily to the calculation of the inner friction, and the model used by Andrade has been adopted here.

ANDRADE'S THEORY OF VISCOSITY

According to Andrade's theory, the molecules of a liquid can be regarded as vibrating with a certain frequency about equilibrium positions which change only slowly with time. The transfer of momentum which occurs in a viscous liquid between layers moving with different velocities is due to temporary unions (collisions) of adjacent molecules which occur at the extremes of each swing, so that for an infinitesmal time the two molecules move as one.

Suppose there is a velocity gradient in the z direction in a liquid, and consider the transfer of momentum between and x-y plane (1) which is moving with velocity v, and an adjacent parallel plane (2) which is moving with velocity $(v + dv)$. If approximately one-third of the molecules are supposed to be vibrating in the z-direction, the number of temporary unions per second which cause momentum transfer between the planes (1) and (2) is

$$\frac{1}{3}\, 2 \cdot v \left(\frac{1}{\sigma}\right)^2 \quad \text{per unit area}$$

where σ is the mean distance between adjacent molecules, so that the number of molecules per unit area is $\left(\frac{1}{\sigma}\right)^2$. The momentum lost by plane (2) and gained by plane (1) at each collision is

$$\frac{m\,dv}{2}$$

where m is the mass of a molecule. The total momentum transferred from plane (2) to plane (1) per second per unit area is

$$\frac{1}{3} v m \left(\frac{1}{\sigma}\right)^2 dv$$

This is equal to the shearing force between the layers

$$F = \frac{1}{3} \frac{vm}{\sigma^2}\, dv$$

The viscosity is defined by the equation

$$F = \eta \frac{dv}{dx}$$

$$= \eta \frac{dv}{\sigma} \text{ in this case}$$

Therefore $$\eta = \frac{1}{3} \frac{vm}{\sigma}$$

This equation involves the assumption that a collision takes place every time a molecule arrives at its extreme position. If we write instead

$$\eta = \frac{c}{3} \frac{vm}{\sigma}$$

c is the probability of such a collision and varies as $e^{-\frac{E}{kT}}$, where E is the mutual potential energy of the molecules, k is Boltzmann's constant, and T is the absolute temperature.

EXTENSION OF THE THEORY TO A MIXTURE OF TWO LIQUIDS

The relaxation time of a polar molecule (B) in a non-polar solvent (A), depends on the transfer of momentum between a molecule A and a molecule B. This type of momentum transfer will also influence the viscosity of a mixture of the two liquids, therefore it is of interest to extend the above theory to the case of a mixture.

In this case the transfer of momentum is due to three different types of collision, which can be represented by AA, BB and AB respectively. The first type will occur

$$\frac{1}{3} c_A f_A^2 \cdot 2 v_A \frac{1}{(\sigma_m)^2}$$

times per second, and cause a momentum transfer

$$m_A \frac{dv}{2}$$

each time, thus contributing a shearing force

$$f_A^2 \frac{c_A}{3} \frac{v_A m_A}{\sigma_m}$$

where f_A is the mole fraction of the component in the mixture and symbols with suffix A refer to molecules of substance A, symbols with suffix m, to the mixture.

Similarly, the second type of collision contributes a shearing force

$$f_B^2 \frac{c_B}{3} \frac{v_B m_B}{\sigma_m}$$

The third type of collision occurs

$$2 f_A f_B \frac{c_{AB}}{3} \frac{v_A + v_B}{\sigma_m^2}$$

times per second, and causes a momentum transfer

$$\frac{m_A m_B \, dv}{m_A + m_B}$$

each time, thus contributing a shearing force

$$2 f_A f_B \frac{c_{AB}}{3} \frac{m_A m_B}{m_A + m_B} \frac{v_A + v_B}{\sigma_m^2} \, dv$$

The total shearing force is

$$\left(f_A^2 \frac{c_A}{3} \frac{m_A v_A}{\sigma_m^2} + f_B^2 \frac{c_B}{3} \frac{m_B v_B}{\sigma_m^2} + 2 f_A f_B \frac{c_{AB}}{3} \frac{m_A m_B}{m_A + m_B} \cdot \frac{v_A + v_B}{\sigma_m^2} \right) dv$$

and the viscosity is

$$\eta_m = f_A^2 \eta_A \frac{\sigma_A}{\sigma_m} + f_B^2 \eta_B \frac{\sigma_B}{\sigma_m} + 2 f_A f_B \eta_{AB} \frac{\sigma_{AB}}{\sigma_m} \qquad 2.1$$

where η_A and η_B are the viscosities of the pure liquids A and B and η_{AB}, the "mutual viscosity" is defined by

$$\eta_{AB} = \frac{C_{AB}}{3} \frac{m_A m_B}{m_A + m_B} \frac{r_A + r_B}{\sigma_{AB}}$$

being the mean distance between a molecule of type A and an adjacent molecule of type B in the mixture.

COMPARISON WITH EXPERIMENTAL DATA

A good summary of the types of viscosity-concentration curve which are found experimentally, and the relations which have been suggested to account for them, is given by Jaeger[19] in the Second Report on Viscosity and Plasticity, Amsterdam, 1938.

The experimental curves fall mostly into three classes:-

1. Those which sag below the straight line $\eta = f_A \eta_A + f_B \eta_B$. This is the most common type.
2. Those which rise above the straight line. η may become greater than both η_A and η_B.
3. Those which exhibit a point of inflexion. These are relatively uncommon and in many of the reported cases (e.g., the ether-chloroform mixture quoted by Jaeger) the appearance of the point of inflexion is due to the viscosity being plotted against the weight or volume rather than the molar concentration.

The empirical relations which have been proposed are:-

1. $\eta = f_A \eta_A + f_B \eta_B$
2. $\log \eta = f_A \log \eta_A + f_B \log \eta_B$ (Arrhenius, 1887)
3. $\frac{1}{\eta} = f_A \frac{1}{\eta_A} + f_B \frac{1}{\eta_B}$ (Bingham, 1922)

4. $$\eta^{\frac{1}{3}} = f_A \eta_A^{\frac{1}{3}} + f_B \eta_B^{\frac{1}{3}}$$ (Kendall and Monroe, 1917)

None of these relations is capable of predicting cases 2 and 3 above.

There are also a number of relations based on empirical formulae for the viscosity, e.g.

McLeod[20] $$\eta = f_A \eta_A \frac{x_A}{x} + f_B \eta_B \frac{x_B}{x}$$

(x_A, x_B, x are the free spaces of the pure components and mixture)

Kottler[21] $$\phi = \frac{f_A C_A \phi_A + f_B C_B \phi_B + \Delta V}{(C_A)^{f_A} (C_B)^{f_B} (C_{AB})^{f_A f_B}}$$

where ϕ is the reciprocal of the viscosity, C is the constant of Batschinski's[22] empirical relation, on which the relation is based and has the form $e^{F/RT}$, and ΔV is the change of volume on mixing.

Lima[23] $$\log \log \eta = \frac{(f_A I_A + f_B I_B)(d-k)}{f_A M_A + f_B M_B}$$

where I is Souders'[24] viscosity constant, a constitutive property for any group of atoms, and is additive in compounds, d is the density and k is a constant independent of concentration and temperature. Souders' formula is

$$\log_{10}(\log_{10} \eta) = \frac{I}{M} d - 2.9$$

M being the molecular weight.

The number of relations which have a theoretical basis is much smaller. Stuart[25] (1948) proposed a formula derived from van Wijk and Seeders' theory of viscosity. In the notation used above this is

$$\eta = C_A^2 \eta_A \frac{\rho_m^2}{\rho_A^2} + C_B^2 \eta_B \frac{\rho_m^2}{\rho_B^2} + 2 C_A C_B \eta_{AB}$$

where C_A, C_B are the weight concentrations of the two components and the ρ's are densities. On converting to mole concentrations this becomes

$$\eta = f_A^2 \eta_A \left(\frac{\sigma_A}{\sigma_m}\right)^6 + f_B^2 \eta_B \left(\frac{\sigma_B}{\sigma_m}\right)^6 + 2 f_A f_B \left(\frac{\sigma_A}{\sigma_m}\right)^3 \left(\frac{\sigma_B}{\sigma_m}\right)^3 \frac{\rho_A \rho_B}{\rho_e^2} \eta_{AB} \qquad 2.2$$

The η_{AB} of Stuart's relation is not, of course, defined in the same way as the η_{AB} in the theory above, but it has a similar significance.

Yang[26] (1949), applying the kinetic theory of simple liquids developed by Born and Green to the case of a mixture, also derives an expression containing three terms, the third term taking into account the interaction between molecules of different kinds. Yang himself abandons the task of numerical calculation from the formula, but since Born and Green's equation for the viscosity of a pure liquid reduces to an equation very similar to Andrade's, if certain assumptions are made, it seems probable that in similar circumstances Yang's formula will tend to equation 2·1 above.

Balaz[27] (1951), using as a model structureless particles moving in a periodic field of force, obtained

$$\log\eta = f_A \log\eta_A + f_B \log\eta_B - \beta f_A f_B \frac{\omega_{AB}}{kT} \qquad 2.3$$

where β is a fraction which is the same for pure liquids and mixtures, and ω_{AB} is an energy term which becomes zero for perfect solutions. For such solutions the equation becomes

$$\log\eta = f_A \log\eta_A + f_B \log\eta_B$$

which is the same as the empirical relation proposed by Arrhenius.

In the tables below, these three relations

1. $\eta = f_A^2\eta_A\frac{\sigma_A}{\sigma_m} + f_B^2\eta_B\frac{\sigma_B}{\sigma_m} + 2f_Af_B\frac{\sigma_{AB}}{\sigma_m}$
2. $\eta = f_A^2\eta_A\left(\frac{\sigma_A}{\sigma_m}\right)^6 + f_B^2\eta_B\left(\frac{\sigma_B}{\sigma_m}\right)^6 + 2f_Af_B\frac{\rho_A\rho_B}{\rho_r^{*}}\eta_{AB}\left(\frac{\sigma_A}{\sigma_m}\right)^2\left(\frac{\sigma_B}{\sigma_m}\right)^2$ (Stuart)
3. $\log\eta = f_A\log\eta_A + f_B\log\eta_B - \beta f_Af_B\frac{\omega_{AB}}{kT}$ (Balaz)

are compared with experimental values taken from the International Critical Tables. σ is calculated from

$$\sigma = \sqrt[3]{\frac{M}{N\rho}}$$

where M and ρ are the molecular weight and density of the mixture. The choice of pairs of substances for this purpose is based on the following considerations: the molecules involved must be compact, so that the assumption of rigid molecules is justifiable; pairs in which both large and small ranges of η and of ρ occur should be included; and all types of viscosity curve should be represented. In each relation there is an unknown parameter ($\eta_{AB}\sigma_{AB}$ in the first, $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2}$ in the second and $\beta\frac{\omega_{AB}}{\kappa T}$ in the third). These have been calculated in each case from a value of η at approximately $f_B = 50\%$. The "mean error" is the mean calculated without regard to sign. The relations are shown graphically in figures 2.1 to 2.4, for those substances for which data is available at a sufficient number of concentrations.

BROMOBENZENE (A) AND BENZENE (B)

$f_A\%$	$\eta_{exp.}$ c.poise	ρ gm. cm.$^{-3}$	$\eta_{calc.}$ c.poise			% error		
			1.	2.	3.	1.	2.	3.
0.0	0.652	0.88	-	-	-	-	-	-
12.65	0.713	1.03	0.723	0.758	0.711	+1.4	+6.3	-0.3
33.4	0.795	1.22	0.828	0.854	0.813	+4.1	+7.4	+2.2
59.5	0.940	1.36	0.940	0.940	0.940	-	-	-
100.0	1.118	1.50	-	-	-	-	-	-

Range of $\sqrt[3]{N}\sigma$, 4.46-4.71 cm. ~~Angstrom units~~

1. $\sqrt[3]{N}\,\eta_{AB}\sigma_{AB} = 3.95$ c.poise cm. Mean error 2.8%

2. $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2} = 0.623$ c.poise Mean error 6.9%

3. $\beta\frac{\omega_{AB}}{\kappa T}\log_{10}e = -0.0823$ Mean error 1.3%

CHLOROBENZENE (A) AND BENZENE (B)

f_A%	$\eta_{exp.}$ c.poise	ρ gm.cm.$^{-3}$	$\eta_{calc.}$ c.poise			% error		
			1.	2.	3.	1.	2.	3.
0.0	0.652	0.88	-	-	-	-	-	-
17.6	0.676	0.99	0.685	0.689	0.683	+1.3	+1.9	+1.0
39.3	0.715	1.01	0.715	0.715	0.715	-	-	-
65.1	0.751	1.05	0.745	0.731	0.746	-0.8	-2.7	-0.7
100.0	0.768	1.11	-	-	-	-	-	-

Range of $\sqrt[3]{N}\sigma$, 4.46-4.80 ~~A.U.~~ cm.

1. $\sqrt[3]{N}\,\eta_{AB}\sigma_{AB} = 3.42$ c.poise cm. Mean error 1.1%

2. $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2} = 0.651$ c.poise Mean error 2.3%

3. $\frac{3\omega_{AB}}{kT}\log_{10} e = -0.0507$ Mean error 0.9%

FORMAMIDE (A) AND ACETIC ACID (B)

f_A%	$\eta_{exp.}$ c.poise	ρ gm.cm.$^{-3}$	η calc. c.poise			% Error		
			1.	2.	3.	1.	2.	3.
0.0	3.356	1.132	-	-	-	-	-	-
9.6	3.381	1.128	3.84	3.99	3.94	+0.2	+4.2	+2.8
20.4	4.149	1.120	4.20	4.43	4.38	+1.2	+ 6.8	+5.5
29.7	4.31	1.115	4.37	4.53	4.62	+1.4	+5.1	+7.2
40.6	4.348	1.112	4.36	4.37	4.56	+0.2	+0.5	+4.8
49.8	4.219	1.102	4.22	4.22	4.22	-	-	-
59.9	3.861	1.094	3.93	3.82	3.78	+1.86	-1.0	- 2.0
69.4	3.483	1.085	3.50	3.36	3.18	+0.6	-3.5	-8.6
79.0	2.857	1.076	2.94	2.76	2.52	+2.8	-3.1	-11.5
90.1	2.000	1.062	2.06	2.00	1.82	+3.0	0.0	-9.0
100.0	1.280	1.046	-	-	-	-	-	-

Range of $\sqrt[3]{N}\sigma$ 3.41-3.86 ~~A.~~U cm.

1. $\sqrt[3]{N}\eta_{AB}\sigma_{AB}$ = 22.45 c.poise cm. Mean error 1.4%

2. $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2}$ = 6.28 c.poise Mean error 3.0%

3. $\beta\frac{\omega_{AB}}{kT}\log_{10}e$ = -1.255 Mean error 6.4%

CARBON DISULPHIDE (A) AND ETHYL ALCOHOL (B)

f_B%	η_{exp} c.poise	ρ gm.cm.$^{-3}$	$\eta_{calc.}$ c.poise 1.	2.	3.	% Error 1.	2.	3.
0.0	0.363	1.18	-	-	-	-	-	-
28.0	0.493	1.145	0.447	0.183	0.477	-9.3	-63.0	-3.2
37.4	0.547	1.095	0.503	0.312	0.537	-8.0	-43.0	-1.8
41.6	0.567	1.073	0.528	0.393	0.552	-6.9	-22.2	- 2.6
58.7	0.667	0.985	0.667	0.667	0.667	-	-	-
71.8	0.763	0.928	0.80	0.86	0.779	+5.2	+12.7	+ 2.1
77.6	0.842	0.902	0.853	0.928	0.837	+1.3	+10.0	-0.6
82.7	0.908	0.880	0.908	0.988	0.892	-	+ 8.8	+ 1.7
87.0	0.954	0.860	0.970	1.017	0.941	+1.7	+ 6.6	-1.4
89.0	0.946	0.842	0.979	1.012	0.967	+ 3.4	+ 7.0	+ 2.2
100.0	1.115	0.802	-	-	-	-	-	-

Range of $\sqrt[3]{N}\sigma$ 3.39 - 4.56 $\frac{\text{cm}}{\text{cm.}}$ ~~Att~~

1. $\sqrt[3]{N}\,\eta_{AB}\sigma_{AB}$ = 1.478 c.poise cm. Mean error 4.5%

2. $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2}$ = -0.424 c.poise Mean error 21.7%

3. $\beta\frac{\omega_{AB}}{\kappa T}\log_{10}e$ = -0.0896 Mean error 2.0%

The calculation from relation 2 has no real significance, because a negative value must be given to η_{AB} to make the relation fit at f = 58.7%, and this has no physical significance.

FORMIC ACID (A) AND FORMAMIDE(B)

f_B%	$\eta_{exp.}$ c.poise	$\eta_{calc.}$ c.poise		% Error	
		1. and 2	3.	1 and 2	3
0.0	1.60	–	–	–	–
10.0	1.95	1.99	1.92	+2.0	−1.2
20.0	2.32	2.32	2.25	+0.3	−2.9
30.1	2.56	2.62	2.57	+2.3	+0.4
40.0	2.85	2.86	2.87	+0.35	+0.7
50.0	3.06	3.06	3.06	–	–
60.0	3.20	3.22	3.33	+0.6	+4.1
70.0	3.29	3.32	3.46	+0.9	+5.2
80.0	3.31	3.38	3.51	+2.1	+6.0
90.0	3.35	3.40	3.48	+1.3	+3.9
100.0	3.36	–	–	–	–

Range of $\sqrt[3]{N\sigma}$ 3.36-3.38 cm. This variation is negligible and the relations 2.1 and 2.2 are identical in this case, except that the significance of η_{AB} is different.

1. $\eta_{AB} = 3.64$ c. poise — Mean error 1.3%

2. $\eta_{AB}\dfrac{\rho_A\rho_B}{\rho_e^2} = 3.64$ c. poise — Mean error 1.3%

3. $\dfrac{\beta\,\omega_{AB}}{kT}\log_{10}e = -0.521$ — Mean error 3.1%

CHLOROFORM (A) AND BROMOBENZENE (B)

f%	η exp. c.poise	η calc. c.poise 1.	2.	3.	% Error 1.	2.	3.
0.0	0.700	-	-	-	-	-	-
8.5	0.753	0.772	0.784	0.763	+2.5	+4.11	+1.3
23.5	0.860	0.888	0.922	0.876	+3.3	+7.2	+1.9
40.2	1.015	1.015	1.015	1.015	-	-	-
64.7	1.198	1.204	1.191	1.213	-0.5	-0.6	+1.2
86.9	1.380	1.369	1.395	1.380	-0.8	+1.1	0.0
100.0	1.470	-	-	-	-	-	-

Range of $\sqrt[3]{N}\sigma$ 4.28-4.69 cm.

1. $\sqrt[3]{N}\eta_{AB}\sigma_{AB}$ = 4.87 c.poise cm. Mean error 1.8%

2. $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2}$ = 1.045 c.poise Mean error 3.9%

3. $\beta\frac{\omega_{AB}}{\kappa T}\log_{10}e$ = -0.0756 Mean error 1.1%

CARBON TETRACHLORIDE (A) AND ACETONE (B)

f_A %	η exp. c.poise	ρ gm.cm.$^{-3}$	η calc. c. poise			% Error		
			1.	2.	3.	1.	2.	3.
0.0	1.332	1.63	-	-	-	-	-	-
11.4	1.138	1.57	1.165	1.184	1.171	+2.4	+4.0	+2.9
36.4	0.854	1.38	0.863	0.880	0.879	+1.0	+3.0	+2.9
51.2	0.735	1.27	0.735	0.735	0.735	-	-	-
73.6	0.562	1.09	0.545	0.529	0.559	-3.0	-5.9	-0.5
86.5	0.481	0.95	0.454	0.448	0.474	-5.2	-6.8	-1.5
96.7	0.421	0.85	0.415	0.421	0.417	-1.0	0.0	-1.0
100.0	4.00	0.81	-	-	-	-	-	-

Range of $\sqrt[3]{N}\sigma$ 4.15-4.55 cm

1. $\sqrt[3]{N}\eta_{AB}\sigma_{AB}$ = 2.56 c.poise cm. Mean error 2.5%

2. $\eta_{AB}\frac{\rho_A\rho_B}{\rho_e^2}$ = 0.938 c.poise Mean error 3.9%

3. $\beta\frac{\omega_{AB}}{kT}\log_{10}e = -0.036$ Mean error 1.8%

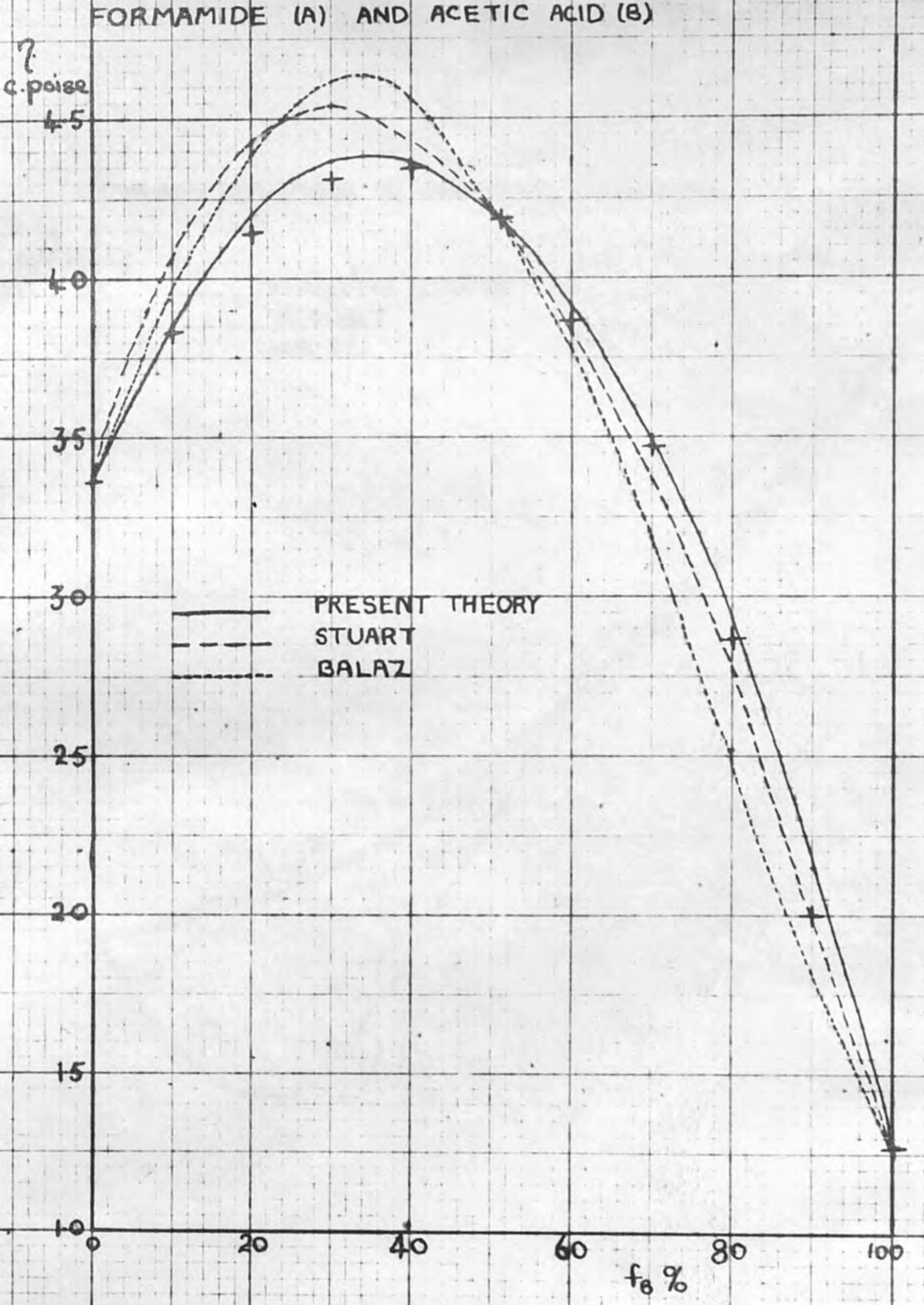

FORMAMIDE (A) AND ACETIC ACID (B)
η
c.poise
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
20
40
60
80
100
f_B %
PRESENT THEORY
STUART
BALAZ

FIGURE 2.1

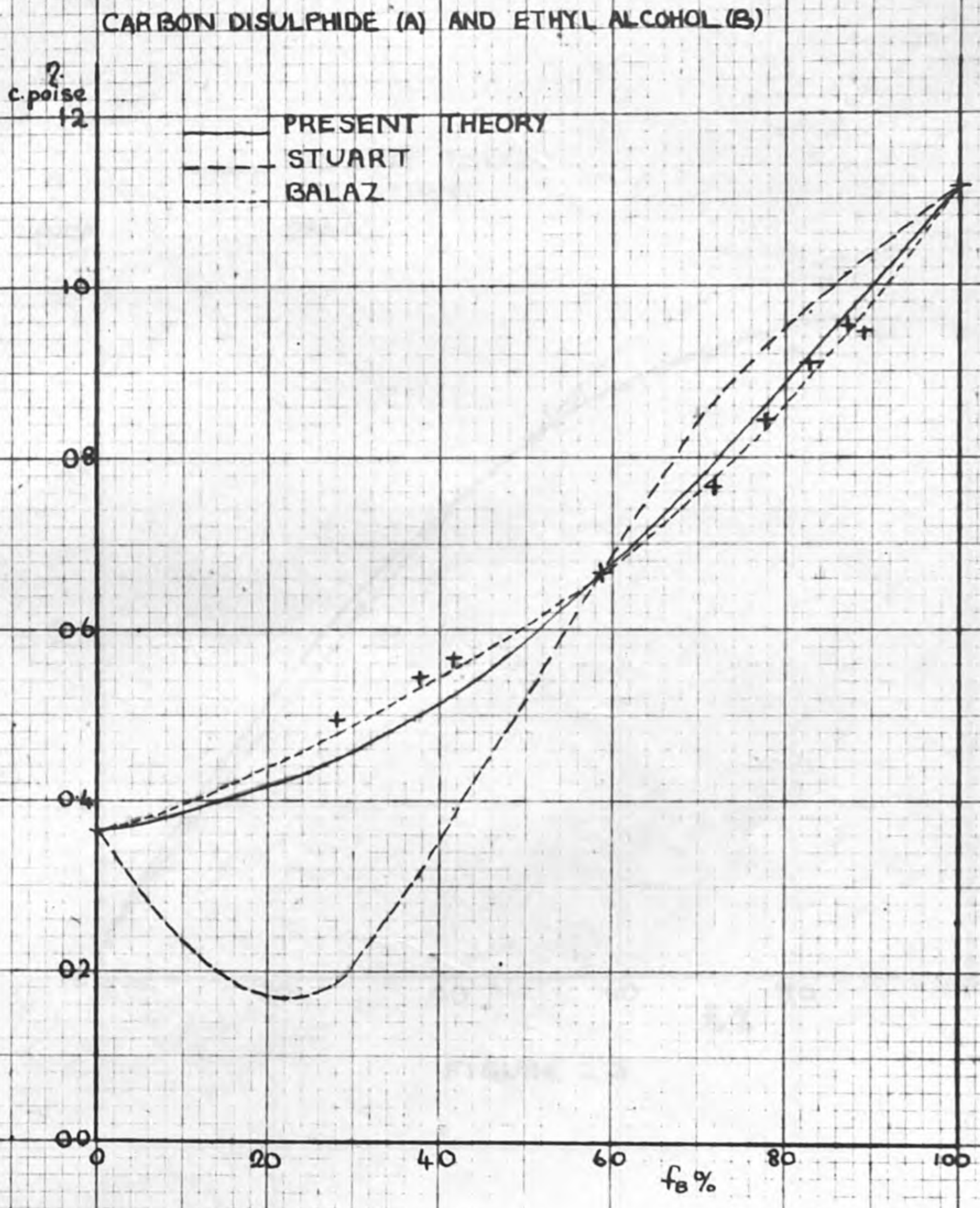

CARBON DISULPHIDE (A) AND ETHYL ALCOHOL (B)
η
c.poise
1·2
1·0
0·8
0·6
0·4
0·2
0·0
PRESENT THEORY
STUART
BALAZ
0
20
40
60
80
100
f_B %

FIGURE 2.2

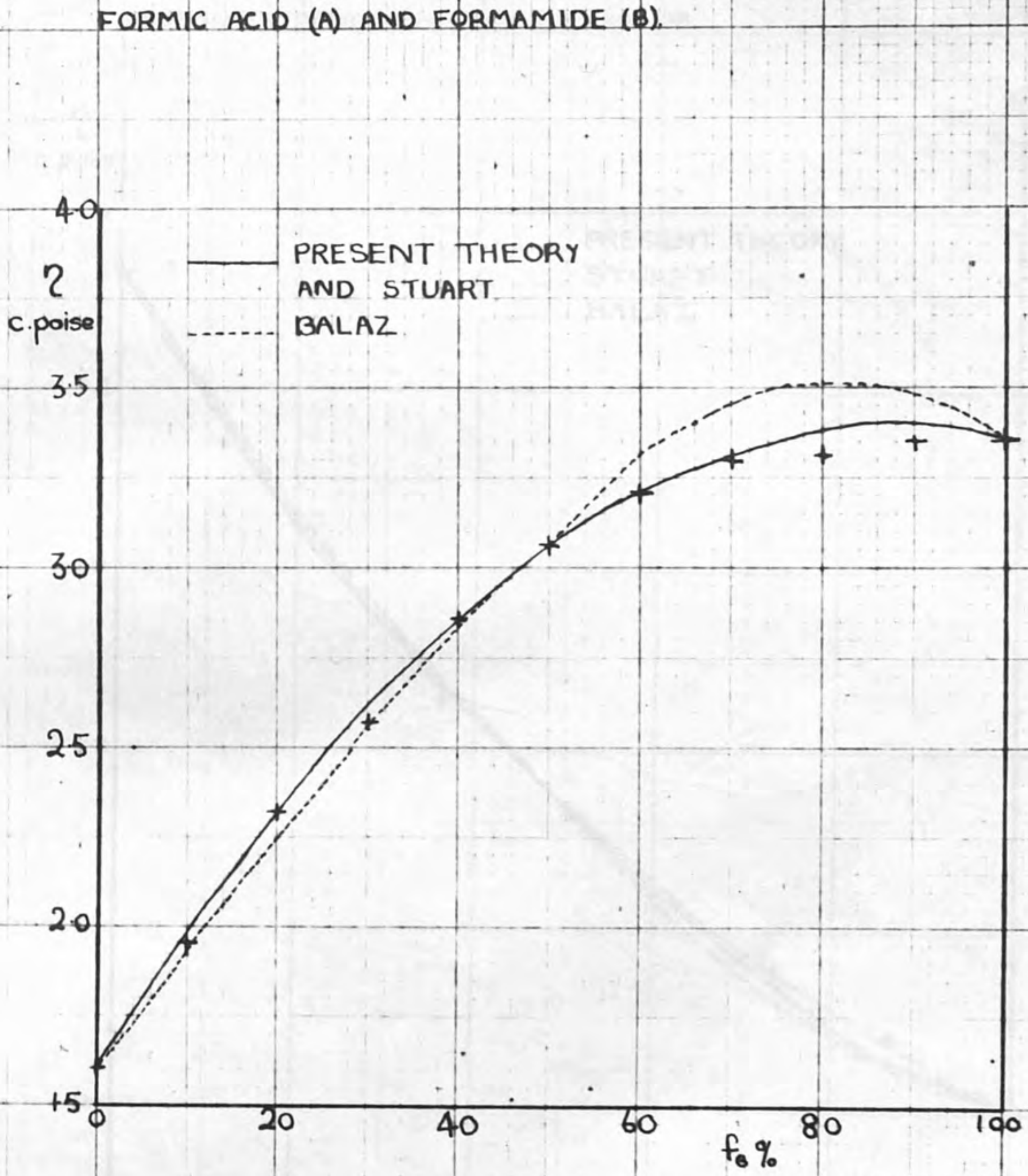

FORMIC ACID (A) AND FORMAMIDE (B).
PRESENT THEORY
AND STUART
BALAZ
η
c.poise
4.0
3.5
3.0
2.5
2.0
1.5
0
20
40
60
80
100
f_B %

FIGURE 2.3

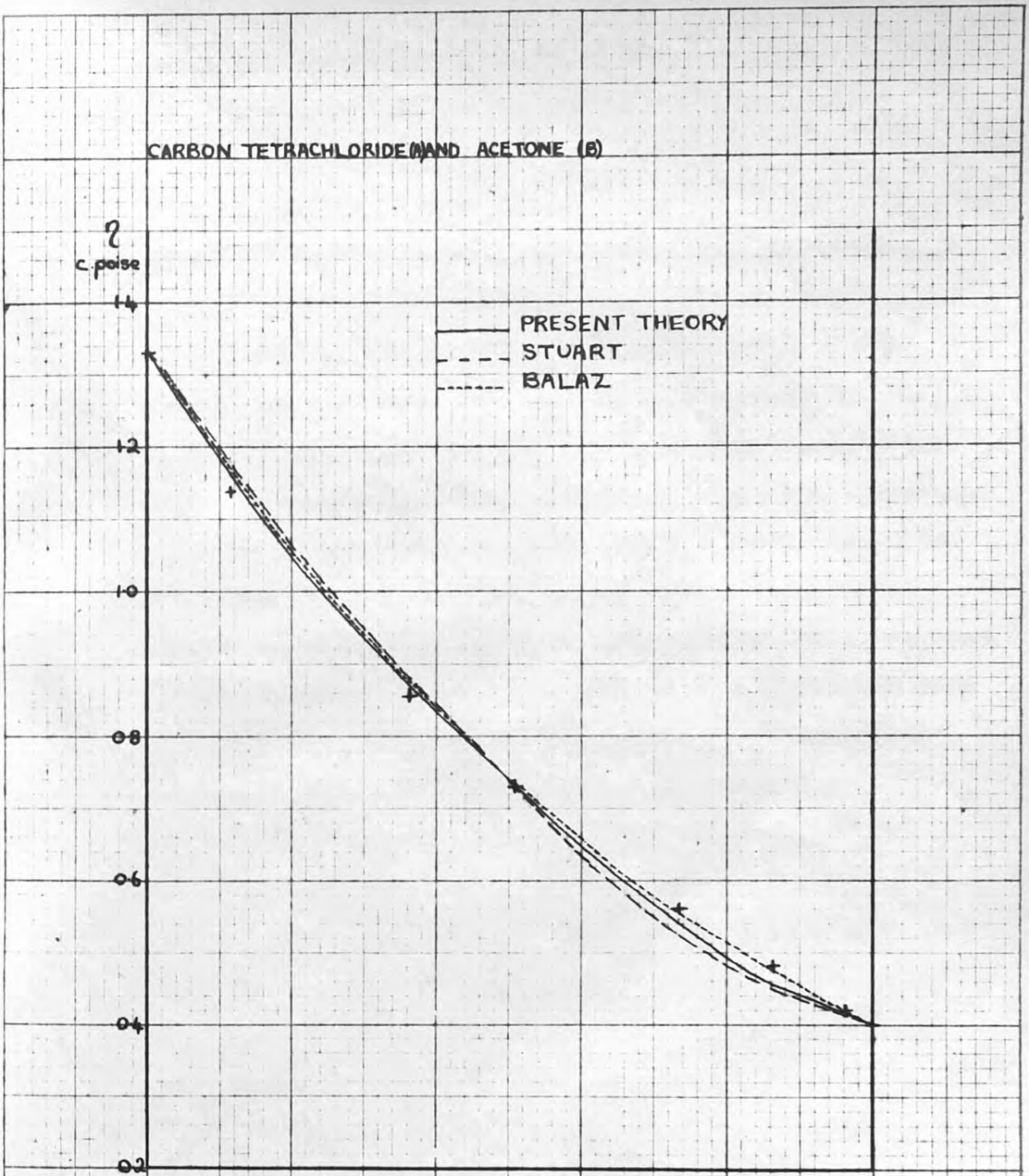

CARBON TETRACHLORIDE (A) AND ACETONE (B)
η
c.poise
1·4
1·2
1·0
0·8
0·6
0·4
0·2
PRESENT THEORY
STUART
BALAZ
0
20
40
60
80
100
f_A%

FIGURE 2.4

The overall mean and maximum errors for the three theories are

1. Mean 2.2% Maximum 9.3%
2. Mean 6.1% Maximum 63.0%
3. Mean 2.4% Maximum 11.5%

Stuart's relation evidently has too great a dependence on the inter-molecular distances σ, since when there is a large variation of this quantity, the theoretical curve differs widely from the experimental (fig. 2.2). Balaz' theory and the present one show similar results, except when the curve is strongly concave to the f-axis, when the present theory agrees more closely with experiment.

It appears from these results that this theory accounts for the experimental results as well as any other, probably better, so that the mutual viscosity may justifiably be regarded as a measure of the interaction between the two types of molecule in the mixture. It remains to calculate how the relaxation time of a molecule in solution in another liquid is related to this quantity.

3. THE MUTUAL VISCOSITY AND THE INNER FRICTION

The resistive force which a rotating polar molecule experiences in a non-polar liquid depends chiefly on the mutual viscosity of the two liquids, if the resistive force arises in a similar way to the viscous forces. The polar molecule collides with one of the surrounding molecules once in every $\frac{1}{c}$ times that it or one of its neighbours is at the extreme limit of its swing, where c is a probability as before.

Suppose a rigid polar molecule (B), rotating with an angular velocity ω, collides with a neighbouring non-polar molecule (A). Conservation of momentum requires that the molecule B loses momentum

$$d\omega = \frac{I_{AB}}{I_B + I_{AB}}\,\omega$$

where I_B is the moment of inertia of the molecule B about its centre of mass, and I_{AB} is the moment of inertia of the molecule A about the centre of mass of B. The angular momentum lost by B is

$$\frac{I_B\, I_{AB}\, \omega}{I_B + I_{AB}} .$$

Such a momentum loss occurs twice in every $\frac{1}{f_A c_{AB}}$ complete oscillations of B and twice in every $\frac{n}{f_A c_{AB}}$ complete oscillations of A, where n is the number of "near neighbours", (because it is assumed that any molecule has the probability c of colliding with <u>one</u> of its neighbours at every extreme position).

The number of collisions of any molecule B with a neighbouring molecule A per second is

$$f_A c_{AB}\, 2\nu_B + f_B n \frac{c_{AB}}{n}\, 2\nu_A$$

The loss of angular momentum per second due to such collisions (which is also the contribution to the resistive force of this type of collision) is

$$F_A = f_A \frac{I_A I_B}{I_{AB}+I_B} 2 c_{AB} (v_A + v_B) \omega$$
$$= f_A 6. \frac{I_A I_B}{I_{AB}+I_B} \frac{m_A + m_B}{m_A m_B} \sigma_{AB} \eta_{AB} \omega.$$

The resistive force due to a neighbouring polar molecule depends in a similar way on η_B, but the alignment of the molecules by the field alters both the probability of collision and the amount of momentum transferred. For simplicity suppose that one-half of the polar molecules is at any instant rotating about each of two axes at right-angles to one another and to the external electric field. In a collision between two molecules rotating about axes at right-angles to one another both molecules lose angular momentum

$$I_B \left(1 - \frac{1}{\sqrt{2}}\right) \omega$$

This is the case for one-half of the total number of collisions. For the remaining collisions the momentum loss is

$$0 \quad \text{or} \quad I_B \omega$$

according to whether the rotations are in the same or opposite senses. The mean momentum loss per second due to this type of collision is

$$\frac{1}{4}\left\{2 I_B \left(1 - \frac{1}{\sqrt{2}}\right) + I_B\right\}\omega$$

the number of collisions per second between polar molecules is

$$4 f_B v_B c_{B'}$$

where $c_{B'}$ is the probability of collision, and may vary with the degree of alignment of the polar molecules, and therefore with the frequency of the external field. Some recent results of Andrade and Dodd[28] on the effect of an electric field on the viscosity of a polar liquid indicate that $c_{B'}$ does not differ much from c_B, the probability in the absence of a field.

The resistive force due to the polar molecules is

$$F_B = 4 f_B v_B c_B' \frac{I_B}{4} \left\{ 2\left(1-\frac{1}{\sqrt{2}}\right)+1 \right\} \omega$$
$$= 3(3-\sqrt{2}) f_B \frac{c_B'}{c_B} \frac{I_B}{m_B} \eta_B \sigma_B \omega$$

Therefore the total resistive force is

$$F = \left(f_A 6 \frac{I_{AB} I_B}{I_{AB}+I_B} \frac{m_A+m_B}{m_A m_B} \eta_{AB} \sigma_{AB} + f_B 3(3-\sqrt{2}) \frac{c_B'}{c_B} \frac{I_B}{m_B} \eta_B \sigma_B \right) \omega$$

the coefficient of inner friction is

$$\varsigma = f_A 6 \frac{I_{AB} I_B}{I_{AB}+I_B} \frac{m_A+m_B}{m_A m_B} \eta_{AB} \sigma_{AB} + f_B 3(3-\sqrt{2}) \frac{c_B'}{c_B} \frac{I_B}{m_B} \eta_B \sigma_B$$

and the relaxation time of the polar molecule

$$\tau = \frac{1}{2kT} \left\{ f_A 6 \frac{I_{AB} I_B}{I_{AB}+I_B} \cdot \frac{m_A+m_B}{m_A m_B} \eta_{AB} \sigma_{AB} + f_B 3(3-\sqrt{2}) \frac{c_B'}{c_B} \frac{I_B}{m_B} \eta_B \sigma_B \right\}$$

I_B must be regarded as a mean moment of inertia - the sum of the products of the moments of inertia about the different possible axes of rotation and the probabilities of rotation about these axes. Since the resistance to rotation is different for different axes, these probabilities, and therefore I_B vary in general with frequency. This will cause a broadening of the dispersion curve, or if the moments of inertia about different axes differ widely, the appearance of more than one region of dispersion in the frequency spectrum. Only for a spherically symmetrical molecule can a single relaxation time be defined.

COMPARISON WITH EXPERIMENTAL RESULTS

1. For pure polar liquids

For the relaxation time of a pure polar liquid Debye gave

$$\tau = \frac{4\pi\eta_B}{kT} a_B^3 \qquad 3.1$$

The present theory gives

$$\tau = \frac{3(3-\sqrt{2})}{2kT} \frac{c_B'}{c_B} \eta \, k_B^2 \sigma_B , \quad (m_B k_B^2 = I_B) \qquad 3.2$$

Since $k_B^2 \sigma_B$ will be of the same order of magnitude as a_B^3, the chief difference between the two expressions lies in the numerical factor, and the appearance in the second expression of the ratio $\frac{C_B'}{C_B}$ which is the ratio of the probabilities of collision between two molecules in the presence and absence of an external field.

The ratio of the numerical factors is

$$\frac{3(3-\sqrt{2})}{8\pi} \doteq \frac{1}{5}$$

so that equation 3.2 predicts relaxation times smaller by a factor of about five than those predicted by the Debye theory, and in better agreement with the results of Conner and Smyth[6] and Hennelly, Heston Jr. and Smyth,[7] who found a discrepancy between the Debye theory and the experimental results of about this amount.

According to Andrade's model of a liquid, $\frac{C_B'}{C_B}$ may be written $e^{-\frac{E'-E}{kT}}$ where E' and E are the mutual potential energies of two molecules in the presence and absence of an external field respectively and are negative. Andrade and Dodd's[28] experiments indicate that the deviation of $\frac{C_B'}{C_B}$ from unity is positive and is certainly within experimental error of relaxation time measurements. This is supported by some recent observations by Lane and Saxton[29] who find $E' \equiv E$ for water, methyl alcohol and ethyl alcohol. Whiffen and Thompson,[11] however, found $|E|$ slightly greater than $|E'|$ for toluene, p-cymene and o-xylene, although the difference was almost within the experimental error, while Hennelly, Heston Jr. and Smyth[7] found $\frac{E'}{E}$ about 0.6 for a series of organic halides. The latter set of results, however, refers chiefly to large molecules which do not satisfy the assumptions of the theory.

Equation 3.2 agrees with the Debye relation in predicting an increase of τ with increasing η and molecular size.

2. For a polar solute in a non-polar solvent

For a very dilute solution of a polar substance in a non-polar solvent, the Debye relation is

$$\tau_D = \frac{4\pi\eta_A a_B^3}{KT} \qquad 3.3$$

and the present theory gives

$$\tau = \frac{3}{kT} \cdot \frac{I_{AB} I_B}{I_{AB} + I_B} \cdot \frac{m_A + m_B}{m_A m_B} \eta_{AB} \sigma_{AB}$$

The chief difference here is that the viscosity of the solvent in the Debye relation is replaced by the mutual viscosity of the solute and solvent in equation 3.4. This offers an immediate explanation of the different relaxation times found for one solute in different solvents of the same viscosity, and the relatively low relaxation times found for solutes in high viscosity solvents.

In the table below values of $\eta_{AB}\sigma_{AB}$ calculated from data taken from the International Critical Tables, are compared with the relaxation times determined by Willis Jackson and Powles,[10] Whiffen and Thomson[11] and Curtis, McGreer, Rathmann and Smyth[13] for various pairs of substances. The last column is ℓ, the distance of closest approach between a polar and a non-polar molecule, calculated from the estimated radii of gyration of the molecules and the value of I_{AB} found from the relaxation time. Considering the crudeness of the model on which the theory is based, and the high sensitivity of ℓ to the numerical factor in the equation for τ, the values of ℓ are very reasonable, except for chloroform in benzene, where the estimated moments of inertia are such that

l becomes negative. Figures 3.1 and 3.2 are graphs of τ against η_A and τ against η_{AB} respectively. Neglecting the variation of molecular size, both graphs should be straight lines passing through the origin, if the theories on which they are based are correct. The superiority of equation 3.4 is clearly demonstrated.

TABLE 3.1

Solutions at 20°C	Relaxation time $\times 10^{12}$ sec.	$\eta_{AB}\sigma_{AB}$ $\times 10^{10}$ poise cm.	$\frac{kT}{3}\frac{\tau}{\eta_{AB}\sigma_{AB}}$ $\times 10^{16}$ cm.	$l \times 10^{8}$ cm.
In benzene $\eta = 0.65$ cpoise				
1. Chlorobenzene	7.5	3.9	2.6	0.87
2. Bromobenzene	10.0	4.2	3.2	1.27
3. Nitrobenzene	11.5	4.1	3.8	1.55
4. Ethyl benzoate	12.0	5.9	2.7	-
5. Acetone	3.2	2.0	2.2	-
6. Chloroform	7.7	3.1	3.35	negative
In carbon tetrachloride $\eta = 0.97$ cpoise				
7. Chloroform	5.0	3.15	2.1	0.90

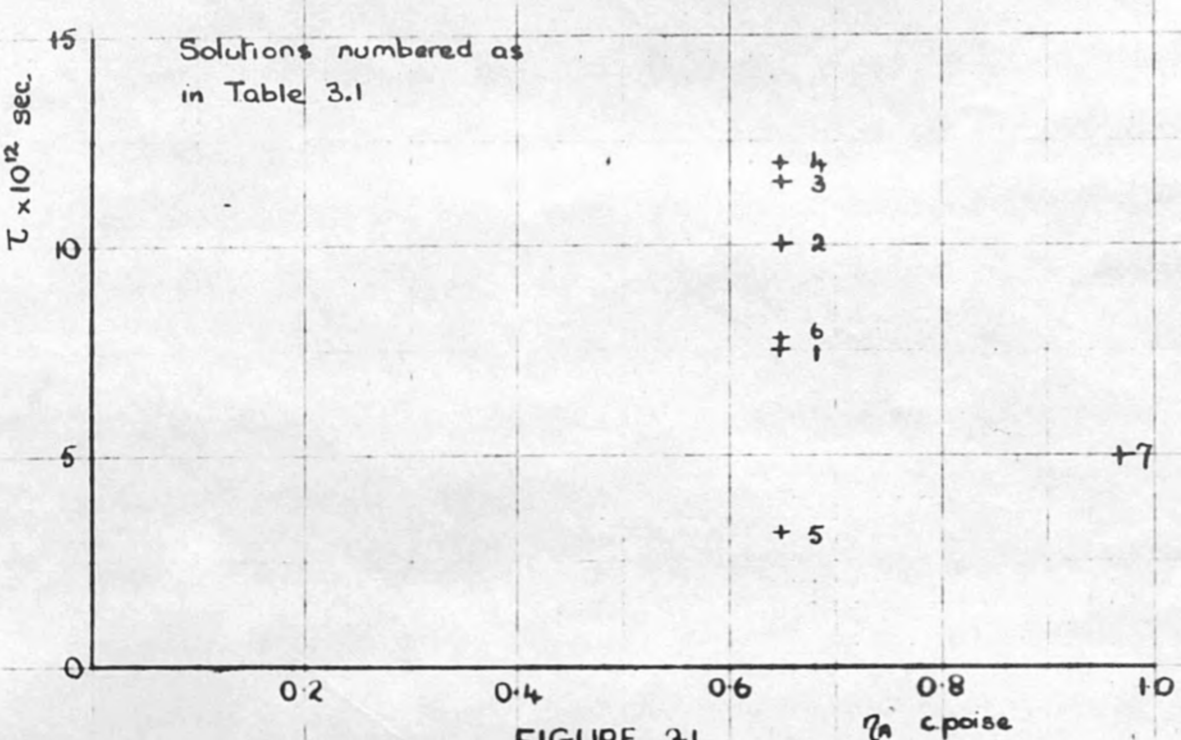


FIGURE 3.1

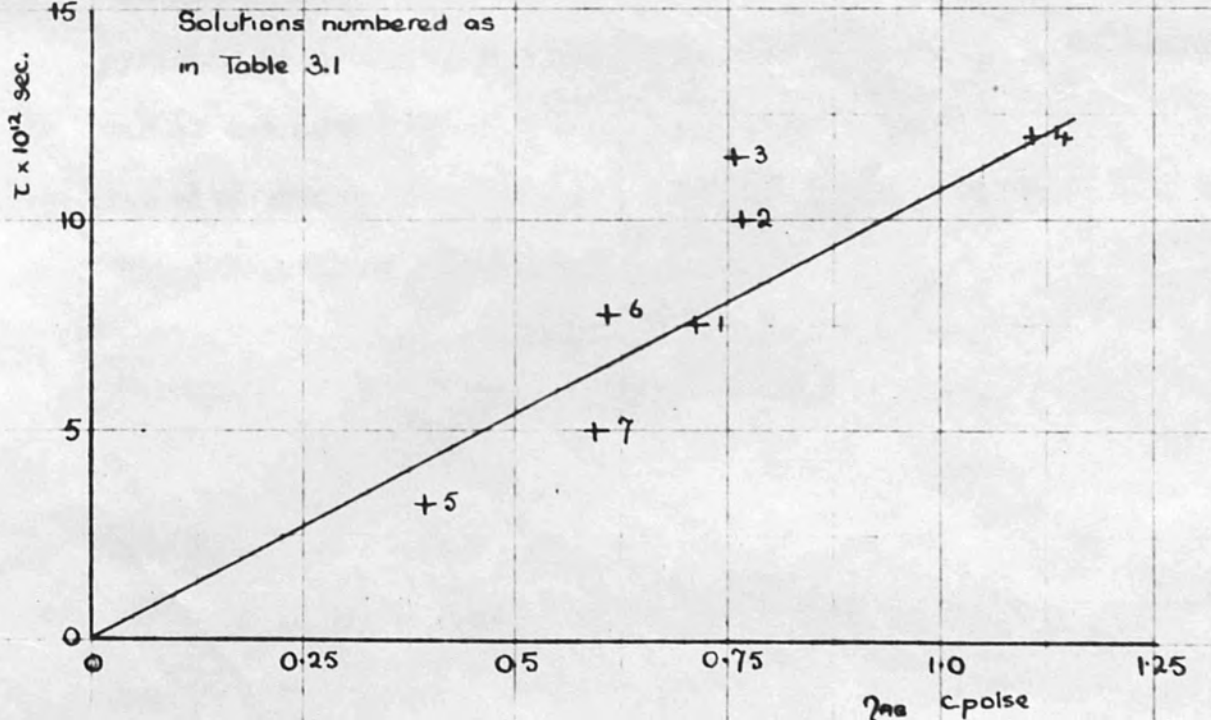


FIGURE 3.2

4. EXPERIMENTAL METHODS

The experimental evidence available for comparison between the theory developed above and the Debye theory consists almost entirely of results for various polar solutes (mostly benzene derivatives) in benzene, since the mutual viscosities are not known for other combinations. These results are better correlated by the present theory, but present no real evidence against the Debye theory, because the variation of the relaxation time can be attributed to the varying size and shape of the molecules. It was therefore proposed to make measurements which would enable the two theories to be compared in cases where the Debye relation is known to fail, namely when the same solute is used in two different solvents which have the same viscosity and when very viscous solvents are used. Measurements have been made of the relaxation time of pyridine in solution in carbon tetrachloride and in cyclohexane, and of the mutual viscosity of each polar-non-polar combination. The viscosities of these substances at 20°C are given in Timmerman's "Physico-chemical Constants"as

carbon tetrachloride	0.965 c.poise
cyclohexane	0.97 c.poise
pyridine	0.958 c.poise

The choice of a polar substance with a viscosity similar to that of the solvents ensures that the small concentration of polar substance present in the solution does not alter the viscosity appreciably. It was originally intended to make measurements of the relaxation time over the whole range of concentrations, but this was not possible because at the higher concentrations pyridine attacks the brass of the transmission line in which the measurements were made. The commercial pyridine and cyclohexane were used without further purification. The carbon tetrachloride was distilled with mercury to remove sulphur compounds. Measurements were also made of the mutual viscosities of monochlorbenzene-medicinal paraffin, chloroform-carbon tetrachloride, chloroform-cyclohexane, nitrobenzene-carbon tetrachloride and nitrobenzene-cyclohexane, for comparison with the relaxation times measured by Whiffen and Thompson[11] and by Curtis, McGreer, Rathmann and Smyth.[13]

EXPERIMENTAL METHODS

MEASUREMENT OF RELAXATION TIME

Ideally, to measure relaxation time for a polar molecule in solution, one should measure the real and imaginary parts (ε' and ε'') of the dielectric constant, over the whole range of frequency in which anomalous dispersion occurs. Debye[1] showed that for such a solution, provided ε''^2 is negligible compared with ε'^2

$$\frac{\varepsilon'-1}{\varepsilon'+2}\frac{M}{\rho} = \frac{4\pi N}{3}\left\{f_A\alpha_A + f_B\left(\alpha_B + \frac{\mu^2}{3kT}\frac{1}{1+\omega^2\tau^2}\right)\right\} \qquad 4.1$$

$$\frac{3\varepsilon''}{(\varepsilon'+2)^2}\frac{M}{\rho} = \frac{4\pi N}{3} f_B \frac{\omega\tau}{1+\omega^2\tau^2}\frac{\mu^2}{3kT} \qquad 4.2$$

where M and ρ are the molecular weight and density of the solution. The quantity $\frac{3\varepsilon''}{(\varepsilon'+2)^2}$ is thus proportional to $\frac{\omega\tau}{1+\omega^2\tau^2}$ if f_B is held constant and the frequency is varied. It reaches a maximum when $\omega\tau = 1$. From the position of this maximum on the frequency scale, τ can be found.

If it is not possible to make measurements over the whole range of frequency, it is still possible to find τ provided it can be assumed that the absorption follows the law given by the above equations. Eliminating μ between the two equations

$$\omega\tau = \frac{\frac{3\varepsilon''}{(\varepsilon'+2)^2}}{\frac{\varepsilon'-1}{\varepsilon'+2} - \frac{n^2-1}{n^2+2}}$$

where n is the refractive index of the solution. Alternatively, since the dipole moment of pyridine is known, $\frac{\omega\tau}{1+\omega^2\tau^2}$ can be found directly from equation 4.2, and the ambiguity in the value of removed by considering the order of magnitude of $\omega\tau$ required by equation 4.1. Thus τ can be found from measurements of the real and imaginary parts of the dielectric constant.

In practice, the real and imaginary parts of the dielectric constant were measured in terms of the real and imaginary parts of the propagation constant of a transmission line filled with the liquid. If

$$P = \alpha + j\beta$$

is the propagation constant of such a line, and

$$P_o = j\beta_o$$

is the propagation constant of a similar air-filled line

$$\frac{\alpha + j\beta}{j\beta_o} = \sqrt{\frac{\varepsilon' - j\varepsilon''}{\varepsilon_o}}$$ 30 (Willis Jackson)

where ε_o is the dielectric constant of air

Hence

$$\varepsilon' = \frac{\beta^2 - \alpha^2}{\beta_o^2} \qquad (\varepsilon_o = 1)$$

$$\varepsilon'' = \frac{2\alpha\beta}{\beta_o^2}$$

MEASUREMENT OF THE PROPAGATION CONSTANT OF A LIQUID-FILLED TRANSMISSION LINE.

The phase and attenuation constants (α and β) of a transmission line filled with the liquid were measured by a method developed by H.T. Flint and G. Williams.[31] A vertical transmission line short-circuited at its lower end, is filled to a depth s with the liquid. It is excited by an input probe at its upper end, and the ratio of the voltages at points distant $(2n+1)\frac{\lambda_0}{4}$ and $n\frac{\lambda_0}{2}$ from the surface of the liquid is measured by means of probes connected through crystal rectifiers to sensitive galvanometers (λ_0 being the wave-length in air). The length s of the line filled with the liquid and terminated by a short-circuit constitutes an impedance

$$Z_T = Z_0' \tanh(\alpha + j\beta)s$$ (Willis Jackson)[32]

where Z_0' is the characteristic impedance of the liquid-filled line.

The voltage at a distance y from this termination is

$$V = A\left\{e^{P_0 y} + \frac{Z_T - Z_0}{Z_T + Z_0} e^{-P_0 y}\right\}$$ (Willis Jackson)

where A is a constant and Z_0 and P_0 are the characteristic impedance and propagation constant of the air-filled line. The ratio of the voltages at the points $y = (2n+1)\frac{\lambda}{4}$, $y = 2n\frac{\lambda}{4}$ is

$$\frac{V_{\frac{\lambda}{4}}}{V_{\frac{\lambda}{2}}} = \frac{(Z_T + Z_0)e^{j(2n+1)\frac{\pi}{2}} + (Z_T - Z_0)e^{-j(2n+1)\frac{\pi}{2}}}{(Z_T + Z_0)e^{jn\pi} + (Z_T - Z_0)e^{-jn\pi}}$$

$$= \mp j\frac{Z_T}{Z_0}$$

according as n is even or odd.

The ratio is independent of the input voltage (which determines A). This is the chief advantage of the method.

The quantity measured experimentally is $\left|\frac{V_{\lambda/4}}{V_{\lambda/2}}\right|^2$

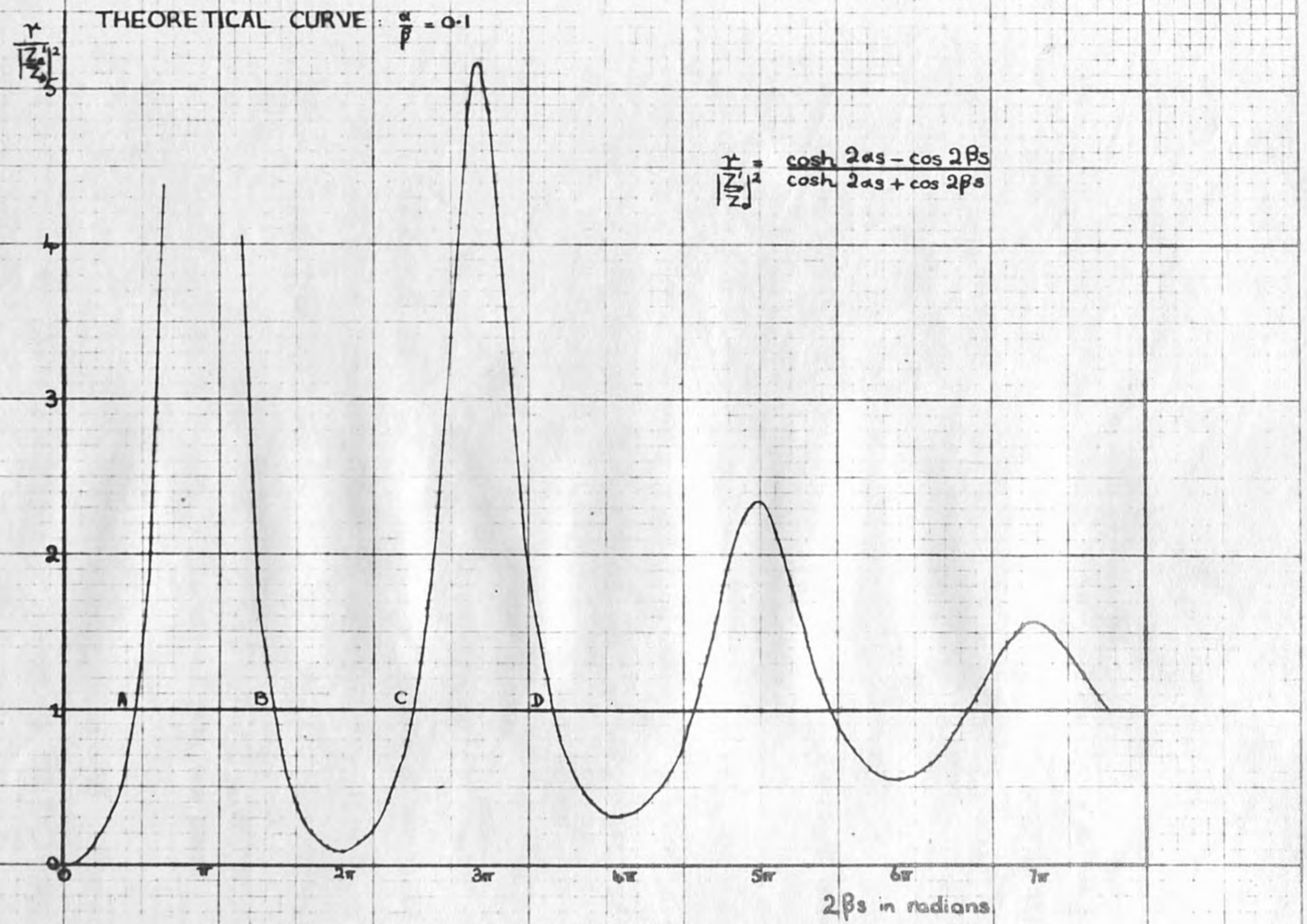

THEORETICAL CURVE : $\frac{\alpha}{\beta} = 0{\cdot}1$
$\frac{r}{\left|\frac{Z'}{Z_0}\right|^2}$
$\frac{r}{\left|\frac{Z'}{Z_0}\right|^2} = \frac{\cosh 2\alpha s - \cos 2\beta s}{\cosh 2\alpha s + \cos 2\beta s}$
5
4
3
2
1
0
A
B
C
D
0
π
2π
3π
4π
5π
6π
7π
2βs in radians

FIGURE 4.1

$$\left|\frac{V_{\lambda/4}}{V_{\lambda/2}}\right|^2 = \left|\frac{Z_T}{Z_0}\right|^2$$
$$= \left|\frac{Z_0' \tanh(\alpha + j\beta)s}{Z_0}\right|^2$$
$$= \left|\frac{Z_0'}{Z_0}\right|^2 \frac{\cosh 2\alpha s - \cos 2\beta s}{\cosh 2\alpha s - \cos 2\beta s}$$

The variation of this quantity with s is shown in figure 4.1

The calculation of α and β from this equation depends on the following properties:-

1. When $\beta s = (2n+1)\pi/2$

$$r = \left|\frac{V_{\lambda/4}}{V_{\lambda/2}}\right|^2 = \left|\frac{Z_0'}{Z_0}\right|^2$$

This means that the line $r = \left|\frac{Z_0'}{Z_0}\right|^2$ (the equal intercept line) cuts the curve at the points

$\beta s = \frac{\pi}{2},\ 3\frac{\pi}{2},\ 5\frac{\pi}{2} \ldots (2n+1)\frac{\pi}{2}$ (A,B,C,...... in figure 4.1)

This line is easily located allowing both β and $\left|\frac{Z_0'}{Z_0}\right|^2$ to be evaluated.

2. When $\beta s = n\pi$, $\cos\beta s = \pm 1$, according as n is odd or even.

$$r = \left|\frac{Z_0'}{Z_0}\right|^2 \frac{\cosh 2\alpha s \mp 1}{\cosh 2\alpha s \pm 1} \qquad \text{n even or odd}$$
$$= \left|\frac{Z_0'}{Z_0}\right|^2 \tanh^2 \alpha s \qquad \text{n even}$$
$$\text{or} \quad = \left|\frac{Z_0'}{Z_0}\right|^2 \coth^2 \alpha s \qquad \text{n odd}$$

The former set of points lie near the minima of the curve, the latter near the maxima, and either set may be used to find α.

3. The gradient of the curve is

$$\frac{dr}{ds} = -\left|\frac{Z_0'}{Z_0}\right|^2 \frac{4\beta \sin 2\beta s \cosh 2\alpha s + 4\alpha \cos 2\beta s \sinh 2\alpha s}{(\cosh 2\alpha s + \cos 2\beta s)^2}$$

At the points $s = (2n+1)\pi/2$ (the intersections with the equal intercept line)

$$\frac{dr}{ds} = \mp\left|\frac{Z_0'}{Z_0}\right|^2 \frac{4\beta}{\cosh 2\alpha s} \qquad \text{(n even or odd)}$$

This provides an alternative method of finding α, but is less useful when the absorption is small, because whereas $\tanh^2\alpha s$ is proportional to $(\alpha s)^2$ when αs is small, $\cosh 2\alpha s$ is proportional to $\left[1 + \left(\frac{2\alpha}{2} s\right)^2\right]$ and is therefore less sensitive to a small change in α.

GENERAL CRITICISM OF THE METHOD

An ideal system for the measurement of the electrical properties of a liquid should have the following properties:

1. It should be a completely enclosed system, so that it is not affected by the surroundings, and in particular by the position of the observer.
2. It should be independent of fluctuations of the input power.
3. It should be independent of the law of the detector.
4. The quantity of liquid required should be small.
5. Measurement procedure should be rapid.
6. The required constants should be simply related to the quantities measured.

Actual methods can be divided into four classes, namely, free wave methods, resonant systems, systems in which a standing wave is explored by a travelling probe and systems in which a fixed detector indicates the variation of the impedance of a liquid-filled line or guide with its length. The present method belongs to the fourth class.

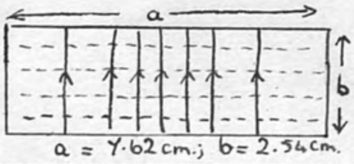
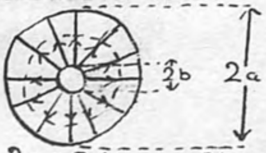
All free wave methods fail to satisfy the first condition, which is very important at centimetre wave-lengths. Also they require the use of large specimens to avoid edge effects. Resonant systems are probably best for the measurement of very low absorption, but become very complicated when a liquid of high absorption is used, because the amount of liquid in the resonant cavity has to be made very small. They are, however, still capable of yielding results of high accuracy, provided the apparatus itself is accurately made.

Standing wave methods in general cannot satisfy the first condition, because the detectors must have access to the field over a considerable length of the transmission line or wave guide, but if the apparatus is well designed the amount of radiation is small. The fourth type of method requires relative motion between the termination of the line or guide and the detector. In the present case this has been achieved by moving the detectors rather than the short circuit, because it is difficult to obtain a satisfactory moveable short-circuit.

All systems which rely on a single detector are sensitive to both fluctuations of the input and variations of the detector law, but the first fault is avoided and the second reduced in the present method because the measurements are made in terms of the ratio of the signal at two similar detectors at different positions in the line.

The method can be used with any guide system. In the original form it was used with Lecher lines, but the advantage of a closed system makes a wave guide or transmission line preferable. A rectangular wave guide was used successfully by V.I. Little[33] for liquids with absorptions between 0.01 and 0.5 cm.$^{-1}$ A coaxial transmission line was first used by G. Williams (unpublished), but his measurements were not sufficient to provide an adequate test of the method. Further measurements were made by Miss M.F. Newitt,[34] using a wave-length of 8.44 cm. The results for non-absorbing liquids were consistent with the theory, but when ethyl alcohol was used, the experimental curve showed considerable distortion. An attempt to make measurements on water was abandoned because the high surface tension and phase constant of water made the initial setting so difficult. These difficulties were partly due to the small dimensions of the line (inner diameter 0.31 cm., outer diameter 1.25 cm.), partly to the method used for setting the liquid level, which must have introduced a considerable systematic error.

The choice between a wave-guide and a transmission line is chiefly determined by the cross-sectional area (which determines the quantity of liquid required) and the narrowest width (which determines the surface tension effect) when the dimensions have been chosen so that the required mode is propagated without appreciable attenuation, and all other modes are cut off. The controlling factors are summarized below. (See, for example, Lamont, Wave Guides, Methuen 1942)

	Rectangular wave guide	Concentric transmission line
	 $a = 7.62$ cm.; $b = 2.54$ cm.	 $2a = 3.46$ cm.; $2b = 0.93$ cm.
To prevent cut off of required mode	$a > \frac{\lambda}{2}$ ($a = 7.62$ cm > 5 cm.) no limit to b	no limit
To cut off higher modes	$a < \lambda$ ($a = 7.62$ cm. < 10 cm.)	$a + b < \frac{\lambda}{3}$ ($a+b = 2.2$ cm. < 3.2 cm.)
Attenuation due to conductor resistance	$\alpha_c = \left(\frac{\varepsilon f}{\sigma}\right)^{\frac{1}{2}} \frac{\frac{1}{b} + \frac{2}{a}\left(\frac{\lambda}{2a}\right)^2}{\left[1 - \left(\frac{\lambda}{2a}\right)^2\right]^{\frac{1}{2}}}$ ($\alpha_c = 5.4 \times 10^{-3}$ neper. cm.$^{-1}$)	$\alpha_c = \left(\frac{\varepsilon f}{\sigma}\right)^{\frac{1}{2}} \frac{1}{2} \frac{\frac{1}{a} + \frac{1}{b}}{2 \log_e a/b}$ ($\alpha_c = 8.5 \times 10^{-3}$ neper cm.$^{-1}$) α_c is a min. when $\log \frac{a}{b} \doteq 3.6$ ($\frac{a}{b} = 3.7$)
Cross-sectional area	ab (19.35 cm.^{2})	$\pi (a^2 - b^2)$ (8.67 cm.^{2})
Smallest width	b (2.54 cm)	$a - b$ (1.26 cm.)

The figures in brackets give the corresponding quantities for a rectangular wave guide 3" x 1" (Little) and a transmission line with $a = 1.73$ cm., $b = 0.465$ cm., as used in the present case, both being made entirely of brass, for which the conductivity is taken to be $\frac{1}{8} \times 10^{6}$ ohm.$^{-1}$ cm.$^{-1}$ or $\frac{9}{8} \times 10^{17}$ e.s.u. The transmission line has the smaller cross-sectional area and smallest width, but if the narrow dimension of the guide were reduced by a factor of two, the cross section, attenuation and smallest width of the two systems would become approximately equal. The transmission line has, however, the advantage that it can be used without modification for longer wave-lengths.

ACCURACY OF THE METHOD

There are two factors which chiefly determine the accuracy of the method:- firstly, the size of the signal at each detector at the parts of the curve from which the constants are calculated, and, secondly, the accuracy with which the initial settings of the probes and liquid levels are made.

1. Sensitivity of the detectors

$$\frac{V_{\lambda/2}}{V_{\lambda/4}} = \left|\frac{Z_0'}{Z_0}\right|^2 \frac{\cosh 2\alpha s - \cos 2\beta s}{\cosh 2\alpha s + \cos 2\beta s}$$

$$= \frac{1}{\varepsilon'} f(s) \qquad \text{where } f(s) \rightarrow 1 \text{ as } s \rightarrow \infty$$

If k is the ratio of the sensitivity of the detector in the $\frac{\lambda}{2}$ position to that of the detector in the $\frac{\lambda}{4}$ position, the measured ratio of the two signals is

$$r' = \frac{k}{\varepsilon'} f(s)$$

The maximum accuracy is obtained when $r' = 1$, for the signal at either probe must not exceed the value beyond which the rectifier ceases to obey a square law, and therefore if r' differs much from 1 the signal at one probe must be limited to prevent that at the other becoming excessive.

In a liquid which has a high absorption, (say $\alpha > 0.2$), so that $f(s) \to 1$ quite rapidly, it is best to arrange that $r' = 1$ at the equal intercept line, that is to make

$$k \doteq \varepsilon'$$

The accuracy of the value of r' at the maxima and minima is then approximately equal, and both sets of turning points are used to calculate α.

If the liquid has a low absorption, it becomes impossible to obtain high accuracy at both sets of turning points, and it is best to select one set of turning points for the calculation of α, and arrange that the line $r' = 1$ lies somewhere between the equal intercept line and the chosen turning points.

In the present measurements on one solute in different solvents, the relative values of the absorption are of more interest than the absolute values, so that an exact knowledge of k, which affects all the measurements equally, is not necessary. Therefore for these measurements it was arranged to satisfy the conditions at one set of turning points. At the turning points the condition becomes

$$r'_{min} \doteq \frac{k}{\varepsilon'}(\alpha s)^2 \doteq 1$$

or

$$r'_{max} \doteq \frac{k}{\varepsilon'}\frac{1}{(\alpha s)^2} \doteq 1$$

Since $\alpha s \ll 1$, and ε' is about 3 or 4, it is more convenient to use the maxima of r' than the minima.

2. Setting of the probes and liquid surface

The method requires that the probes shall be at a distance $(2n+1)\frac{\lambda_0}{4}$ apart, and at distances $(2n+1)\frac{\lambda_0}{4}$ and $n\frac{\lambda_0}{2}$ respectively from the liquid surface. The first adjustment can easily be made, but since the liquid surface is not flat, owing to surface tension effects, the second is more difficult and small errors here may cause the curve to differ appreciably from its theoretical form. This type of error is considered in some detail, as it seems probable that it sets the lower limit to the dimensions of a transmission line for use with this method.

The general expression for the ratio of the voltages at two probes distant x_1 and x_2 from the liquid surface is

$$\frac{V_1}{V_2} = \frac{jZ_0 \sin\beta_0(x_1+x_2) + Z_T \cos\beta_0(x_1+x_2)}{jZ_0 \sin\beta_0 x_1 + Z_T \cos\beta_0 x_1}$$

If $x_1 = x_2 = (2n+1)\frac{\lambda}{4}$ this reduces to

$$\frac{V_1}{V_2} = \mp j\frac{Z_T}{Z_0} \qquad \text{(n even or odd)}$$

but if instead $x_1 = (2n+1)\frac{\lambda}{4}$, and $x = (2n+1)\frac{\lambda}{4} + d$, where d is small

$$\frac{V_1}{V_2} = \frac{jZ_0\sin\delta - Z_T\cos\delta}{jZ_0\cos\delta + Z_T\sin\delta}$$

$$\frac{V_1}{V_2} \to \frac{jZ_0\delta - Z_T}{jZ_0 + Z_T\delta} \qquad \text{as } \delta \text{ tends to zero}$$

where $\delta = \frac{2\pi d}{\lambda_0}$ and δ^2 is negligible compared to unity.

$$\left|\frac{V_1}{V_2}\right|^2 = \frac{|Z_T|^2 - 2X_T Z_0\delta + Z_0\delta^2}{Z_0^2 + 2X_T Z_0\delta + |Z_T|^2\delta^2}$$

where X_T is the imaginary part of Z_T i.e., $Z_T = R_T + jX_T$

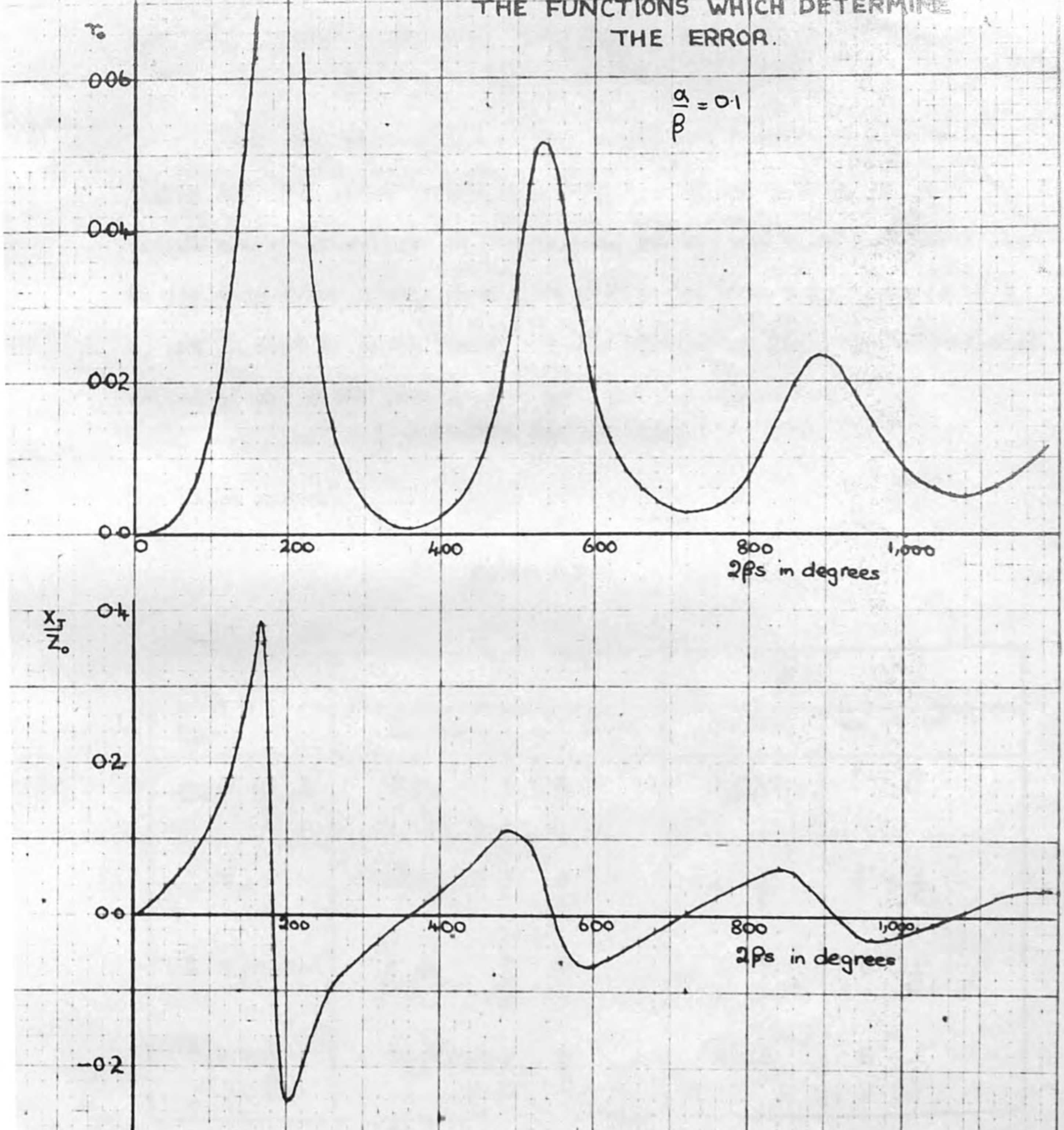
$$\left|\frac{V_1}{V_2}\right|^2 = r_0\left\{\frac{1 - 2\frac{X_T}{Z_0}\frac{\delta}{r_0} + \frac{1}{r_0}\delta^2}{1 + 2\frac{X_T}{Z_0}\delta + r_0\delta^2}\right\}$$

where

$$r_0 = \frac{1}{\varepsilon'}\,\frac{\cosh 2\alpha s - \cos 2\beta s}{\cosh 2\alpha s + \cos 2\beta s}$$

and

$$\frac{X_T}{Z_0} = \frac{\alpha\beta_0 \sinh 2\alpha s + \beta\beta_0 \sin 2\beta s}{(\alpha^2+\beta^2)(\cosh 2\alpha s + \cos 2\beta s)}$$



THE FUNCTIONS WHICH DETERMINE THE ERROR.

FIGURE 4.2

and the term in δ^2 is not necessarily negligible compared with the term in δ, because its coefficient may be very large. If δ is small,

$$\left|\frac{V_1}{V_2}\right|^2 = r_0\left\{1 - \frac{2X_T}{Z_0}\,\delta\left(1+\frac{1}{r_0}\right) + \delta^2\left(\frac{1}{r_0} - r_0\right)\right\}$$

The variation with s of the quantities involved is shown in figure 4.2 The error varies in a complicated way with s, but the effect can be calculated at the turning points and equal intercept line in two particular cases: when s is small; and when s is so large that r_0 and $\frac{X_T}{Z_0}$ tend to their steady values. Table 4.1 gives the approximate values of the coefficients of δ and δ^2 in the expression

$$\frac{r}{r_0} = 1 - A\delta + B\delta^2$$

for these cases.

TABLE 4.1

	A		B	
$2\beta s$	$\alpha s \to 0$	$\alpha s \to \infty$	$\alpha s \to 0$	$\alpha s \to \infty$
$2n\pi$ (min.)	$2\frac{1}{\beta_0 s}$	$\frac{\alpha}{\beta_0}$	$\varepsilon'\frac{1}{(\alpha s)^2}$	$\varepsilon' - \frac{1}{\varepsilon'}$
$2n\pi + \frac{\pi}{2}$	$2\beta\beta_0(\varepsilon'+1)$	$\frac{\alpha}{\beta_0}$	$\varepsilon' - \frac{1}{\varepsilon'}$	$\varepsilon' - \frac{1}{\varepsilon'}$
$2n\pi + \pi$ (max.)	$\frac{2}{\varepsilon'}\,\frac{1}{\beta_0 s}$	$\frac{\alpha}{\beta_0}$	$-\frac{1}{\varepsilon'}\,\frac{1}{(\alpha s)^2}$	$\varepsilon' - \frac{1}{\varepsilon'}$
$2n\pi + \frac{3\pi}{2}$	$-2\beta\beta_0(\varepsilon'+1)$	$\frac{\alpha}{\beta_0}$	$\varepsilon' - \frac{1}{\varepsilon'}$	$\varepsilon' - \frac{1}{\varepsilon'}$

The following facts emerge:-

1. The coefficient of the linear term in general increases with α

2. The coefficient of the square term in general increases with ε'

3. The error at the turning points due to the square term may become very large near the origin, owing to the factor $\frac{1}{(\alpha s)^2}$ in the coefficients.

4. Since $\varepsilon' > 1$, the error is less at the maxima than at the minima.

This source of error is most important in liquids for which both ε' and α are high. This explains why the setting of the liquid level is so critical in the case of water. For dilute solutions of a polar substance in a non-polar solvent the error will be small provided the measurements are not made near $s = 0$. In the present measurements on solutions α was calculated from the ratio r'_{min} at a depth s of about 5 cm. Taking $\alpha = 0.01$, $\beta_0 = 0.6$ $\varepsilon' = 2.5$, the coefficients are

$$A = 0.66$$

$$B = 1{,}000$$

If the error is to be less than 1%, δ must be less than 0.03, i.e., the displacement of the liquid level from its correct position must be less than

$$\frac{\lambda}{2\pi}\,\delta \quad = \quad 0.02 \text{ cm.}$$

It is estimated that the experimental error in setting the level of the liquid in this case is 0.01 cm.

It will be seen that the term in δ^2 has in this case more effect than the term in δ.

DESCRIPTION OF THE APPARATUS

The apparatus is shown diagrammatically in figure 4.3. It

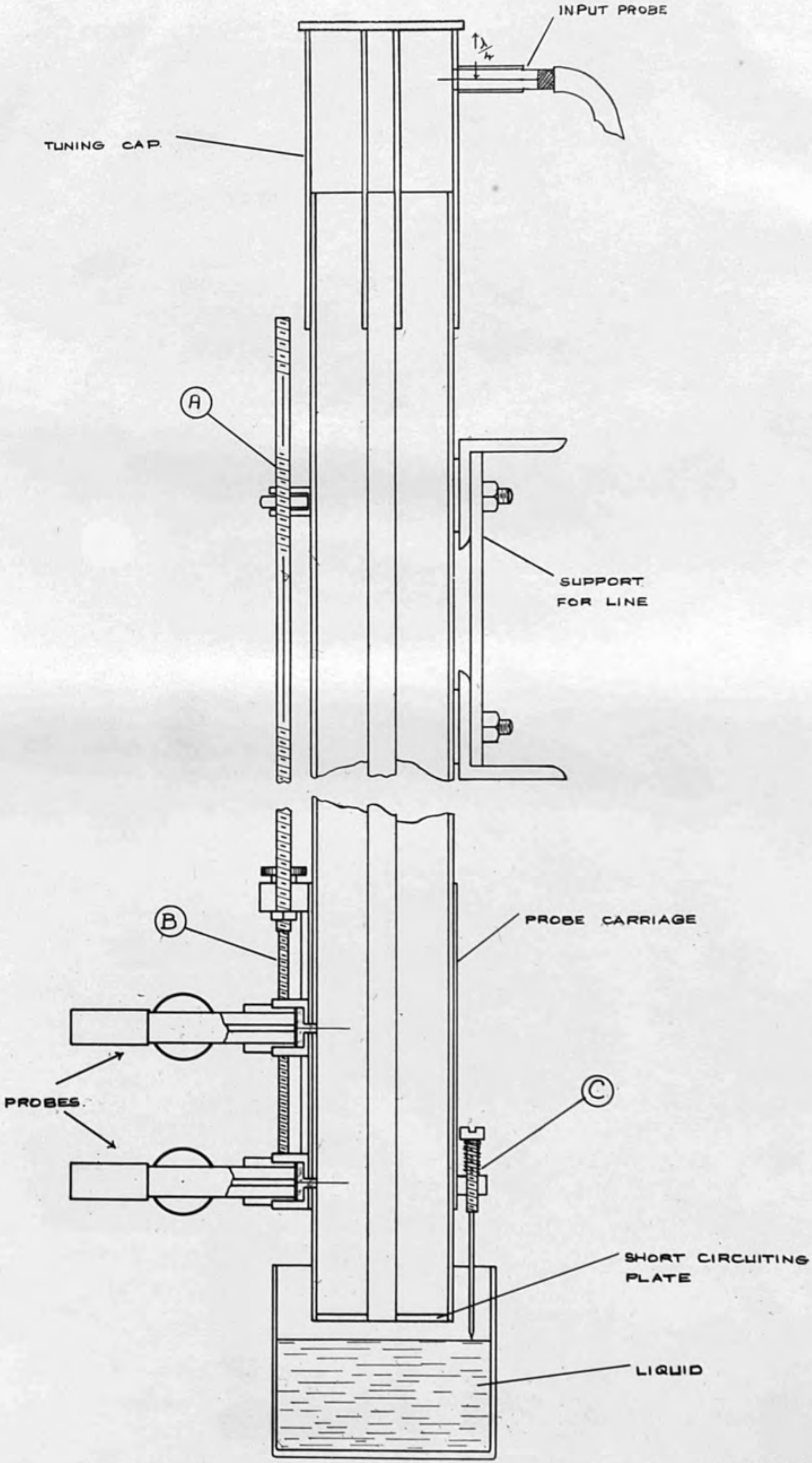

INPUT PROBE
λ/4
TUNING CAP.
A
SUPPORT FOR LINE
B
PROBE CARRIAGE
PROBES.
C
SHORT CIRCUITING PLATE
LIQUID

FIGURE 4·3

consists of a concentric transmission line supported vertically by brackets fixed to the wall of the laboratory. The liquid is contained in a beaker supported on a rising table, and enters the transmission line through three slots in the short-circuiting plate at the end of the line, the slots being cut radially so as not to disturb the flow of current in the plate. The input enters through a side tube in the cap which closes the line at the upper end. This cap provides a moveable short-circuit at the upper end of the line, so that the amplitude of the input voltage can be controlled. The input probe is one-quarter of the wave-length away from the short-circuit, so that it is in the optimum position whatever the position of the tuning cap. The detector probes are mounted on a carriage which can be moved up and down the line by means of the screw A. The pitch of this screw is 1.265 mm., and the milled head which raises the screw is marked in six segments, so that when the head is turned through one division the carriage is raised by 0.21 mm. This setting can be made with an accuracy greater than 0.01 mm., and is used to measure the position of the probes. The lower probe is fixed on the collar, the upper can be moved up or down by the screw B. This allows the distance between the two probes to be adjusted. The carriage also carries a sharp needle attached to the screw C. This is used to mark the correct position of the liquid surface.

Radiation from the line, which caused considerable difficulty at first, was reduced by using a thicker short-circuiting plate at the lower end of the line, so that any waves set up in the slot were attenuated to negligible amplitude before reaching the outer surface of the plate (the ratio of the thickness of the plate to the width of the slots should be not less than 2), and by the use of the cap-shaped tuning piston at the upper end, suggested by Dr. V.I. Little to replace the original piston, which consisted of an annular brass plate mounted on polythene. Radiation from the slot in which the probes move cannot be prevented, but is relatively slight.

Each detector probe forms part of the inner of a short coaxial line closed by a cap piston, which allows the impedance of the detector to be varied. The sensitivities of the detectors can be varied by altering either the tuning of the short coaxial line or the penetration of the probes into the main line. The signal to the detector is rectified by a crystal rectifier situated at the end of a second short length of line in parallel to the first, and is measured by a sensitive moving coil galvanometer.

The input voltage is provided by a reflex klystron. A coaxial cable connects the input probe in the transmission line to a loop which couples the magnetic field in the klystron cavity. A second loop in the klystron cavity is connected by a coaxial cable to a cavity wavemeter. The klystron is tuned to a wavelength of 9.35 cm. by altering the position of the tuning plunger until the galvanometer which measures the output of the wavemeter registers a maximum. Power supplies for the klystron are provided by a stabilised power pack connected to the mains through a constant voltage transformer. Once the klystron has reached thermal equilibrium, its frequency is very stable.

The beaker containing the liquid is provided with a cardboard cover, in which holes are cut to allow the transmission line and indicator pin to pass. This serves the double purpose of reducing evaporation from the liquid surface, and of holding the beaker in a constant position relative to the transmission line, so that the surface tension effects are constant.

EXPERIMENTAL PROCEDURE

The klystron is tuned until the wave-meter galvanometer registers a maximum.

To set the detector probes the correct distance apart, the carriage is moved up the line and the positions of the minima for the two detectors are noted, the sensitivity of each detector being adjusted to a maximum as the detector approaches its minimum. The carriage is then moved down to a position mid-way between the minima of the lower detector, the upper detector is tuned to maximum sensitivity, and moved by the screw B until it is at a minimum. The two probes are then an odd number of quarter wave-lengths apart ($\frac{3\lambda_0}{4}$ was the distance used). This is checked by repeating the observations on the minima of both detectors. The distance between two scratches marked centrally on the blocks supporting the probes was measured with a vernier microscope and found to be 7.0125 cm.

The setting of the liquid surface at the correct level relative to the probes is more difficult because the surface within the line is curved, and it is impossible to know exactly where the effective surface level is, while a small error in this setting may cause a large error in the experimental results. Various methods of setting the liquid level were tried, but the following were found to be best:-

1. For a liquid with a low dielectric constant, and relatively low surface tension, the probe carriage is moved down to the position it should occupy when the liquid is about to enter the line, i.e., one detector is registering a maximum, and the other a minimum, and the liquid is raised until it is seen from above to cover half the base of the transmission line, the line having been previously wetted. The pin C is then moved down until it just touches the surface of the liquid. This method succeeds for most liquids, but not for water, probably owing to its high surface tension.

Since the dielectric constant of water is high it is possible to use the change in the resonant length of the transmission line to indicate the effective level of the water. The detectors are placed as before, and the tuning cap is moved until the line is nearly, but not quite, resonant. When the cap is in this position the entry of the liquid causes a rapid change in the signal at the detector which is placed at a maximum of the standing wave pattern. The liquid is raised into the wetted line in steps of 0.1 mm. as indicated by the scale on the rising table and the signal at the detector is noted at each step. A graph of detector signal against liquid level is plotted, giving a curve as in figure 4.4 The falling part of the curve is extrapolated back to the level part, and the point of intersection taken as the level at which the liquid just entered. The indicator pin is moved so that it just touches the liquid at this level.

This method is not successful with liquids of low dielectric constant because the change in resonance position is not sufficiently rapid. It does not always succeed for water, and slight adjustment

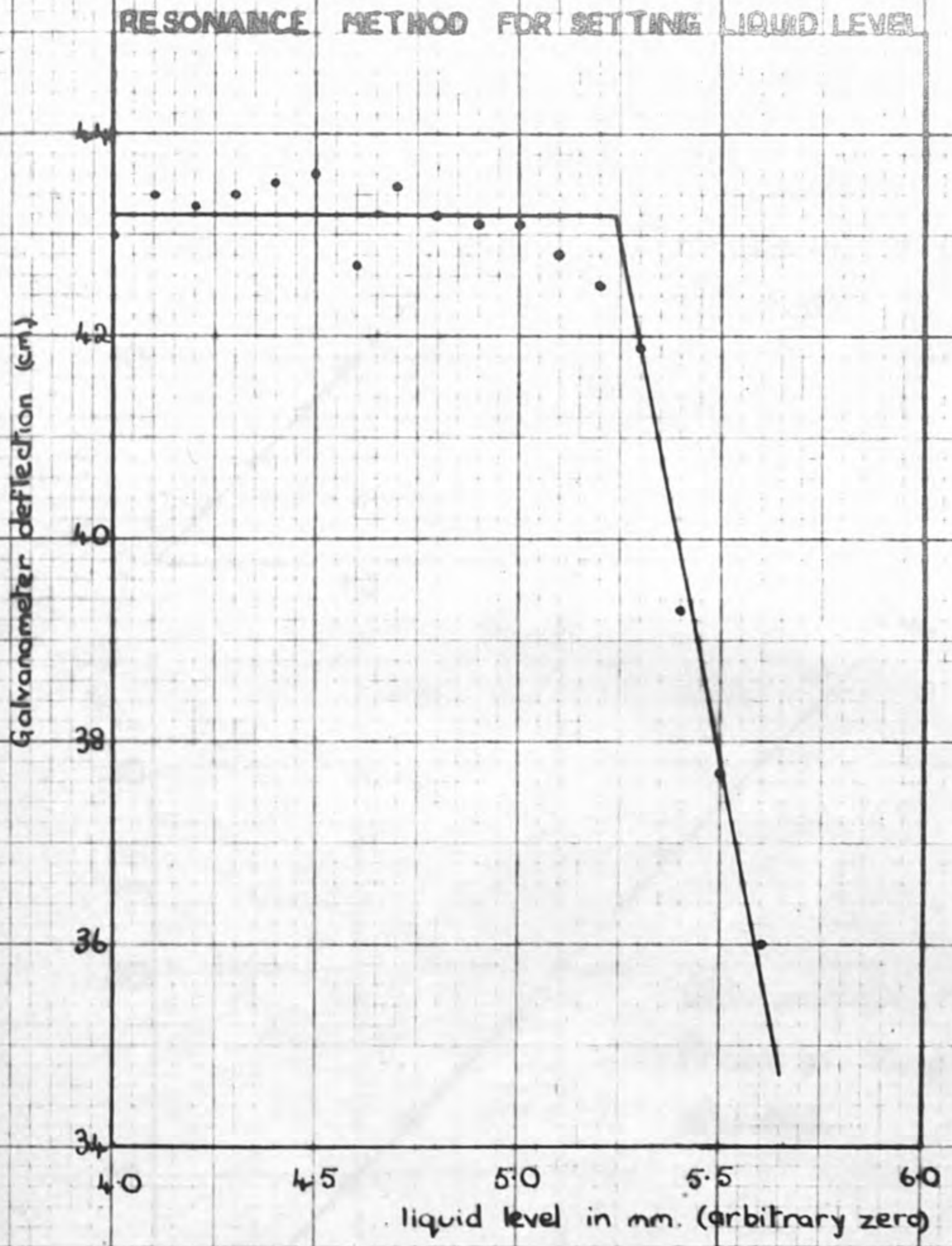

RESONANCE METHOD FOR SETTING LIQUID LEVEL
Galvanometer deflection (cm.)
44
42
40
38
36
34
4·0
4·5
5·0
5·5
6·0
liquid level in mm. (arbitrary zero)

FIGURE 4.4.

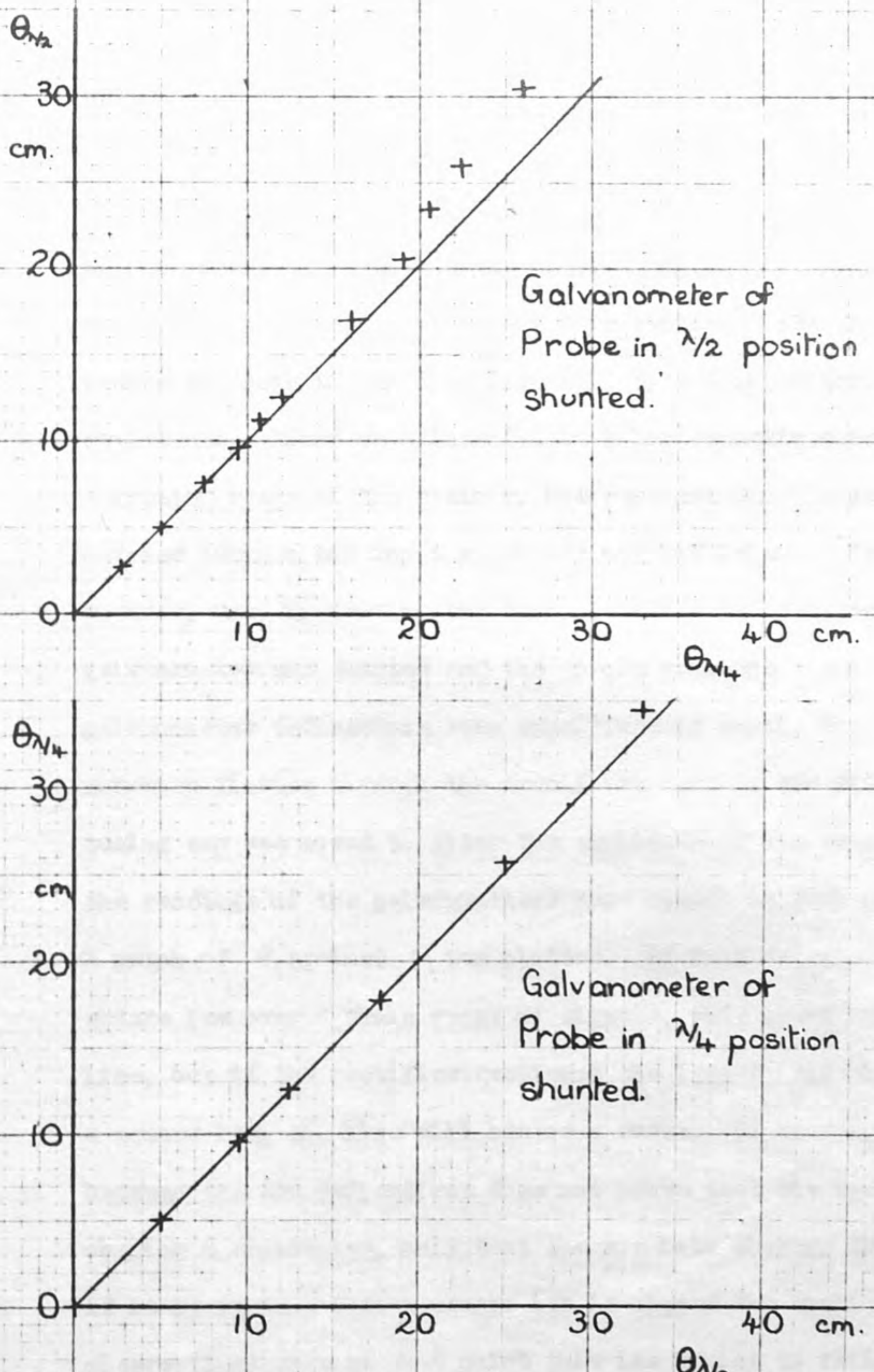

$\theta_{\lambda/2}$
30
cm.
20
10
0
10
20
30
40 cm.
$\theta_{\lambda/4}$
Galvanometer of Probe in λ/2 position shunted.
$\theta_{\lambda/4}$
30
cm
20
10
0
10
20
30
40 cm.
$\theta_{\lambda/2}$
Galvanometer of Probe in λ/4 position shunted.

Figure 4.5

by trial and error may be necessary.

The setting of the indicator pin has to be adjusted for each liquid used, as the surface tension effects are different.

Before measurements are made with this system, it is necessary to know over what range the detectors obey a square law. Each galvanometer connected to the probes was provided with a shunt and series resistance, which could be switched into the circuit to reduce the sensitivity by a factor of 5, without altering the resistance. These were intended to allow accurate measurement over a greater range of the ratio r, but were not finally used for this purpose because the input power was not sufficient. They were, however, used in testing the characteristics of the rectifiers. One galvanometer was shunted and the probe carriage was moved until the galvanometer deflections were approximately equal, that is, the currents flowing through the rectifiers were in the ratio 5:1. The tuning cap was moved to alter the amplitude of the standing waves, and the readings of the galvanometers were noted in each position (θ_1 and θ_2) A graph of θ_1 against θ_2 was plotted. If both detectors obeyed a square law over a whole range of signals, this graph would be a straight line, but if the rectifier receiving the larger signal ceases to obey a square law, the line will become a curve. Of course, a linear relation between the two deflections does not prove that the rectifiers are obeying a square law, only that the are both obeying the same law, but if it is assumed that a square law is obeyed for small signals the observations show at what point this law begins to fail.

By shunting the other galvanometer the limit for the other rectifier can be found in the same way. Figure 4.5 shows the graphs for the two crystals selected.

When these adjustments have been made the carriage is raised by steps of one or more divisions, the liquid is raised each time until it just touches the indicator pin, and the readings of the galvanometers connected to the two detectors are noted, the sensitivities of the two detectors having been adjusted to give the maximum accuracy. The ratio of the two readings is plotted against the carriage position, and the constants are deduced from the graph as described above. For water, to reduce the surface tension effects, readings were taken as the liquid depth was reduced from its maximum to zero. The time taken to make the measurements and plot the complete curve for water (readings being taken at intervals of about 0.2 mm., up to a depth of about 3 cm.) is about 2 hrs.

MEASUREMENT OF THE MUTUAL VISCOSITY

The mutual viscosity is calculated from the relationship

$$\eta\sigma = f_A^2\eta_A\sigma_A + f_B^2\eta_B\sigma_B + 2f_Af_B\eta_{AB}\sigma_{AB}$$

where $\sigma = \sqrt[3]{\frac{M}{N\rho}}$ (M = molecular weight, N = Avogadro's number) and can therefore be found from measurements of the viscosity and density of the pure substances and of mixtures of various concentrations. $\eta_{AB}\sigma_{AB}$ is calculated for each concentration. If it shows a consistent variation with concentration, the extrapolated value at $f_B = 0$ is used since this gives the mutual viscosity under the conditions in which the relaxation times are usually measured. Otherwise the mean value is taken.

The viscosity measurements were made using an Ostwald viscometer (B.S.S. No. 1) in which the flow time for the mixtures used was 2-7 minutes. The viscometer was maintained at a temperature of (20.0 ± 0.1)°C. in a thermostatically controlled water bath, and was calibrated by assuming a viscosity of 0.97 c.poise for cyclohexane at 20°C.

The viscosity of the chlorobenzene-medicinal paraffin mixtures of higher paraffin content were measured by Stokes' method The accuracy of these measurements is not high, but in any case the molecular weight of the paraffin is not accurately known, and a rough estimate of the mutual viscosity is sufficient to indicate whether the theory is applicable in this extreme case.

The densities were measured at (20 ± 1)°C. using a density bottle and a "Chain-dial" balance.

5. EXPERIMENTAL RESULTS

RELAXATION TIMES

WATER AND ETHYL ALCOHOL

Miss Newitt's results [34] suggested that measurements made using a transmission line might be less reliable than those made using a wave-guide, and that if this is the case the difficulties will be greatest when liquids of high phase constant and absorption are used. Measurements were therefore made with the present apparatus on water and ethyl alcohol to discover whether the experimental results are consistent with the theory.

The chief source of error in the case of water appears to arise from the difficulty of setting the initial level of the liquid. Graphs 5.1, a-f, show experimental curves for liquid depths 1.3 to

4.0 cm. for water, with the indicator pin set at distances 9.30, 9.35, 9.40, 9.45, 9.50, 9.55 cm. respectively below the lower probe, the water being contained in a wide vessel so that the surface tension affects would not be altered by slight variations in the position of this vessel relative to the transmission line. The graphs show that under the conditions used, the liquid level is correct when the pin is between 9.45 and 9.50 cm. below the lower probe. (In the absence of surface tension the correct position would be 9.35 cm. below the lower probe). If the liquid level differs by more than 0.05 cm. from its correct position it becomes impossible to draw an "equal intercept line". On each graph a line has been drawn across each segment of the curve at the level at which it has the correct width (i.e. $\frac{\lambda}{4}$), so that the distortion of the curve can be clearly seen. The dotted line has been drawn to show how the general level of the whole curve varies.

Graphs 5.2, 5.3, 5.4, 5.5, show the experimental results for water at various temperatures when the setting of the liquid level is approximately correct, as is proved by the close approximation of the experimental curve to the theoretical form. For graphs 5.2-5.4 the setting of the pin was determined by the resonance method; for graph 5.5 the pin was set at 9.50 cm. below the lower probe and a wide containing vessel was used. In each case values of αs have been calculated from the values of r at $s = n\frac{\lambda}{4}$ and the values of $\frac{dr}{ds}$ at $s = (2n+1)\frac{\lambda}{8}$, (n is an integer), and plotted against s, the former points being marked with rings and the latter, which are less reliable, by crosses. The approximation of this graph to a straight line

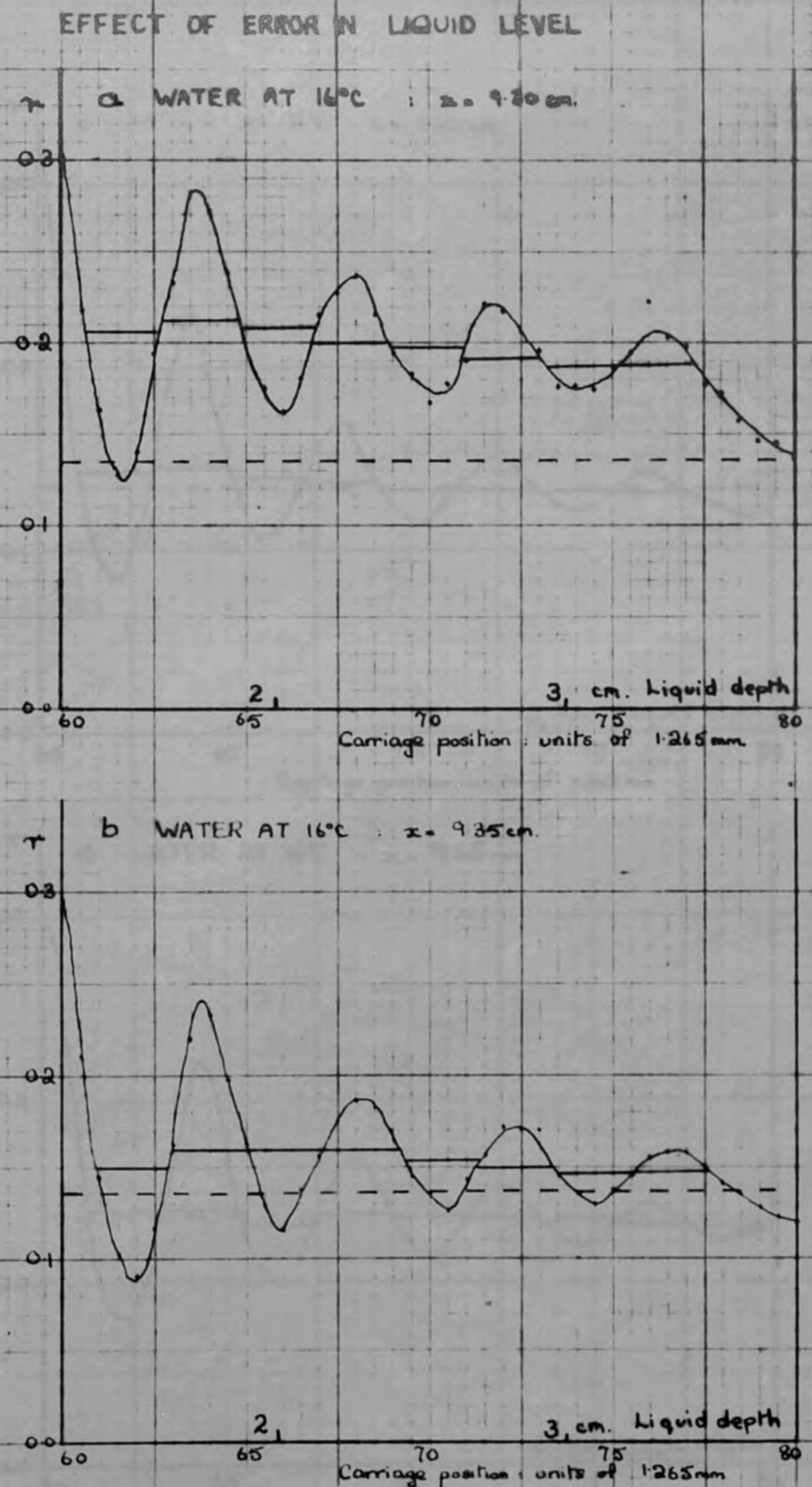


FIGURE 5.1 a and b.

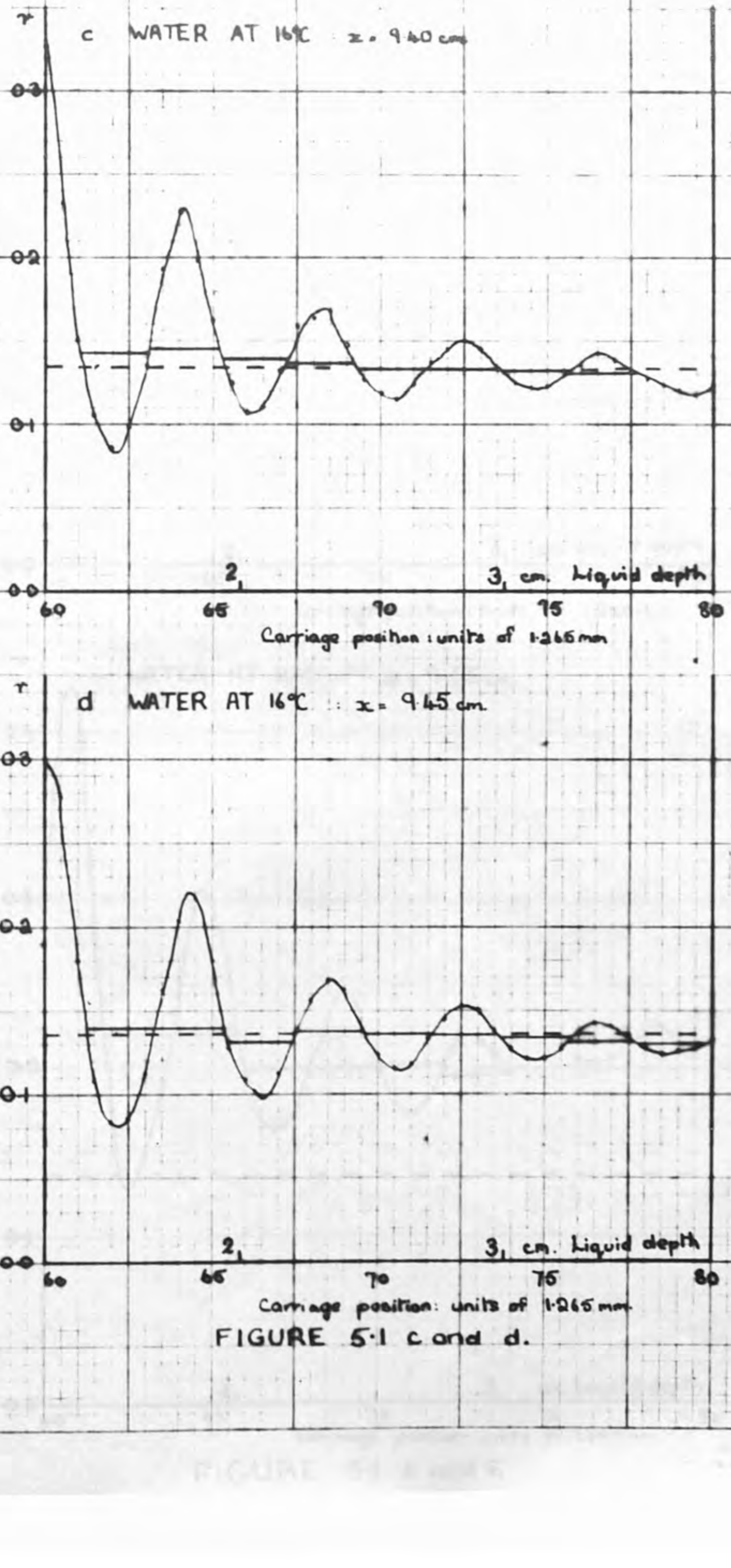


FIGURE 5·1 c and d.

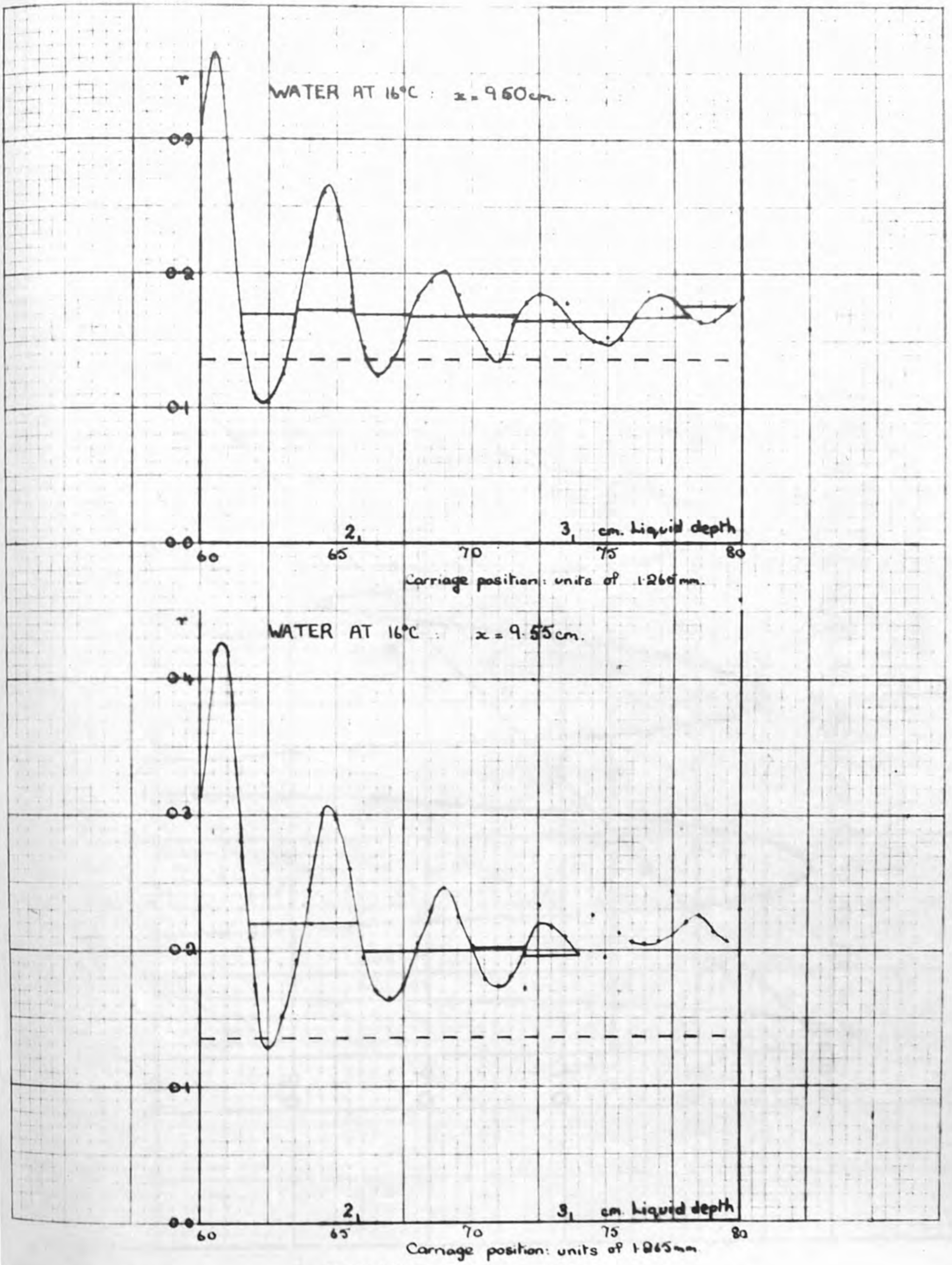


FIGURE 5·1 e and f.

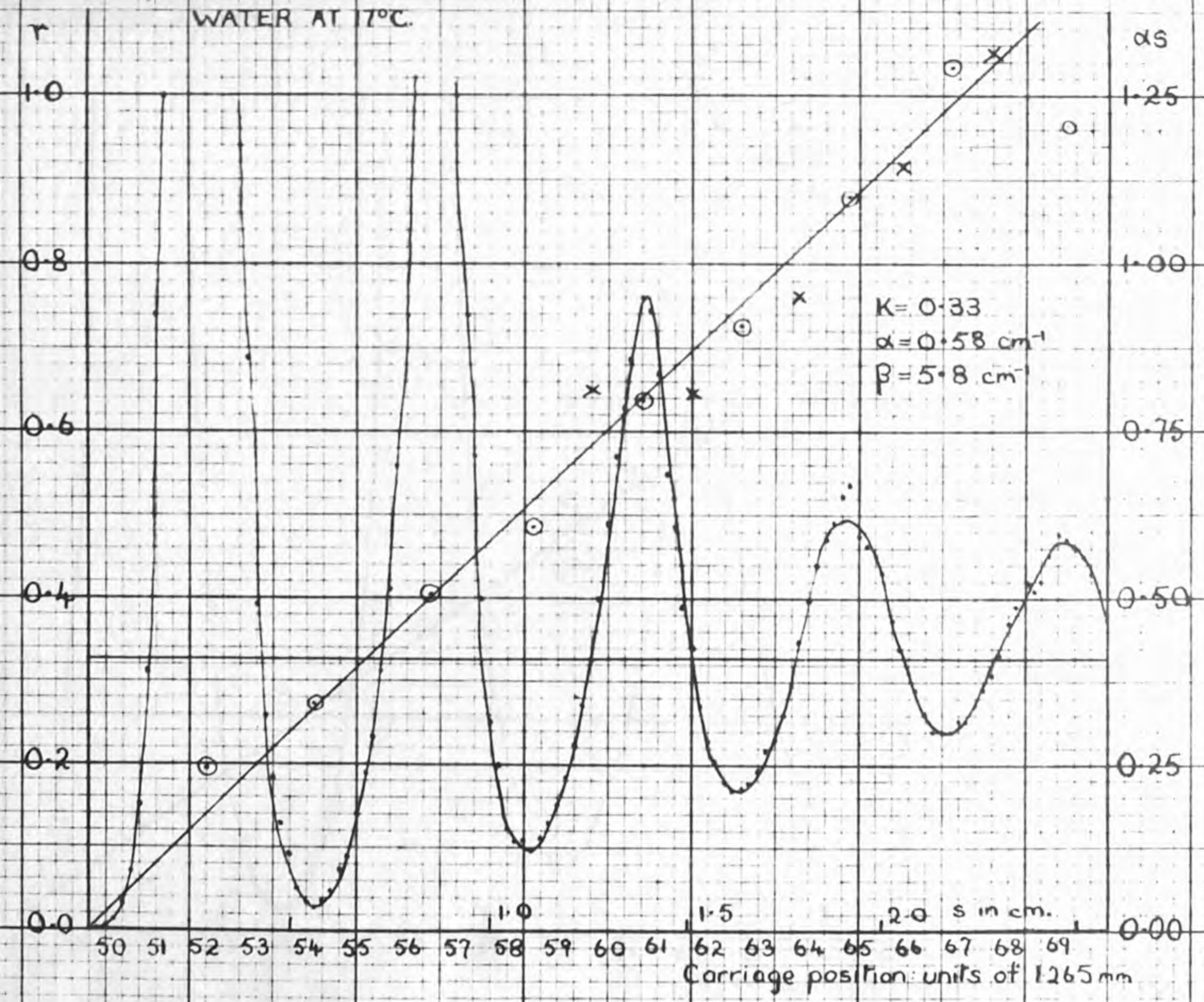

WATER AT 17°C.
r
1·0
0·8
0·6
0·4
0·2
0·0
αs
1·25
1·00
0·75
0·50
0·25
0·00
K= 0·33
α = 0·58 cm⁻¹
β = 5·8 cm⁻¹
1·0
1·5
2·0
s in cm.
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
Carriage position: units of 1·265 mm

FIGURE 5.2

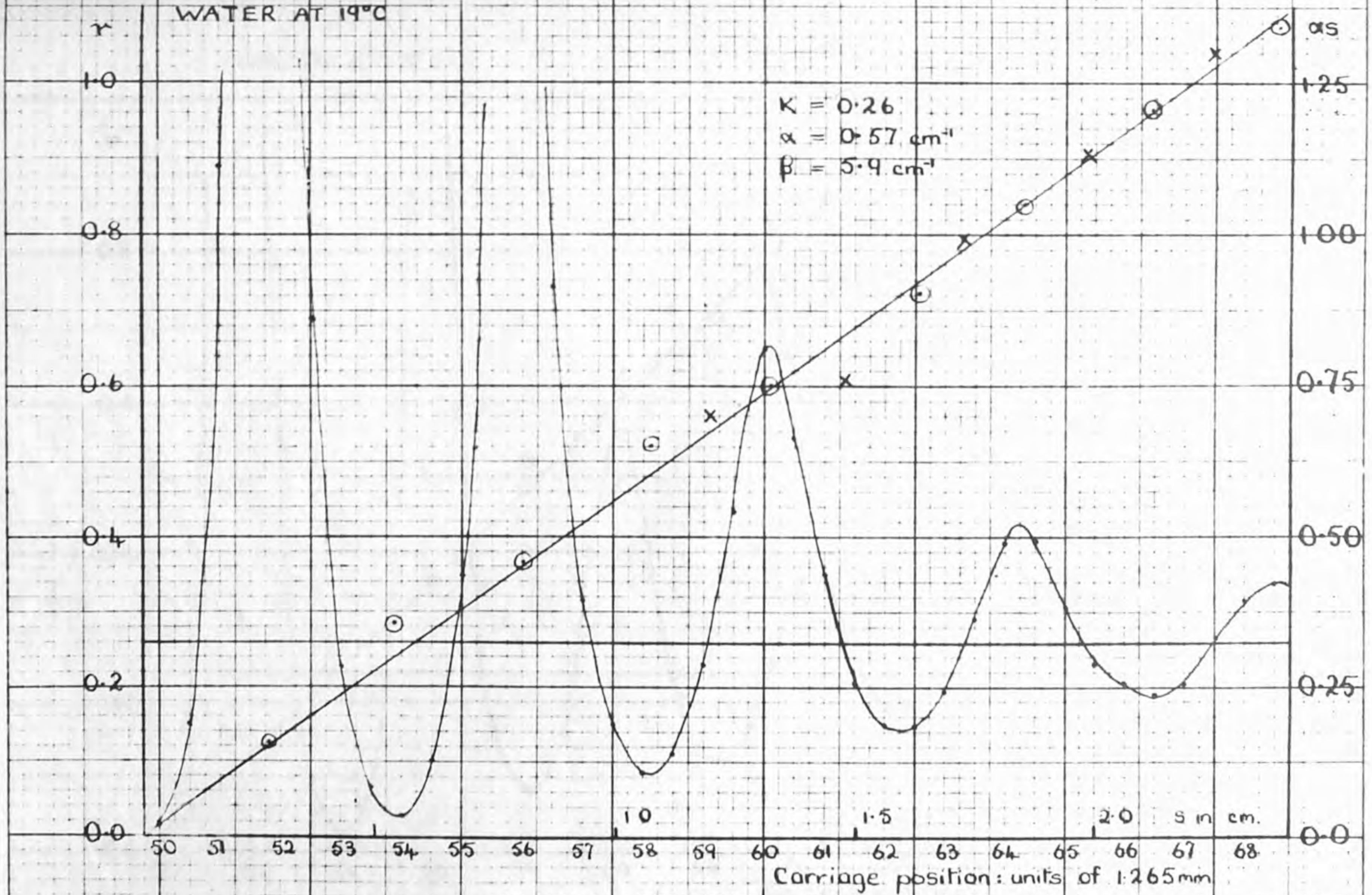

WATER AT 19°C
r
1·0
0·8
0·6
0·4
0·2
0·0
αs
1·25
1·00
0·75
0·50
0·25
0·0
K = 0·26
α = 0·57 cm⁻¹
β = 5·9 cm⁻¹
1·0
1·5
2·0
s in cm.
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
Carriage position: units of 1·265mm

FIGURE 5:3

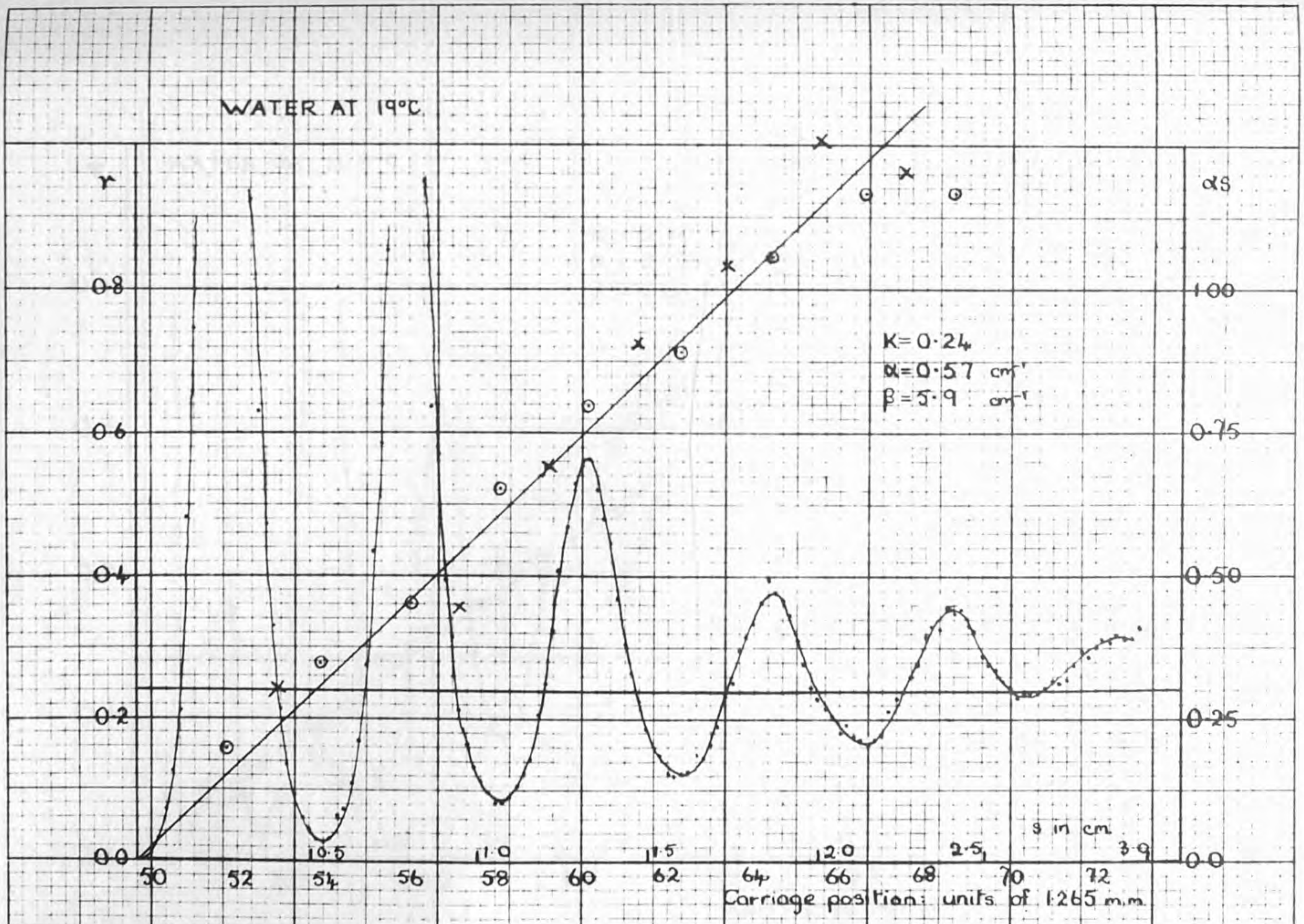

WATER AT 19°C
r
0·0
0·2
0·4
0·6
0·8
αs
0·0
0·25
0·50
0·75
1·00
K = 0·24
α = 0·57 cm⁻¹
β = 5·9 cm⁻¹
s in cm
10·5
11·0
11·5
12·0
2·5
3·9
50
52
54
56
58
60
62
64
66
68
70
72
Carriage position: units of 1·265 m.m.

FIGURE 5-4

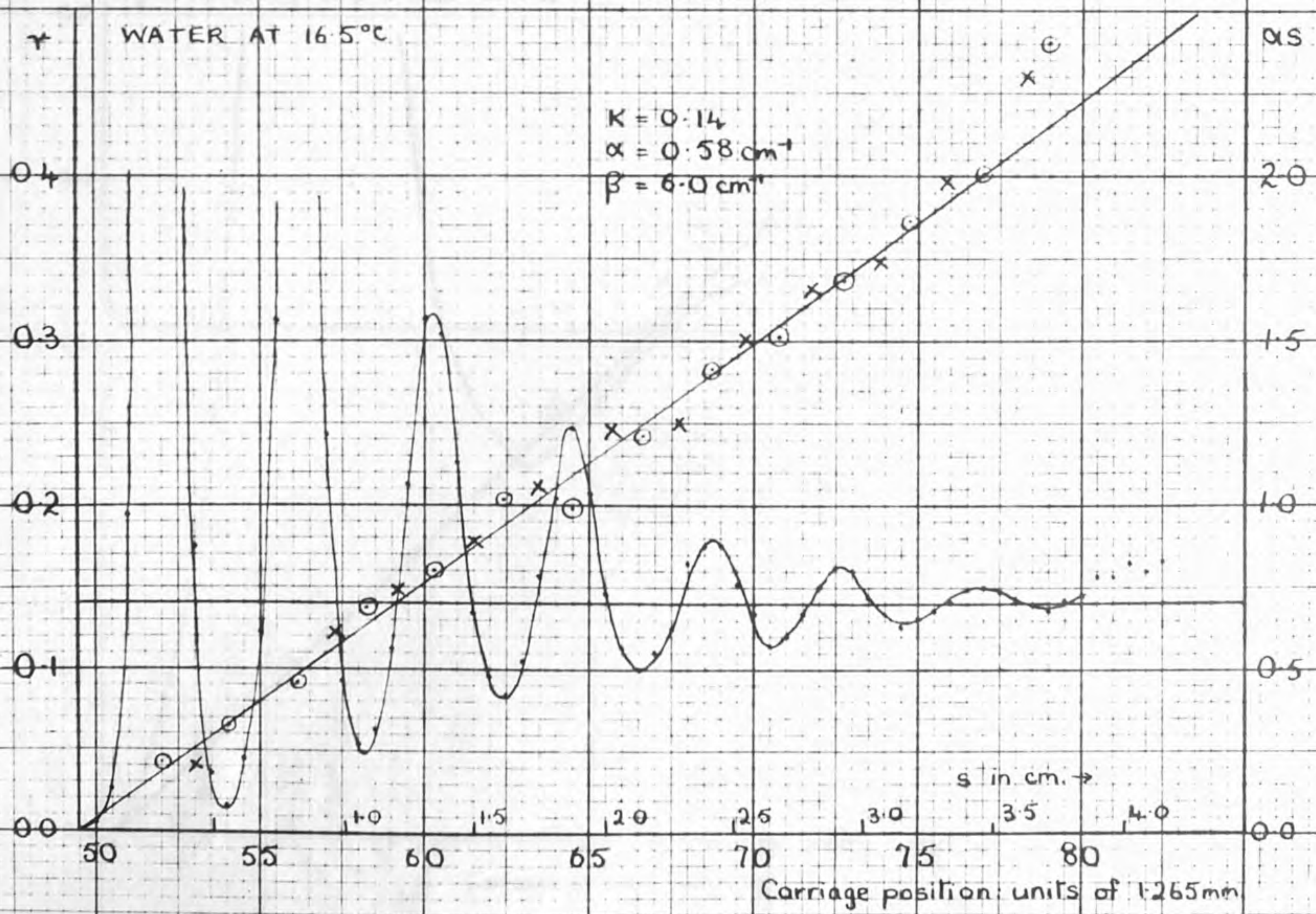

r
WATER AT 16·5°C
K = 0·14
α = 0·58 cm⁻¹
β = 6·0 cm⁻¹
αs
0·0
0·1
0·2
0·3
0·4
0·5
1·0
1·5
2·0
s in cm. →
1·0
1·5
2·0
2·5
3·0
3·5
4·0
50
55
60
65
70
75
80
Carriage position: units of 1·265 mm

FIGURE 5·5

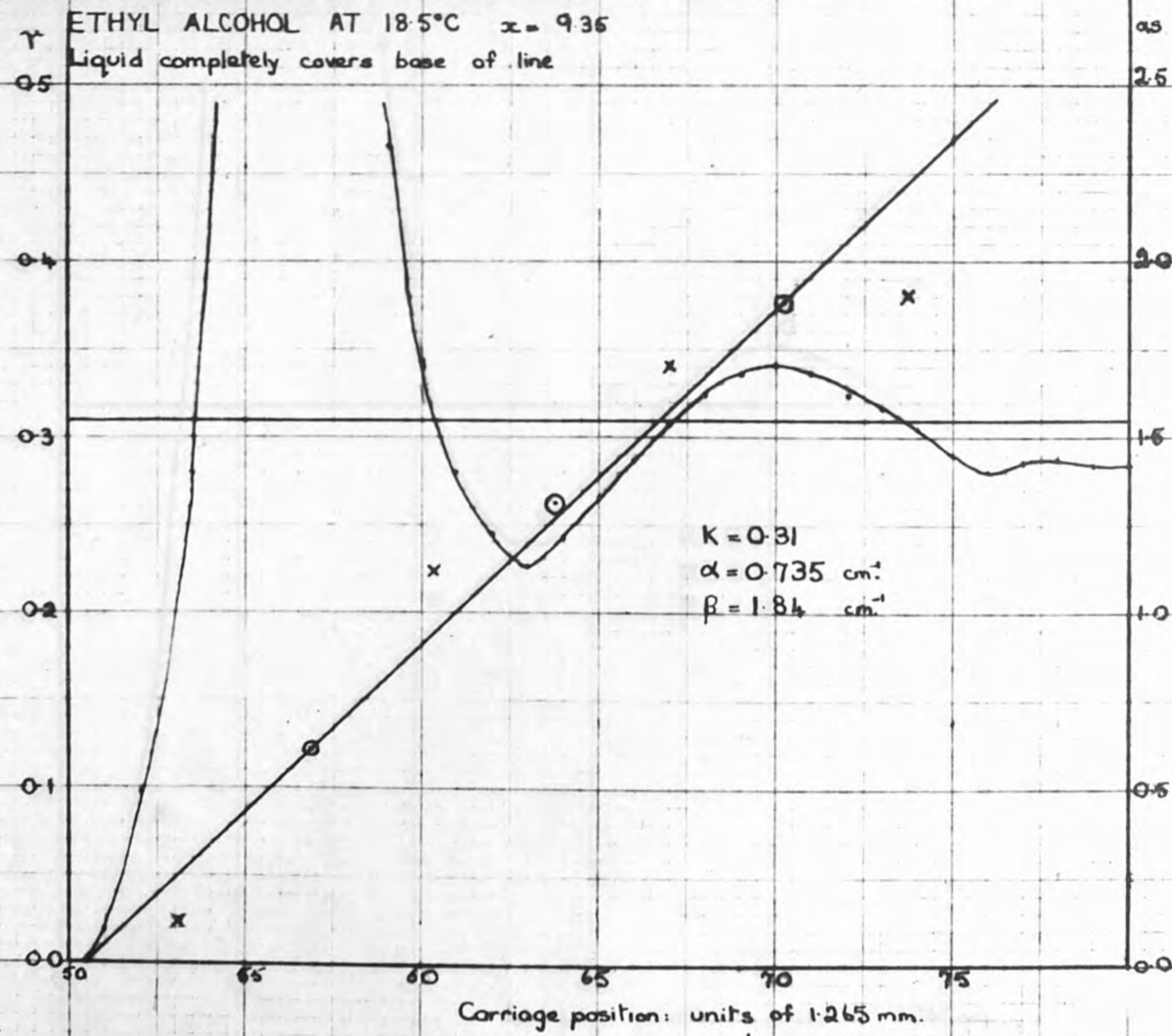

ETHYL ALCOHOL AT 18·5°C x = 9·35
Liquid completely covers base of line
γ
0·5
0·4
0·3
0·2
0·1
0·0
as
2·5
2·0
1·5
1·0
0·5
0·0
K = 0·31
α = 0·735 cm⁻¹
β = 1·84 cm⁻¹
50
55
60
65
70
75
Carriage position: units of 1·265 mm.

FIGURE 5·6a

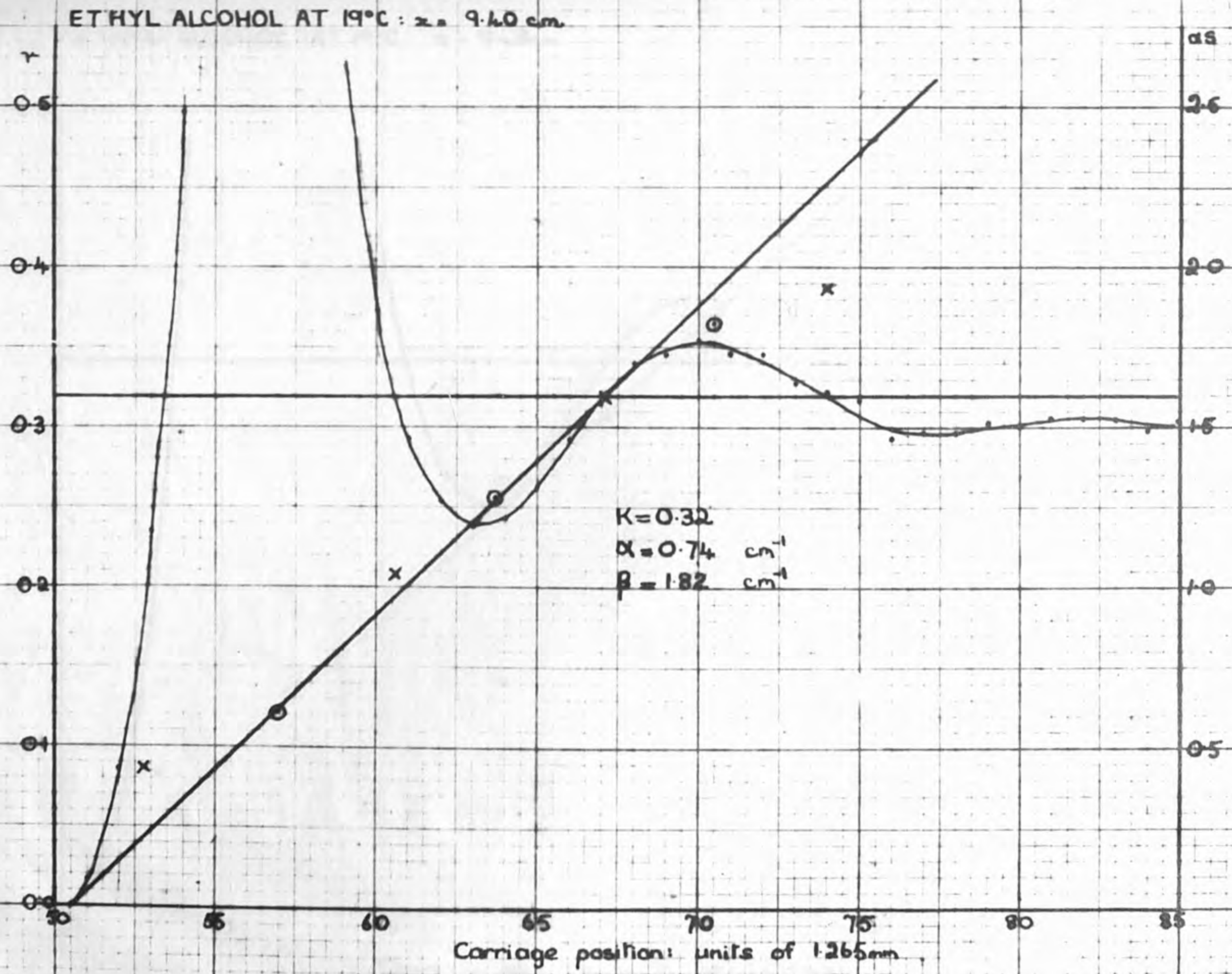

ETHYL ALCOHOL AT 19°C : x = 9·40 cm.
r
0·5
0·4
0·3
0·2
0·1
0·0
as
2·6
2·0
1·5
1·0
0·5
50
55
60
65
70
75
80
85
K = 0·32
α = 0·74 cm⁻¹
β = 1·82 cm⁻¹
Carriage position: units of 1·265mm

FIGURE 5·6b

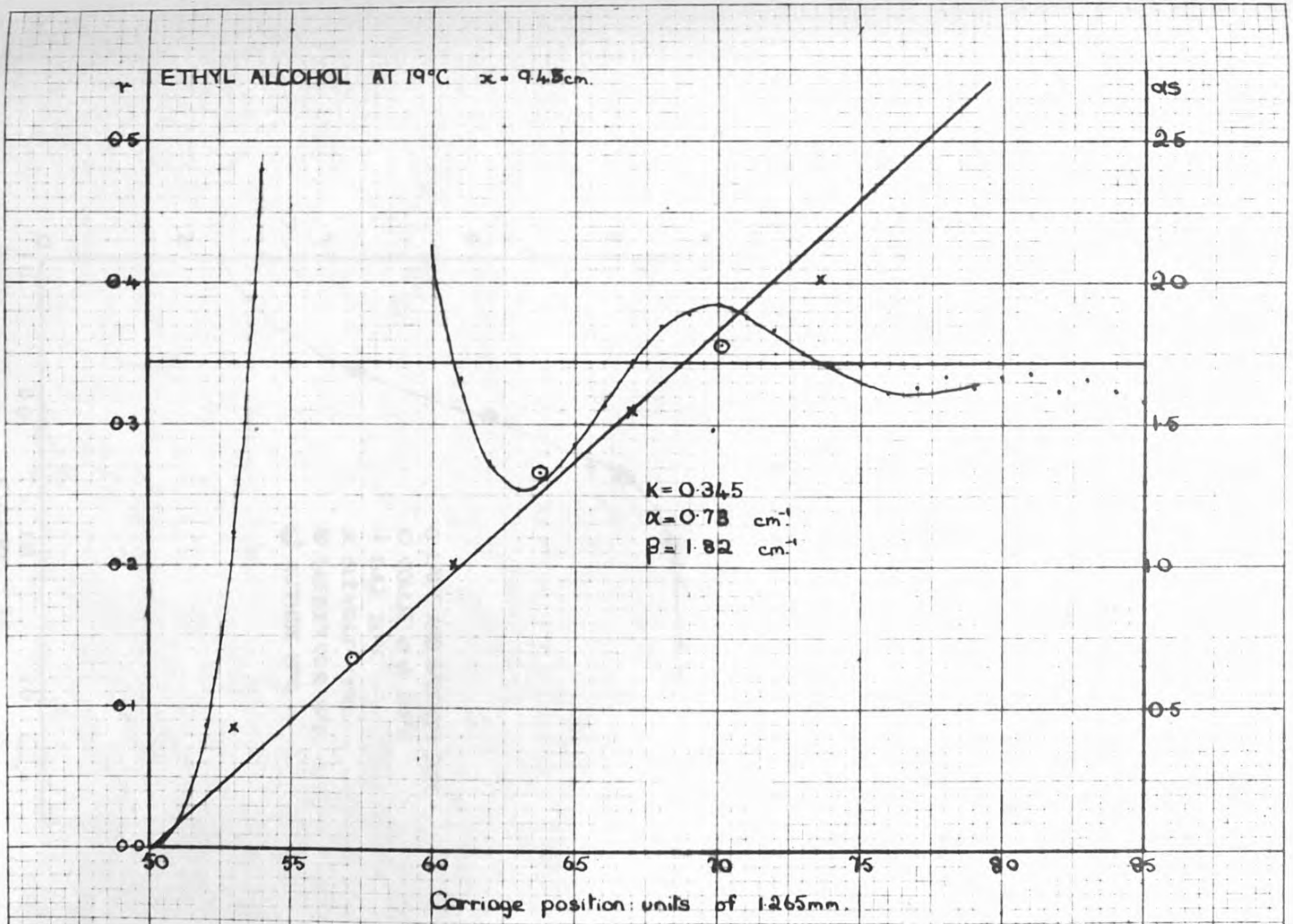

r
ETHYL ALCOHOL AT 19°C x = 9·45cm.
αs
0·0
0·1
0·2
0·3
0·4
0·5
0·5
1·0
1·5
2·0
2·5
K = 0·345
α = 0·78 cm.⁻¹
β = 1·82 cm.⁻¹
50
55
60
65
70
75
80
85
Carriage position: units of 1·265mm.

FIGURE 5·6c.

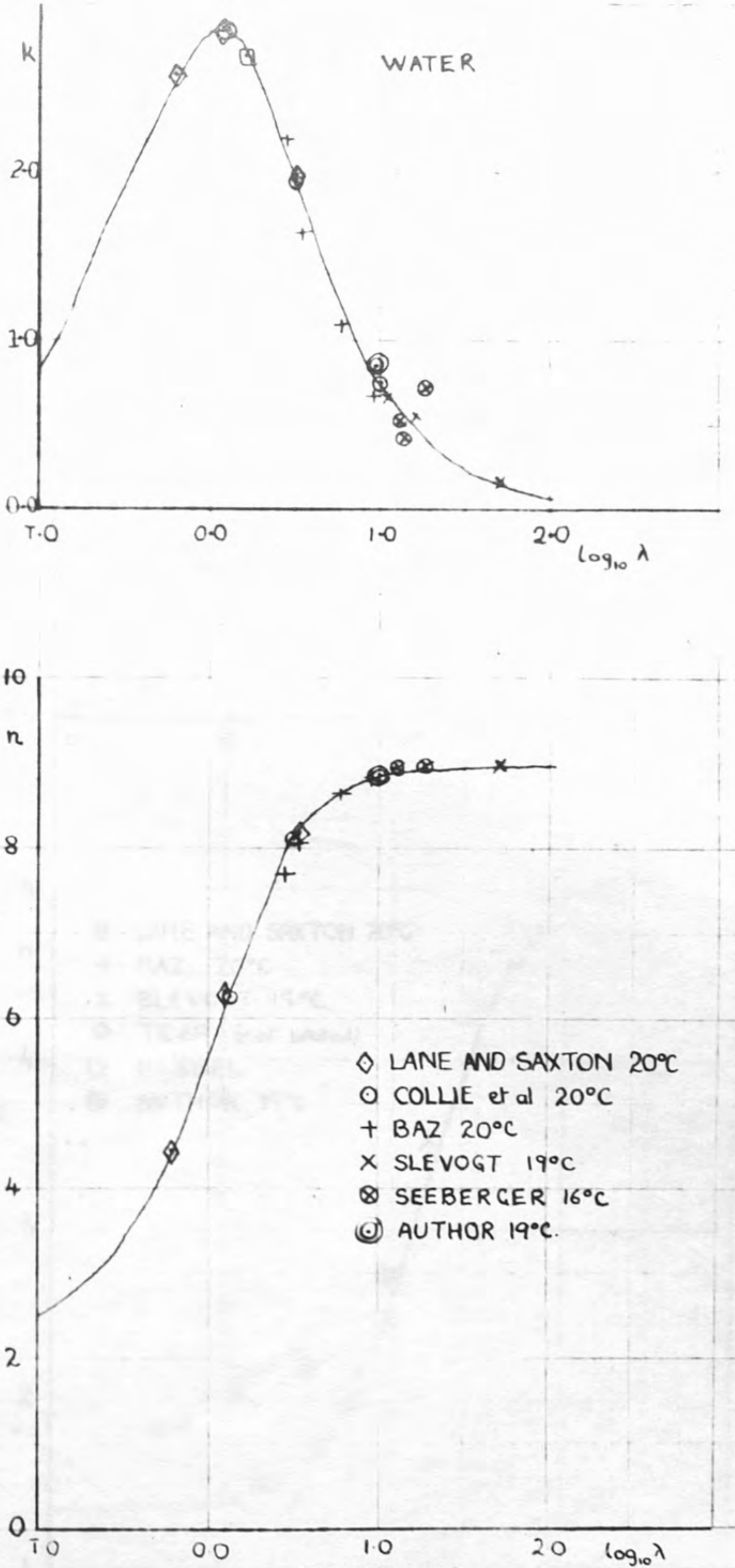

k
WATER
2·0
1·0
0·0
1̄·0
0·0
1·0
2·0
log₁₀ λ
10
n
8
6
4
2
0
1̄0
0.0
1.0
2.0
log₁₀ λ
◇ LANE AND SAXTON 20°C
○ COLLIE et al 20°C
+ BAZ 20°C
× SLEVOGT 19°C
⊗ SEEBERGER 16°C
◎ AUTHOR 19°C.

FIGURE 57a

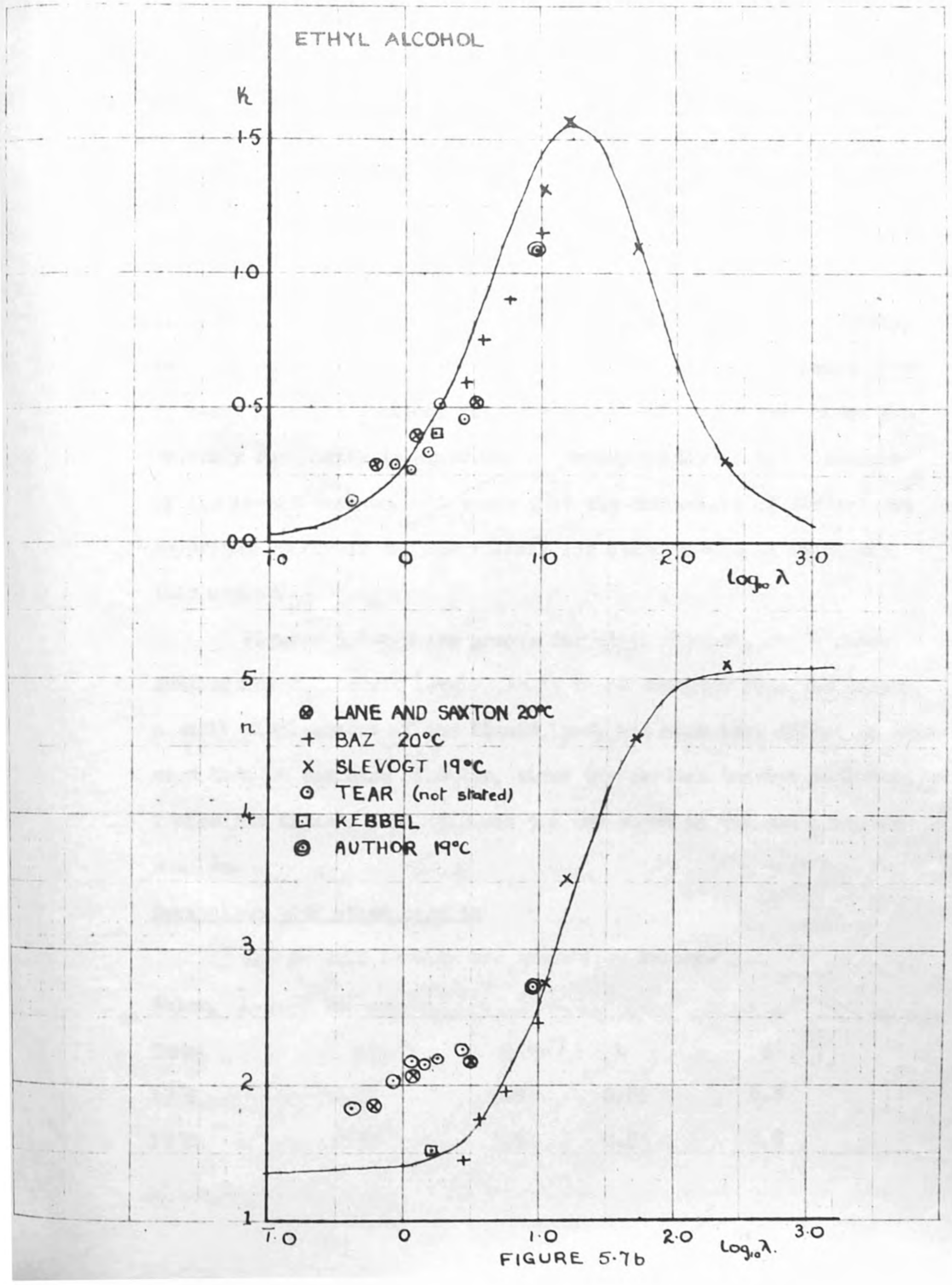

ETHYL ALCOHOL
k
1·5
1·0
0·5
0·0
1̄·0
0
1·0
2·0
3·0
log₁₀ λ
n
5
4
3
2
1
⊗ LANE AND SAXTON 20°C
+ BAZ 20°C
× SLEVOGT 19°C
⊙ TEAR (not stated)
⊡ KEBBEL
◎ AUTHOR 19°C
1̄·0
0
1·0
2·0
3·0
log₁₀ λ.

FIGURE 5·7b

indicates that the error in the absorption coefficient measured by this method is about 2%, and that the curvature of the liquid surface has no serious effect in a line of these dimensions ($a = 1.73$ cm., $b = 0.46$ cm.) provided the correct level for the liquid can be found. On the other hand, not one of the four graphs corresponds exactly to the theoretical curve; for instance, some of the measured gradients near the origin give values of cosh $2\alpha s$ less than unity, and in no case are the intercepts made by the "equal intercept line" constant over the whole of the curve plotted. These deviations are probably due partly to experimental error, partly to the curvature of the liquid surface. It seems that the dimensions of the present apparatus represent the lower limit for measurements on water with this method.

Figures 5.6 a-c are graphs for ethyl alcohol, for various settings of the liquid level. As is to be expected from the theory, a small displacement of the liquid level has much less effect in this case than in the case of water, since the surface tension is lower. Tables for figures 5.1a, 5.2 and 5.6 are shown in the appendix, as samples.

Comparison with other results

The present results are summarised below:-

Water, $\lambda = 9.35$ cm.

Temp.	α (cm^{-1})	β (cm^{-1})	k	n
17°C	0.58	5.9	0.86	8.8
19°C	0.57	5.9	0.85	8.8

Alcohol [illegible] cm.

Alcohol $\lambda = 9.35$ cm.

Temp.	$\alpha\,(cm^{-1})$	$\beta\,(cm^{-1})$	k	n
19°C.	0.73 (5)	1.83	1.09	2.72

The error is estimated to be ±2% in all cases.

In figures 5.7a and 5.7b the theoretical curves for water and alcohol are drawn, the necessary constants being taken from the results of Collie et al.[35] and Baz,[36] respectively.

The relations used are

$$\varepsilon' = n^2 - k^2$$

$$\varepsilon'' = 2nk$$

and

$$\varepsilon' = \varepsilon_0 + \frac{\varepsilon_s - \varepsilon_0}{1 + x^2}$$

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_0}{1 + x^2} \cdot x$$

where according to the Debye theory, $x = \frac{\varepsilon_s + 2}{\varepsilon_0 + 2}\frac{\lambda_s}{\lambda}$ ($\lambda_s = 2\pi c\tau$) while according to Onsager's theory, x is simply $\frac{\lambda_s}{\lambda}$. The form of the theoretical curve is the same in each case, but the interpretation of the constants is different. The values of λ_s quoted refer to Onsager's theory. The constants are:-

Water $\lambda_s = 1.80$ cm., $\varepsilon_s = 80.36$, $\varepsilon_o = 5.5$

Alcohol $\lambda_s = 28.4$ cm., $\varepsilon_s = 25.8$ $\varepsilon_o = 1.85$

The present results are plotted on these graphs together with the results of other observers. (Refs. 35-41). It will be seen that the agreement with other results is good, showing that there is no serious error due to the curvature of the liquid surfaces.

PYRIDINE IN CYCLOHEXANE AND IN CARBON TETRACHLORIDE

Figure 5.8 shows the experimental curve for pure cyclohexane (Table 5.8). From this curve

$$K\left|\frac{Z_o'}{Z_o}\right|^2 = K\left|\frac{\lambda}{\lambda_o}\right|^2 = 23$$

and λ = 6.53 cm.

hence K = 47.2

This value of k was used to calculate $K\left|\frac{Z_o'}{Z_o}\right|^2$ for the solutions.

In figure 5.9 (table 5.9) the second minimum for each solution is shown. The position of each minimum gives the wave length in the liquid. $K\left|\frac{Z_o'}{Z_o}\right|^2$ can then be calculated, and α found from the amplitude at the minimum. The variation of α with concentration is shown in figure 5.10, the values of α being listed, together with the derived constants, in table 5.10. The value of τ is constant within the experimental error over this range of concentration, and the mean value (neglecting the first 3 results).

$$\tau = 2{\cdot}7 \pm 0{\cdot}1 \times 10^{-12} \text{ sec.}$$

is taken as the relaxation time at infinite dilution for a solution of pyridine in cyclohexane at (20±1)°C.

Tables 5.11-5.13, and figures 5.11-5.13 are the corresponding results for pyridine in carbon tetrachloride. From figure 5.13, for pure carbon tetrachloride

$$K\left|\frac{Z_o'}{Z_o}\right|^2 = K\left|\frac{\lambda}{\lambda_o}\right|^2 = 21$$

and $\lambda = 6{\cdot}24$ cm.

hence $K = 47{\cdot}3$

From table 5.13 τ is again seen to be constant within the experimental error, and the relaxation time of pyridine in carbon tetrachloride at infinite dilution is taken to be

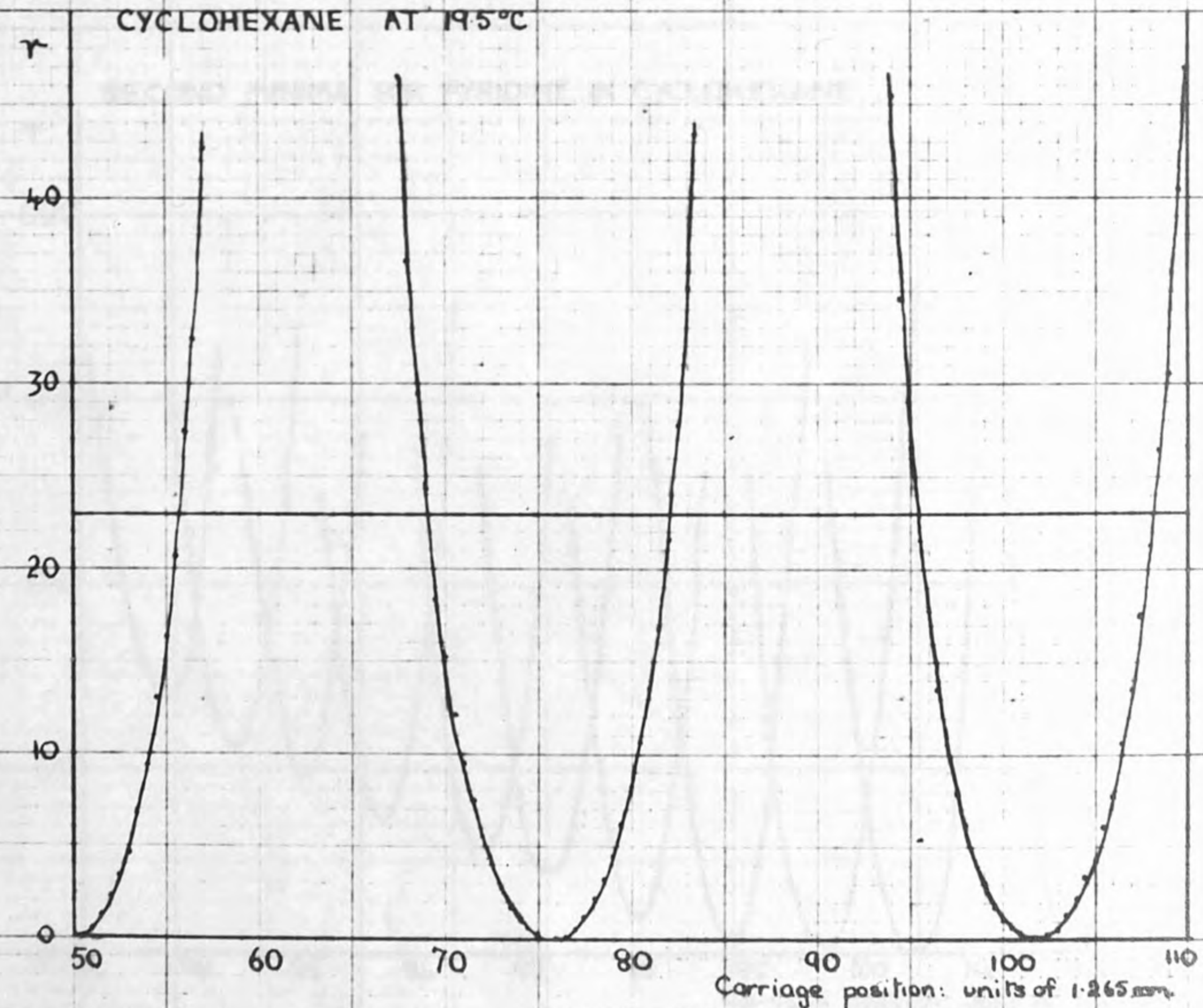

CYCLOHEXANE AT 19·5°C
r
40
30
20
10
0
50
60
70
80
90
100
110
Carriage position: units of 1·265 mm.

FIGURE 5·8

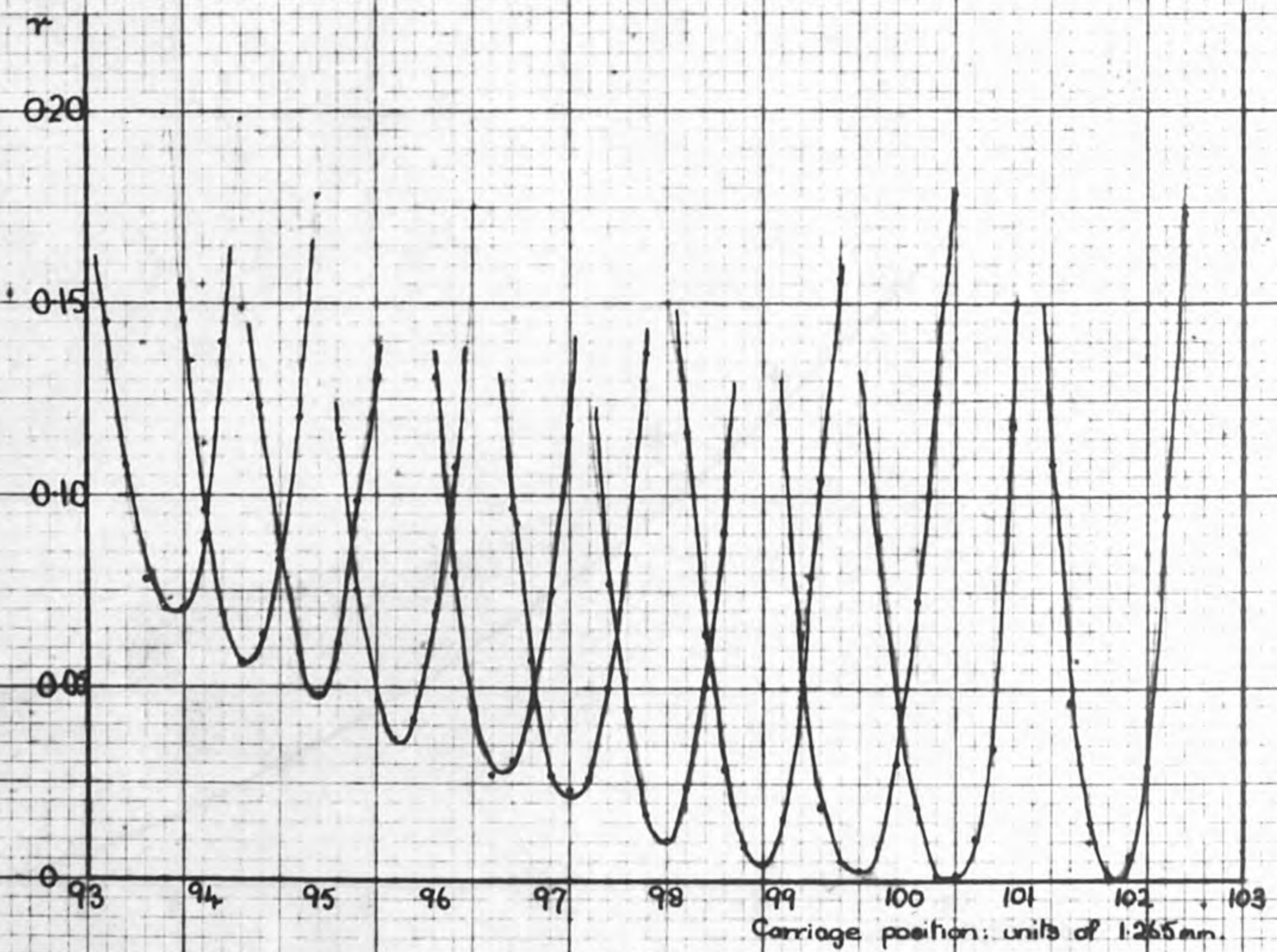

SECOND MINIMA FOR PYRIDINE IN CYCLOHEXANE

FIGURE 5.9

ABSORPTION OF PYRIDINE-CYCLOHEXANE MIXTURES AT 20°C.

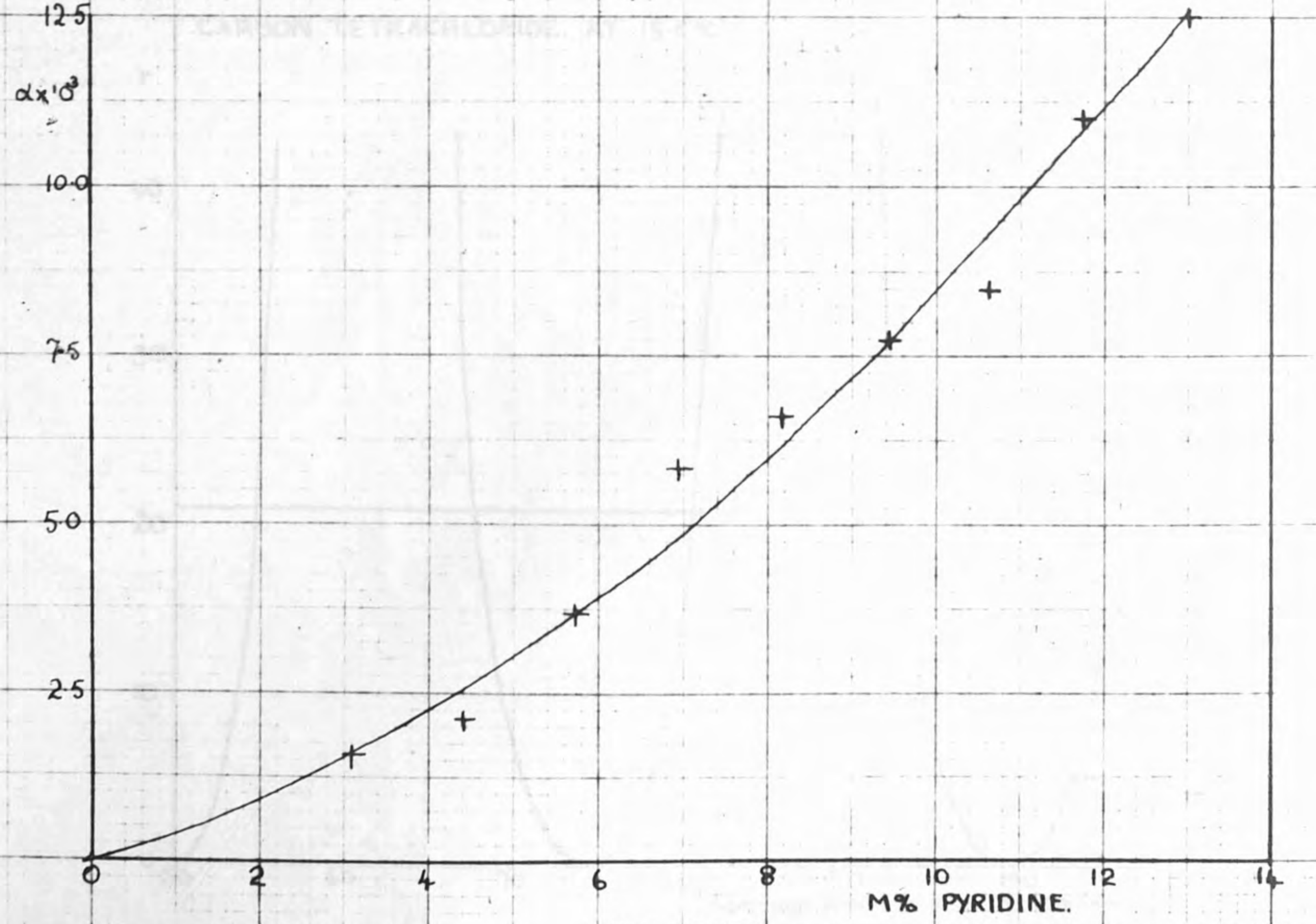


FIGURE 5.10

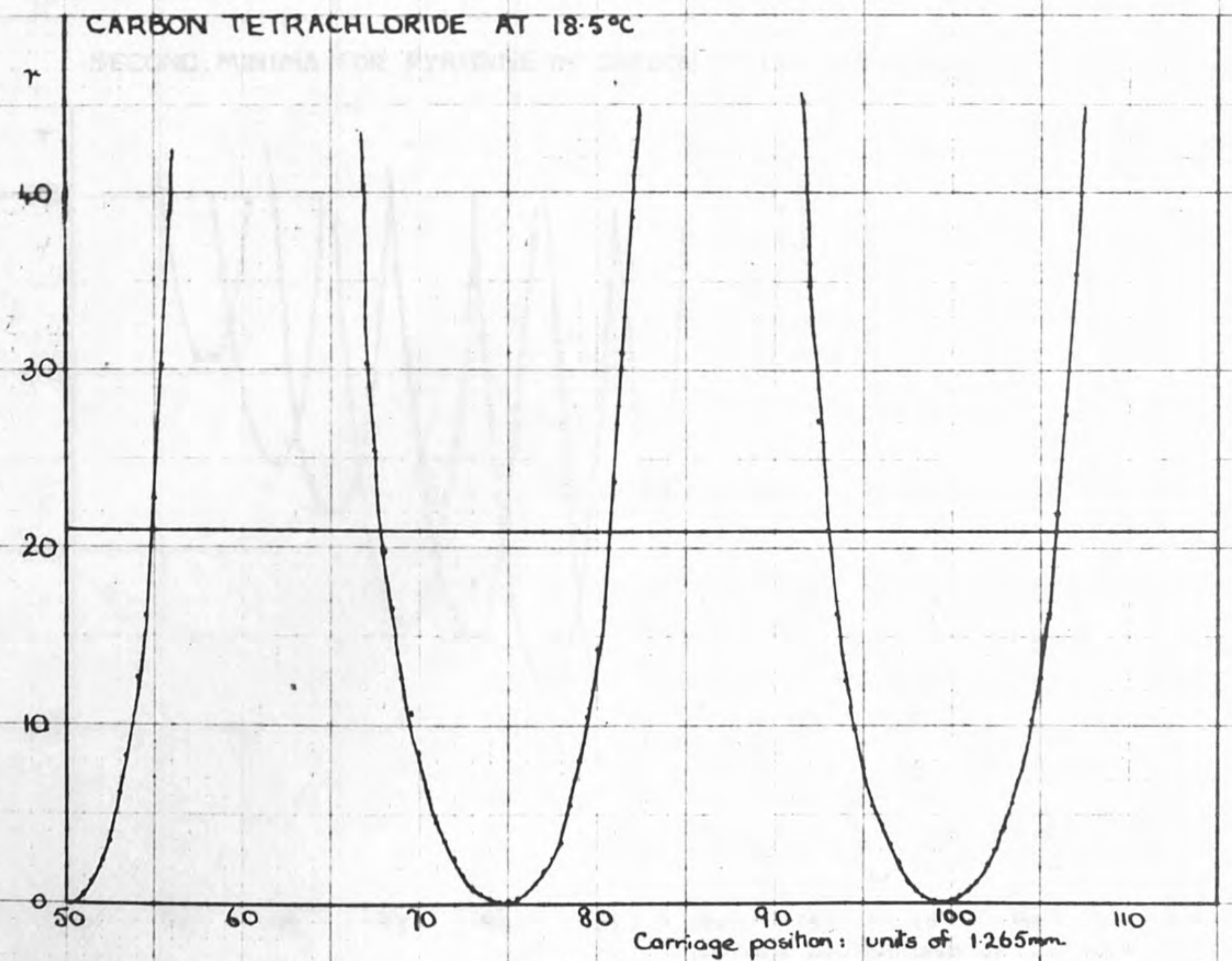

CARBON TETRACHLORIDE AT 18·5°C
r
0
10
20
30
40
50
60
70
80
90
100
110
Carriage position: units of 1·265mm.

FIGURE 5.11.

SECOND MINIMA FOR PYRIDINE IN CARBON TETRACHLORIDE

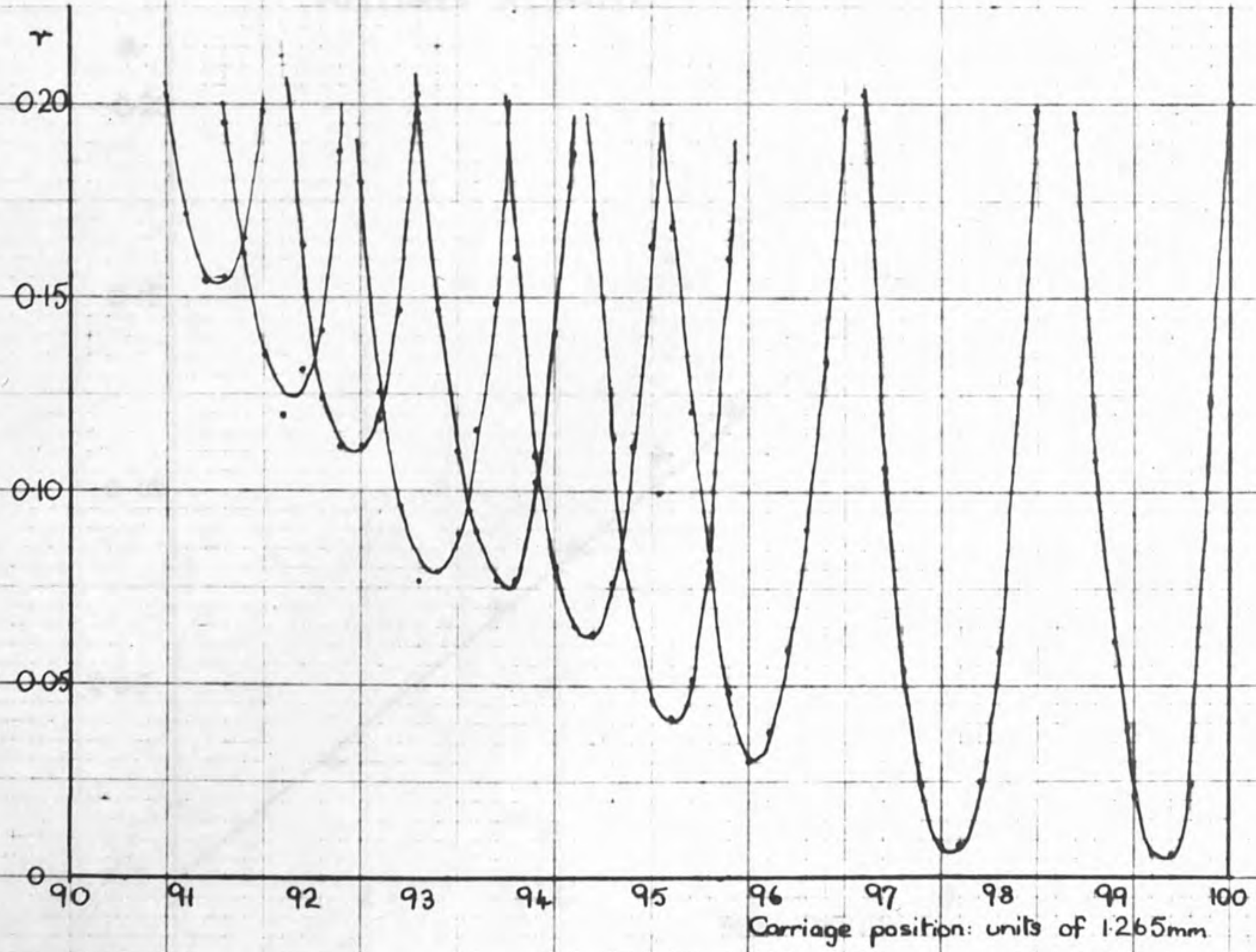


FIGURE 5.12

ABSORPTION OF PYRIDINE-CARBON TETRACHLORIDE MIXTURES AT (19±1)°C.

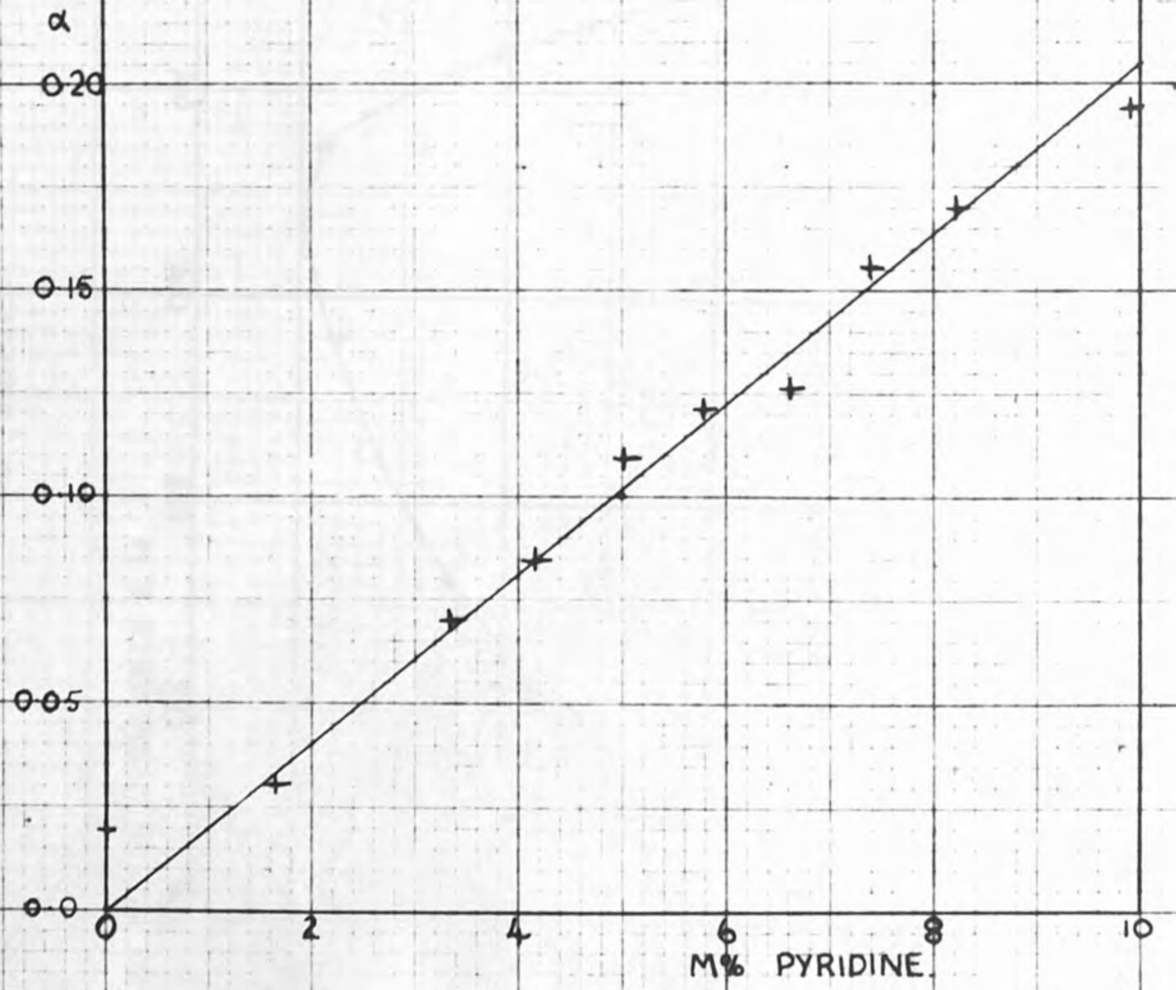


FIGURE 5·13

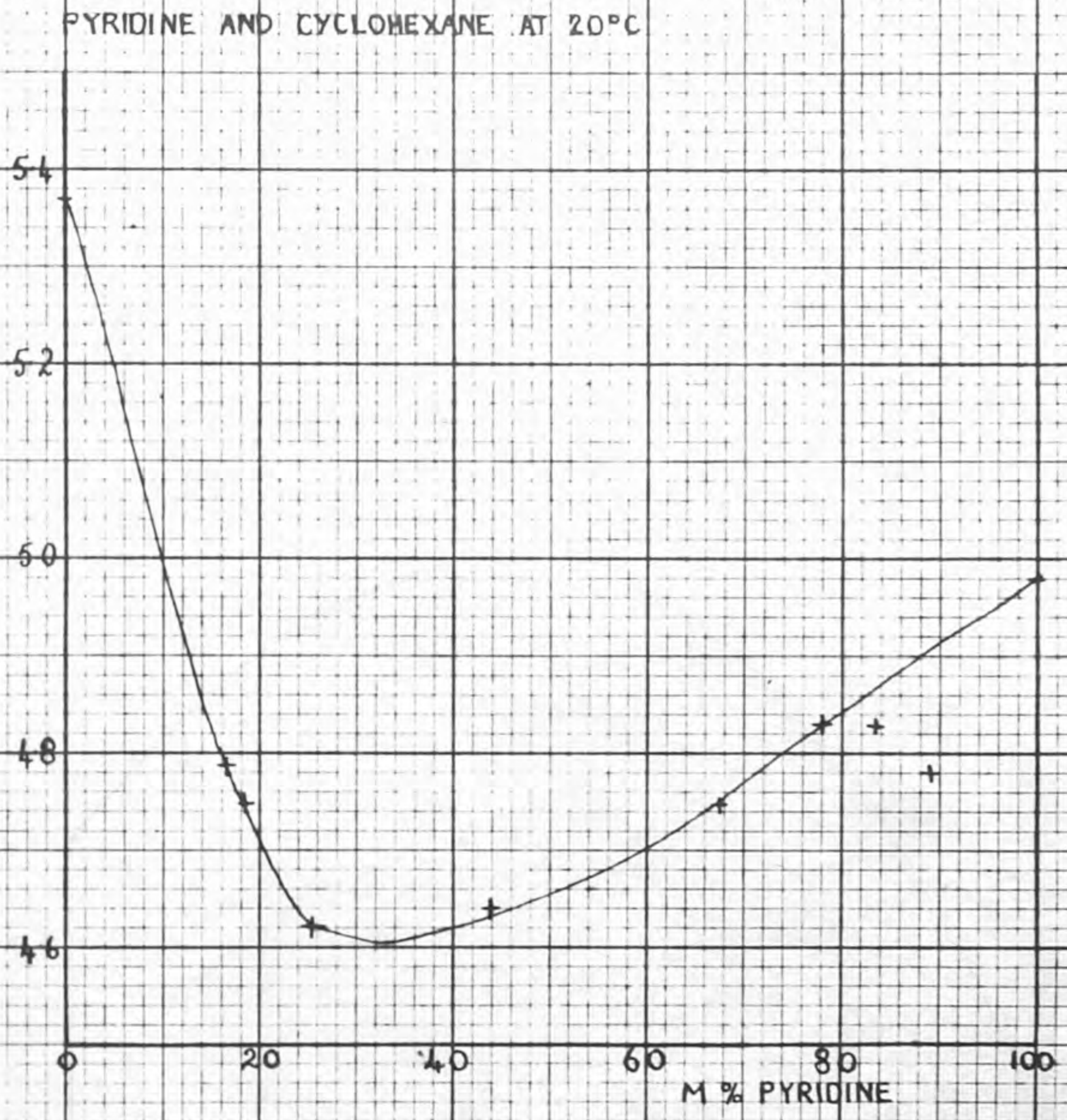

PYRIDINE AND CYCLOHEXANE AT 20°C
54
52
50
48
46
0
20
40
60
80
100
M % PYRIDINE

FIGURE 514

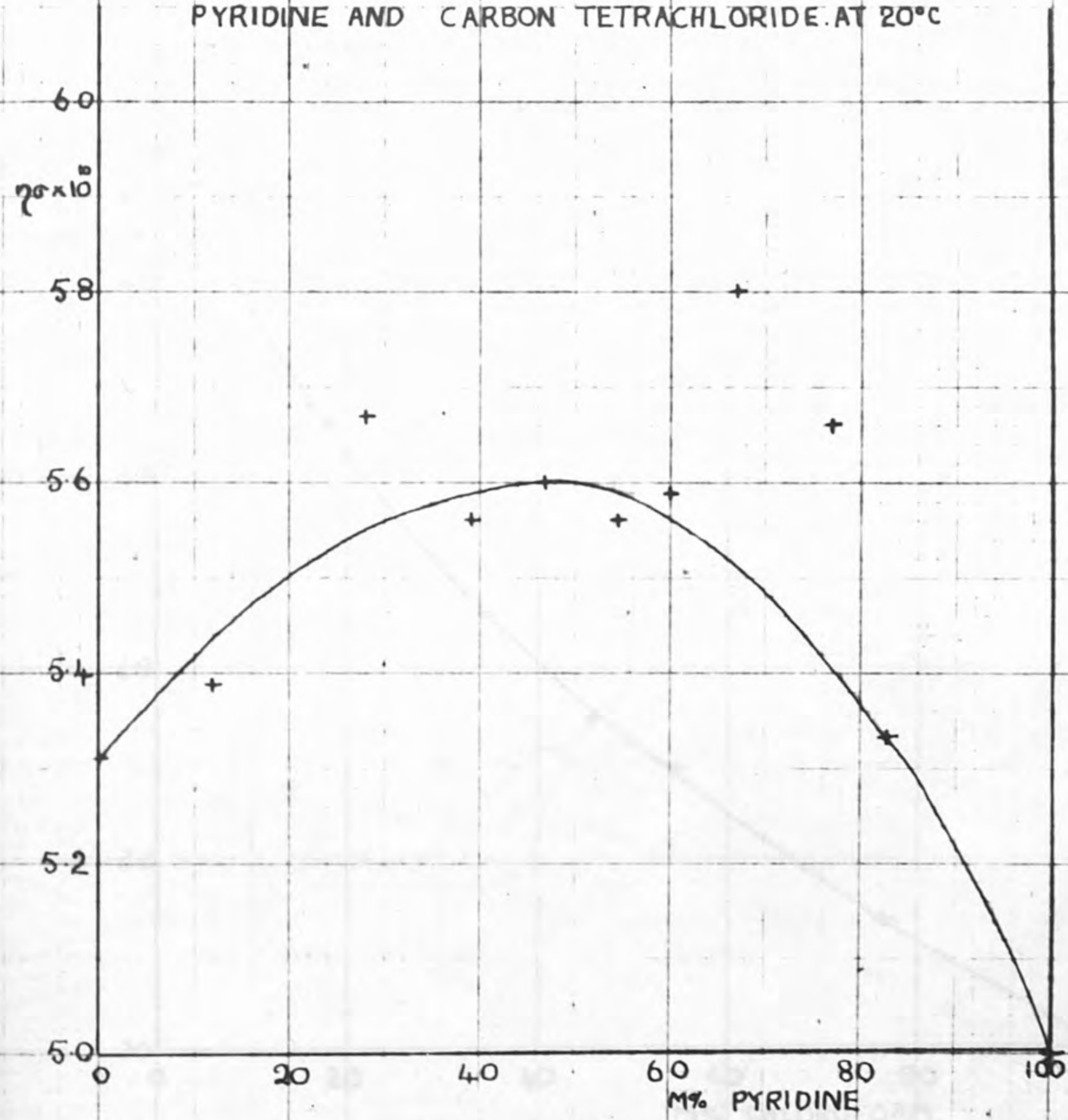

PYRIDINE AND CARBON TETRACHLORIDE AT 20°C
6·0
5·8
5·6
5·4
5·2
5·0
$\eta\sigma \times 10^{10}$
0
20
40
60
80
100
M% PYRIDINE

FIGURE 5.15.

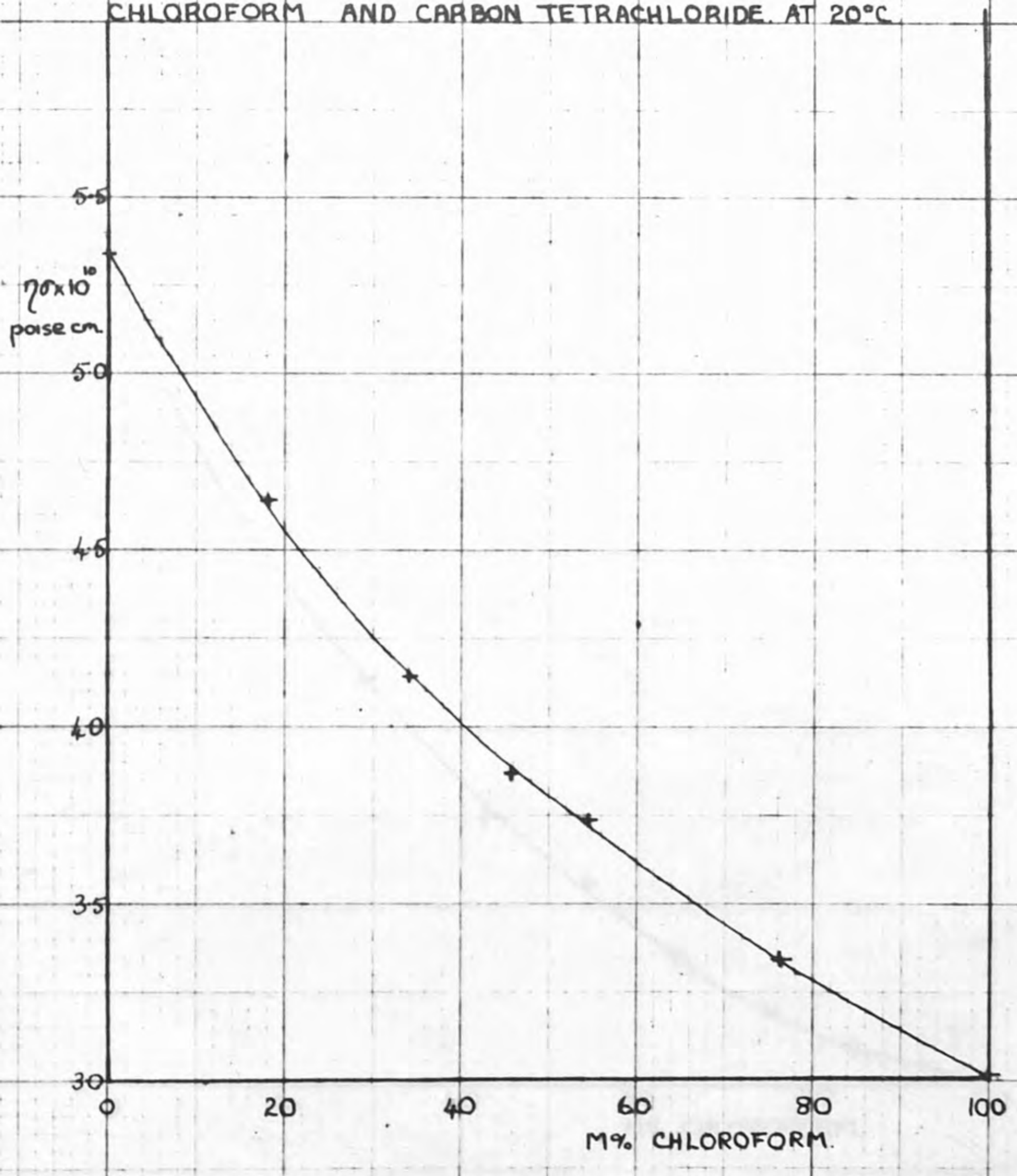
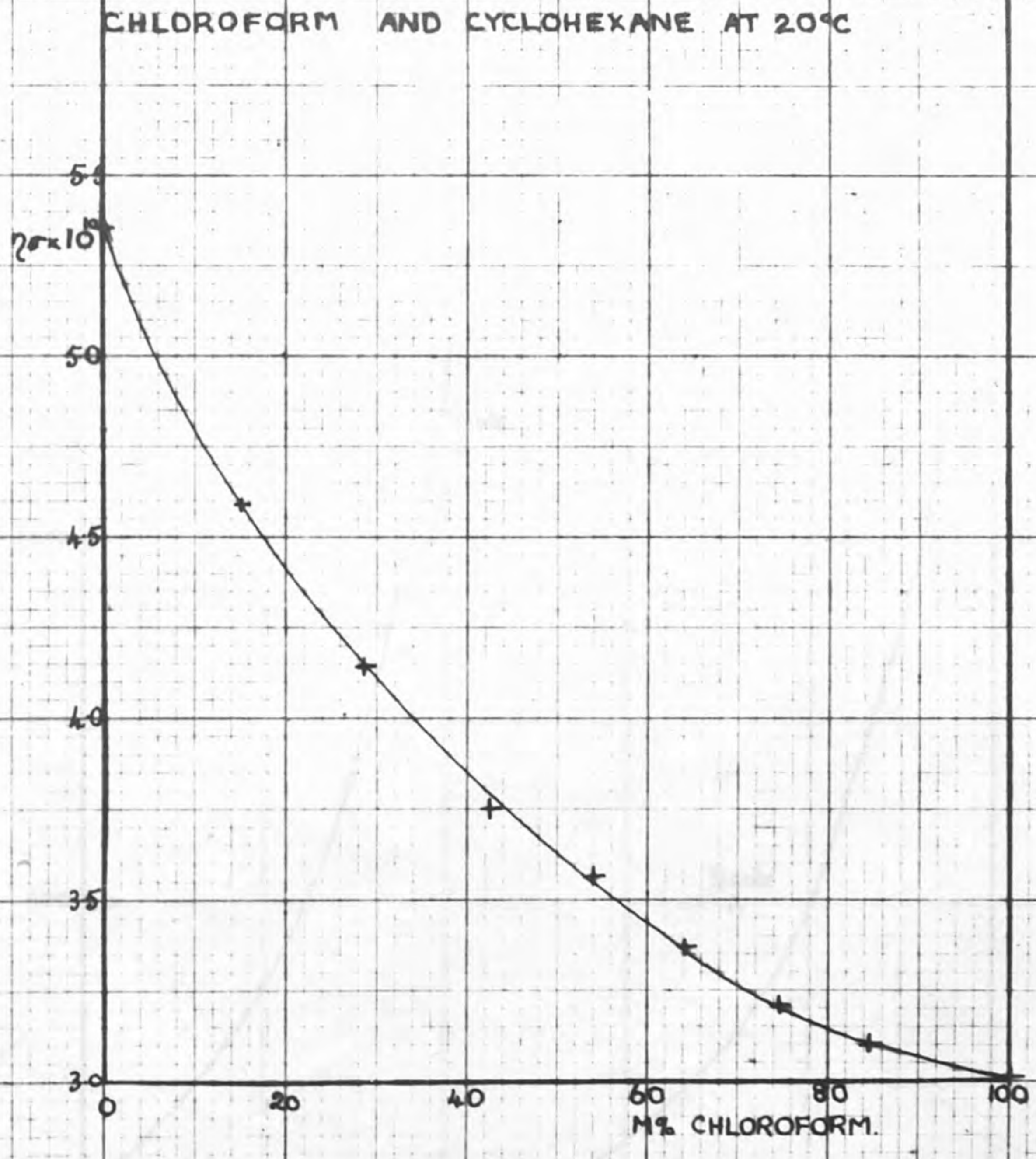

CHLOROFORM AND CARBON TETRACHLORIDE AT 20°C
$\eta\sigma \times 10^{10}$ poise cm.
5·5
5·0
4·5
4·0
3·5
3·0
0
20
40
60
80
100
M% CHLOROFORM.

FIGURE 5·16



CHLOROFORM AND CYCLOHEXANE AT 20°C

FIGURE 5.17.

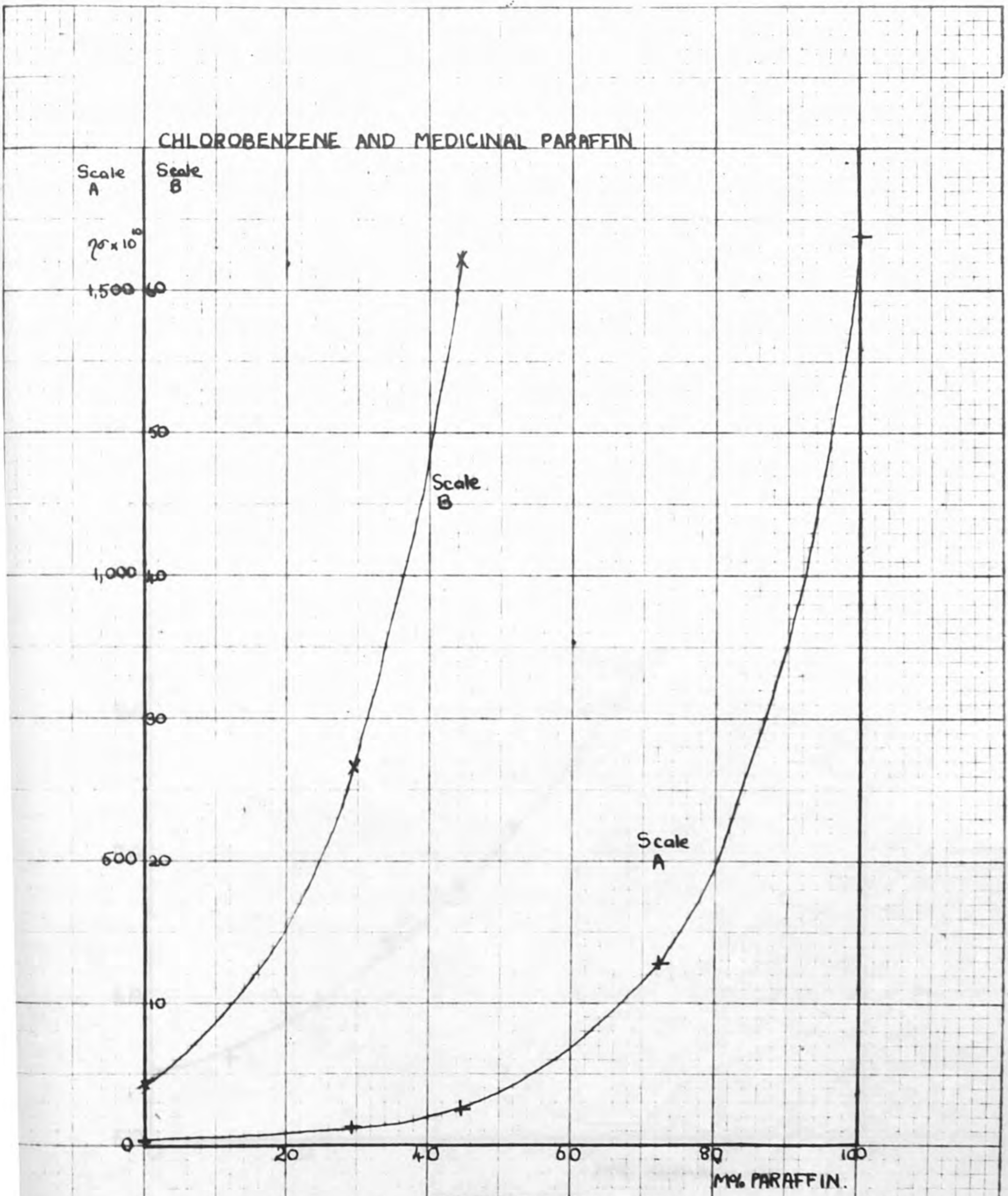

CHLOROBENZENE AND MEDICINAL PARAFFIN
Scale A
Scale B
$\eta\sigma \times 10^{10}$
1,500
60
50
1,000
40
30
600
20
10
0
20
40
60
80
100
M% PARAFFIN.
Scale B
Scale A

FIGURE 5·18.

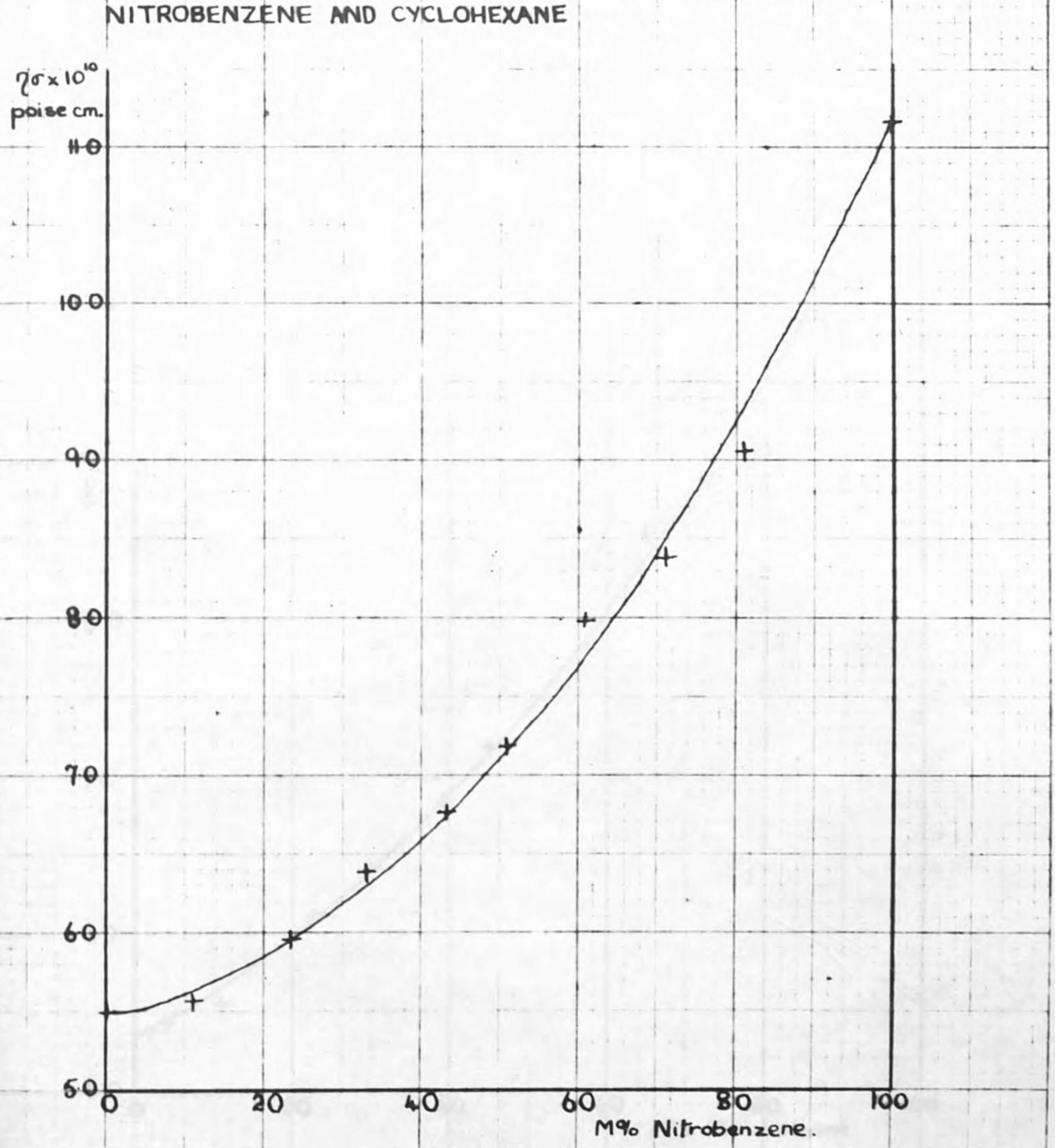

NITROBENZENE AND CYCLOHEXANE
$\eta\sigma \times 10^{10}$ poise cm.
11·0
10·0
9·0
8·0
7·0
6·0
5·0
0
20
40
60
80
100
M% Nitrobenzene.

FIGURE 5.19

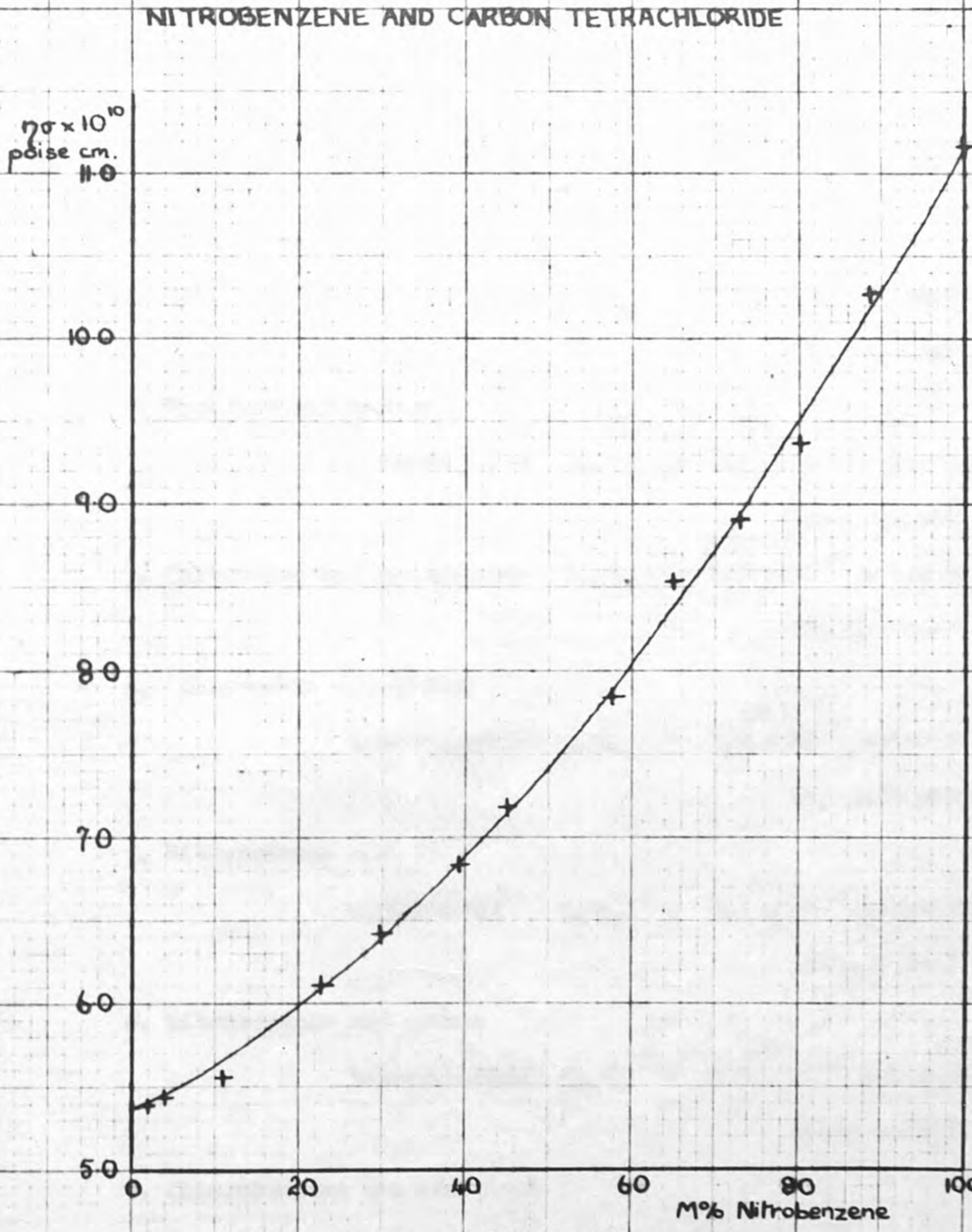

NITROBENZENE AND CARBON TETRACHLORIDE
$\eta\sigma \times 10^{10}$ poise cm.
11·0
10·0
9·0
8·0
7·0
6·0
5·0
0
20
40
60
80
100
M% Nitrobenzene

FIGURE 5.20

$$\tau = 6.2 \pm 0.3 \times 10^{-12} \text{ sec.}$$

at a temperature of $(20 \pm 1)^{\circ}$C.

MUTUAL VISCOSITY

The results are tabulated in tables 5.14-5.20, and shown graphically in figures 5.14-5.20. The values of the mutual viscosities at 20°C are:-

1\. Pyridine and cyclohexane $\eta_{AB}\sigma_{AB} = 3.0\overset{\pm 0.1}{\wedge} \times 10^{-10}$ poise. cm. at $f_B = 0$

(by extrapolation)

2\. Pyridine and carbon

tetrachloride $\eta_{AB}\sigma_{AB} = 6.1\overset{\pm 0.1}{\wedge} \times 10^{-10}$ poise cm.

(mean value)

3\. Chloroform and cyclohexane $\eta_{AB}\sigma_{AB} = \overset{2.3\pm 0.1}{\cancel{1.7}} \times 10^{-10}$ poise cm. at $f_B = 0$

(by extrapolation)

4\. Chloroform and carbon

tetrachloride $\eta_{AB}\sigma_{AB} = 3.1\overset{\pm 0.1}{\wedge} \times 10^{-10}$ poise cm.

(by extrapolation)

5\. Nitrobenzene and

cyclohexane $\eta_{AB}\sigma_{AB} = 5.7\overset{\pm 0.1}{\wedge} \times 10^{-10}$ poise cm.

(mean value)

6\. Nitrobenzene and carbon

tetrachloride $\eta_{AB}\sigma_{AB} = 6.5\overset{\pm 0.1}{\wedge} \times 10^{-10}$ poise cm.

(mean value)

7\. Chlorobenzene and medicinal

paraffin $\eta_{AB}\sigma_{AB} = 23.3 \times 10^{-10}$ poise cm.

In this case $\eta_{AB}\sigma_{AB}$ has been calculated from $\frac{d(\eta\sigma)}{df_A}$ at zero concentration of the paraffin, since in this case the conditions assumed in the theory are more nearly satisfied in the polar than in the non-polar liquid

$$\eta_{AB}\sigma_{AB} = \eta_B\sigma_B + \frac{1}{2}\left(\frac{d(\eta\sigma)}{df_A}\right)_{f_A=0}$$
$$= \left(4.25\times10^{-10} + 19.0\times10^{-10}\right)\text{ poise cm.}$$
$$= 23.3\times10^{-10}\text{ poise cm.}$$

SUMMARY OF THE RESULTS

The measured relaxation times and mutual viscosities of the various pairs of substances are tabulated below, together with some times taken from the results of Curtis, McGreer, Rathmann and Smyth,[13] and of Whiffen and Thompson.[11] The ratios $\frac{kT}{3}\frac{\tau}{\eta_{AB}\sigma_{AB}}$ and $\frac{\tau}{\eta}$ are shown for comparison. The last column shows ℓ, the mean distance of closest approach, calculated from $\frac{kT}{3}\frac{\tau}{\eta_{AB}\sigma_{AB}}$ and the estimated radii of gyration of the molecules.

Solute	Solvent	$\tau\times10^{12}$ sec.	$\eta_{AB}\sigma_{AB}\times10^{10}$ poise cm.	$\frac{kT}{3}\cdot\frac{\tau}{\eta_{AB}\sigma_{AB}}$ $\times10^{16}$ cm.^{2}	$\frac{\tau}{\eta}\times10^{10}$ cm.^{3}	$\ell\times10^8$ cm.
Pyridine	Cyclohexane	2.7	3.0	1.5	2.75	neg.
	Carbon tetrachloride	6.2	6.1	1.35	6.5	neg.
Chloroform	Cyclohexane	3.18	1.7	1.9 ~~2.6~~	3.3	1.07 ~~1.21~~
	Carbon tetrachloride	4.97	3.1	2.2	5.2	0.90
Chlorobenzene	Medicinal paraffin	40.0	23.3	2.3	0.2	—
Nitrobenzene	Cyclohexane	9.55	5.7	2.26	9.95	0.25
	Carbon tetrachloride	15.35	6.54	3.17	15.9	0.87

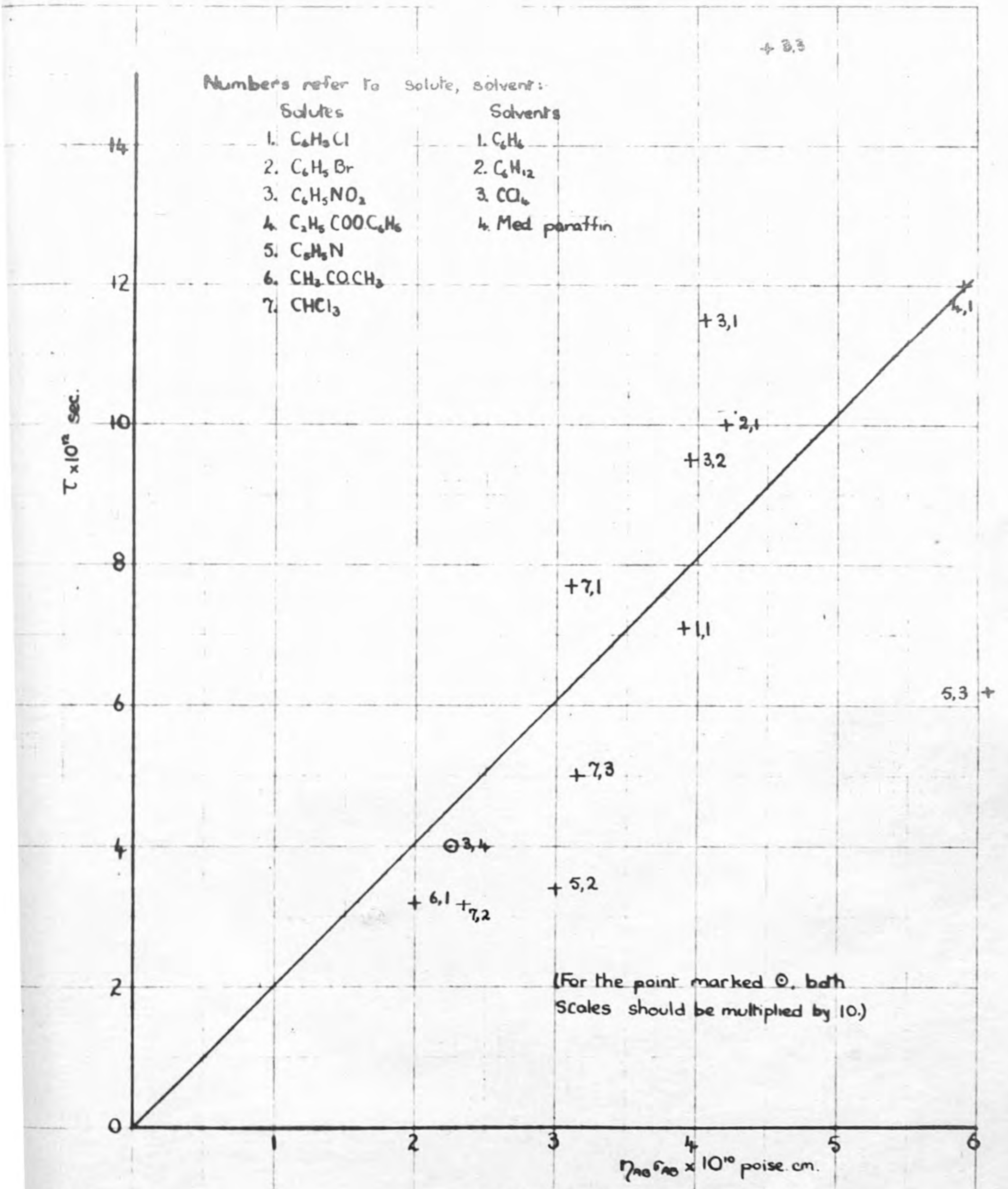

Numbers refer to solute, solvent:
Solutes
1. C_6H_5Cl
2. C_6H_5Br
3. $C_6H_5NO_2$
4. $C_2H_5COOC_6H_5$
5. C_5H_5N
6. $CH_3.CO.CH_3$
7. $CHCl_3$
Solvents
1. C_6H_6
2. C_6H_{12}
3. CCl_4
4. Med paraffin
$\tau \times 10^{12}$ sec.
0
2
4
6
8
10
12
14
1
2
3
4
5
6
$\eta_{AB}\sigma_{AB} \times 10^{10}$ poise cm.
+ 3,3
4,1
+ 3,1
+ 2,1
+ 3,2
+ 7,1
+ 1,1
5,3 +
+ 7,3
⊙ 3,4
+ 5,2
+ 6,1
+ 7,2
(For the point marked ⊙, both Scales should be multiplied by 10.)

FIGURE 6·1.

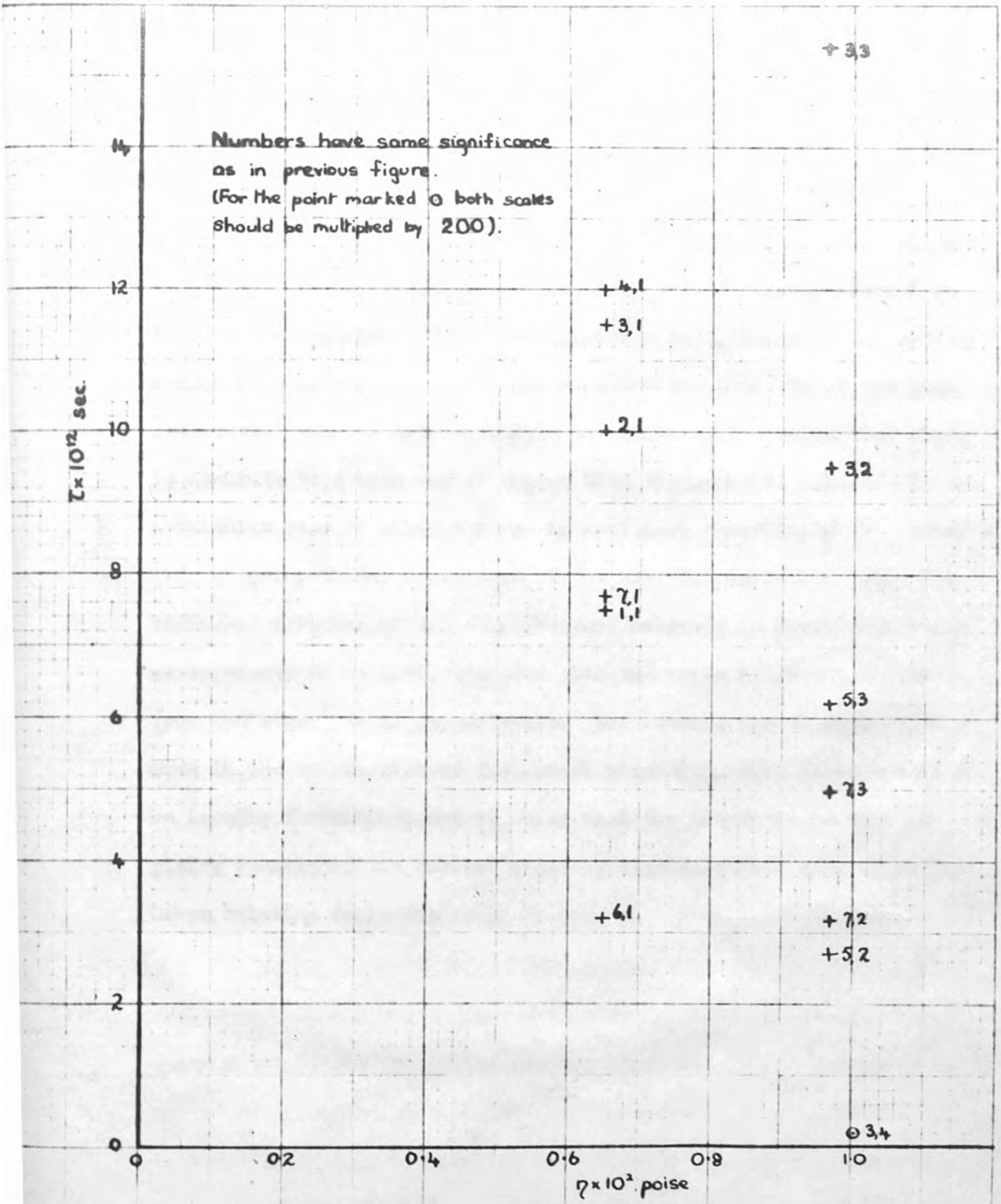

Numbers have same significance
as in previous figure.
(For the point marked ⊙ both scales
should be multiplied by 200).
τ × 10¹² sec.
η × 10² poise
0
2
4
6
8
10
12
14
0
0·2
0·4
0·6
0·8
1·0
+ 3,3
+ 4,1
+ 3,1
+ 2,1
+ 3,2
+ 7,1
+ 1,1
+ 5,3
+ 7,3
+ 6,1
+ 7,2
+ 5,2
⊙ 3,4

FIGURE 6.2

It will be seen that the correlation between $\eta_{AB}\sigma_{AB}$ and τ is much closer than that between η and τ, the ratio $\frac{\tau}{\eta_{AB}\sigma_{AB}}$ being almost constant for any given solute and varying by a factor of only three over the whole range, while $\frac{\tau}{\eta}$ varies by 80. The values of ℓ calculated from $\frac{KT}{3}\frac{\tau}{\eta_{AB}\sigma_{AB}}$ are of the correct order of magnitude, except for pyridine in cyclohexane and in carbon tetrachloride, where ℓ is found to be negative. This probably means that, owing to the crude method of calculation, the values of τ are too low. Since the same method was used for both solutions the ratio of the relaxation times is accurate to a much higher degree than the separate values. In the particular case of chlorobenzene in medicinal paraffin, $\frac{KT}{3}\frac{\tau}{\eta_{AB}\sigma_{AB}}$ tends to K_B^2, owing to the large mass of the paraffin molecule. Thus the radius of gyration of the chlorobenzene molecule is found from these measurements to be 1.5A, compared with the value 1.85A calculated from the structure of the molecule. Considering the approximations made in the calculation of the mutual viscosity, this agreement must be largely fortuitous, but it shows that the theory is capable of giving results of the correct order of magnitude in a case where the Debye relation fails entirely.

6. CONCLUSION

The experimental results recorded above in general support the theory developed in Chapters 2 and 3. In figures 6.1 and 6.2, all the available experimental evidence is displayed. The first graph shows τ plotted against $\eta_{AB}\sigma_{AB}$, and the second shows τ plotted against η , as required by the Debye relation. Each point on both graphs is marked by two numbers. The first indicates the solute and the second the solvent. According to the Debye relation the points (τ,η) for a single solute in a variety of solvents should lie on a straight line through the origin. This is far from being the case in figure 6.2. The present theory requires that points $(\tau, \eta_{AB}\sigma_{AB})$ for all solute-solvent combinations should lie about a straight line through the origin, the deviations being due to the variation of the moment of inertia of the molecules and of the "distance of closest approach" of a solvent and a solute molecule. From figure 6.1 it is seen that the points do in fact lie about a straight line, including the point for chlorobenzene in paraffin, a case for which the Debye law is known to fail. The points for pyridine fall well below the line. This may be due to the crude method used for the calculation of the relaxation time.

Although the theory is here worked out from the very simple and rather crude model suggested by Andrade, it is clear that the general principle; that the relaxation time of a polar substance in a non-polar solvent depends on the solute-solvent interaction viscosity, rather than on the viscosity of the solvent; remains whatever model is used for the calculation, although the nature of the other quantities involved may change. It seems that the next step in the theory will be to interpret this principle in terms of the more detailed kinetic theory of simple liquids developed by Born and Green.

A number of questions remain to be answered, for instance, can the mutual viscosity be related to any of the other physical properties of the mixtures (apart from the relaxation time)? An attempt was made to correlate it with the heat of solution since this must give some measure of the interaction energy between the two types of molecule, but it was not successful. The polarizability of the solvent molecules may have some influence on the mutual viscosity (through the probability constant c_{AB}) - the mutual viscosity of each polar substance investigated with cyclohexane ($\alpha = 1.10 \times 10^{-23}$) is less than that with carbon tetrachloride ($\alpha = 1.14 \times 10^{-23}$). This is in effect the suggestion of Curtis et al. but the difference in the polarizabilities of the two types of solvent is not large enough to account for the whole difference in the mutual viscosities.

Can the activation energy for dielectric relaxation in solution be related to the activation energy of the mutual viscosity, which can be found from the temperature variation of the latter?

Can any information be derived from the apparent variation of the mutual viscosity with concentration, which occurs for some pairs of substances? The simplest explanation is that it is an association effect - clusters of molecules forming as the concentration increases, but it cannot be readily explained in this way.

Further results are also required on the mutual viscosity and relaxation times of a large number of polar-non-polar pairs. The investigation of all these points will provide material for further research.

ACKNOWLEDGEMENTS

The author wishes to express her thanks to Professor H.T. Flint, under whose direction this work was carried out, and to the staff (both academic and technical) of Bedford College Physics Department, for their generous help and encouragement; also to the staff of the Chemistry Department for advice on chemicals, and the calculation of molecular moments of inertia.

APPENDIX

Tables of experimental results.

TABLE 5.1 a. WATER AT 16°C. x = 9.30 cm.

Carriage position		$\theta_{\lambda/2}$	$\theta_{\lambda/4}$	r'	Carriage position		$\theta_{\lambda/2}$	$\theta_{\lambda/4}$	r'
turns,	div.	cm.	cm.		turns,	div.	cm.	cm.	
80,	0	4.0	29.35	0.136	69,	3	5.0	27.5	0.182
79,	3	4.45	30.7	0.145	69,	0	5.15	26.5	0.194
79,	0	4.4	30.1	0.146	68,	3	5.4	25.1	0.215
78,	3	4.7	29.9	0.157	68,	0	5.5	23.3	0.236
78,	0	5.15	30.0	0.172	67,	3	4.85	21.2	0.228
77,	3	5.3	29.7	0.178	67,	0	5.4	25.0	0.216
77,	0	5.8	29.3	0.198	66,	3	5.2	28.8	0.180
76,	3	5.65	27.8	0.201	66,	0	5.4	33.5	0.161
76,	0	5.35	24.0	0.223	65,	3	6.1	35.0	0.174
75,	3	4.6	23.75	0.194	65,	0	6.55	33.0	0.198
75,	0	4.95	26.4	0.187	64,	3	7.2	30.2	0.238
74,	3	4.6	26.2	0.175	64,	0	6.9	25.4	0.271
74,	0	5.05	28.5	0.177	63,	3	6.35	22.5	0.281
73,	3	4.85	27.5	0.176	63,	0	4.55	19.5	0.233
73,	0	5.45	28.0	0.195	62,	3	4.85	25.1	0.193
72,	3	5.05	23.4	0.206	62,	0	4.5	32.0	0.140
72,	0	5.4	24.6	0.219	61,	3	4.5	35.0	0.128
71,	3	5.3	24.0	0.221	61,	0	5.45	33.4	0.163
71,	0	5.3	27.8	0.190	60,	3	6.7	30.7	0.218
70,	3	5.25	29.5	0.178	60,	0	6.6	21.9	0.301
70,	0	4.85	28.75	0.168					

s = 0 at 49 turns, 4 div.

1 turn = 1.265 mm.

Tables for figures 5.1 b-f are similar, and have therefore been omitted

TABLE 5.2. WATER AT 17° C.

Carriage position		$\theta_{\frac{1}{2}}$	$\theta_{\frac{1}{4}}$	τ'	Carriage position		$\theta_{\frac{1}{2}}$	$\theta_{\frac{1}{4}}$	τ'
turns	div.	cm.	cm.		turns	div.	cm.	cm.	
49,	4½	0.00	24.7	0.00	53,	4	1.85	20.75	0.089
50,	0	0.05	24.1	0.002		5	1.2	22.25	0.056
	1	0.35	23.45	0.015	54,	0	0.85	23.85	0.036
	2	0.75	22.0	0.034		1	0.7	22.25	0.033
	3	1.35	19.85	0.068		2	0.85	22.7	0.037
	4	2.95	20.5	0.14		3	1.1	22.9	0.048
	5	5.45	17.65	0.31		4	1.4	21.75	0.065
51,	0	12.35	16.8	0.736		5	2.05	22.05	0.093
	1	22.25	19.9	1.12	55,	0	3.05	22.0	0.14
	2	17.1	7.05	2.43		1	3.95	21.45	0.19
	3	11.8	3.3	3.58		2	5.0	20.65	0.23
	4	8.1	1.45	5.65		3	6.0	19.35	0.31
	5	5.45	0.85	6.4		4	8.5	20.45	0.42
52,	0	6.9	1.5	4.6		5	9.8	17.6	0.56
	1	8.35	2.8	2.98	56,	0	9.85	13.5	0.73
	2	9.3	4.65	2.00		1	9.75	9.6	1.02
	3	9.75	6.95	1.4		2	8.15	6.65	1.22
	4	9.4	10.0	0.94		3	6.9	4.9	1.43
	5	7.75	11.3	0.69		4.	5.1	3.4	1.50
53,	0	6.25	15.85	0.39		5	4.45	3.5	1.27
	1	4.8	18.65	0.26	57,	0	4.0	4.0	1.00
	2.	3.75	20.4	0.19		1	3.4	4.6	0.74
	3	2.75	21.2	0.13		2	2.95	5.15	0.57

continued

TABLE 5.2 contd.

Carriage position turns	div.	$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	r'	Carriage position turns	div.	$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	r'
57,	3	3.25	8.1	0.40	61,	2	3.25	6.7	0.49
	4	2.4	9.65	0.25		3	3.1	7.85	0.40
	5	2.3	11.5	0.20		4	2.95	8.7	0.34
58,	0	1.9	15.7	0.12		5	2.75	10.25	0.27
	1	1.85	17.45	0.11	62,	0	2.45	10.8	0.23
	2	1.85	16.5	0.11		1	2.3	11.2	0.21
	3	1.95	19.7	0.10		2	2.25	12.5	0.18
	4	2.25	20.1	0.11		3	2.3	13.5	0.17
	5	2.6	20.25	0.13		4	2.45	14.05	0.18
59,	0	3.0	19.95	0.15		5	2.6	14.55	0.18
	1	3.55	19.95	0.18	63,	0	2.9	14.75	0.20
	2	4.0	18.1	0.22		1	3.1	14.25	0.22
	3	4.5	16.75	0.27		2	3.2	13.7	0.23
	4	4.05	12.5	0.32		3	3.3	12.65	0.26
	5	4.1	10.2	0.40		4	3.55	12.0	0.30
60,	0	4.45	9.0	0.50		5	3.75	10.85	0.35
	1	4.6	8.05	0.57	64,	0	3.85	9.65	0.40
	2	4.1	6.5	0.63		1	3.8	8.65	0.44
	3	4.75	6.95	0.68		2	3.65	7.8	0.47
	4	4.9	6.45	0.76		3	3.35	6.85	0.49
	5	4.35	5.85	0.74		4	3.15	6.0	0.53
61,	0	3.4	5.05	0.67		5	2.9	5.4	0.54
	1	3.45	6.25	0.55	65,	0	3.7	7.8	0.48

Continued

TABLE 5.2 continued

Carriage position turns	div.	$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	r'	Carriage position turns	div.	$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	r'
65,	1	3.65	7.9	0.46	67,	4	3.3	10.95	0.30
	2	3.45	7.8	0.46		5	3.5	10.5	0.33
	3	3.35	7.85	0.43	68,	0	3.5	9.5	0.37
	4	3.0	8.0	0.38		1	3.4	8.65	0.39
	5	3.4	10.0	0.34		2	3.3	7.9	0.42
66,	0	3.25	10.3	0.32		3	2.9	7.1	0.41
	1	2.9	10.5	0.29		4	3.75	8.85	0.42
	2	2.8	10.65	0.26		5	4.0	8.8	0.45
	3	2.7	11.15	0.24	69,	0	4.05	8.45	0.48
	4	2.75	11.3	0.24		1	3.85	8.1	0.48
	5	2.9	12.0	0.24		2	3.55	7.7	0.46
67,	0	3.05	12.15	0.25		3	3.35	7.5	0.45
	1	3.1	12.15	0.25		4	3.1	7.2	0.43
	2	3.25	11.85	0.27		5	3.35	8.25	0.41
	3	3.35	11.5	0.29	70,	0	3.25	8.55	0.38

$s = 0$ at 49 turns, $4\frac{1}{2}$ div. 1 turn = 1.265 mm.

Tables for figures 5.3 to 5.5 are similar and have therefore been omitted.

TABLE 5.6a. ALCOHOL AT 18.5°C. $x = 9.35$ cm.

Carriage position		$\theta_{\frac{\lambda}{2}}$	$\theta_{\frac{\lambda}{4}}$	τ'	Carriage position		$\theta_{\frac{\lambda}{2}}$	$\theta_{\frac{\lambda}{4}}$	τ'
turns	div.	cm.	cm.		turns	div.	cm.	cm.	
50,	½	0.0	30.5	0.0	66,	0	9.0	31.2	0.288
51,	0	0.6	30.3	0.02	67.	0	9.6	31.0	0.309
52,	0	2.85	29.3	0.097	68,	0	9.85	30.3	0.325
53,	0	8.4	30.0	0.280	69,	0	10.1	30.25	0.334
54,	0	18.1	29.5	0.614	70,	0	9.95	29.2	0.340
55,	0	30.4	30.25	1.003	71,	0	10.35	30.8	0.336
56,	0	29.9	25.1	1.190	72,	0	9.85	30.4	0.324
57,	0	22.0	22.15	0.994	73,	0	9.8	30.8	0.318
58,	0	15.2	22.5	0.675	74,	0	9.15	30.1	0.304
59,	0	9.2	19.8	0.465	75,	0	8.65	29.8	0.290
60,	0	10.1	29.4	0.344	76,	0	8.35	29.8	0.280
61,	0	9.4	33.6	0.280	77,	0	8.8	30.6	0.287
62,	0	7.5	30.8	0.243	78,	0	8.6	29.75	0.289
63,	0	6.9	30.15	0.226	79,	0	8.85	31.0	0.285
64,	0	7.55	31.4	0.242	80,	0	8.2	28.9	0.284
65,	0	8.15	31.1	0.262					

$s = 0$ at 50 turns, ½ div. 1 turn = 1.265 mm.

Tables for figures 5.6 b–c are similar, and have therefore been omitted.

TABLE 5.8 CYCLOHEXANE AT 19.5°C.

Carriage position units, div.		$\theta_{\frac{\lambda}{2}}$ cm	$\theta_{\frac{\lambda}{4}}$ cm	σ'	Carriage position units, div.		$\theta_{\frac{\lambda}{2}}$ cm	$\theta_{\frac{\lambda}{4}}$ cm	σ'
110,	0	28.2	0.6	47.0	98,	3	33.1	7.45	4.44
109,	3	34.3	0.85	40.5	98,	0	31.8	5.2	6.11
109,	0	29.0	0.95	30.5	97,	3	29.3	3.7	7.91
108,	3	32.0	1.2	26.6	97,	0	31.5	3.0	10.5
108,	0	34.0	1.6	21.2	96,	3	32.3	2.4	13.5
107,	3	35.1	2.05	17.3	96,	0	27.5	1.55	17.75
107,	0	32.0	2.4	13.3	95,	3	32.3	1.5	21.5
106,	3	30.6	2.9	10.6	95,	0	30.6	1.15	26.6
106,	0	31.8	4.0	7.95	94,	3	31.1	0.9	34.5
105,	3	30.2	4.95	6.09	94,	0	29.5	0.65	45.4
105,	0	31.7	7.15	4.43					
104,	3	34.3	10.3	3.23	83,	3	32.5	0.75	43.3
104,	0	32.6	15.1	2.16	83,	0	31.6	0.9	35.1
103,	3	19.4	14.9	1.30	82,	3	30.5	1.1	27.7
103,	0	17.8	27.0	0.66	82,	0	30.2	1.4	21.6
102,	3	7.45	27.4	0.27	81,	3	31.2	1.85	16.8
102,	0	1.15	27.25	0.04	81,	0	32.0	2.35	13.6
101,	3	0.65	27.4	0.02	80,	3	33.1	3.1	10.65
101,	0	5.7	27.2	0.21	80,	0	32.7	4.05	8.08
100,	3	15.1	27.4	0.55	79,	3	29.6	4.85	6.10
100,	0	31.3	26.6	1.18	79,	0	29.35	6.8	4.32
99,	3	32.2	16.75	1.92	78,	3	30.2	9.65	3.13
99,	0	33.8	11.0	3.08	78,	0	29.5	14.6	2.02

continued

TABLE 5·8 contd.

Carriage position turns, div.		$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	r'	Carriage position turns, div.		$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	r'
77,	3	31.2	24.3	1.28	68,	0	31.2	0.85	36.7
77,	0	20.55	31.4	0.66	67,	3	30.3	0.65	46.5
76,	3	8.1	31.5	0.26					
76,	0	0.85	32.0	0.03	57,	0	30.0	0.7	42.9
75,	3	0.8	32.35	0.02	56,	3	30.8	0.95	32.5
75,	0	7.4	32.3	0.23	56,	0	31.6	1.15	27.5
74,	3	19.9	32.2	0.62	55,	3	32.0	1.55	20.6
74,	0	29.9	25.2	1.19	55,	0	32.1	1.95	16.4
73,	3	30.65	15.8	1.94	54,	3	31.2	2.4	13.0
73,	0	29.8	10.1	2.95	54,	0	30.9	3.35	9.3
72,	3	29.9	7.35	4.06	53.	3	30.3	4.4	6.9
72,	0	29.9	5.25	5.69	53,	0	33.0	6.85	4.8
71,	3	30.0	4.1	7.31	52,	3	32.0	9.65	3.3
71,	0	28.85	3.0	9.62	52,	0	29.0	13.0	2.2
70,	3	31.5	2.6	12.1	51,	3	30.6	23.4	1.3
70,	0	29.5	1.95	15.1	51,	0	14.1	22.3	0.63
69,	3	30.2	1.65	18.3	50,	3	4.95	22.5	0.22
69,	0	30.3	1.25	24.3	50,	0	0.55	22.5	0.02
68,	3	29.6	1.0	29.6	49,	5	0.0	23.0	0.00

s = 0 at 49 turns, 5 div. 1 turn = 1.265 mm.

TABLE 5.9 SECOND MINIMA FOR SOLUTIONS OF PYRIDINE IN CYCLOHEXANE

s = 0 at 49 turns, 5 div.
1 turn = 1.265 mm.

1. Pure C_6H_{12}

Carriage position turns div.	$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	σ
102, 3	7.1	28.8	0.246
102, 2	4.9	28.3	0.173
102, 1	2.8	29.0	0.095
102, 0	0.85	28.9	0.029
101, 5	0.2	29.0	0.007
101, 4	0.1	29.5	0.003
101, 3	0.45	29.7	0.015
101, 2	1.35	29.6	0.046
101, 1	3.3	29.6	0.108

Temperature 19.5°C.

2. Volume of C_6H_{12} = 248 cc.

C_5H_5N added = 3.6 cc.

V% C_5H_5N = 1.43, M% = 1.91

101 0	1.3	19.1	0.068
100, 5	0.65	18.9	0.034
100, 4	0.2	19.0	0.011
100, 3	0.05	18.6	0.003
100, 2	0.05	19.1	0.003
100, 1	0.35	19.0	0.018
100, 0	0.85	18.9	0.045
99, 5	1.55	17.7	0.088

Temperature 19.7 C.

3. Volume of mixture 2 = 250 cc.

C_5H_5N added = 2.4 cc.

V% C_5H_5N = 2.36, M% = 3.09

n = 1.4282

100, 3	3.45	19.4	0.178
100, 2	2.45	19.6	0.126
100, 1	1.45	20.2	0.072
100, 0	0.6	20.2	0.030
99, 5	0.15	20.2	0.008
99, 4	0.05	19.9	0.003
99, 3	0.10	20.2	0.005
99, 2	0.35	20.0	0.018
99, 1	0.95	18.5	0.051

Temperature 19.7°C

TABLE 5.9 continued

4. Volume of mixture 3 = 249 cc.

C_5H_5N added = 2.55 cc.

V% = 3.36, M% = 4.40

n = 1.4282

99, 3	2.5	16.0	0.156
99, 2	1.65	15.8	0.104
99, 1	0.8	16.5	0.048
99, 0	0.25	15.7	0.016
98, 5	0.05	16.0	0.004
98, 4	0.15	15.9	0.009
98, 3	0.45	16.0	0.028
98, 2	1.0	16.0	0.063
98, 1	1.85	16.1	0.116

Temperature 19.8°C.

5. Volume of mixture 4 = 249.5 cc.

C_5H_5N added = 2.6 cc.

V% C_5H_5N = 4.38, M% = 5.74

n = 1.4289

98, 3	1.35	15.2	0.09
98, 2	0.75	14.35	0.050
98, 1	0.35	14.5	0.023
98, 0	0.15	14.6	0.010
97, 5	0.25	14.8	0.017
97, 4	0.65	14.6	0.043
97, 3	1.15	14.2	0.077

Temperature 19.9°C.

6. Volume of mixture 5 = 250 cc.

C_5H_5N added = 2.6 cc.

V% C_5H_5N = 5.35, M% = 6.98

n = 1.4295

98, 0	3.0	14.5	0.207
97, 5	2.05	14.5	0.137
97, 4	1.25	14.75	0.085
97, 3	0.75	14.8	0.050
97, 2	0.4	14.9	0.027
97, 1	0.35	14.8	0.023
97, 0	0.4	15.1	0.027
96, 5	0.85	15.0	0.057
96, 4	1.45	14.8	0.097

Temperature 19.9°C

TABLE 5.9 continued

7. Volume of mixture 6 = 250 cc.

C_5H_5N added = 2.6 cc.

V% C_5H_5N = 6.31, M% = 8.19

n = 1.4303

97, 0	1.7	14.4	0.119
96, 5	1.1	14.2	0.075
96, 4	0.65	14.05	0.045
96, 3	0.45	13.9	0.031
96, 2	0.4	14.6	0.028
96, 1	0.6	14.1	0.043
96, 0	1.15	14.5	0.079
95, 5	1.9	14.65	0.131

Temperature 19.8°C.

8. Volume of mixture 7 = 250 cc.

C_5H_5N added = 2.6 cc.

V% C_5H_5N = 7.27, M% = 9.43

n = 1.4310

96, 3	3.35	14.0	0.239
96, 2	2.45	13.7	0.175
96, 1	1.5	14.0	0.107
96, 0	0.95	13.8	0.068
95, 5	0.6	14.3	0.041
95, 4	0.5	13.8	0.036
95, 3	0.65	14.2	0.046
95, 2	1.05	13.9	0.075

8. continued

95, 1	1.65	14.05	0.117
95, 0	2.8	14.2	0.198

Temperature 19.8°C

9. Volume of mixture 8 = 250 cc.

C_5H_5N added = 2.55 cc.

V% C_5H_5N = 8.22, M% = 10.64

n = 1.4318

95, 3	1.7	12.5	0.131
95, 2	1.3	13.1	0.099
95, 1	0.8	13.05	0.061
95, 0	0.6	13.1	0.048
94, 5	0.75	13.2	0.058
94. 4	1.1	13.15	0.085
94, 3	1.6	13.5	0.123

10. Volume of mixture = 250 cc.

C_5H_5N added = 2.45 cc.

V% C_5H_5N = 9.11, M% = 11.73

n = 1.4326

95, 0	2.2	12.3	0.178
94, 5	1.5	12.4	0.120
94, 4	1.05	12.55	0.084
94, 3	0.8	12.4	0.064
94, 2	0.7	12.3	0.057
94, 1	0.85	12.9	0.066

continued

TABLE 5.9 continued

10. continued

94,	0	1.25	13.0	0.096
93,	5	1.95	13.1	0.148
93,	4	2.55	12.7	0.200

11. Volume of mixture 10 = 250 cc.

C_5H_5N added =2.6 cc.

V% C_5H_5N = 10.05, M% = 13.0

n = 1.4330

94,	3	3.55	13.5	0.263
94,	2	2.5	12.7	0.197
94,	1	1.85	13.2	0.140
94,	0	1.15	13.1	0.088
93,	5	0.95	13.5	0.070
93,	4	0.95	13.5	0.070
93,	3	1.05	13.6	0.077
93,	2	1.4	13.0	0.107
93,	1	1.9	13.1	0.145

TABLE 5.10. PYRIDINE AND CYCLOHEXANE

M%	λ cm.	γ_{min}	$\alpha \times 10^{-2}$ cm^{-1}	β cm^{-1}	ε''	ε'	$\tau \times 10^{12}$ sec.
0.0	6.53	0.0	0.0	0.962	0.0	2.05	–
1.89	6.38	0.0	0.0	0.985	0.0	2.15	-
3.10	6.30	0.003	0.16	0.996	0.007	2.20	2.1
4.40	6.18	0.004	0.21	1.017	0.0095	2.28	1.8
5.74	6.07	0.010	0.37	1.035	0.010	2.38	1.4
6.98	5.96	0.023	0.58	1.052	0.027	2.45	2.9
8.19	5.86	0.028	0.66	1.070	0.031	2.53	2.7
9.43	5.78	0.036	0.77	1.085	0.037	2.61	2.6
10.64	5.70	0.048	0.84	1.101	0.041	2.69	2.5
11.73	5.61	0.056	1.10	1.119	0.055	2.78	2.8
13.00	5.42	0.073	1.25	1.160	0.065	2.97	2.7

TABLE 5.11. CARBON TETRACHLORIDE AT 18.5°C.

Carriage position turns	div.		$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	τ'	Carriage position turns	div		$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	τ
50,	$\frac{1}{4}$		0.0	27.4	0.0	68,	0	s	30.65	5.85	19.9
50,	3		2.0	27.4	0.073	68,	3	s	27.9	6.35	16.65
51,	0		14.15	26.0	0.54	69,	0	s	30.85	9.15	12.8
51,	3		29.2	25.9	1.13	69,	3	s	31.5	11.3	10.55
52,	0		27.8	11.4	2.44	70,	0	s	30.5	14.0	8.28
52,	3		24.8	6.95	3.57	70,	3	s	30.6	17.45	6.66
53,	0		29.0	4.8	6.05	71,	0	s	30.4	23.85	4.84
53,	3		31.2	3.8	8.22	71,	3	s	31.6	32.3	3.72
54,	0		30.2	2.5	12.08	72,	0	s	26.0	39.8	2.48
54,	3		29.95	1.85	16.1	72,	3		31.0	18.2	1.70
55,	0		29.7	1.3	22.9	73,	0		27.3	28.1	0.97
55,	3	s	34.3	4.3	30.2	73,	3		15.45	28.6	0.54
56,	0	s	29.7	2.7	42.3	74,	0		5.25	27.2	0.19
56,	3	s	35.1	2.4	55.6	74,	3		1.0	27.8	0.04
57,	0	s	29.3	1.55	71.8	75,	0		0.95	26.35	0.04
						75,	0		5.95	31.0	0.19
66,	0	s	28.65	1.95	55.8	76,	0		18.65	31.3	0.60
66,	3	s	28.75	2.5	43.7	76,	3		32.3	30.55	1.06
67,	0	s	29.3	3.7	30.1	77,	0		31.55	16.3	1.94
67,	3	s	28.7	4.3	25.4	77,	3		29.9	11.1	2.70

For those readings marked "s" the "$\frac{\lambda}{2}$" galvanometer has been shunted and its deflection has to be multiplied by 3.8

continued

TABLE 5.11 continued

Carriage position turns	div.		$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	τ'	Carriage position turns,	div.		$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	τ'
78,	0	s	28.1	25.1	4.26	96,	0		28.7	6.5	4.42
78,	3	s	30.75	20.75	5.64	96,	3		31.8	10.0	3.18
79,	0	s	31.25	14.7	8.08	97,	0		31.0	15.0	2.06
79,	3	s	32.05	11.55	10.55	97,	3		28.2	22.0	1.28
80,	0	s	30.2	8.1	14.15	98,	0		20.8	30.35	0.69
80,	3	s	29.2	6.6	16.8	98,	3		10.05	30.6	0.33
81,	0	s	30.55	4.85	23.9	99,	0		2.3	30.8	0.08
81,	3	s	29.4	3.6	31.0	99,	3		0.35	31.3	0.01
82,	0	s	29.0	2.85	38.7	100,	0		1.85	18.1	0.10
82,	3	s	31.0	2.35	50.1	100,	3		5.75	17.9	0.32
83,	0	s	31.75	1.75	68.8	101,	0		13.0	17.4	0.75
						101,	3		23.05	18.0	1.28
91,	0	s	32.6	2.15	57.6	102,	0		30.2	13.7	2.20
91,	3	s	31.4	2.65	45.1	102,	3		31.7	10.4	3.04
92,	0	s	32.0	3.5	34.8	103,	0		26.9	6.2	4.33
92,	3	s	30.8	4.3	27.2	103,	3	s	32.3	21.0	5.84
93,	0	s	32.6	5.9	21.0	104,	0	s	27.6	13.9	7.54
93,	3	s	29.2	6.9	16.1	104,	3	s	32.8	12.25	10.18
94,	0	s	29.9	9.1	12.5	105,	0	s	31.8	9.35	12.9
94,	3	s	28.9	11.1	9.9	105,	3	s	30.25	7.05	16.3
95,	3	s	19.75	14.1	5.32	106,	3	s	31.8	4.4	27.5
						107,	0	s	32.0	3.45	35.3

TABLE 5.12. SECOND MINIMA FOR SOLUTIONS OF PYRIDINE IN CARBON TETRACHLORIDE

s = 0 at 49 turns, 5 div.

1 turn = 1.265 mm.

1. Pure CCl_4

$n = 1.460$ at 20.5°C.

Carriage position turns, div.	$\theta_{\frac{\lambda}{2}}$ cm.	$\theta_{\frac{\lambda}{4}}$ cm.	τ
100, 0	3.2	16.1	0.198
99, 5	1.15	15.9	0.072
99, 4	0.4	16.4	0.024
99, 3	0.1	16.3	0.006
99, 2	0.1	16.3	0.006
99, 1	0.35	15.7	0.021
99, 0	0.95	15.7	0.061
98, 5	1.7	16.8	0.108
98, 4	3.1	16.0	0.194

Temperature 18.5°C.

2. Volume of CCl_4 = 240 cc.

C_5H_5N added = 5.0 cc.

V% C_5H_5N = 2.02, M% = 1.68

$n = 1.462$ at 20.5°C

2. cont.

98, 2	2.4	12.1	0.198
98, 1	1.55	12.0	0.129
98, 0	0.7	12.2	0.059
97, 5	0.3	12.0	0.025
97, 4	0.1	12.1	0.008
97, 3	0.1	12.3	0.008
97, 2	0.3	12.3	0.024
97, 1	0.65	12.35	0.053
97, 0	1.3	12.25	0.106
96, 5	2.4	11.9	0.202

Temperature 18.5°C.

3. Volume of mixture 2 = 242 cc.

C_5H_5N added = 5.05 cc.

V% C_5H_5N = 4.02, M% = 3.36

$n = 1.463$ at 20.5°C.

96, 4	2.35	12.0	0.196
96, 3	1.5	11.25	0.133
96, 2	1.05	11.65	0.090
96, 1	0.7	11.9	0.059
96, 0	0.45	12.0	0.037
95, 5	0.4	12.4	0.030
95, 4	0.6	12.45	0.048
95, 3	1.0	12.2	0.082
95, 2	1.5	12.5	0.120
95, 1	2.1	12.4	0.169

Temperature 18.6°C

TABLE 5.12 cont.

4. Volume of mixture 3 = 245 cc.

C_5H_5N added = 2.45 cc.

V% C_5H_5N = 4.97, M% = 4.16

n = 1.4638 at 20.0°C.

95,	5	2.65	10.6	0.250
95,	4	1.75	10.9	0.110
95,	3	0.8	10.3	0.078
95,	2	0.55	10.85	0.051
95,	1	0.45	10.7	0.042
95,	0	0.5	10.8	0.046
94,	5	0.8	11.05	0.072
94,	4	1.25	11.0	0.114
94,	3	1.9	11.15	0.171
94,	2	2.5	11.1	0.225

Temperature 18.9°C.

5. Volume of mixture 4 = 245.5 cc.

C_5H_5N added = 2.6 cc.

V% C_5H_5N = 5.97, M% = 5.00

n = 1.4642 at 20.0°C.

95,	0	1.85	11.4	0.163
94,	5	1.3	11.5	0.113
94,	4	0.9	11.8	0.076
94,	3	0.75	11.7	0.064
94,	2	0.75	11.5	0.065

5. contd.

94,	1	0.9	11.5	0.078
94,	0	1.25	11.4	0.109
93,	5	1.8	11.25	0.160
93,	4	2.75	11.15	0.246

Temperature 19.0°C.

6. Volume of mixture 4 = 246 cc.

C_5H_5N added = 2.5 cc.

V% C_5H_5N = 6.90, M% = 5.80

n = 1.4650 at 20.0°C.

94,	3	2.65	10.9	0.243
94,	2	2.05	10.95	0.187
94,	1	1.55	11.0	0.141
94,	0	1.1	10.75	0.102
93,	5	0.85	11.0	0.077
93,	4	0.85	11.1	0.077
93,	3	1.0	11.25	0.089
93,	2	1.25	11.35	0.110
93,	1	1.65	11.25	0.147
93,	0	2.35	11.35	0.207

Temperature 19.5°C

continued

TABLE 5.12 contd.

7. Volume of mixture 6 = 246 cc.

C_5H_5N added = 2.5 cc.

V% C_5H_5N = 7.85, M% = 616.

n = 1.4655 at 20.0°C.

94, 0	3.15	10.3	0.306
93, 5	2.35	10.5	0.224
93, 4	1.55	10.5	0.148
93, 3	1.2	10.35	0.116
93, 2	0.95	10.8	0.088
93, 1	0.85	10.8	0.079
93, 0	0.8	10.75	0.074
92, 5	1.05	11.0	0.096
92, 4	1.4	11.2	0.125
92, 3	2.0	11.1	0.180

Temperature 19.5°C.

8. Volume of mixture 7 = 246 cc.

C_5H_5N added = 2.5 cc.

V% C_5H_5N = 8.78, M% = 7.40

n = 1.4660 at 20.2°C

93, 0	2.0	10.1	0.198
92, 5	1.45	9.9	0.147
92, 4	1.2	9.95	0.118
92, 3	1.1	10.05	0.111
92, 2	1.15	10.35	0.111

8. contd.

92, 1	1.3	10.55	0.123
92, 0	1.7	10.45	0.163
91, 5	2.3	10.8	0.213

Temperature 19.5°C

9. Volume of mixture 8 = 246 cc.

C_5H_5N added = 2.55 cc.

V% C_5H_5N = 9.71, M% = 8.21

92, 3	2.15	8.85	0.242
92, 2	1.7	9.0	0.189
92, 1	1.35	9.5	0.142
92, 0	1.2	9.1	0.132
91, 5	1.1	9.35	0.118
91, 4	1.25	9.25	0.135
91, 3	1.5	9.2	0.162
91, 2	1.8	9.2	0.195

Temperature 19.5°C.

TABLE 5.12 contd.

10. Volume of mixture 9 = 246 cc.

C_5H_5N added = 2.55 cc.

V% C_5H_5N = 10.65, M% = 9.94

n = 1.4671 at 20.8°C.

92,	0	2.85	8.9	0.320
91,	5	2.25	9.1	0.247
91,	4	1.8	9.1	0.198
91,	3	1.55	9.4	0.165
91,	2	1.45	9.35	0.155
91,	1	1.45	9.4	0.154
91,	0	1.6	9.35	0.171
90,	5	1.9	9.4	0.202
90,	4	2.45	9.05	0.271

Temperature 19.4°C.

Time for observations on these 10 mixtures, 2 hrs.

TABLE 5.13. PYRIDINE IN CARBON TETRACHLORIDE

M%	λ cm.	$r_{min.}$	$\alpha \times 10^2$	β cm.$^{-1}$	ε''	ε'	$\tau \times 10^{12}$ sec.
0.00	6.24	0.003	0.19	1.005	0.0085	2.25	
1.68	6.03	0.007	0.31	1.040	0.0143	2.40	6.3
3.36	5.80	0.030	0.70	1.081	0.034	2.60	7.1
4.16	5.72	0.041	0.84	1.097	0.041	2.67	6.7
5.00	5.62	0.063	1.09	1.117	0.054	2.78	6.7
5.80	5.55	0.075	1.21	1.130	0.061	2.85	6.3
6.61	5.46	0.077	1.26	1.150	0.065	2.94	5.7
7.40	5.37	0.110	1.56	1.170	0.081	3.05	6.1
8.21	5.30	0.122	1.70	1.183	0.090	3.12	5.8
9.94	5.24	0.152	1.93	1.199	0.103	3.20	5.4

TABLE 5.14. PYRIDINE AND CYCLOHEXANE at 20°C

M% pyridine	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^{8}$ cm.	$\eta\sigma \times 10^{10}$ poise cm.	$\eta_{AB}\sigma_{AB}$ poise cm.
0.0	340	0.780	0.970	5.65	5.37	-
16.2	293	0.803	0.861	5.56	4.79	3.14
18.2	290	0.806	0.856	5.55	4.75	3.35
25.7	280	0.821	0.841	5.50	4.62	3.46
44.8	275	0.855	0.861	5.39	4.64	4.05
67.8	271	0.905	0.898	5.29	4.75	4.47
78.4	270	0.937	0.926	5.21	4.83	4.40
83.6	270	0.942	0.930	5.19	4.83	4.27
89.1	265	0.955	0.925	5.16	4.78	3.94
100.0	270	0.985	0.975	5.11	4.98	-

TABLE 5.15. PYRIDINE AND CARBON TETRACHLORIDE AT 20°C

M% pyridine	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^8$ cm.	$\eta\sigma \times 10^{10}$ poise cm.	$\eta_{AB}\sigma_{AB}$ poise cm.
0.0	168	1.597	0.98	5.42	5.31	-
11.95	178	1.537	1.000	5.39	5.39	5.84
28.1	197	1.474	1.062	5.34	5.67	6.5
39.4	205	1.408	1.056	5.26	5.56	5.9
47.2	215	1.357	1.065	5.25	5.60	6.05
54.5	222	1.308	1.061	5.24	5.56	6.05
60.0	231	1.269	1.070	5.21	5.59	6.12
66.8	249	1.223	1.114	5.20	5.80	6.74
73.7	253	1.183	1.095	5.17	5.66	6.62
83.3	256	1.107	1.037	5.15	5.34	6.15
100.0	269	0.985	0.970	5.09	5.00	-

TABLE 5.16. CHLOROFORM AND CYCLOHEXANE AT 20°C.

M%	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^8$ cm.	$\eta\sigma \times 10^{10}$ poise cm.	$\eta_{AB}\sigma_{AB}$ poise cm.
0.0	333	0.780	0.951	5.64	5.35	
15.3	263	0.856	0.824	5.56	4.58	2.27
28.7	220	0.929	0.749	5.51	4.13	2.74
42.6	185	1.020	0.690	5.44	3.75	2.90
54.1	164	1.100	0.661	5.38	3.56	3.08
64.3	147	1.175	0.632	5.32	3.36	3.06
74.9	133	1.253	0.610	5.26	3.21	3.12
84.7	121	1.345	0.596	5.20	3.10	3.10
100.0	109	1.475	0.589	5.12	3.02	

TABLE 5.17. CHLOROFORM AND CARBON TETRACHLORIDE AT 20°C.

M%	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^8$ cm.	$\eta\sigma \times 10^{10}$ poise cm.	$\eta_{AB}\sigma_{AB}$ poise cm.
0.0	168	1.595	0.980	5.43	5.33	-
18.5	149	1.573	0.858	5.39	4.63	3.26
34.5	136	1.555	0.774	5.34	4.13	3.27
45.7	129	1.548	0.731	5.29	3.86	3.36
54.7	126	1.535	0.708	5.26	3.73	3.52
76.2	116	1.510	0.642	5.20	3.34	3.70
100.0	109	1.475	0.589	5.12	3.01	-

TABLE 5.18. CHLOROBENZENE AND MEDICINAL PARAFFIN AT $(18 \pm 1)^{\circ}$C

Using an Ostwald viscometer

W% paraffin	M% paraffin	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^{8}$ cm.	$\eta\sigma \times 10^{10}$ poise cm.
0.0	0.0		1.11	0.77	5.52	4.25
48	29.4	1176	0.983	4.2	6.33	26.6
64	44.5	2651	0.948	9.2	6.66	62.1

Using a falling sphere viscometer

Steel ball of diameter (2r) 0.157 cm. falling in a tube of diameter (2r) 1.19 cm. Density of steel (ρ') 7.87 gm. cm.

$$\eta = \frac{2}{9}\,\frac{(\rho' - \rho) g r^{2}}{v\left(1 + 2.4\frac{r}{R}\right)\left(1 + 3.3\frac{r}{h}\right)}$$

W%	M%	Terminal velocity cm. sec.	Density (ρ) gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^{8}$ cm.	$\eta\sigma \times 10^{10}$ poise cm.
85	72.5	15.95	0.905	45.0	7.03	316
100	100.0	3.52	0.88	205	7.78	1595

(The molecular weight of medicinal paraffin is assumed to be 250)

TABLE 5.19. NITROBENZENE AND CYCLOHEXANE

M% Nitrobenzene	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^8$ cm.	$\eta\sigma \times 10^{10}$ poise cm.	$\eta_{AB}\sigma_{AB} \times 10^{10}$ poise cm.
0.0	341	0.782	0.976	5.62	5.49	-
11.0	327	0.827	0.989	5.61	5.55	5.39
23.6	331	0.877	1.062	5.60	5.96	5.95
32.9	341	0.916	1.142	5.59	6.39	6.14
43.5	345	0.960	1.211	5.58	6.76	5.91
51.0	355	0.996	1.292	5.57	7.18	5.73
61.2	367	1.040	1.438	5.56	7.98	6.24
71.0	384	1.075	1.510	5.55	8.39	5.43
81.3	399	1.120	1.630	5.54	9.05	4.78
100.0	458	1.205	2.015	5.54	11.18	-

TABLE 5.20. NITROBENZENE AND CARBON TETRACHLORIDE

M% Nitrobenzene	Flow time sec.	Density gm. cm.$^{-3}$	Viscosity c. poise	$\sigma \times 10^{8}$ cm.	$\eta\sigma \times 10^{10}$ poise cm.	$\eta_{AB}\sigma_{AB} \times 10^{10}$ poise cm.
0.0	169	1.600	0.989	5.43	5.37	-
1.8	171	1.587	0.991	5.43	5.39	5.65
3.8	172	1.580	0.995	5.44	5.43	5.88
10.7	180	1.555	1.02	5.44	5.56	5.91
22.3	207	1.510	1.14	5.45	6.22	7.00
29.6	217	1.480	1.175	5.46	6.41	6.65
38.9	237.5	1.440	1.25	5.46	6.82	6.55
45.2	253	1.427	1.32	5.47	7.19	6.67
57.5	286	1.370	1.43	5.48	7.84	6.50
64.8	316	1.343	1.555	5.49	8.54	6.96
73.2	339	1.306	1.62	5.50	8.90	6.54
79.9	364	1.281	1.71	5.50	9.38	6.88
88.5	407	1.249	1.86	5.52	10.29	7.28
100.0	458	1.207	2.02	5.54	11.19	-

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