A DIELECTRIC STUDY OF PLASTICIZED POLYVINYLIDENE CHLORIDE

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PREFACE

Since a great deal of work has been published on plasticized polyvinyl chloride, it was thought that attention should be directed to studies on other plasticized polymers. For this reason, a chemically similar polymer, polyvinylidene chloride was chosen to be investigated.

Another objective of the study was to evolve a method, using a series of more or less empirical equations, to describe the temperature, frequency and concentration dependance of the dielectric and the thermodynamic activation properties of plasticized polymers. By this method a mass of data could possibly be reduced to a few equations eliminating the necessity of bulky tables and graphs for the presentation of experimental results.

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THEORETICAL INTRODUCTION

A. POLYMERS

The Structure of Linear Polymers

The properties of linear polymers vary quite widely from the hard brittle substances through soft resilient rubbers to viscous liquids. Although they are nearly all composed of a long chain carbon backbone, it is the substituent group on the carbon atom which causes the variations in physical properties from one polymer to another of similar molecular weight.

The novelty of the polymer is limited to the long chain of carbon atoms joined by primary valence bonds. The basic concepts of physical chemistry which apply to simpler molecules are also attendant in the case of polymers, modified only by the abnormal length and molecular weight of the polymer.

Macromolecules possess internal flexibility due to vibration and rotation of segments of the polymer chains. The flexibility and strength of a polymer is determined by the nature of the groups on the chain, the interchain and intrachain forces, the degree of coiling or kinking of the chains and the length of the chains.

A minimum degree of polymerization is necessary for mechanical strength. Below a certain degree of polymerization the tensile strength of a film is negligible, and above this the tensile strength increases in proportion to the degree of polymerization. On reaching higher degrees of polymerization the dependancy of tensile strength tapers off and tends to become independent of the chain length. This is due to the fact that the strength of the polymer largely depends upon the mechanical entanglement of the chains.

In a crystalline solid, each molecule (or atom or ion as the case may be) is held, by forces of attraction and repulsion, in an equilibrium position. The molecule may undergo rapid vibrations in this position but diffusion is extremely infrequent since the average amplitude is only of the order of five percent of the distance between equilibrium positions. The material is rigid, hard and has a definite shape. As the temperature is increased the vibrations increase and at the melting point the crystal structure breaks down and far reaching geometric order is absent. The molecule is not in a fixed equilibrium position but possesses translational energy, as evidenced by Brownian motion, and self diffusion is possible. The resulting material can retain no definite shape but assumes that of the container. This liquid can be supercooled, the viscosity increasing exponentially, and at low enough temperatures becomes hard and brittle - a glass. The transition from a rigid glass to a viscous liquid occurs in narrow temperature intervals, the softening point, with no change in structure and no discontinuity in the primary thermodynamic variables (heat capacity, free energy, etc.).

Therefore, for low molecular weight materials, we have in the crystalline state long range order and a high viscosity; in the glassy state very short range order and a high viscosity; and in the liquid state very short range order and a low viscosity. The situation with respect to high polymeric materials is more complicated. In this case the "molecule" or monomer unit is joined to two adjacent "molecules" by primary valence bonds and to four others by relatively weak Van der Waal's forces, the magnitude of which depends on the substituent groups of the "molecule". Thus there is very great strength along the axis of the macromolecule for all polymers and at right angles to this the forces are relatively weak and the intermolecular bonds (Van der Waal's) are easily broken. Long range entanglement of polymeric materials thus replaces long range crystallinity of simpler molecules.

In rubbery polymers there are very small interchain forces and a very kinked and coiled chain. The distance between chains is further increased by the introduction of alkyl groups at regular intervals and the presence of double bonds increases the possibility of a more kinked and coiled chain (e.g. natural rubber which is cis-polyisoprene). The presence of low interchain forces means lower potential barriers which allows chains to slip past one another more easily. The coiled and kinky nature of the chain is responsible for the springiness of rubber. The low interchain forces are responsible for the speed at which elastic recovery takes place. In rubbers, a certain amount of crosslinking is necessary to prevent displacement of the linear molecule as a whole. Fix-points from chain to chain are necessary at widely spaced intervals (just as in the case of bedsprings) to provide a co-operative motion of all polymer molecules resulting in a motion of segments of the chain rather than the whole molecule.

Mark (M1) considers these properties on the basis of Brownian motion - a. microbrownian motion or movement of segments of the molecule and b. macrobrownian motion or motion of the molecules relative to one another. Hence rubber would be described as a substance possessing rapid microbrownian motion and no macrobrownian motion. Just as glasses are liquids with high viscosities, Mark describes rubbers as liquids with long range entanglements.

Usually rubbers, unless stretched, do not give X-ray patterns and in the normal relaxed state are not crystalline.

Vinyl polymers with polar side groups generally possess different properties from rubbers. Unless monomer is present there are no unsaturated linkages along the main carbon chain. This restricts the chain from assuming the kinky and coiled up configuration of the rubbers. Polar groups closely spaced along the chain interact with such polar groups on adjacent chains, thus segment motion is reduced due to these strong attractions. Hence we have a material which at normal temperatures has little or no rubbery properties. The properties may be between the extremely brittle polyvinylidene chloride, which will neither bend nor stretch without breaking, to the alkyl polyacrylates which are soft and elastic, behaving much like rubber latex. The difference in physical properties of the vinyl polymers depends to a large extent on the strength of the interaction of the polar side groups and on their size.

The presence of polar side groups tends to provide a large number of fix-points thus limiting segmental motion. The polar attraction may be so great as to produce crystallization in a number of vinyl polymers where the polar group is relatively small (e.g. polyvinyl chloride, polyvinylidene chloride).

The microbrownian motion of polar vinyl polymers is determined by the strength of the polar interaction. From the standpoint of macrobrownian motion the vinyl polymer chain is stiffer and less subject to coiling than in the case of rubber, chain entanglement is not as great as in the case of rubbers and so macrobrownian motion depends to a greater extent on the polar interaction. Hence in polymers where polar interaction is small, more rubbery properties will be exhibited but at the same time a greater tendency to creep or cold flow is produced in the absence of crosslinking agents. Whereas rubber has been described as a liquid with long range entanglements polar vinyl polymers have been described as glasses.

Mark describes the properties of polymers as the combination of three physical states of polymers. For fibres the solid crystalline state is accentuated with only enough of the rubbery state to give resiliency. A typical rubber requires the bulk of the material in the rubbery state with a fix-point system. The plastic material is a combination of the solid and liquid states with very little rubberiness. The interrelation of the three states can be shown in the following way:

Brittle Point

Flow Point

SOLID	RUBBERY	LIQUID
microbrownian motion frozen in	microbrownian motion rapid	microbrownian motion rapid
macrobrownian motion frozen in	macrobrownian motion frozen in	macrobrownian motion activated
sustains external forces	sustains external forces	does not sustain external forces
high modulus of elasticity	low modulus of elasticity	flows and has medium viscosity

Plasticizers

Plasticizers are materials which are added to polymers to alter their physical properties in order to increase the scope of their commercial uses. Plasticizers facilitate processing by softening or increasing the tack of the resulting composition. They are used to modify the mechanical properties (e.g. reducing the brittleness) and the electrical properties of polymers. Some of these effects can be accomplished by other means which are usually, however, deleterious to the polymer. Raising the temperature for instance will soften the polymer but might result in slight decomposition of the material. If the degree of polymerization is reduced the polymer will become softer but with a resulting decrease in its tensile strength and a greater tendency to creep. Copolymerization is an excellent method for altering the properties of polymers but is limited to some extent by the degree to which two (or more) monomers can be combined and also by the number of monomers which are available for copolymerization. Hence plasticizers are the modifiers most commonly used today.

There are certain basic requirements which must be considered in choosing a plasticizer for a given polymer.

Compatibility refers to the maximum amount of plasticizer which can be added to a polymer without causing phase separation (i.e. the plasticizer must be miscible with the polymer). If such is not the case, the plasticizer molecules will aggregate, weakening the structure, and will eventually exude or sweat out.

Permanence: In most cases it is essential that plasticizer is not lost from the composition. In only a few instances the plasticizer is incorporated merely to facilitate processing operations such as molding and the loss of plasticizer from the finished article is not a serious consideration. When the plasticizer is added to effect relatively permanent changes in the mechanical or electrical properties of the polymer, it is essential that the loss of plasticizer be extremely small. Consequently plasticizers are chosen which have low vapour pressures and which are relatively large in size to decrease diffusion to the surface of the material and hence eliminating evaporation from the surface. This usually means that the molecular weight be high relative to the molecular weights of common solvents (which are plasticizers but lack permanence). The plasticizer must also be stable to light and heat to avoid production of objectionable by-products. Certain plasticizers are chosen for specific purposes (e.g. tricresyl phosphate imparts flame resistant properties to compositions containing it).

Efficiency concerns how much a given property of the plastic (brittle point, second order transition temperature, flexibility, hardness, etc.) is altered by the addition of a fixed amount of polymer. Most theories of plasticizer action so far have dealt with the subject of efficiency as the manner in which a certain property changes with composition.

Mechanism of Plasticizer Action

An excellent summary of the findings of various investigators with regard to plasticizer action is given by Stickney and Cheyney (S1). From this paper an overall picture of the polymer-plasticizer interaction is given from a more or less kinetic viewpoint.

The modification of the mechanical properties of a polymer by plasticization must result from a modification of the mechanical binding or intermolecular forces. The effect of plasticizer addition reduces the number of interchain linkages which are not due to primary valence bonds. In polar polymers, solvation is necessary for compatibility resulting in the masking of polymer active centres. According to Stickney and Cheyney the efficiency of a plasticizer depends on the surface it presents in the composition and hence on its shape. Hence on a weight basis low molecular weight plasticizer should be more efficient since small molecules present a greater surface than an equal weight of large molecules. However, on a molar basis high molecular weight plasticizers should be more effective.

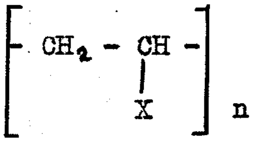
The shape of the plasticizer is not determined by the molecular model shape but by its form in the plasticized composition and is thus affected by the polymer-plasticizer interaction. The physical or mechanical properties are determined by the shape of the polymer-plasticizer complex.

The effect of temperature on a plasticized polymer is generally less than on the unplasticized polymer especially in the case of polar polymers. In the unplasticized polymer the interchain links are broken at higher temperatures and polymer-polymer interaction is reduced. In plasticized polymers there are fewer polymer-polymer links and these of course will be reduced as the temperature increases but at the same time polymer-plasticizer links will be broken with the possible reforming of more polymer-polymer links.

The efficiency of a plasticizer has been determined by the changes produced in certain properties of the polymer (e.g. the brittle point, second order transition temperature, Young's modulus, dielectric loss, etc.). As a result the efficiency of various plasticizers may be described, with fair success, in terms of the property studied (e.g. the variation of brittle point with composition). Since these methods elicit different responses from the plasticized compositions it is often difficult to compare data from one to another. A great number of these tests are time dependant which also introduces further sources of incongruity.

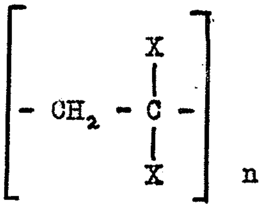
B. THE DIELECTRIC METHOD OF INVESTIGATION

In the dielectric method of investigation of polar polymers with structures of the type



$$\left[-CH_2-\underset{X}{\underset{|}{CH}}-\right]_n$$

or



$$\left[-CH_2-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\right]_n$$

(where X is a polarizable group) a force is applied directly to the polar groups and the properties measured provide an indication as to the magnitudes of the binding forces present and the relative freedom of the dipoles from one polymer to another.

If we apply an alternating electromotive force to a capacitor having a polar polymer as its dielectric, a current flows through the dielectric. The magnitude of this current depends on the structure of the polymer, the frequency of the applied voltage and the temperature. At high frequencies dipoles present are not able to follow the applied field and the current flowing is due to electronic polarization plus the Maxwell displacement current. This current is a capacitative current as it leads the applied voltage by 90° and is present at all frequencies. At very low frequencies the dipoles are able to follow the field and the current carried is proportional to the magnitude of the dipole moment of the polar group. Thus a further current is superimposed on the electronic displacement current, both being purely capacitative. As the frequency is lowered the dielectric constant approaches that found by d.c. measurements and is designated by e_o. As the frequency is increased the dielectric constant approaches the optical dielectric constant ϵ_∞ which is equal to (according to Clausius (C1) and Mosotti (M2))the square of the index of refraction.

At intermediate frequencies an interesting process takes place. At lower frequencies the dipole is oscillating in the alternating field and the current being carried is purely capacitative. As the frequency is increased the dipole becomes less and less able to keep up with the applied field and begins to lag. This lag results in a current being produced which is out of phase with the electronic polarization. A purely capacitative current is represented by a vector at right angles to the voltage vector, and a purely resistive current is represented by a vector lying along the voltage vector (Fig. 1). If the dipolar oscillation lags behind the electronic polarization, the current flowing through the capacitor has a component in phase with the voltage and hence can be represented as a resistive component which results in the dissipation of heat in the dielectric. This lag becomes greatest when the frequency of the field is of the same order of magnitude as the relaxation time τ of the dipole. This relaxation time τ is defined as the time required for a steady state orientation to decay to $^1/e$ of its value. As the frequency of the field is increased further the dipole is less able to follow the field due to "viscous drag" and eventually becomes "frozen in" at which point the electronic displace-

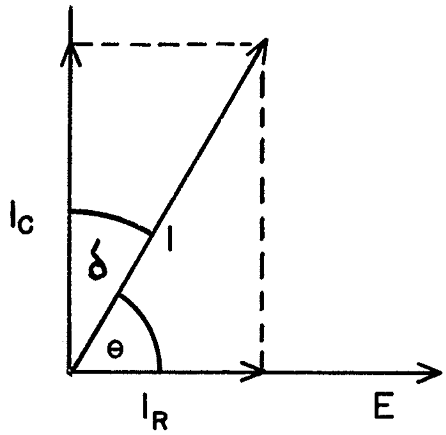


Fig. 1

ment current only is present and there is no resistive component.

Debye introduced the complex dielectric constant

$$\epsilon = \epsilon' - j\,\epsilon'' \qquad 1.$$

where ϵ' is the dielectric constant, ϵ'' is the loss factor (a measure of the energy dissipated in a dielectric) and j is the operator for 90° rotation and is equal to $\sqrt{-1}$.

Thus going from low to high frequencies at a given temperature it is found that the dielectric constant ϵ' goes through a sigmoidal increase and the loss factor ϵ'' goes through a maximum, and on an ϵ'' versus log f graph is symmetrical about its critical frequency. As the temperature is raised the maximum in the loss factor is shifted to higher frequencies as is the point of inflection of the dielectric constant curve.

Quite similar curves are obtained if ϵ' and ϵ'' are plotted against temperature. The loss factor ϵ'' goes through a maximum at a given temperature, and as the frequency is increased the peak occurs at higher temperatures, the point of inflection of the ϵ' curve occurring at higher temperatures as the frequency is increased.

If a plasticizer is added to the polymer, the peak in the ϵ'' versus log f curve, at a given temperature, is shifted to higher frequencies or in the corresponding ϵ'' versus temperature plot, the peak at a given frequency is shifted to lower temperatures.

To provide a qualitative, if not quantitative, picture, the so-called Debye equations are employed. The complex dielectric constant given in equation (1) is also given by the equation

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \qquad 2.$$

where ϵ_0 is the static or low frequency value of the dielectric constant.

ϵ_∞ is the value of the dielectric constant at optical frequencies.

ω is the angular frequency of the applied field and is equal to $2\pi f$ where f is the frequency of the field.

j is the operator for 90° rotation and is equal to $\sqrt{-1}$

τ is known as the relaxation time.

If the second term of equation 2. is multiplied by its complex conjugate and placed in the form of equation 1. thus

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

we find that ϵ' and ϵ'' in equation 1. are given by the following expressions.

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + \omega^2 \tau^2} \qquad 4.$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2 \tau^2} \qquad 5.$$

Rearrangement of these give the following equations which are more amenable to discussion.

$$\frac{\epsilon' - \epsilon_\infty}{(\epsilon_0 - \epsilon_\infty)} = \frac{1}{1 + \omega^2 \tau^2} \qquad 4a.$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\omega\tau}{1 + \omega^2 \tau^2} \qquad 5a.$$

Plotting the left hand side of equations 4a. and 5a. against log $\omega\tau$

the symmetrical curves of figures 3 and 2 are obtained. The corresponding curves of ϵ' and ϵ'' against $\log\omega$ are also symmetrical and give curves similar to those of figures 2 and 3. The maximum in the absorption curve can be found by setting $\frac{\partial\, \epsilon''}{\partial\, \omega\tau} = 0$. It is thus found that the maximum occurs when $\omega\tau = 1$ or at $\log\omega\tau = 0$. The value of ω at the maximum is usually designated by ω_m and the value of the frequency corresponding to ω_m is known as the critical frequency, f_c .

The values of ϵ' and ϵ'' at ω_m are designated by ϵ'_m and ϵ''_m and are found by setting $\omega\tau = 1$ in equations 4. and 5.

$$\epsilon'_m = \frac{\epsilon_0 + \epsilon_\infty}{2} \qquad 4b.$$

$$\epsilon''_m = \frac{\epsilon_0 - \epsilon_\infty}{2} \qquad 5b.$$

The relaxation time τ used in equation 2. and subsequent equations is commonly called the relaxation time and is a measure of the decay of the macroscopic polarization of the medium. For this reason Powles (P1) prefers to designate it as the decay time. This relaxation time τ is related to the intrinsic relaxation time τ^* which is of the order of magnitude of the time required for a given molecule, if fixed and released, to revert to random orientation in the absence of resulting macroscopic polarization resulting from the surrounding molecules. The intrinsic relaxation time τ^* is independent of the value of the internal field, but its relation to τ , the experimentally determined quantity, can only be determined by assuming an expression for the internal field. The resulting relation between τ and τ^* will then depend on the choice of the expression for the internal field. However, the difference between the two relaxation times diminishes as the ratio of $\epsilon_0/\epsilon_\infty$ decreases. The tendency of the polarization to maintain itself

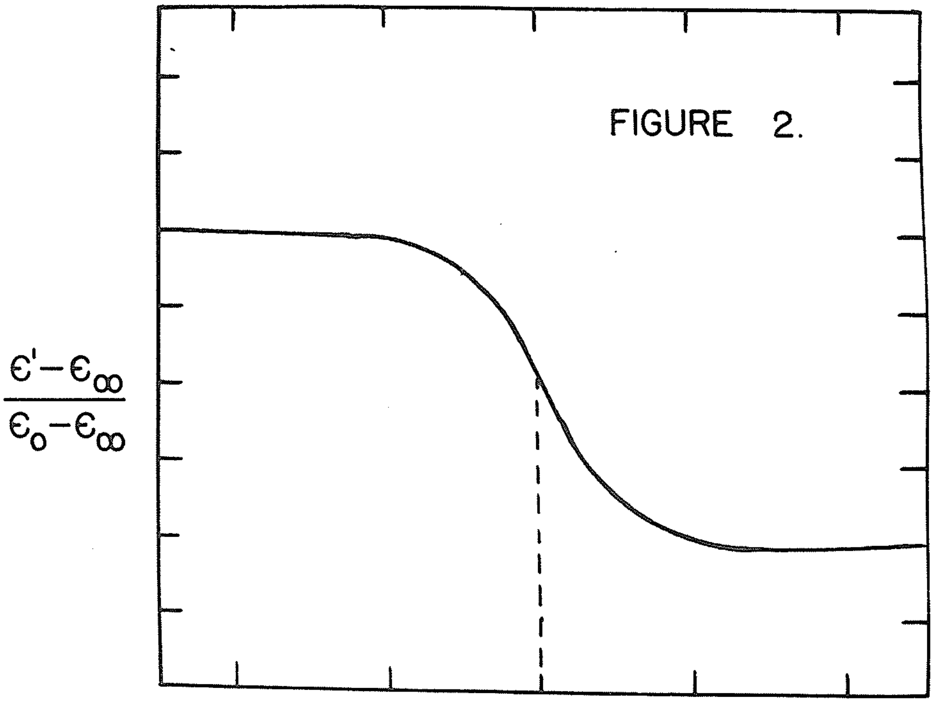


FIGURE 2.

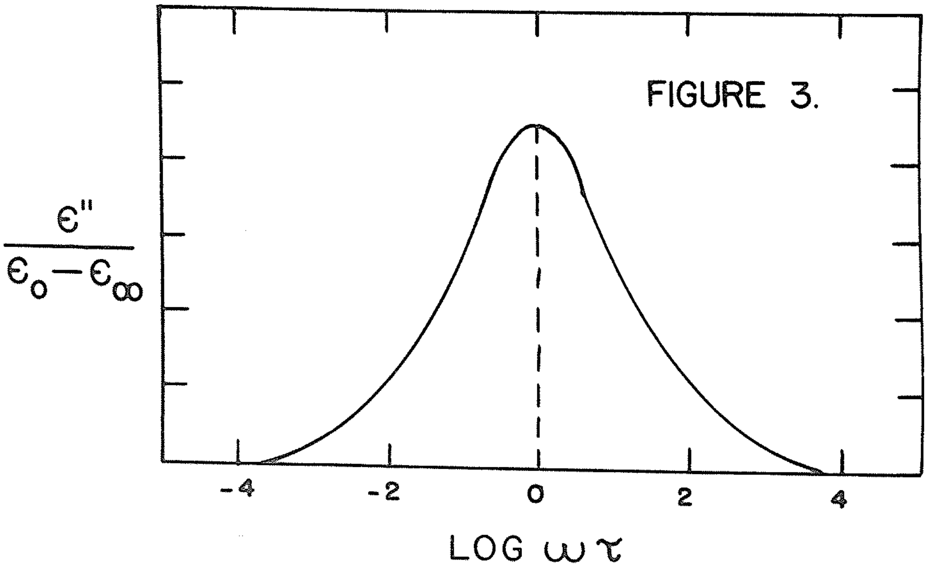


FIGURE 3.

is always active to some extent so that τ is always greater than τ^*. Most experimental results now are expressed in terms of τ or ω_m.

Distribution of Relaxation Times

If ϵ'' is plotted against ϵ' a semicircular plot should be obtained (Fig. 4) which is described by the equation

$$\left(\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2}\right)^2 + (\epsilon'')^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2}\right)^2 \qquad 6.$$

This curve is predicted from equations 4. and 5. on the assumption of a single relaxation time. However, ideal behaviour is quite rare in condensed phases, the experimental curves deviating from the curves predicted. Cole and Cole (C2) showed that generally the experimental curve is still circular, with the centre of the circle shifted below the ϵ' axis (i.e. to negative values of ϵ'') (Fig. 5).

The model upon which this theory is based is obviously too simple. The forces of interaction and thermal motions vary from place to place and from time to time and consequently every dipole in its particular situation has, at any moment, its own intrinsic relaxation time. When in measurements an average is taken over all conditions, a distribution of relaxation times about a most probable value will result. Consequently equations 4. and 5. should be written

$$\epsilon' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \int_0^\infty \frac{G(\tau)\, d\tau}{1 + \omega^2 \tau^2} \qquad 4c.$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) \int_0^\infty \frac{G(\tau)\, d\tau}{1 + \omega^2 \tau^2} \qquad 5c.$$

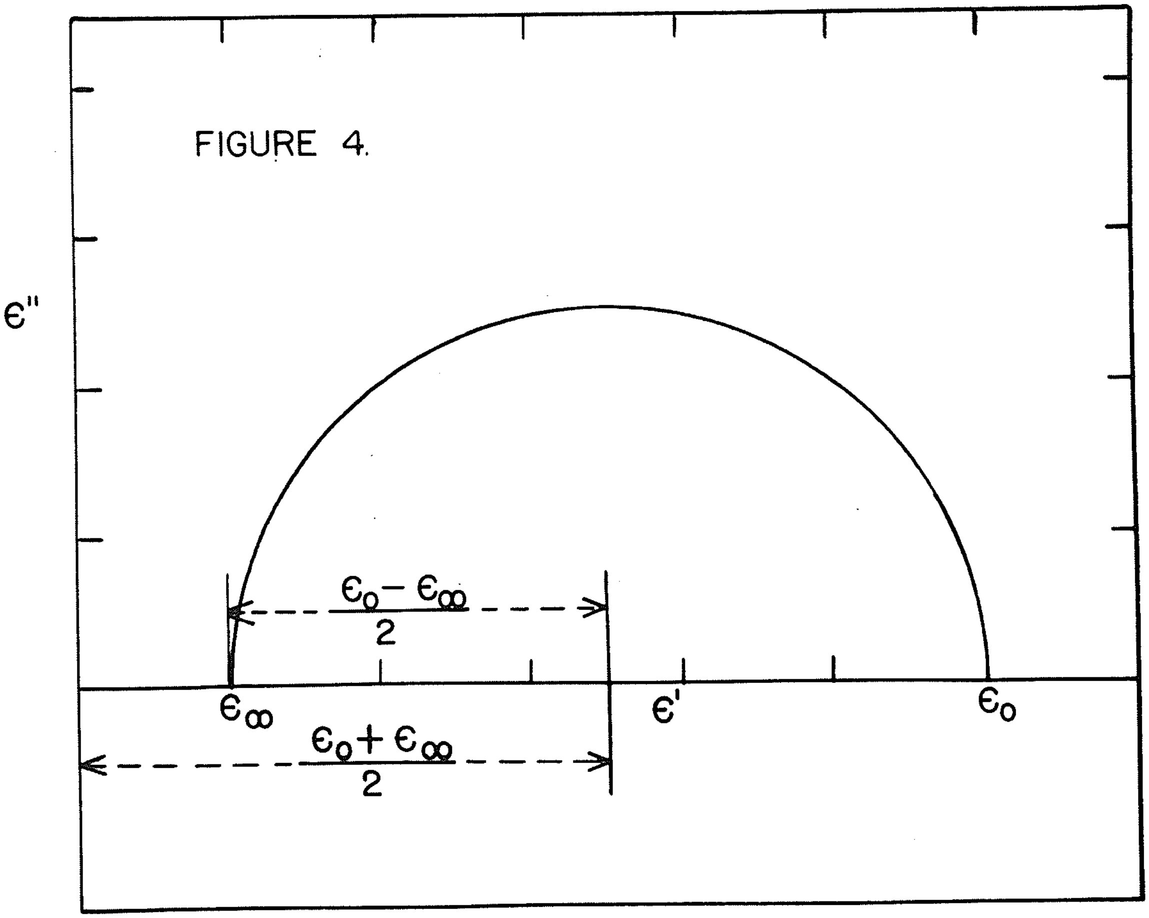


FIGURE 4.

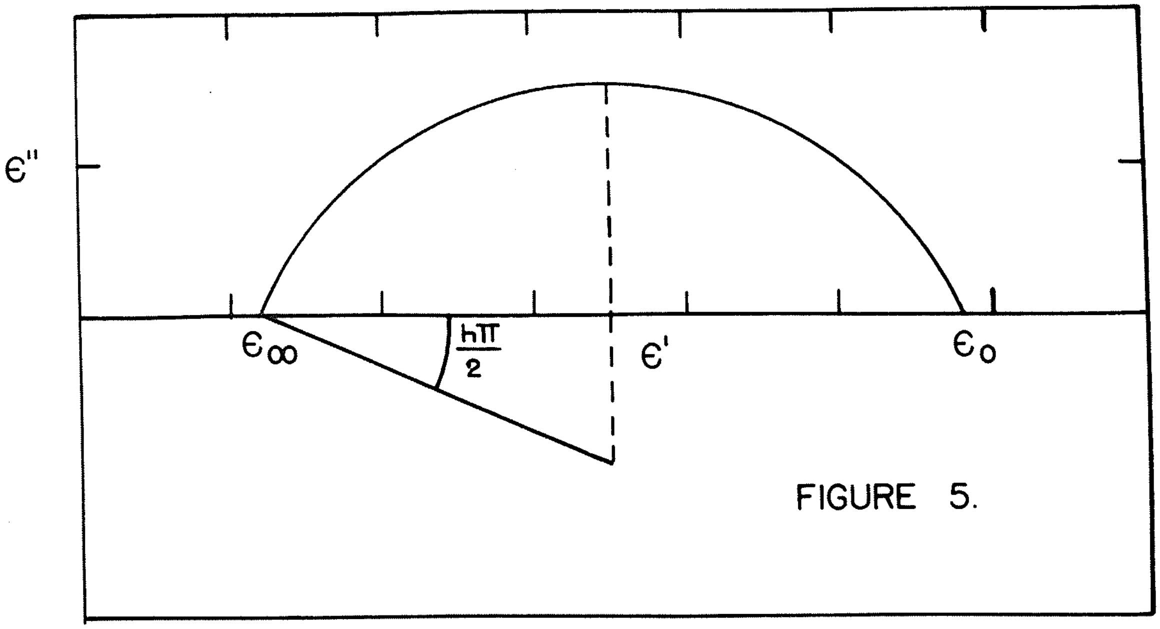


FIGURE 5.

Where $G(\tau)$ is the distribution function of relaxation times and $G(\tau)$ $d\tau$ is the fraction of molecules at a given instant associated with relaxation times between τ and $\tau + d\tau$. Various types of distribution functions have been tried with varying degrees of success. Cole and Cole adopted an empirical function which still permitted interpretation from a circular arc plot. These authors showed that in the case of a distribution of relaxation times the locus of the $\epsilon' - \epsilon''$ curve is a circular arc with the centre of the circle lying below the ϵ' axis. Equation 2. was modified to give

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau)^{1-h}} \qquad 7.$$

For a single distribution time h is zero giving the original equation. For a distribution of relaxation times h lies between zero and unity. The value of h can be determined relatively simply from the circular arc plot (Fig. 5).

From equation 7. it can be shown that the maximum in the ϵ'' curve occurs when $\omega m = \frac{1}{\tau_0}$. In the case of a single relaxation time $\tau = \tau_0$, but in the case of a distribution of relaxation time τ_0 is some average value about which the relaxation times are spread and is referred to as the average relaxation time.

In 1937 Fuoss began his series of papers entitled "Electrical Properties of Solids" in which he did much to elucidate the nature of Debye dispersion in vinyl polymers. His work led to an attempt by Kirkwood and Fuoss (K1), to derive theoretically an expression for the distribution of relaxation times. The result obtained

$$G(\tau) = \frac{1}{2 \cosh y + 2} \qquad 8.$$

$$\text{where } y = \ln \frac{\tau}{\tau_o}$$

was not too successful however, but a more empirical relation developed about the same time by Fuoss and Kirkwood (F1) proved more successful:

$$\epsilon'' = \epsilon''_m \cdot \operatorname{sech} \left[\beta \ln \frac{\omega}{\omega_m} \right] \qquad 9.$$

where β is a parameter and ω_m is the angular frequency corresponding to the maximum value ϵ''_m of ϵ''. This equation for a single relaxation time with $\beta = 1$ can be derived from equations 5. 5b. and 6. The β factor serves to flatten the curve out to match the experimental results and can have values between zero and unity. An analysis by Böttcher (B1) shows that the Cole-Cole and Fuoss-Kirkwood expressions are in agreement and a constant value of β in the latter corresponds to a constant value of h in the former.

C. INTERPRETATION OF DIELECTRIC DATA

When the dielectric data has been obtained, the problem then arises as to how to interpret the data.

Frank (F2) enumerated a number of methods for determining activation energies for the relaxation process and the relative merits of the various modes. The main variation in the procedures is in the evaluation of the temperature dependence of the relaxation time and the relaxation time at a given temperature. Knowing these it is possible, through the Arrhenius equation

$$\frac{1}{\tau} = Ce^{-A/RT} \qquad 10.$$

to evaluate the activation energy A. The method deemed to be most reliable involved finding at various frequencies the temperature at which the loss factor, ϵ'', reached its maximum.

Following a suggestion by Eyring (E1) that the theory of absolute reaction rates could be applied to the process of dielectric relaxation, it became possible to interpret the results in terms of the free energy, enthalpies and entropies of activation. The mathematical expression of the absolute rate theory is

$$K = \kappa \frac{kT}{h} e^{-\Delta F^{*}/RT} \qquad 11.$$

where K is the specific reaction rate

κ is a probability factor (usually taken as unity)

k is the Boltzman constant

T is the absolute temperature

h is Planck's constant

ΔF^* is the free energy of activation

R is the gas constant

Using the thermodynamic relation $\Delta F = \Delta H - T\Delta S$, equation 11. can also be written

$$K = \cdot\ \cdot \frac{kT}{h} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \qquad 11a.$$

where ΔH^* is the enthalpy of activation

and ΔS^* is the entropy of activation.

In the case of dielectric relaxation, K is the rate of decay of the polarization (due to the uncertainty in the calculation of the internal field, K will refer to the rate of decay of the macroscopic polarization) and is inversely proportional to the relaxation time, τ, (i.e. the decay time) of the dielectric. Hence we may now write

$$\frac{1}{\tau} = \frac{kT}{h} \cdot e^{-\Delta F^*/RT} \qquad 12.$$

as the expression for dielectric relaxation, and by a similar substitution to that performed above an equation analogous to 11a. is obtained

$$\frac{1}{\tau} = \frac{kT}{h} \cdot e^{-\Delta H^*/RT}\ e^{\Delta S^*/R} \qquad 12a.$$

Thus if τ is known at a given temperature, ΔF^* can be calculated from equation 12. and by plotting $\ln \frac{1}{\tau}$ against $\frac{1}{T}$ (neglecting T in the $\frac{kT}{h}$ term since this is usually insignificant) a straight line is usually obtained whose slope is found to be $-\Delta H^*/R$ and hence ΔS^* can readily be found.

According to Kauzmann (K2) the most reliable method of determining the dielectric relaxation time is to take $\frac{1}{\tau}$ as equal to 2π times the frequency giving the maximum loss factor at each temperature. This method is analogous to the one recommended by Frank for the Arrhenius equation.

Fuoss (F3) and Davies, Miller and Busse (D1) employed a method of calculation suggested by equation 5. These authors assumed that the value of x in the equation $\epsilon'' = 2\,\epsilon''_{max}\,\frac{x}{1 + x^2}$ is at a given frequency and at different temperatures proportional to the relaxation time. Thus from the temperature dependence of ϵ'' at a given frequency, the relaxation rate can be determined at various temperatures, and hence the activation energy for the process. However, the activation energies determined by this method are not in agreement with those determined by the method of Kauzmann. The reason for this is that the distribution of relaxation times is usually quite broad and changes with temperature (K2 , Fig. 8) so that ϵ'' decreases much more slowly from the maximum than would be expected from the dispersion equation for a single relaxation time. This method is very similar to one suggested by Frank and found, by him, to give an underestimate of the activation energy.

Another method which was quite recently developed by Ferry et al (F4, F5, F6) deserves mention at this time. From their work on the dynamic mechanical properties of plasticized polyvinyl chloride they found that mechanical loss data at any temperature could be reduced to one temperature to give a single composite curve rather than a spectrum. Since the curves obtained in the mechanical case bear a startling resemblance to dielectric constant and loss factor curves obtained in dielectric dispersion, they applied their method to reducing dielectric data with considerable success.

The reduction of data in the case of dielectrics is effected by the following equations:

$$\epsilon'_p = \epsilon' T\rho_0/T_0\rho + \epsilon_\infty(1 - T\rho_0/T_0\rho) \qquad 13.$$

$$\epsilon''_p = \epsilon'' T\rho_0/T_0\rho \qquad 14.$$

$$\omega_p = \omega b_T \qquad 15.$$

Where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant

ϵ_∞ is the limiting high frequency value

ρ_0 is the density at T_0, the temperature to which the data is to be reduced

ρ is the density at temperature T

ω is the angular frequency

b_T is a factor chosen empirically at each temperature to superpose both the ϵ' and ϵ'' data.

The subscript p denotes the reduced values.

The factor $T\rho_0/T_0\rho$ was arrived at as a consequence of the fact that the dielectric constant and loss factor vary inversely as the absolute temperature and directly as the density of the material.

Equations 13. to 15. have been found applicable in the reduction of the data for two polyvinyl chloride samples (F5) and a sample of polyvinyl acetal (F7). However, if the shapes of individual curves of ϵ' and ϵ'' versus log ω do not coincide with horizontal shifting, they found it necessary to use reduced variables to normalize the magnitude of the individual curves. That is, instead of using ϵ' and ϵ'', the reduced dielectric constant $(\epsilon' - \epsilon_\infty) / (\epsilon_0 - \epsilon_\infty)$ and the reduced loss factor $\epsilon'' / (\epsilon_0 - \epsilon_\infty)$ were used, where ϵ_0 is the limiting value of ϵ' at low frequencies.

The method appears to be applicable to all cases in which the maximum value of the loss factor remains the same or decreases with increasing temperature. However, in cases in which the loss factor maximum increases with increasing temperature (F3, F8) it was found that the data would not superpose.

The factor b_T describes the temperature dependance of relaxation times and hence could apparently be used to determine the activation energy for dielectric relaxation. This can be done in two ways by plotting

a. log b_T against T and finding the slopes at various temperatures and substituting them into the equation

$$\Delta H_b = -RT^2 \frac{d \ln b_T}{dT} \qquad 16.$$

b. log b_T against 1/T and determining the slopes at various temperatures and substituting them into the equation

$$\Delta H_b = \frac{-Rd \ln b_T}{d\,1/T} \qquad 17.$$

Activation energies determined in this manner were found to vary quite widely (F6, Fig. 6), the value at the highest temperature being in one case less than one third of the value at the lowest temperature. In all cases there was a remarkable decrease shown as the temperature was increased, a fact which is in some disagreement with the Kauzmann-Eyring approach which predicts a fairly constant activation energy.

EXPERIMENTAL

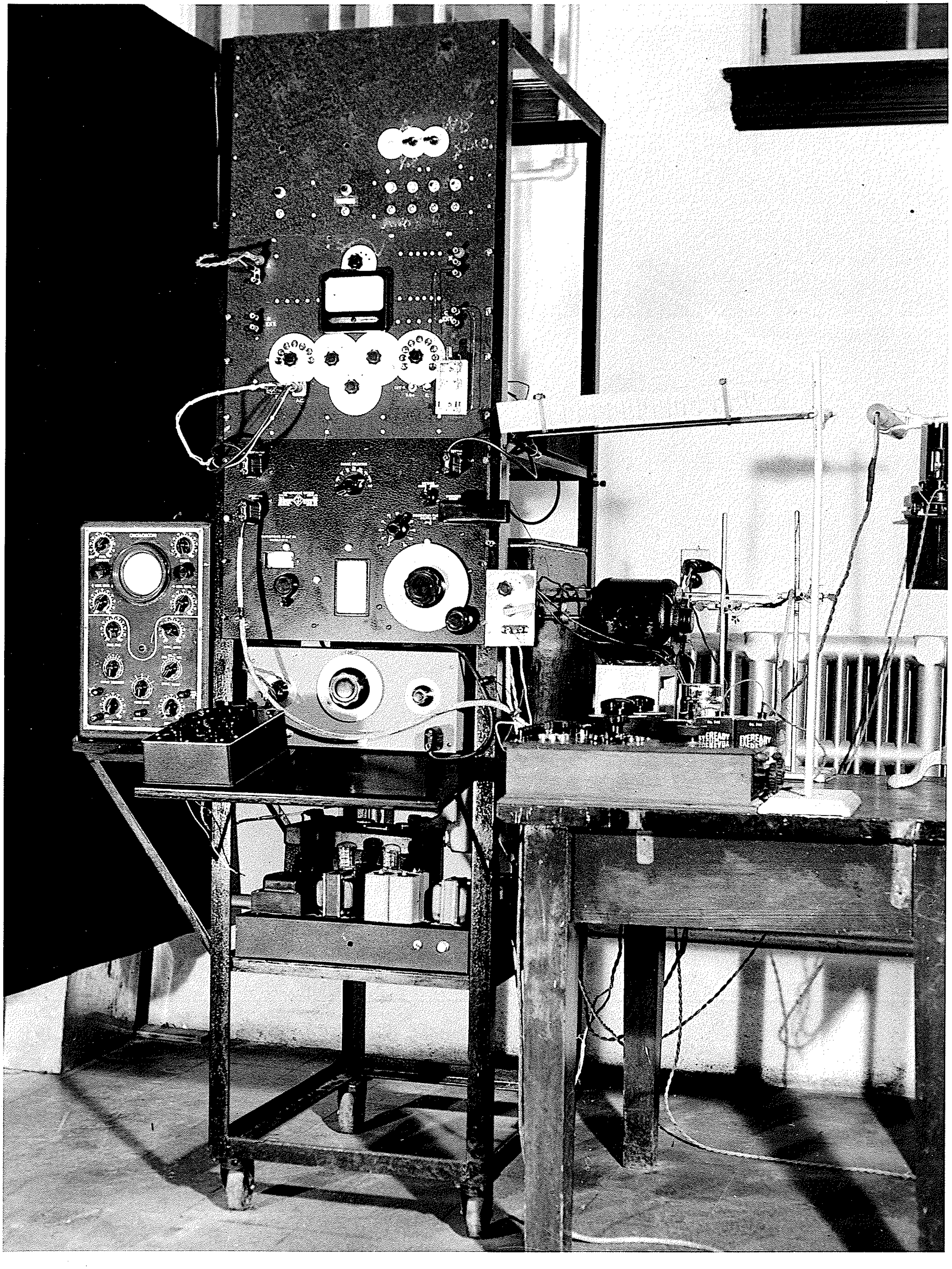


FIGURE 6

Apparatus

A picture of the apparatus is given in Fig. 6. Measurements of the capacitance and dissipation factor were made on a General Radio Capacitance Bridge 716-C. The A.C. signal was supplied by a Hewlett Packard Oscillator, continuously variable from 20 c.p.s. to 200 kc. The null point was determined by amplifying the signal from the bridge by a stabilized amplifier and observing the signal on a Simpson milliammeter with a 100 m.a. movement.

The sample disks, 2 inches in diameter, were placed in a General Radio precision sample holder type 1690-A with the sides removed for the purpose of ventilation (Fig. 7). A wooden box insulated with glass wool and lined with sheet aluminum served as an air thermostat. The temperature was controlled by an Aminco bimetallic thermoregulator which activated a Fisher-Serfass electronic relay. Heat was supplied by two toaster elements, both controlled by powerstats, one of which was operated by the relay, the other was set to maintain the thermostat just below the regulating temperature. A fan in the box provided air circulation through the cell. For experimental runs below room temperature air was passed through a series of drying tubes and then through a copper coil immersed in a dry ice-acetone bath and then into the box. An air pump which was activated by the relay forced the air through the cooling system into the box. At lower temperatures pieces of dry ice were dropped into the box to facilitate temperature control. Above room temperature it was possible to maintain the temperature within ±0.05°C while below room temperature it was only possible to hold the temperature to within

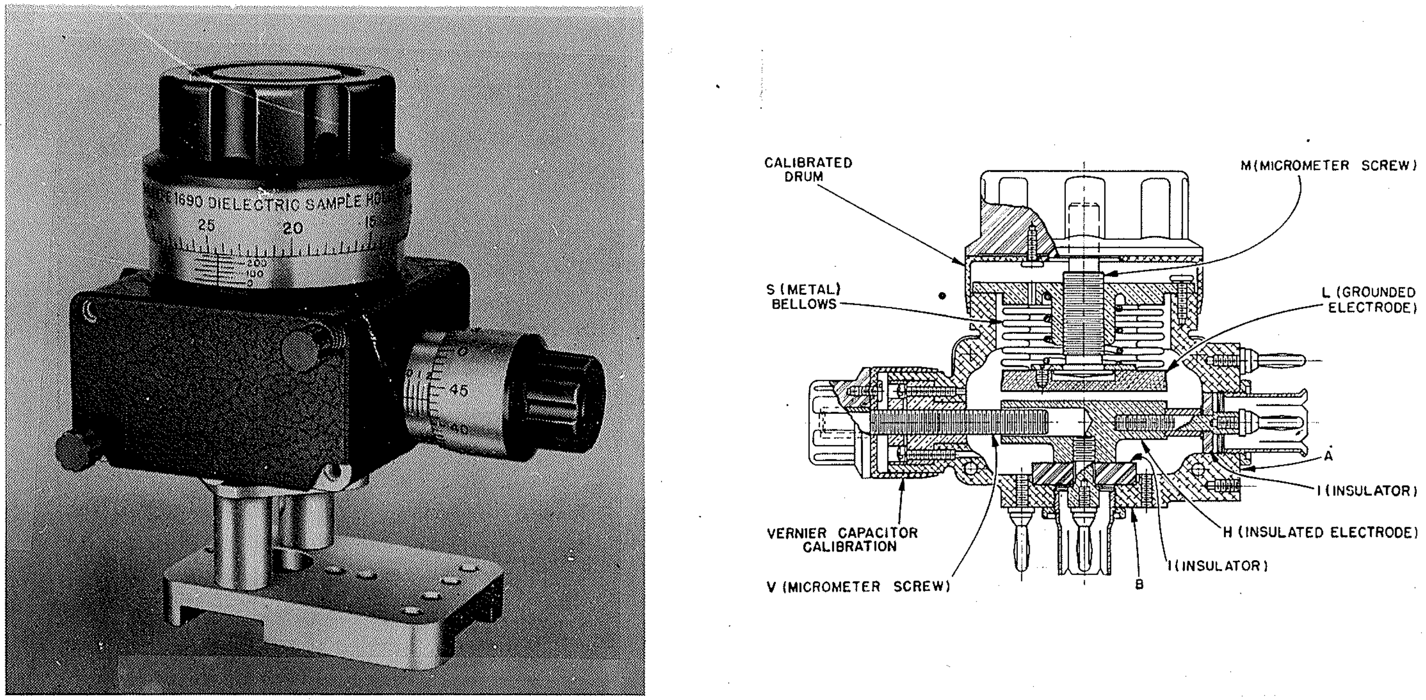

1690 DIELECTRIC SAMPLE HO
25
20
15
45
40
CALIBRATED DRUM
M (MICROMETER SCREW)
S (METAL) BELLOWS
L (GROUNDED ELECTRODE)
A
I (INSULATOR)
VERNIER CAPACITOR CALIBRATION
H (INSULATED ELECTRODE)
I (INSULATOR)
V (MICROMETER SCREW)
B

FIGURE 7

a few tenths of a degree, the lower the temperature the poorer the control. A calibrated chromel-constantan thermocouple was placed in the housing of the dielectric sample holder and e.m.f. readings were made on a Leeds and Northrup potentiometer.

Resistance readings were also taken on the sample. For this purpose a Wheatstone Bridge was constructed according to a paper by Avins (A1) modified slightly by Funt. A circuit diagram is given on the following page (Fig. 8). All resistors up to 10,000 ohms in the ratio arms were I.R.C. 0.1% precision wire wound resistors. The 1 megohm resistor and the bank of 20 megohm resistors comprising the 100 megohm arm of the bridge were special high stability carbon deposited I.R.C. resistors. A Rubicon decade resistance box served as the third arm of the bridge.

Materials

Saran: Two samples of Saran A were obtained from the Dow Chemical Company. One was a sample of molecular weight in the neighbourhood of 10,000 and the other had a molecular weight of around 100,000. These are designated in the following work as Saran (M.W. 10,000) and Saran (M.W. 100,000). They were given no treatment except pulverization. The chlorine contents of these samples are respectively 73.8% and 75.2%.*

Vinylidene Chloride: This monomer was also obtained from the Dow Chemical Company. The monomer was distilled and the fraction was collected which boiled between 30.8 - 31.2°C at a pressure of 750 mm of Hg. The refractive

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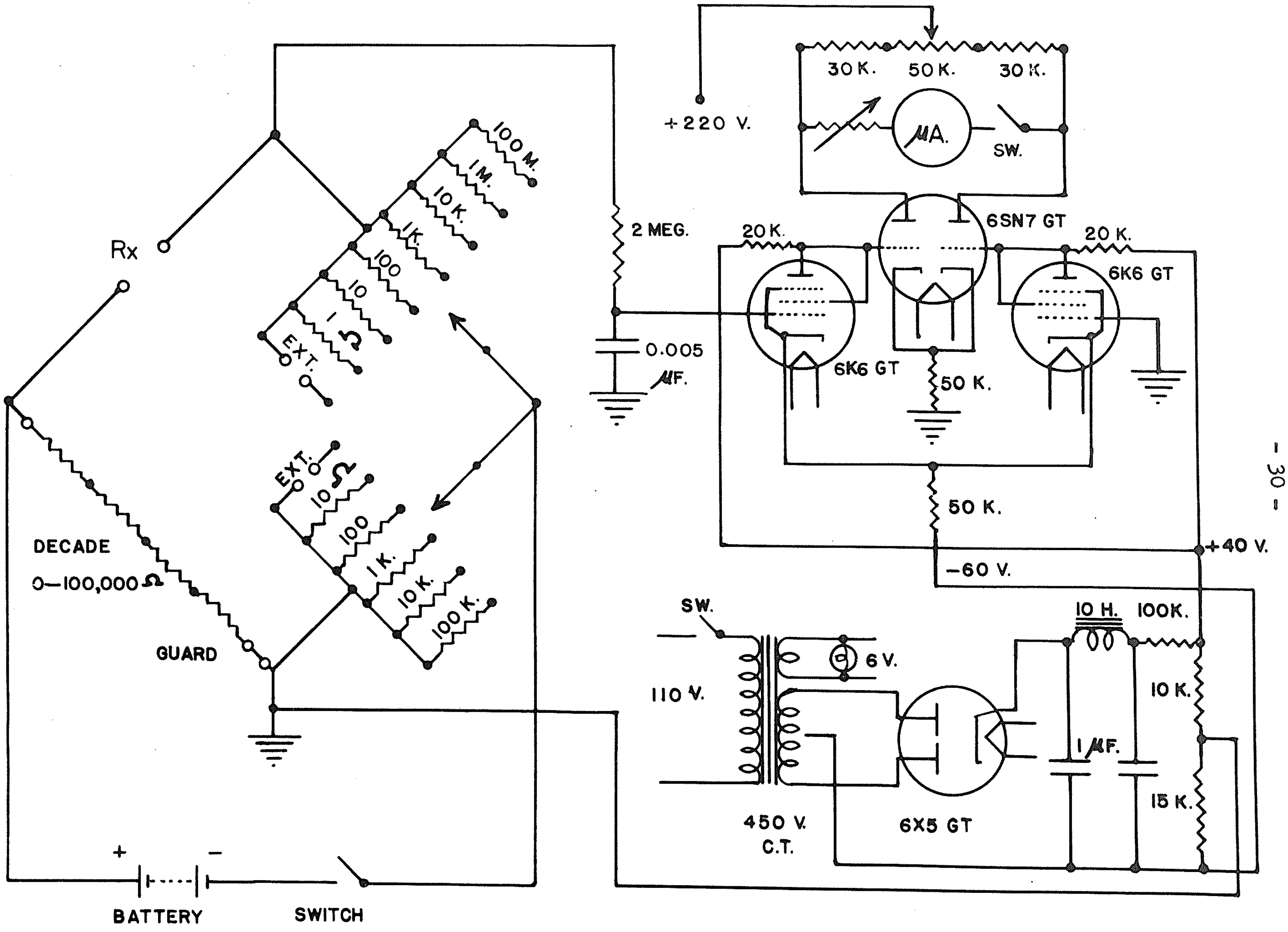
* (chlorine determination by National Testing Laboratories, Winnipeg, Man.)



WHEATSTONE BRIDGE AND AMPLIFIER (FIGURE 8.)

index was found to be 1.4272 at 16°C.

<u>Polyvinylidene Chloride</u>: The polymer was obtained by the emulsion polymerization of the monomer. The following recipe was used:

Water	300 ml.
Vinylidene Chloride	250 ml.
Sodium Bisulphite	0.25 g.
Potassium Persulphate	0.60 g.
Antarox A-400	4 ml.

The polymerization was carried on at room temperature under nitrogen for nine hours with agitation. The emulsion was broken by addition of aluminum sulphate. The polymer was then washed with voluminous quantities of water to remove salts and emulsifying agents.

The sodium bisulphite was added to remove oxygen from the water and monomer. The potassium persulphate supplied free radicals for the polymerization. Antarox A-400 is an emulsifying agent. The polymer was found to contain 74.6% chlorine.*

<u>Hexachloro Benzene</u>: This compound was recrystallized three times from benzene. Long white needle-like crystals were obtained having a melting point of 225 - 226°C.

<u>Mineral Oil</u>: The mineral oil used was medicinal grade Nujol. It was not given any treatment. A distillation of the material produced no distillate below 300°C.

<u>α-Chloronaphthalene</u>: This plasticizer was a Fisher Reagent grade chemical and was given no treatment.

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* (chlorine determination by National Testing Laboratories, Winnipeg, Man.)

Lead Stearate: This compound was used as a stabilizer in the plasticized compositions. It is a Witco Chemical Company product known as Witco Stayrite No. 30.

Toluene: Eastman Reagent grade toluene was used in the making of the various compositions.

2-Butanone: This was obtained by redistilling the technical product in a fractionating column. The fraction boiling between 77.8 - 78.8°C was used. Its refractive index (n_D) was 1.3784 at 22°C.

Method of Plasticization

Since no equipment was available for milling and calendering the plasticized mixture, other methods were necessary to obtain a homogeneous sample.

It was found that a mixture of 70% toluene and 30% 2-butanone peptized and partially dissolved the saran after a short period (2 - 3 hours) of heating. On evaporation of the solvent a paste resulted which could be handled quite easily. By repeated stirring and mixing of the paste a relatively homogeneous sample was obtained.

The following method of preparing the samples was adopted. The saran, which was coarsely granular, was ground in a mortar until a fine powder was obtained. About 5 grams of the powder was weighed accurately and transferred to a 100 ml beaker. A weight of Lead Stearate corresponding to about 1% of the total sample weight was added to the beaker.

Plasticizer was added by one of two methods depending on the nature of the plasticizer. The hexachloro benzene which was crystalline was weighed accurately on a watch glass and transferred to the beaker. Nujol and α-chloronaphthalene were liquids and were dispensed from a hypodermic syringe which served as a weight burette.

To the mixture in the beaker, 75 ml of the 70 - 30 toluene - 2-butanone mixture were added. The beaker was then placed on a hot plate and allowed to reflux for 2 - 3 hours. On cooling,a paste formed and this was stirred at frequent intervals and heat was again applied to evaporate the solvent.

A powder resulted which still contained a trace of solvent. The latter was removed by vacuum drying, which, in the case of hexachloro benzene and Nujol, was for a period of 48 hours. The α-chloronaphthalene which was more volatile than the hexachloro benzene was only dried for a period of 24 hours.

The powder was then added to a die (Fig. 9) which had previously been heated to a temperature of 130 - 160°C depending upon the nature of the composition. The die was placed in a Carver press and a pressure of about 12,000 psi applied to the sample. The die was allowed to cool to room temperature and the sample freed from between the plates. A circle was scribed on the disk 2.0 inches in diameter and the material outside the line removed.

After the edges were trimmed on the sample, 18 micrometer readings were taken at regular intervals on the 2 inch disk. Three measurements of the diameter were taken 60° apart. The disk was then coated with aquadag (colloidal graphite) and placed in the dielectric sample holder for dielectric measurements.

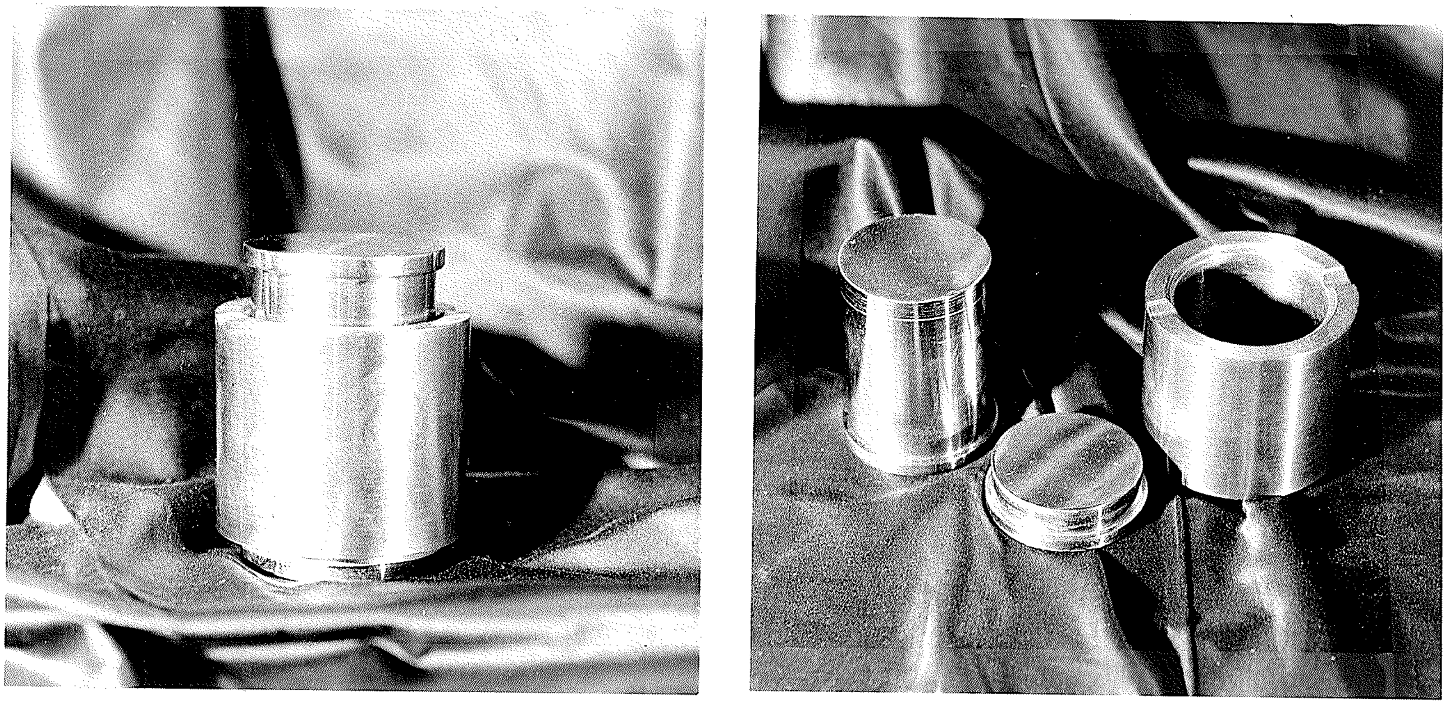


FIGURE 9

EXPERIMENTAL RESULTS

TABLE 1

SARAN (M.W. 100,000)

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
-13.3	2.88	0.027	2.86	0.028	2.84	0.035	2.83	0.032	2.80	0.050	2.77	0.094	2.68	0.144	2.53	0.146
- 3.4	2.93	0.034	2.92	0.038	2.89	0.043	2.87	0.039	2.85	0.058	2.80	0.100	2.71	0.154	2.55	0.152
4.5	3.02	0.056	2.99	0.057	2.96	0.060	2.92	0.053	2.89	0.067	2.84	0.105	2.75	0.156	2.59	0.161
10.7	3.16	0.101	3.11	0.097	3.05	0.090	2.99	0.077	2.95	0.087	2.88	0.125	2.78	0.176	2.59	0.169
16.0	3.34	0.164	3.27	0.154	3.18	0.134	3.08	0.113	3.02	0.115	2.93	0.147	2.82	0.192	2.63	0.182
21.3	3.60	0.221	3.50	0.216	3.36	0.197	3.22	0.166	3.12	0.155	3.01	0.176	2.87	0.217	2.66	0.199
27.0	3.92	0.237	3.80	0.255	2.63	0.260	3.42	0.244	3.27	0.222	3.10	0.222	2.95	0.244	2.73	0.223
31.5	4.12	0.214	4.02	0.243	3.84	0.280	3.60	0.287	3.41	0.276	3.21	0.269	3.03	0.282	2.77	0.251
36.8	4.30	0.162	4.23	0.196	4.09	0.255	3.85	0.308	3.64	0.327	3.37	0.330	3.15	0.333	2.86	0.305
42.5	4.43	0.114	4.38	0.140	4.29	0.200	4.11	0.278	3.90	0.347	3.59	0.393	3.32	0.405	2.97	0.340
48.1	4.50	0.088	4.46	0.104	4.40	0.147	4.27	0.224	4.11	0.317	3.81	0.412	3.51	0.470	3.08	0.425
53.5	4.54	0.080	4.51	0.086	4.46	0.116	4.37	0.172	4.25	0.263	4.00	0.396	3.68	0.502	3.20	0.467
58.7	4.57	0.082	4.53	0.081	4.49	0.096	4.42	0.134	4.33	0.214	4.15	0.334	3.88	0.488	3.38	0.526
64.0	4.58	0.101	4.55	0.087	4.51	0.089	4.44	0.111	4.38	0.161	4.25	0.279	4.03	0.452	3.54	0.539
69.7	4.60	0.132	4.57	0.105	4.52	0.089	4.46	0.095	4.41	0.131	4.31	0.228	4.14	0.397	3.70	0.523
74.1	4.61	0.170	4.57	0.121	4.52	0.092	4.46	0.086	4.42	0.113	4.33	0.194	4.20	0.354	3.79	0.507
81.3	4.66	0.278	4.60	0.185	4.54	0.113	4.48	0.087	4.44	0.098	4.38	0.157	4.28	0.295	3.94	0.458

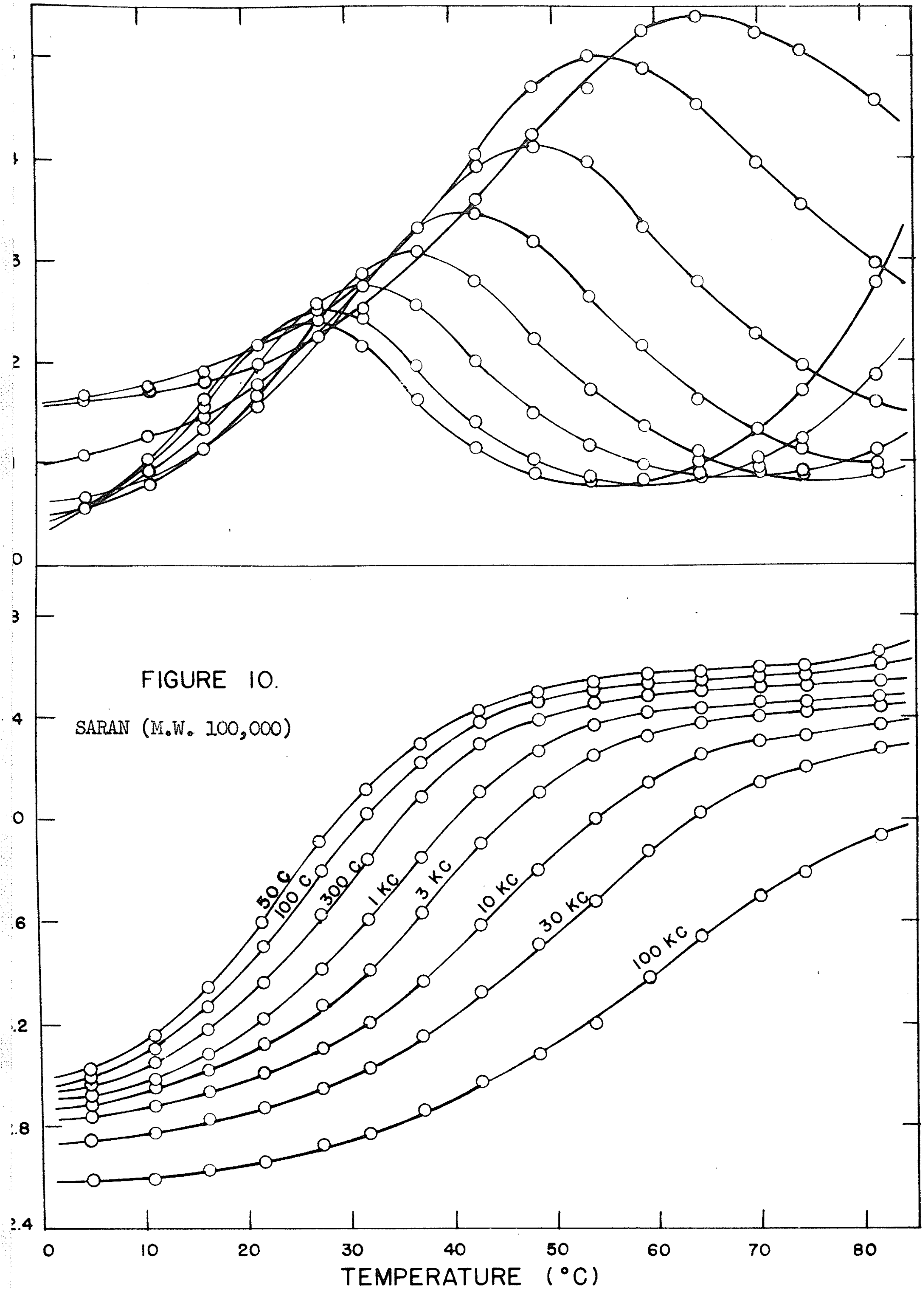


FIGURE 10.
SARAN (M.W. 100,000)
50 C
100 C
300 C
1 KC
3 KC
10 KC
30 KC
100 KC
3
2
0
8
4
0
6
2
8
2.4
0
10
20
30
40
50
60
70
80
TEMPERATURE (°C)

TABLE 2

SARAN (M.W. 10,000)

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
- 9.2	3.13	0.025	3.12	0.025	3.09	0.027	3.07	0.026	3.05	0.028	3.04	0.033	3.02	0.058	2.97	0.133
0.5	3.22	0.049	3.19	0.049	3.16	0.049	3.12	0.043	3.09	0.044	3.07	0.048	3.04	0.081	2.97	0.169
9.1	3.45	0.141	3.39	0.126	3.31	0.105	3.23	0.087	3.18	0.075	3.13	0.075	3.09	0.102	3.00	0.190
15.0	3.77	0.259	3.66	0.236	3.52	0.194	3.38	0.152	3.29	0.123	3.20	0.112	3.15	0.135	3.03	0.224
21.1	4.20	0.340	4.04	0.336	3.81	0.303	3.58	0.248	3.43	0.199	3.30	0.167	3.21	0.178	3.06	0.262
25.5	4.52	0.337	4.36	0.364	4.11	0.372	3.79	0.327	3.60	0.273	3.40	0.224	3.29	0.226	3.09	0.293
32.0	4.88	0.263	4.75	0.310	4.52	0.382	4.17	0.411	3.89	0.382	3.60	0.324	3.42	0.305	3.17	0.358
36.8	5.05	0.182	4.97	0.232	4.81	0.323	4.49	0.408	4.20	0.442	3.82	0.422	3.57	0.404	3.24	0.442
42.1	5.15	0.112	5.10	0.148	5.00	0.227	4.78	0.341	4.52	0.444	4.11	0.503	3.78	0.519	3.32	0.550
47.2	5.19	0.081	5.15	0.102	5.09	0.156	4.94	0.261	4.76	0.388	4.38	0.517	4.02	0.599	3.46	0.645
52.8	5.21	0.059	5.19	0.069	5.15	0.106	5.06	0.183	4.93	0.297	4.65	0.464	4.30	0.627	3.68	0.735
57.9	5.23	0.053	5.20	0.056	5.17	0.077	5.11	0.128	5.03	0.216	4.83	0.380	4.56	0.595	3.93	0.788
63.1	5.23	0.056	5.21	0.052	5.18	0.061	5.13	0.097	5.08	0.161	4.94	0.302	4.73	0.529	4.16	0.796
68.7	5.24	0.067	5.22	0.057	5.19	0.055	5.15	0.074	5.11	0.118	5.02	0.226	4.89	0.437	4.40	0.771
74.0	5.24	0.088	5.22	0.066	5.19	0.055	5.15	0.064	5.11	0.093	5.05	0.179	4.96	0.367	4.56	0.713
79.6	5.25	0.116	5.22	0.086	5.19	0.059	5.15	0.060	5.12	0.081	5.06	0.146	5.00	0.308	4.68	0.637

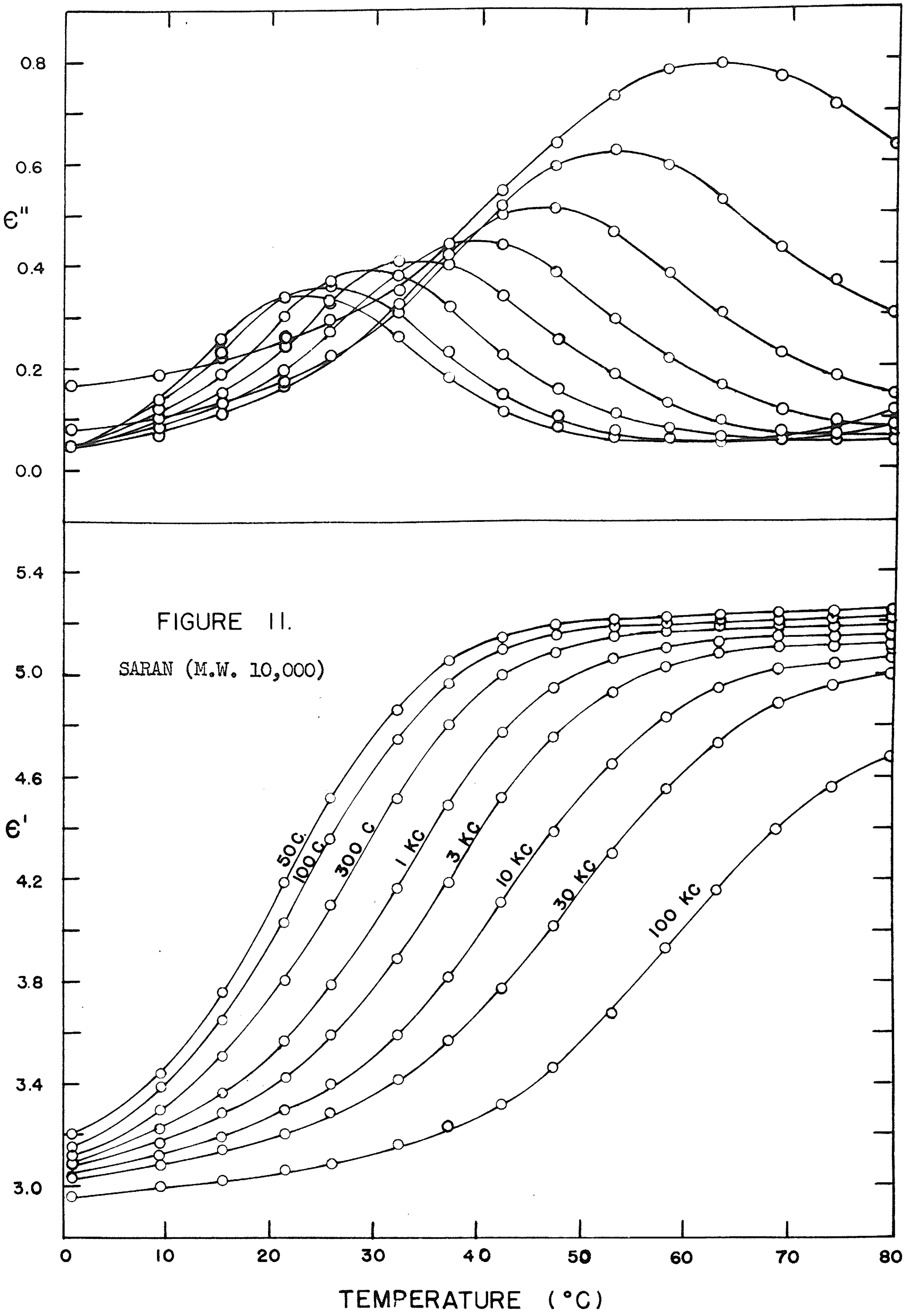


FIGURE 11.

SARAN (M.W. 10,000)

TABLE 3

VINYLIDENE CHLORIDE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
- 2.3	2.53	0.023	2.52	0.021	2.50	0.080	2.48	0.016	2.47	0.016	2.46	0.023	2.44	0.034	2.42	0.056
6.3	2.63	0.058	2.60	0.054	2.57	0.044	2.54	0.034	2.52	0.030	2.50	0.034	2.47	0.044	2.45	0.066
12.3	2.75	0.100	2.71	0.091	2.65	0.077	2.59	0.058	2.56	0.050	2.53	0.048	2.50	0.055	2.46	0.075
16.7	2.86	0.120	2.80	0.115	2.73	0.102	2.65	0.080	2.60	0.066	2.56	0.062	2.52	0.067	2.48	0.079
22.0	3.00	0.127	2.94	0.133	2.85	0.131	2.74	0.112	2.68	0.095	2.60	0.083	2.55	0.081	2.50	0.090
26.9	3.12	0.121	3.06	0.133	2.96	0.143	2.84	0.139	2.75	0.122	2.65	0.105	2.59	0.096	2.53	0.102
31.9	3.22	0.107	3.16	0.118	3.08	0.139	2.96	0.151	2.85	0.147	2.73	0.138	2.65	0.125	2.56	0.123
36.8	3.28	0.088	3.24	0.098	3.17	0.121	3.06	0.147	2.95	0.159	2.81	0.162	2.71	0.150	2.60	0.144
41.5	3.33	0.077	3.30	0.083	3.24	0.105	3.15	0.130	3.05	0.157	2.91	0.180	2.79	0.177	2.64	0.173
47.1	3.38	0.067	3.34	0.070	3.30	0.086	3.23	0.111	3.15	0.142	3.02	0.183	2.88	0.201	2.71	0.200
52.4	3.41	0.065	3.38	0.066	3.34	0.074	3.28	0.091	3.22	0.122	3.11	0.172	2.98	0.209	2.80	0.228
57.2	3.44	0.068	3.41	0.065	3.37	0.068	3.32	0.077	3.27	0.103	3.18	0.152	3.07	0.202	2.87	0.247
62.8	3.48	0.081	3.45	0.073	3.40	0.069	3.35	0.070	3.31	0.087	3.24	0.129	3.15	0.186	2.97	0.248
67.7	3.51	0.095	3.48	0.081	3.43	0.070	3.38	0.065	3.34	0.078	3.28	0.110	3.20	0.170	3.04	0.242
73.0	3.55	0.113	3.51	0.095	3.46	0.077	3.41	0.066	3.37	0.070	3.32	0.099	3.25	0.150	3.11	0.223
80.1	3.62	0.154	3.58	0.126	3.51	0.094	3.45	0.074	3.41	0.069	3.36	0.087	3.31	0.129	3.18	0.198

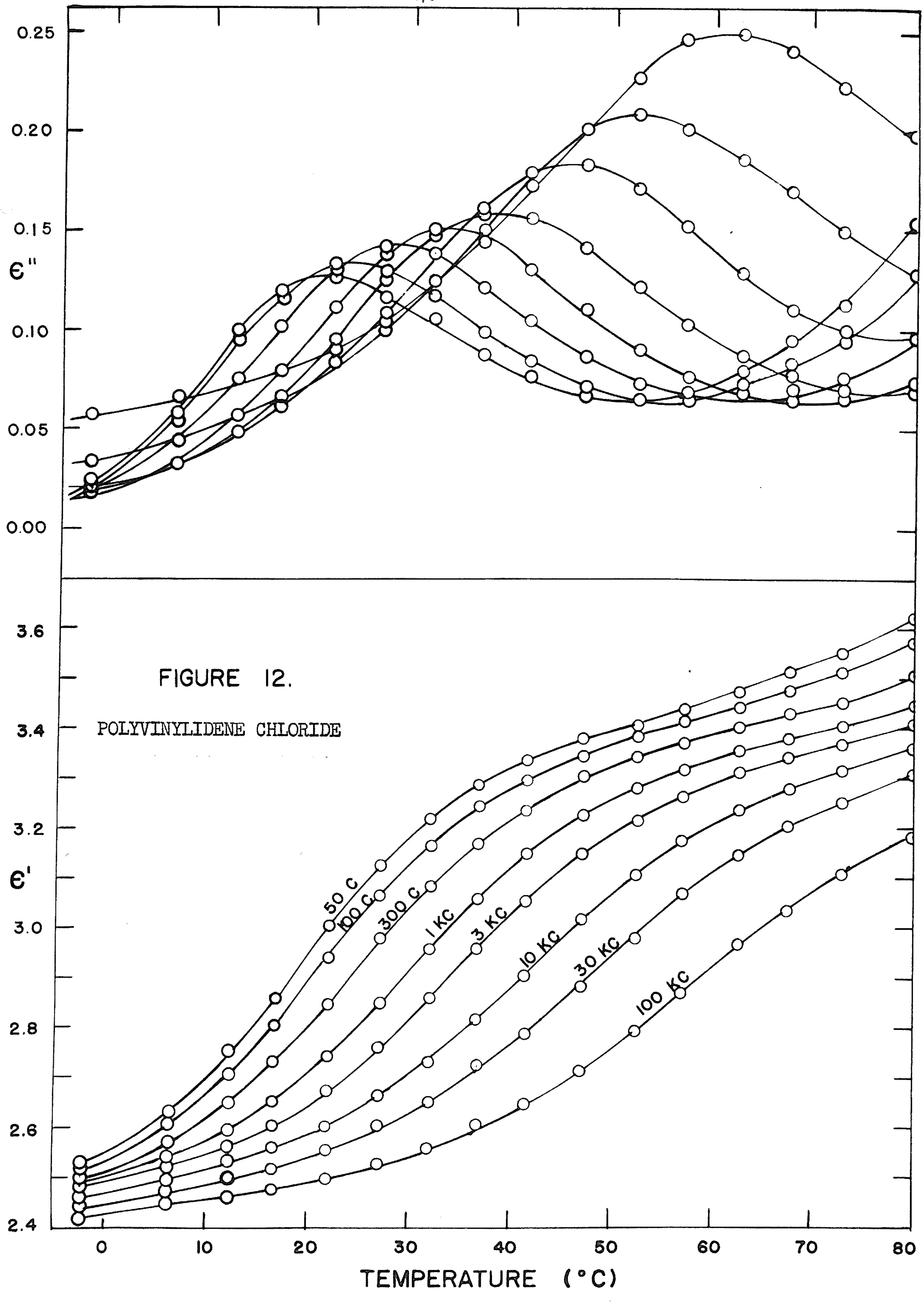


FIGURE 12.

POLYVINYLIDENE CHLORIDE

TABLE 4

99.0% SARAN (M.W. 10,000) - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
- 9.9	3.14	0.032	3.13	0.041	3.11	0.032	3.08	0.027	3.06	0.032	3.04	0.040	3.02	0.065	2.98	0.139
- 3.0	3.24	0.064	3.21	0.059	3.18	0.055	3.14	0.046	3.11	0.047	3.08	0.056	3.05	0.087	2.98	0.180
3.7	3.43	0.137	3.37	0.124	3.30	0.103	3.23	0.084	3.18	0.074	3.13	0.079	3.09	0.105	3.00	0.189
11.0	3.81	0.260	3.70	0.242	3.56	0.205	3.41	0.163	3.32	0.136	3.22	0.121	3.16	0.131	3.06	0.199
15.4	4.12	0.316	3.98	0.310	3.78	0.282	3.57	0.231	3.44	0.191	3.30	0.164	3.21	0.165	3.09	0.229
20.6	4.48	0.311	4.33	0.335	4.11	0.346	3.82	0.314	3.63	0.274	3.43	0.229	3.30	0.217	3.15	0.266
26.0	4.76	0.252	4.65	0.293	4.44	0.349	4.13	0.372	3.88	0.352	3.60	0.310	3.43	0.287	3.21	0.326
32.1	4.94	0.178	4.86	0.214	4.72	0.287	4.45	0.362	4.19	0.397	3.85	0.385	3.62	0.362	3.34	0.380
36.6	5.02	0.136	4.96	0.164	4.86	0.228	4.65	0.312	4.42	0.390	4.07	0.428	3.80	0.431	3.45	0.453
42.5	5.07	0.102	5.03	0.114	4.96	0.157	4.82	0.231	4.66	0.327	4.35	0.428	4.05	0.489	3.63	0.534
47.8	5.09	0.088	5.05	0.094	5.00	0.118	4.90	0.175	4.78	0.261	4.54	0.383	4.27	0.500	3.81	0.596
54.0	5.09	0.080	5.06	0.079	5.01	0.090	4.94	0.124	4.87	0.185	4.71	0.304	4.49	0.465	4.04	0.638
59.0	5.08	0.081	5.05	0.076	5.01	0.078	4.95	0.098	4.89	0.145	4.78	0.241	4.62	0.404	4.22	0.625
64.4	5.08	0.088	5.05	0.078	5.01	0.072	4.95	0.083	4.91	0.115	4.82	0.193	4.71	0.341	4.37	0.592
69.8	5.07	0.102	5.04	0.085	5.00	0.070	4.95	0.072	4.91	0.091	4.84	0.154	4.76	0.280	4.50	0.532
75.1	5.07	0.108	5.03	0.097	4.99	0.074	4.94	0.068	4.90	0.081	4.85	0.126	4.78	0.234	4.58	0.472

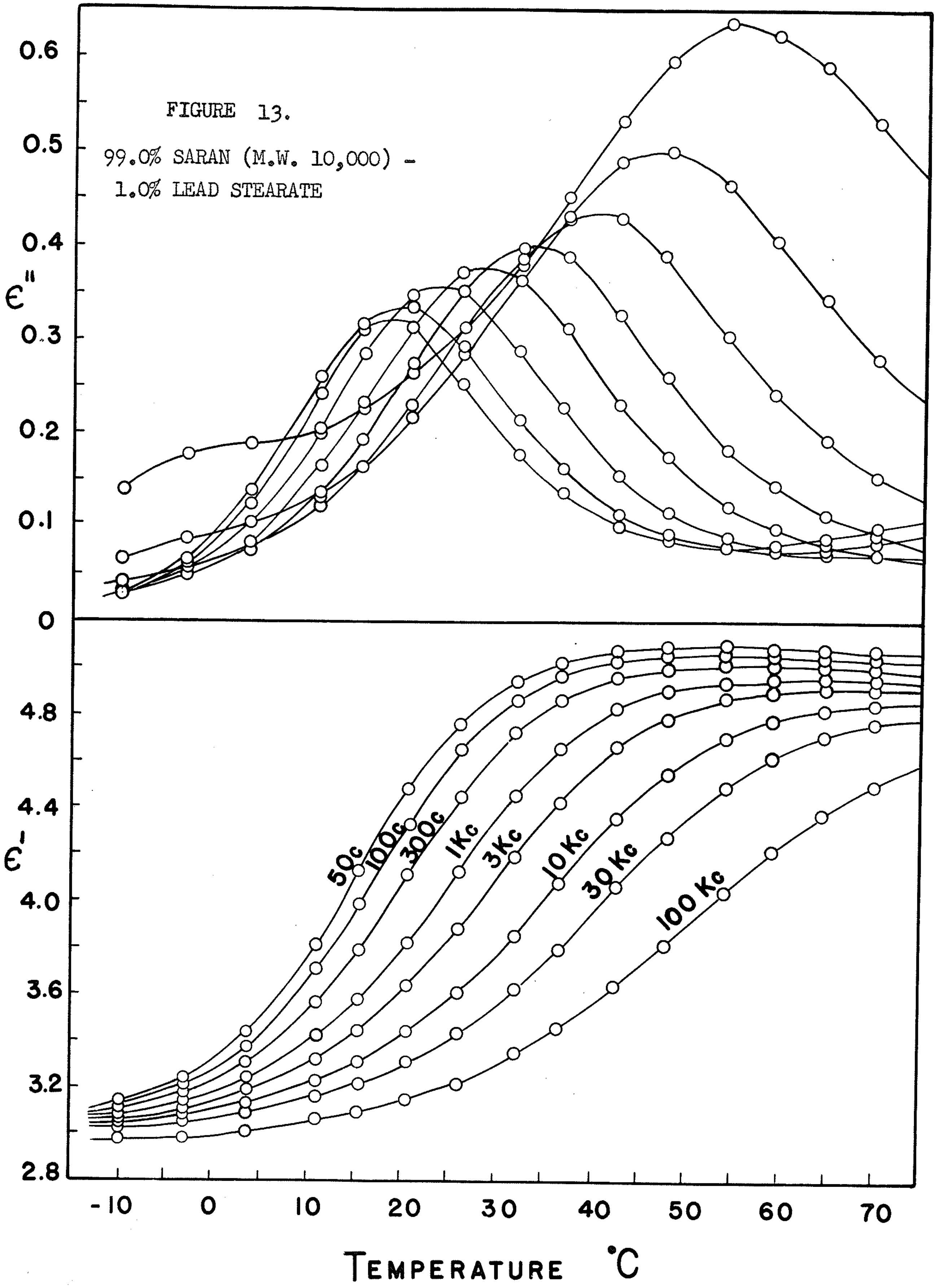


FIGURE 13.

99.0% SARAN (M.W. 10,000) -
1.0% LEAD STEARATE

TABLE 5

96.0% SARAN - 3.0% NUJOL - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-19.6	3.03	0.027	3.02	0.024	3.00	0.024	2.97	0.028	2.95	0.031	2.92	0.038	2.90	0.060	2.85	0.140
- 8.3	3.11	0.050	3.09	0.044	3.06	0.040	3.02	0.042	2.99	0.044	2.96	0.049	2.93	0.067	2.88	0.137
- 0.8	3.29	0.104	3.24	0.095	3.19	0.083	3.11	0.077	3.06	0.072	3.01	0.071	2.97	0.086	2.90	0.151
5.5	3.55	0.181	3.47	0.167	3.37	0.144	3.25	0.129	3.17	0.113	3.09	0.104	3.03	0.119	2.95	0.168
10.9	3.83	0.241	3.72	0.233	3.57	0.209	3.40	0.184	3.29	0.156	3.17	0.141	3.09	0.138	2.99	0.190
16.1	4.12	0.268	4.00	0.274	3.82	0.266	3.60	0.248	3.44	0.216	3.28	0.190	3.17	0.179	3.03	0.222
21.5	4.40	0.241	4.29	0.268	4.10	0.294	3.84	0.302	3.64	0.279	3.42	0.250	3.28	0.231	3.10	0.263
26.9	4.60	0.202	4.51	0.228	4.35	0.271	4.10	0.314	3.89	0.323	3.62	0.311	3.43	0.310	3.18	0.367
31.8	4.70	0.156	4.63	0.178	4.51	0.230	4.29	0.295	4.08	0.337	3.78	0.350	3.56	0.357	3.27	0.397
36.7	4.77	0.113	4.72	0.131	4.64	0.178	4.47	0.252	4.29	0.320	3.99	0.374	3.74	0.405	3.39	0.451
41.7	4.82	0.088	4.78	0.097	4.73	0.130	4.60	0.197	4.47	0.276	4.20	0.371	3.95	0.439	3.56	0.508
47.2	4.85	0.075	4.82	0.075	4.78	0.095	4.69	0.144	4.60	0.216	4.39	0.326	4.16	0.439	3.74	0.556
52.7	4.86	0.068	4.83	0.065	4.79	0.073	4.74	0.108	4.67	0.165	4.52	0.269	4.33	0.406	3.92	0.577
58.4	4.86	0.069	4.83	0.062	4.80	0.062	4.75	0.084	4.70	0.123	4.60	0.211	4.46	0.350	4.11	0.565
64.1	4.87	0.079	4.84	0.066	4.80	0.058	4.75	0.071	4.71	0.097	4.63	0.164	4.54	0.291	4.25	0.523
71.3	4.88	0.104	4.85	0.083	4.81	0.065	4.76	0.069	4.72	0.080	4.66	0.127	4.60	0.231	4.37	0.451

TABLE 6

93.0% SARAN - 6.0% NUJOL - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-14.4	3.01	0.031	3.00	0.029	2.98	0.029	2.96	0.030	2.93	0.031	2.91	0.029	2.89	0.035	2.87	0.064
- 2.0	3.18	0.079	3.15	0.071	3.10	0.063	3.05	0.058	3.01	0.052	2.97	0.050	2.94	0.054	2.90	0.079
4.8	3.37	0.042	3.31	0.129	3.23	0.109	3.14	0.096	3.08	0.082	3.02	0.073	2.98	0.074	2.93	0.097
10.5	3.64	0.209	3.55	0.198	3.42	0.173	3.28	0.149	3.19	0.124	3.10	0.107	3.04	0.100	2.97	0.119
15.6	3.91	0.240	3.81	0.240	3.65	0.228	3.45	0.208	3.32	0.176	3.19	0.148	3.11	0.130	3.02	0.139
20.3	4.16	0.225	4.06	0.243	3.89	0.261	3.66	0.260	3.49	0.231	3.31	0.202	3.19	0.170	3.07	0.167
26.5	4.37	0.190	4.29	0.213	4.14	0.249	3.91	0.284	3.71	0.286	3.48	0.262	3.32	0.233	3.15	0.227
31.8	4.47	0.138	4.41	0.162	4.30	0.205	4.11	0.264	3.92	0.299	3.66	0.303	3.46	0.287	3.24	0.276
36.3	4.54	0.108	4.48	0.123	4.41	0.164	4.25	0.227	4.09	0.285	3.83	0.325	3.61	0.333	3.34	0.335
41.6	4.58	0.084	4.54	0.091	4.48	0.118	4.38	0.177	4.25	0.244	4.02	0.318	3.79	0.361	3.48	0.384
47.4	4.60	0.071	4.57	0.070	4.53	0.085	4.45	0.123	4.37	0.182	4.20	0.269	4.00	0.360	3.67	0.435
53.5	4.60	0.067	4.57	0.063	4.54	0.065	4.48	0.089	4.42	0.131	4.31	0.213	4.16	0.320	3.85	0.447
58.3	4.59	0.076	4.57	0.065	4.53	0.061	4.48	0.075	4.44	0.105	4.35	0.174	4.24	0.274	3.97	0.433
64.1	4.62	0.100	4.58	0.082	4.54	0.067	4.49	0.068	4.45	0.084	4.38	0.134	4.30	0.223	4.09	0.386
70.6	4.67	0.132	4.63	0.110	4.57	0.086	4.50	0.079	4.46	0.081	4.40	0.112	4.34	0.179	4.18	0.337

TABLE 7

89.0% SARAN - 10.0% NUJOL - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"
-13.8	3.02	0.026	3.01	0.025	2.99	0.026	2.96	0.031	2.94	0.038	2.91	0.060	2.87	0.114	2.73	0.167
- 3.2	3.09	0.040	3.08	0.039	3.05	0.038	3.01	0.044	2.98	0.051	2.94	0.076	2.89	0.127	2.75	0.170
5.1	3.22	0.079	3.19	0.073	3.14	0.065	3.08	0.068	3.04	0.069	2.99	0.083	2.92	0.140	2.77	0.186
10.5	3.38	0.132	3.32	0.121	3.25	0.104	3.16	0.098	3.10	0.091	3.03	0.109	2.96	0.151	2.81	0.195
14.0	3.52	0.169	3.44	0.156	3.35	0.134	3.24	0.121	3.16	0.113	3.08	0.125	3.00	0.166	2.83	0.203
20.8	3.88	0.223	3.78	0.228	3.63	0.216	3.45	0.201	3.33	0.182	3.19	0.179	3.08	0.206	2.88	0.230
28.0	4.18	0.204	4.09	0.226	3.93	0.251	3.70	0.263	3.53	0.250	3.33	0.244	3.18	0.259	2.95	0.266
32.5	4.31	0.164	4.24	0.188	4.11	0.234	3.88	0.284	3.69	0.304	3.44	0.319	3.23	0.349	2.91	0.336
37.8	4.39	0.120	4.34	0.135	4.25	0.181	4.07	0.252	3.89	0.310	3.62	0.359	3.37	0.397	3.01	0.386
42.3	4.42	0.099	4.38	0.106	4.32	0.141	4.18	0.212	4.03	0.288	3.77	0.369	3.50	0.433	3.10	0.426
47.7	4.43	0.088	4.40	0.079	4.35	0.100	4.26	0.156	4.16	0.233	3.94	0.347	3.67	0.456	3.23	0.481
53.4	4.43	0.092	4.40	0.069	4.36	0.076	4.30	0.115	4.23	0.186	4.06	0.299	3.83	0.447	3.37	0.511
58.4	4.43	0.110	4.40	0.074	4.37	0.070	4.31	0.093	4.26	0.141	4.13	0.254	3.95	0.418	3.49	0.521
63.5	4.46	0.129	4.42	0.102	4.37	0.078	4.31	0.085	4.27	0.117	4.17	0.213	4.02	0.373	3.61	0.516
69.1	4.56	0.210	4.48	0.165	4.40	0.115	4.32	0.098	4.28	0.108	4.20	0.179	4.08	0.321	3.73	0.486
75.2	4.69	0.295	4.59	0.237	4.46	0.170	4.35	0.130	4.29	0.115	4.21	0.158	4.11	0.275	3.82	0.456

TABLE 8

84.1% SARAN - 14.9% NUJOL - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-16.8	2.82	0.025	2.80	0.024	2.79	0.026	2.77	0.024	2.75	0.025	2.74	0.026	2.72	0.043	2.69	0.098
- 7.4	2.87	0.034	2.86	0.034	2.83	0.036	2.81	0.033	2.78	0.035	2.76	0.035	2.74	0.051	2.70	0.102
3.1	2.97	0.058	2.95	0.055	2.91	0.054	2.89	0.050	2.84	0.049	2.80	0.048	2.78	0.061	2.73	0.110
9.7	3.12	0.104	3.07	0.096	3.02	0.085	2.97	0.076	2.90	0.070	2.85	0.066	2.82	0.075	2.76	0.122
15.1	3.30	0.156	3.23	0.146	3.14	0.128	3.05	0.110	2.98	0.097	2.90	0.088	2.86	0.093	2.79	0.134
20.5	3.51	0.192	3.43	0.191	3.30	0.178	3.16	0.155	3.07	0.134	2.97	0.117	2.91	0.114	2.82	0.052
26.6	3.77	0.184	3.68	0.200	3.54	0.214	3.36	0.208	3.23	0.190	3.08	0.172	2.99	0.171	2.86	0.218
32.3	3.91	0.151	3.84	0.164	3.73	0.203	3.55	0.229	3.39	0.232	3.21	0.216	3.08	0.211	2.92	0.249
37.4	4.00	0.102	3.95	0.121	3.87	0.164	3.72	0.212	3.56	0.248	3.35	0.257	3.19	0.259	3.00	0.288
44.1	4.05	0.072	4.02	0.080	3.97	0.108	3.88	0.160	3.76	0.221	3.55	0.278	3.36	0.307	3.11	0.333
50.9	4.06	0.057	4.03	0.059	4.00	0.074	3.94	0.107	3.87	0.164	3.71	0.245	3.54	0.319	3.25	0.389
56.8	4.07	0.063	4.04	0.055	4.01	0.060	3.97	0.080	3.92	0.120	3.81	0.200	3.67	0.299	3.39	0.409
62.9	4.09	0.106	4.06	0.086	4.02	0.066	3.98	0.066	3.94	0.090	3.87	0.152	3.77	0.256	3.52	0.405
68.6	4.23	0.239	4.15	0.186	4.06	0.124	3.99	0.088	3.95	0.084	3.89	0.122	3.82	0.211	3.62	0.372
74.5	4.44	0.395	4.30	0.313	4.14	0.217	4.01	0.138	3.95	0.095	3.89	0.108	3.84	0.172	3.69	0.327

TABLE 9

98.0% SARAN - 1.0% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-11.9	3.22	0.039	3.20	0.038	3.18	0.039	3.15	0.033	3.12	0.032	3.10	0.033	3.09	0.051	3.05	0.107
- 5.7	3.31	0.068	3.28	0.063	3.24	0.058	3.19	0.049	3.16	0.046	3.13	0.044	3.11	0.060	3.07	0.114
1.7	3.50	0.135	3.45	0.126	3.37	0.107	3.29	0.089	3.24	0.075	3.19	0.067	3.15	0.080	3.09	0.129
7.3	3.77	0.215	3.68	0.203	3.55	0.174	3.42	0.144	3.34	0.117	3.25	0.101	3.20	0.104	3.13	0.146
11.4	4.01	0.271	3.89	0.259	3.73	0.232	3.55	0.193	3.44	0.157	3.32	0.132	3.25	0.127	3.16	0.164
16.2	4.35	0.300	4.22	0.310	4.01	0.303	3.77	0.263	3.60	0.225	3.43	0.185	3.33	0.170	3.21	0.198
20.6	4.61	0.286	4.48	0.312	4.26	0.331	3.98	0.341	3.78	0.285	3.56	0.242	3.42	0.219	3.26	0.236
27.0	4.91	0.221	4.81	0.258	4.63	0.322	4.34	0.364	4.09	0.366	3.79	0.335	3.59	0.314	3.35	0.323
32.0	5.02	0.163	4.95	0.197	4.82	0.266	4.57	0.340	4.32	0.381	3.99	0.390	3.75	0.377	3.46	0.382
36.6	5.08	0.126	5.03	0.146	4.93	0.202	4.75	0.282	4.54	0.362	4.22	0.414	3.94	0.428	3.59	0.449
42.0	5.11	0.091	5.07	0.106	5.01	0.143	4.88	0.211	4.73	0.301	4.45	0.399	4.17	0.468	3.76	0.519
47.2	5.12	0.080	5.08	0.084	5.04	0.104	4.95	0.155	4.85	0.230	4.63	0.344	4.38	0.464	3.95	0.566
52.9	5.11	0.072	5.09	0.073	5.04	0.085	4.98	0.115	4.91	0.168	4.76	0.273	4.57	0.419	4.16	0.583
58.1	5.10	0.073	5.08	0.069	5.04	0.074	4.98	0.091	4.93	0.129	4.82	0.219	4.68	0.362	4.32	0.566
63.1	5.09	0.075	5.06	0.067	5.02	0.067	4.97	0.075	4.93	0.102	4.85	0.169	4.75	0.297	4.46	0.519
69.9	5.08	0.087	5.05	0.073	5.01	0.064	4.96	0.064	4.93	0.079	4.87	0.128	4.80	0.231	4.59	0.440

TABLE 10

94.6% SARAN - 4.4% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
-14.2	3.07	0.035	3.06	0.031	3.04	0.030	3.01	0.028	2.99	0.028	2.97	0.034	2.95	0.059	2.91	0.132
- 5.9	3.22	0.087	3.18	0.077	3.14	0.065	3.08	0.055	3.05	0.050	3.01	0.051	2.99	0.071	2.93	0.137
2.4	3.52	0.186	3.45	0.172	3.34	0.142	3.23	0.117	3.17	0.096	3.10	0.088	3.05	0.098	2.97	0.155
7.1	3.81	0.250	3.70	0.241	3.55	0.212	3.35	0.178	3.28	0.146	3.18	0.125	3.11	0.124	3.02	0.168
12.6	4.14	0.280	4.01	0.287	3.82	0.278	3.59	0.247	3.44	0.212	3.28	0.178	3.19	0.165	3.06	0.200
17.1	4.40	0.263	4.28	0.287	4.08	0.309	3.81	0.304	3.61	0.275	3.40	0.233	3.27	0.212	3.12	0.237
22.7	4.63	0.209	4.53	0.243	4.36	0.296	4.09	0.333	3.86	0.332	3.58	0.304	3.40	0.279	3.19	0.289
27.6	4.76	0.152	4.69	0.186	4.56	0.250	4.33	0.316	4.11	0.357	3.79	0.361	3.57	0.344	3.30	0.348
32.9	4.85	0.116	4.80	0.141	4.71	0.193	4.53	0.273	4.33	0.341	4.02	0.386	3.76	0.395	3.44	0.402
37.8	4.91	0.085	4.86	0.102	4.79	0.141	4.66	0.212	4.51	0.295	4.24	0.381	3.97	0.438	3.59	0.479
43.1	4.91	0.066	4.88	0.076	4.84	0.102	4.75	0.157	4.64	0.233	4.43	0.339	4.18	0.441	3.77	0.527
48.3	4.92	0.057	4.89	0.061	4.86	0.076	4.79	0.116	4.72	0.177	4.56	0.280	4.36	0.408	3.96	0.542
54.1	4.91	0.054	4.89	0.051	4.86	0.060	4.81	0.086	4.76	0.129	4.65	0.216	4.51	0.350	4.16	0.536
60.7	4.91	0.056	4.89	0.050	4.86	0.052	4.82	0.066	4.78	0.094	4.70	0.163	4.61	0.280	4.33	0.483
65.3	4.91	0.062	4.88	0.053	4.86	0.048	4.82	0.057	4.78	0.078	4.72	0.133	4.65	0.237	4.43	0.440
71.1	4.91	0.078	4.88	0.062	4.85	0.050	4.81	0.052	4.79	0.065	4.74	0.107	4.68	0.195	4.51	0.390

TABLE 11

91.1% SARAN - 7.9% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t \ f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-12.8	3.08	0.038	3.06	0.034	3.04	0.033	3.01	0.031	2.99	0.032	2.96	0.040	2.95	0.071	2.88	0.155
- 4.4	3.22	0.080	3.18	0.073	3.13	0.064	3.08	0.055	3.05	0.053	3.01	0.056	2.98	0.085	2.90	0.164
2.7	3.44	0.153	3.38	0.140	3.29	0.119	3.20	0.104	3.13	0.088	3.07	0.084	3.03	0.104	2.93	0.174
7.0	3.65	0.202	3.56	0.192	3.44	0.167	3.31	0.146	3.22	0.122	3.13	0.111	3.07	0.122	2.97	0.189
12.0	3.92	0.248	3.81	0.246	3.65	0.227	3.47	0.204	3.34	0.172	3.21	0.153	3.13	0.154	3.00	0.211
16.6	4.21	0.253	4.09	0.271	3.90	0.277	3.67	0.262	3.50	0.233	3.32	0.203	3.21	0.196	3.05	0.241
22.0	4.44	0.225	4.34	0.253	4.16	0.289	3.90	0.304	3.70	0.289	3.47	0.259	3.32	0.250	3.12	0.282
28.1	4.64	0.173	4.57	0.200	4.43	0.252	4.20	0.308	3.98	0.338	3.69	0.344	3.48	0.347	3.19	0.392
33.4	4.72	0.124	4.67	0.147	4.57	0.199	4.39	0.273	4.19	0.332	3.89	0.375	3.64	0.394	3.31	0.445
38.3	4.78	0.097	4.74	0.110	4.66	0.152	4.52	0.222	4.37	0.301	4.09	0.379	3.83	0.436	3.43	0.501
43.8	4.80	0.074	4.77	0.082	4.72	0.105	4.63	0.164	4.51	0.242	4.29	0.348	4.04	0.454	3.61	0.554
50.4	4.80	0.063	4.78	0.064	4.74	0.075	4.67	0.115	4.60	0.174	4.45	0.282	4.25	0.424	3.82	0.591
54.9	4.80	0.061	4.77	0.057	4.74	0.064	4.68	0.093	4.63	0.138	4.51	0.235	4.36	0.384	3.95	0.594
60.9	4.79	0.064	4.76	0.056	4.73	0.055	4.68	0.074	4.64	0.104	4.56	0.183	4.45	0.324	4.11	0.549
66.2	4.78	0.071	4.75	0.059	4.72	0.051	4.68	0.063	4.63	0.086	4.58	0.148	4.50	0.273	4.21	0.505
71.0	4.76	0.080	4.74	0.063	4.71	0.053	4.66	0.057	4.63	0.075	4.58	0.125	4.51	0.236	4.28	0.461

TABLE 12

86.7% SARAN - 12.4% HEXACHLOROBENZENE - 0.9% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
- 5.7	3.16	0.053	3.14	0.048	3.11	0.043	3.08	0.036	3.06	0.036	3.03	0.039	3.01	0.057	2.97	0.106
1.4	3.34	0.118	3.29	0.107	3.23	0.089	3.16	0.070	3.12	0.062	3.08	0.060	3.04	0.073	2.99	0.115
6.8	3.58	0.194	3.50	0.178	3.39	0.151	3.28	0.120	3.21	0.101	3.14	0.089	3.09	0.095	3.02	0.132
11.5	3.83	0.248	3.73	0.236	3.58	0.210	3.41	0.174	3.31	0.143	3.21	0.123	3.14	0.119	3.05	0.150
16.7	4.15	0.265	4.03	0.277	3.84	0.276	3.62	0.245	3.47	0.208	3.31	0.176	3.21	0.158	3.11	0.177
21.8	4.41	0.229	4.31	0.260	4.12	0.296	3.86	0.299	3.67	0.276	3.45	0.235	3.31	0.207	3.17	0.210
27.8	4.60	0.158	4.52	0.192	4.39	0.253	4.15	0.311	3.93	0.328	3.65	0.306	3.46	0.276	3.26	0.262
33.1	4.68	0.113	4.63	0.139	4.54	0.196	4.35	0.272	4.15	0.328	3.86	0.350	3.63	0.340	3.36	0.327
37.8	4.73	0.084	4.69	0.102	4.62	0.146	4.49	0.216	4.33	0.293	4.06	0.359	3.78	0.384	3.49	0.381
43.3	4.76	0.065	4.72	0.075	4.68	0.104	4.59	0.160	4.48	0.237	4.26	0.335	4.01	0.402	3.65	0.439
48.9	4.77	0.056	4.74	0.059	4.71	0.076	4.64	0.114	4.57	0.177	4.41	0.279	4.20	0.385	3.83	0.478
54.0	4.77	0.054	4.75	0.053	4.72	0.061	4.67	0.087	4.62	0.133	4.50	0.226	4.34	0.345	4.01	0.478
59.8	4.77	0.058	4.75	0.052	4.72	0.052	4.68	0.066	4.65	0.098	4.56	0.171	4.45	0.285	4.18	0.454
64.8	4.77	0.070	4.75	0.056	4.72	0.052	4.69	0.057	4.65	0.079	4.59	0.136	4.51	0.234	4.29	0.405
71.7	4.78	0.093	4.75	0.068	4.72	0.054	4.68	0.050	4.66	0.063	4.61	0.103	4.55	0.180	4.39	0.337

TABLE 13

79.2% SARAN - 19.8% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t/f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"
-11.1	3.11	0.035	3.09	0.033	3.07	0.033	3.04	0.029	3.02	0.031	3.00	0.037	2.99	0.067	2.93	0.163
- 4.9	3.21	0.071	3.18	0.065	3.14	0.058	3.10	0.050	3.07	0.045	3.04	0.048	3.02	0.075	2.96	0.162
0.1	3.33	0.111	3.29	0.102	3.23	0.087	3.16	0.074	3.12	0.065	3.07	0.065	3.04	0.092	2.97	0.185
5.3	3.54	0.173	3.47	0.161	3.37	0.138	3.26	0.116	3.19	0.098	3.13	0.092	3.08	0.113	2.99	0.201
9.5	3.74	0.217	3.64	0.208	3.52	0.186	3.37	0.160	3.28	0.133	3.18	0.118	3.12	0.133	3.01	0.214
14.9	4.03	0.241	3.92	0.248	3.75	0.243	3.55	0.218	3.41	0.190	3.28	0.165	3.19	0.169	3.06	0.234
20.1	4.26	0.217	4.16	0.240	4.00	0.268	3.76	0.269	3.59	0.249	3.40	0.218	3.28	0.213	3.11	0.270
25.1	4.42	0.175	4.34	0.206	4.20	0.254	3.97	0.287	3.77	0.291	3.54	0.273	3.38	0.267	3.18	0.319
28.1	4.49	0.150	4.42	0.176	4.30	0.225	4.09	0.277	3.90	0.298	3.64	0.295	3.46	0.296	3.23	0.339
32.6	4.55	0.110	4.50	0.133	4.41	0.181	4.24	0.246	4.06	0.297	3.80	0.325	3.59	0.340	3.31	0.390
36.9	4.59	0.084	4.55	0.101	4.49	0.138	4.36	0.202	4.21	0.271	3.96	0.333	3.74	0.375	3.42	0.440
41.6	4.61	0.068	4.60	0.078	4.54	0.104	4.44	0.160	4.33	0.228	4.11	0.315	3.90	0.393	3.54	0.476
47.4	4.62	0.053	4.59	0.058	4.56	0.074	4.49	0.113	4.42	0.170	4.27	0.262	4.08	0.376	3.72	0.506
52.5	4.63	0.051	4.61	0.051	4.58	0.060	4.53	0.088	4.47	0.132	4.36	0.218	4.21	0.347	3.87	0.528
57.3	4.63	0.052	4.62	0.049	4.59	0.052	4.54	0.072	4.50	0.104	4.41	0.181	4.30	0.312	3.99	0.522
63.1	4.63	0.057	4.61	0.050	4.59	0.047	4.55	0.059	4.52	0.081	4.45	0.139	4.38	0.257	4.13	0.477
68.1	4.63	0.064	4.61	0.054	4.58	0.048	4.54	0.053	4.51	0.069	4.46	0.116	4.40	0.218	4.20	0.435

TABLE 14

74.3% SARAN - 24.7% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"
- 8.0	3.19	0.038	3.18	0.036	3.15	0.033	3.13	0.029	3.11	0.030	3.09	0.043	3.07	0.081	2.99	0.179
0.4	3.38	0.101	3.34	0.090	3.28	0.076	3.22	0.064	3.18	0.059	3.14	0.062	3.11	0.096	3.02	0.188
6.8	3.62	0.170	3.54	0.157	3.45	0.134	3.34	0.114	3.27	0.095	3.21	0.092	3.16	0.116	3.06	0.201
11.2	3.83	0.206	3.73	0.202	3.61	0.182	3.46	0.156	3.36	0.131	3.27	0.120	3.21	0.138	3.09	0.221
15.7	4.05	0.218	3.95	0.228	3.80	0.224	3.61	0.205	3.48	0.175	3.36	0.158	3.27	0.170	3.13	0.246
20.4	4.28	0.195	4.18	0.222	4.02	0.243	3.81	0.246	3.65	0.227	3.47	0.207	3.35	0.208	3.18	0.275
25.5	4.42	0.157	4.35	0.186	4.22	0.230	4.00	0.261	3.82	0.266	3.61	0.254	3.46	0.255	3.26	0.312
29.7	4.50	0.123	4.45	0.150	4.34	0.199	4.15	0.253	3.97	0.280	3.74	0.285	3.56	0.293	3.32	0.341
33.3	4.56	0.104	4.51	0.122	4.42	0.164	4.26	0.229	4.10	0.281	3.84	0.323	3.64	0.360	3.32	0.443
38.2	4.60	0.078	4.56	0.091	4.50	0.121	4.38	0.184	4.25	0.249	4.02	0.328	3.80	0.393	3.45	0.488
43.2	4.61	0.061	4.59	0.067	4.55	0.088	4.46	0.140	4.36	0.204	4.17	0.302	3.96	0.406	3.58	0.529
48.2	4.62	0.053	4.60	0.056	4.56	0.068	4.50	0.108	4.42	0.162	4.28	0.261	4.12	0.393	3.70	0.555
52.6	4.62	0.050	4.60	0.048	4.57	0.055	4.51	0.086	4.46	0.128	4.35	0.222	4.20	0.363	3.83	0.567
57.9	4.61	0.053	4.59	0.047	4.57	0.047	4.52	0.069	4.48	0.098	4.40	0.177	4.29	0.313	3.97	0.543
62.5	4.61	0.059	4.59	0.049	4.56	0.045	4.52	0.058	4.48	0.080	4.42	0.144	4.34	0.269	4.07	0.505
69.1	4.61	0.078	4.59	0.060	4.56	0.047	4.52	0.053	4.49	0.066	4.44	0.114	4.38	0.219	4.17	0.450

TABLE 15

49.5% SARAN - 49.5% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"
-12.9	3.14	0.020	3.13	0.018	3.12	0.018	3.11	0.015	3.09	0.016	3.09	0.022	3.08	0.047	3.04	0.118
- 4.7	3.21	0.042	3.20	0.038	3.17	0.034	3.15	0.028	3.13	0.027	3.11	0.032	3.09	0.053	3.06	0.121
0.6	3.31	0.075	3.28	0.067	3.24	0.057	3.19	0.047	3.16	0.042	3.14	0.043	3.11	0.062	3.07	0.126
6.0	3.46	0.114	3.41	0.108	3.35	0.094	3.27	0.078	3.23	0.066	3.18	0.062	3.15	0.077	3.09	0.136
9.7	3.63	0.141	3.56	0.140	3.47	0.129	3.37	0.113	3.30	0.096	3.23	0.086	3.19	0.095	3.12	0.149
16.0	3.78	0.142	3.72	0.149	3.62	0.152	3.49	0.143	3.39	0.127	3.30	0.117	3.23	0.118	3.15	0.168
21.5	3.93	0.120	3.88	0.136	3.78	0.158	3.63	0.169	3.53	0.162	3.39	0.153	3.30	0.152	3.20	0.193
26.5	4.02	0.091	3.97	0.111	3.89	0.141	3.76	0.170	3.64	0.180	3.49	0.182	3.38	0.184	3.24	0.224
31.8	4.07	0.075	4.04	0.087	3.98	0.116	3.87	0.154	3.76	0.184	3.60	0.211	3.47	0.233	3.28	0.297
36.8	4.10	0.057	4.08	0.064	4.04	0.087	3.96	0.123	3.87	0.164	3.72	0.212	3.58	0.253	3.37	0.320
41.8	4.12	0.047	4.10	0.050	4.07	0.066	4.01	0.095	3.95	0.135	3.82	0.198	3.69	0.259	3.46	0.341
47.2	4.12	0.040	4.10	0.040	4.08	0.048	4.04	0.068	3.99	0.101	3.90	0.166	3.79	0.246	3.56	0.357
52.5	4.12	0.042	4.10	0.038	4.08	0.040	4.05	0.053	4.02	0.079	3.95	0.133	3.86	0.215	3.66	0.343
58.7	4.11	0.049	4.09	0.039	4.08	0.037	4.05	0.042	4.03	0.059	3.98	0.102	3.92	0.178	3.75	0.320
66.4	4.12	0.070	4.10	0.053	4.08	0.041	4.05	0.038	4.03	0.046	4.00	0.075	3.96	0.136	3.84	0.272

TABLE 16

24.8% SARAN - 74.2% HEXACHLOROBENZENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"	ε'	ε"
- 4.4	3.30	0.018	3.29	0.019	3.28	0.019	3.27	0.012	3.26	0.013	3.25	0.022	3.24	0.052	3.21	0.130
1.7	3.35	0.041	3.33	0.037	3.31	0.031	3.29	0.022	3.27	0.022	3.26	0.028	3.25	0.055	3.21	0.135
7.9	3.45	0.061	3.42	0.057	3.38	0.051	3.35	0.039	3.32	0.035	3.28	0.040	3.28	0.066	3.24	0.145
13.0	3.55	0.074	3.51	0.075	3.46	0.069	3.40	0.060	3.37	0.053	3.33	0.056	3.31	0.077	3.25	0.152
17.7	3.62	0.077	3.58	0.083	3.52	0.083	3.46	0.075	3.41	0.068	3.36	0.069	3.33	0.087	3.27	0.161
22.8	3.70	0.066	3.66	0.076	3.61	0.087	3.53	0.090	3.47	0.085	3.41	0.086	3.36	0.103	3.28	0.170
28.9	3.75	0.048	3.73	0.055	3.69	0.072	3.62	0.094	3.55	0.105	3.46	0.115	3.40	0.138	3.29	0.226
34.1	3.78	0.037	3.77	0.042	3.74	0.057	3.68	0.081	3.62	0.103	3.53	0.125	3.45	0.153	3.33	0.237
39.2	3.80	0.030	3.79	0.032	3.77	0.044	3.72	0.065	3.68	0.091	3.59	0.126	3.51	0.165	3.37	0.253
45.1	3.81	0.027	3.80	0.026	3.79	0.031	3.76	0.047	3.72	0.070	3.66	0.114	3.59	0.170	3.43	0.269
51.5	3.82	0.029	3.80	0.025	3.79	0.025	3.77	0.034	3.75	0.053	3.71	0.093	3.64	0.158	3.49	0.277
56.9	3.83	0.036	3.81	0.028	3.79	0.024	3.78	0.027	3.76	0.040	3.73	0.076	3.69	0.142	3.55	0.269
62.1	3.83	0.044	3.81	0.034	3.80	0.026	3.78	0.024	3.77	0.033	3.74	0.064	3.71	0.123	3.59	0.249
67.3	3.85	0.059	3.83	0.045	3.80	0.033	3.78	0.027	3.77	0.030	3.75	0.053	3.72	0.106	3.62	0.224
73.0	3.89	0.083	3.85	0.066	3.82	0.048	3.79	0.036	3.77	0.032	3.75	0.047	3.73	0.092	3.65	0.202

TABLE 17

95.9% SARAN - 3.1% α-CHLORONAPHTHALENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
- 9.7	3.14	0.058	3.12	0.053	3.09	0.047	3.05	0.039	3.03	0.045	3.00	0.069	2.95	0.129	2.80	0.178
- 3.3	3.31	0.118	3.26	0.104	3.20	0.086	3.14	0.070	3.10	0.070	3.05	0.090	2.99	0.144	2.82	0.186
1.7	3.52	0.196	3.45	0.177	3.34	0.144	3.24	0.114	3.18	0.103	3.11	0.114	3.03	0.158	2.85	0.199
6.3	3.80	0.267	3.69	0.252	3.54	0.212	3.38	0.172	3.28	0.148	3.17	0.145	3.08	0.180	2.90	0.220
11.4	4.14	0.304	4.00	0.303	3.80	0.288	3.58	0.246	3.43	0.209	3.28	0.190	3.17	0.204	2.97	0.249
16.6	4.43	0.282	4.30	0.303	4.09	0.324	3.82	0.309	3.62	0.281	3.41	0.253	3.26	0.256	3.03	0.289
21.0	4.65	0.230	4.55	0.265	4.36	0.314	4.08	0.342	3.85	0.341	3.57	0.317	3.38	0.319	3.10	0.330
26.9	4.82	0.179	4.74	0.208	4.60	0.266	4.36	0.331	4.13	0.369	3.80	0.380	3.57	0.380	3.24	0.393
32.4	4.90	0.142	4.84	0.159	4.74	0.209	4.55	0.280	4.35	0.357	4.03	0.412	3.75	0.441	3.37	0.448
37.2	4.95	0.111	4.90	0.121	4.83	0.157	4.69	0.219	4.54	0.305	4.26	0.404	3.97	0.472	3.54	0.508
42.7	4.98	0.097	4.94	0.098	4.88	0.119	4.79	0.160	4.68	0.235	4.46	0.355	4.21	0.472	3.75	0.560
47.8	4.99	0.087	4.95	0.088	4.90	0.097	4.83	0.126	4.75	0.185	4.59	0.294	4.38	0.439	3.93	0.585
53.5	4.98	0.088	4.94	0.081	4.90	0.081	4.85	0.096	4.79	0.136	4.68	0.233	4.52	0.379	4.13	0.571
58.8	4.97	0.094	4.93	0.081	4.89	0.073	4.84	0.076	4.80	0.105	4.72	0.179	4.60	0.313	4.29	0.528
65.8	4.95	0.110	4.92	0.089	4.87	0.073	4.83	0.065	4.79	0.080	4.73	0.135	4.66	0.241	4.42	0.440

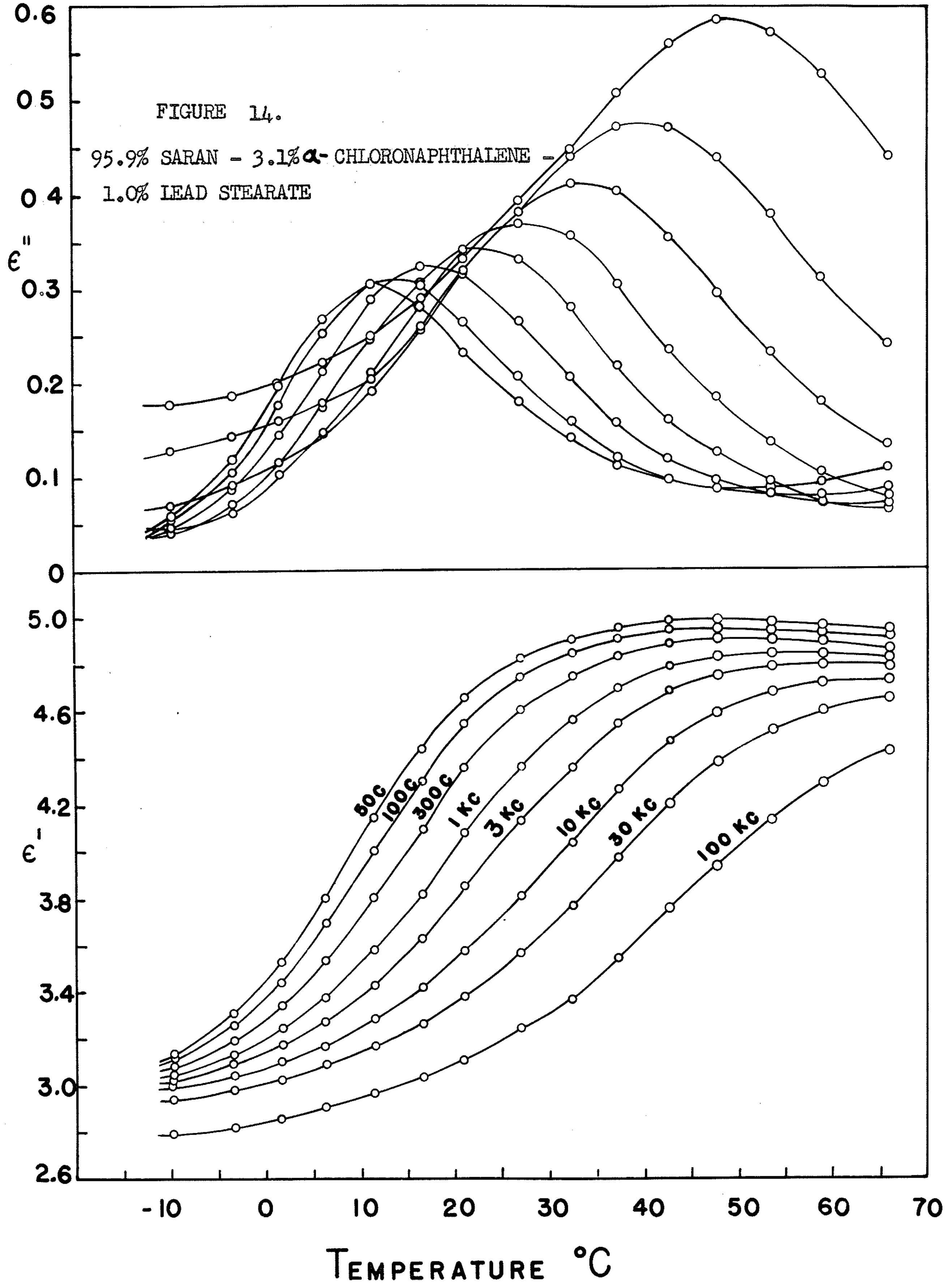


FIGURE 14.

95.9% SARAN - 3.1% α- CHLORONAPHTHALENE - 1.0% LEAD STEARATE

TABLE 18

93.0% SARAN - 6.0% α-CHLORONAPHTHALENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-14.8	3.34	0.068	3.31	0.059	3.28	0.055	3.23	0.047	3.20	0.045	3.17	0.045	3.15	0.067	3.10	0.141
- 7.7	3.52	0.137	3.46	0.121	3.39	0.098	3.32	0.080	3.26	0.070	3.22	0.064	3.18	0.082	3.12	0.149
- 3.1	3.74	0.214	3.66	0.196	3.54	0.162	3.42	0.130	3.35	0.108	3.27	0.093	3.22	0.106	3.14	0.172
1.6	4.06	0.292	3.94	0.276	3.76	0.239	3.58	0.196	3.46	0.157	3.35	0.132	3.28	0.133	3.18	0.197
6.7	4.42	0.320	4.28	0.326	4.06	0.317	3.80	0.275	3.63	0.229	3.46	0.190	3.37	0.176	3.23	0.223
11.3	4.71	0.290	4.57	0.320	4.35	0.351	4.05	0.337	3.83	0.303	3.60	0.252	3.46	0.225	3.29	0.257
16.6	4.95	0.220	4.85	0.261	4.67	0.324	4.37	0.365	4.12	0.373	3.81	0.337	3.62	0.305	3.39	0.320
22.0	5.08	0.164	5.00	0.198	4.87	0.266	4.62	0.340	4.38	0.390	4.03	0.393	3.78	0.375	3.49	0.376
26.6	5.15	0.126	5.09	0.152	4.99	0.205	4.80	0.289	4.59	0.370	4.26	0.419	3.97	0.432	3.61	0.438
31.8	5.20	0.104	5.15	0.121	5.08	0.161	4.94	0.229	4.78	0.314	4.48	0.402	4.20	0.464	3.80	0.504
36.5	5.23	0.085	5.19	0.095	5.13	0.123	5.03	0.176	4.91	0.254	4.67	0.365	4.41	0.472	3.97	0.560
41.4	5.24	0.082	5.21	0.082	5.16	0.100	5.08	0.137	4.99	0.201	4.81	0.308	4.59	0.445	4.17	0.589
47.5	5.24	0.080	5.21	0.073	5.17	0.078	5.11	0.100	5.05	0.143	4.94	0.236	4.78	0.381	4.40	0.586
52.8	5.24	0.092	5.21	0.074	5.17	0.069	5.12	0.081	5.08	0.112	4.99	0.186	4.88	0.320	4.56	0.543
57.8	5.24	0.109	5.20	0.082	5.17	0.066	5.12	0.068	5.09	0.090	5.01	0.149	4.93	0.267	4.68	0.489
63.1	5.23	0.135	5.20	0.097	5.16	0.069	5.11	0.062	5.08	0.075	5.03	0.123	4.96	0.223	4.76	0.435

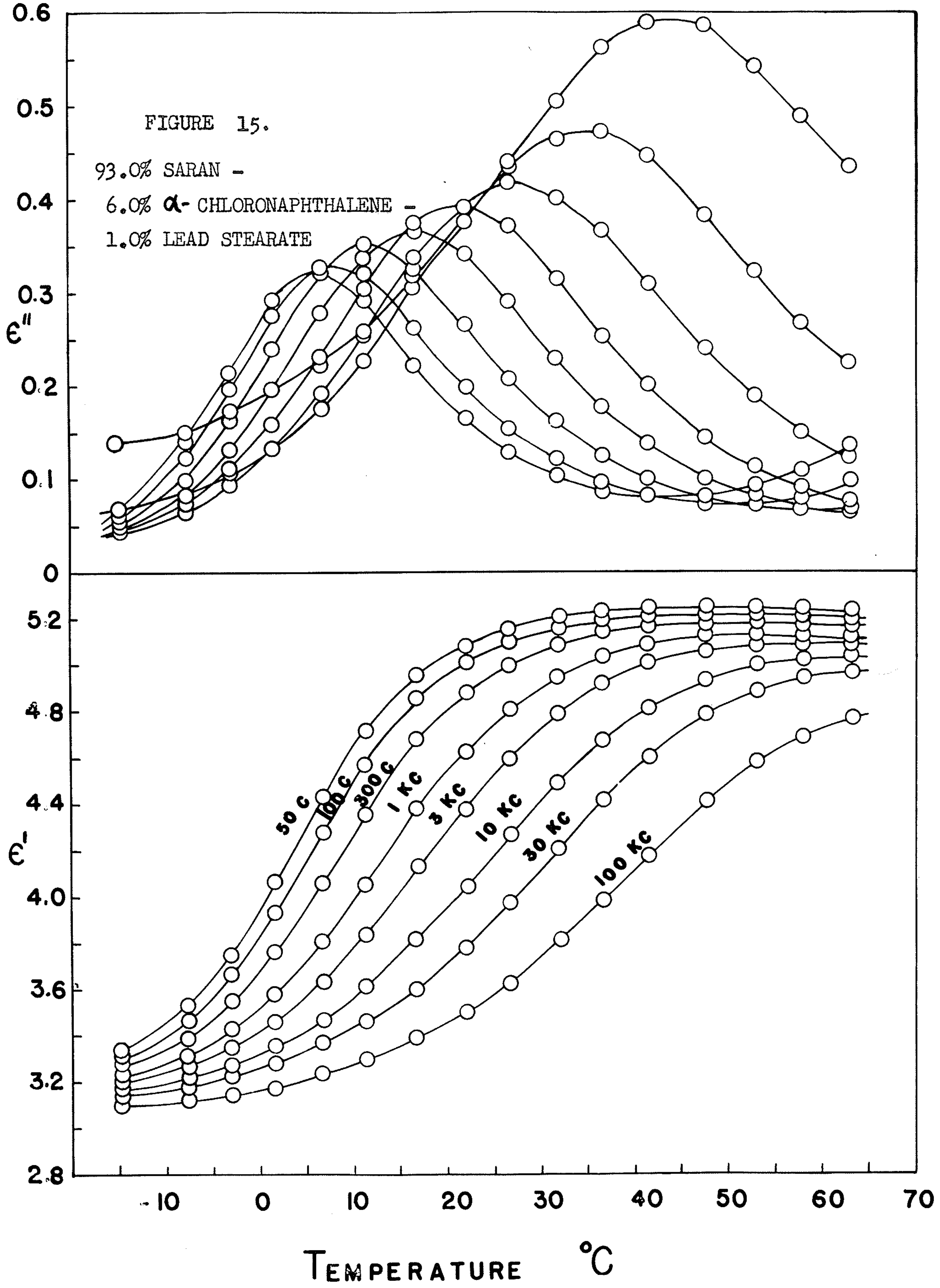


FIGURE 15.
93.0% SARAN -
6.0% α- CHLORONAPHTHALENE -
1.0% LEAD STEARATE
0.6
0.5
0.4
0.3
0.2
0.1
0
ε''
5.2
4.8
4.4
4.0
3.6
3.2
2.8
ε'
50 C
100 C
300 C
1 KC
3 KC
10 KC
30 KC
100 KC
-10
0
10
20
30
40
50
60
70
TEMPERATURE °C

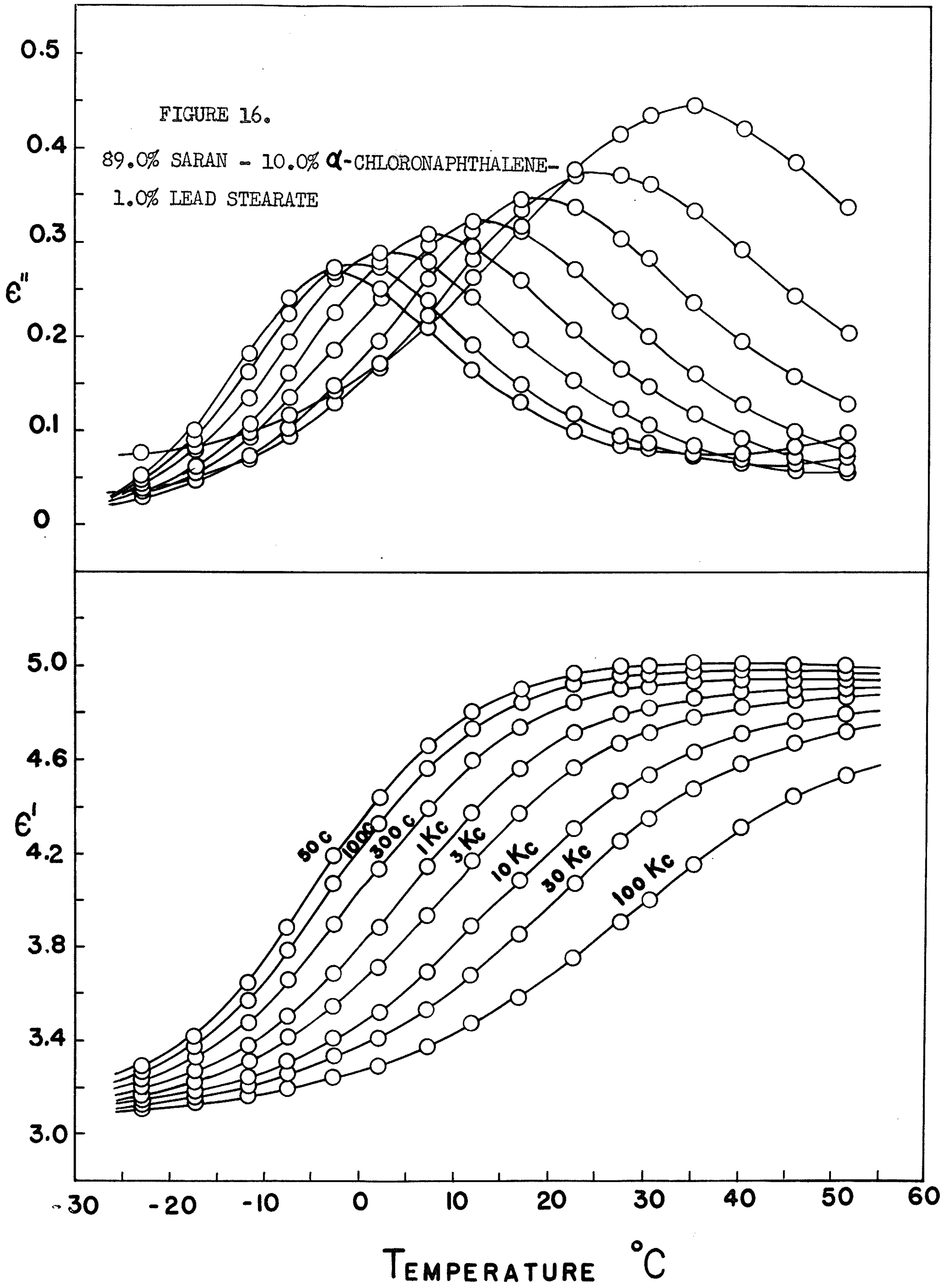


FIGURE 16.

89.0% SARAN - 10.0% α-CHLORONAPHTHALENE- 1.0% LEAD STEARATE

TABLE 20

84.0% SARAN - 15.0% α- CHLORONAPHTHALENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-30.4	3.41	0.073	3.37	0.076	3.32	0.066	3.28	0.053	3.24	0.048	3.22	0.047	3.19	0.073	3.13	0.153
-22.7	3.70	0.182	3.63	0.165	3.53	0.139	3.43	0.111	3.36	0.092	3.30	0.080	3.26	0.096	3.19	0.163
-17.2	4.01	0.251	3.90	0.235	3.75	0.209	3.59	0.171	3.51	0.141	3.39	0.117	3.32	0.122	3.23	0.180
-12.5	4.29	0.280	4.16	0.278	3.98	0.269	3.77	0.231	3.63	0.195	3.49	0.163	3.40	0.157	3.29	0.204
- 8.4	4.54	0.273	4.42	0.285	4.22	0.298	3.97	0.278	3.79	0.250	3.60	0.217	3.48	0.199	3.34	0.235
- 4.0	4.76	0.235	4.66	0.260	4.48	0.302	4.22	0.312	4.01	0.304	3.77	0.272	3.61	0.256	3.42	0.278
0.6	4.93	0.191	4.85	0.218	4.70	0.267	4.46	0.310	4.24	0.331	3.96	0.326	3.75	0.315	3.51	0.332
6.2	5.06	0.151	4.99	0.173	4.88	0.219	4.68	0.276	4.49	0.329	4.20	0.362	3.96	0.377	3.66	0.405
11.0	5.12	0.119	5.07	0.136	4.98	0.174	4.83	0.228	4.67	0.297	4.40	0.364	4.15	0.413	3.80	0.459
16.5	5.17	0.099	5.13	0.110	5.06	0.137	4.94	0.184	4.82	0.247	4.60	0.335	4.36	0.425	3.98	0.515
21.9	5.19	0.089	5.16	0.092	5.10	0.111	5.01	0.147	4.91	0.202	4.74	0.292	4.53	0.404	4.15	0.545
25.2	5.21	0.091	5.17	0.093	5.12	0.104	5.03	0.135	4.95	0.184	4.79	0.264	4.62	0.386	4.25	0.562
30.1	5.21	0.096	5.18	0.087	5.14	0.088	5.07	0.111	5.00	0.151	4.87	0.230	4.73	0.355	4.39	0.560
34.6	5.21	0.105	5.18	0.086	5.14	0.079	5.08	0.094	5.02	0.126	4.92	0.196	4.80	0.319	4.51	0.542
39.8	5.20	0.127	5.17	0.093	5.13	0.074	5.09	0.078	5.04	0.105	4.96	0.164	4.86	0.278	4.61	0.510
45.2	5.21	0.162	5.16	0.114	5.12	0.075	5.08	0.068	5.04	0.085	4.98	0.137	4.91	0.244	4.69	0.473
49.6	5.21	0.208	5.16	0.140	5.11	0.083	5.07	0.065	5.04	0.075	4.99	0.120	4.92	0.218	4.73	0.441

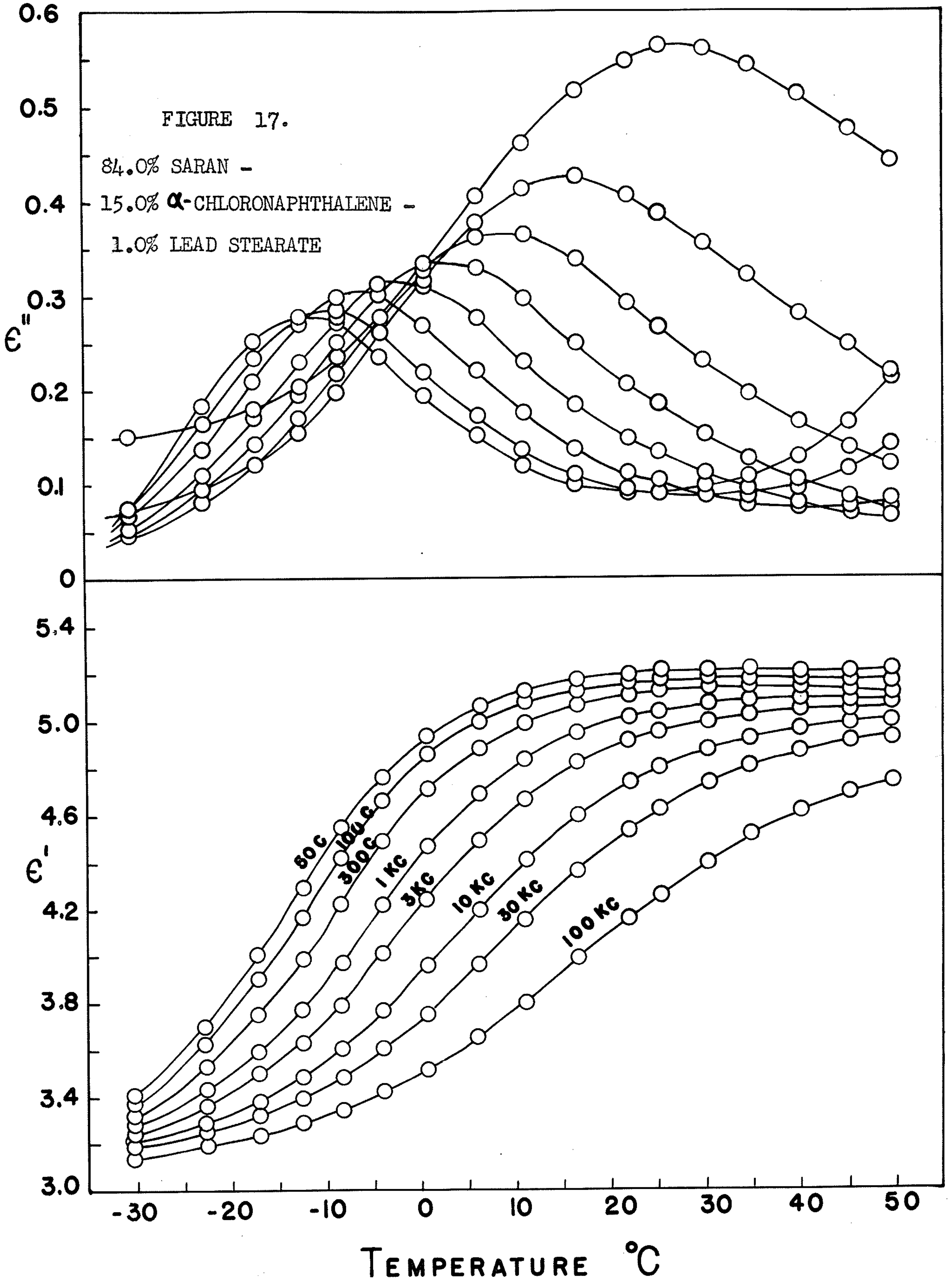


FIGURE 17.

84.0% SARAN –
15.0% α-CHLORONAPHTHALENE –
1.0% LEAD STEARATE

TABLE 21

73.9% SARAN - 25.1% α-CHLORONAPHTHALENE - 1.0% LEAD STEARATE

t\f	50c.		100c.		300c.		1kc.		3kc.		10kc.		30kc.		100kc.	
°C	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
-41.4	3.63	0.095	3.59	0.092	3.53	0.082	3.47	0.067	3.42	0.059	3.39	0.060	3.35	0.092	3.27	0.185
-35.6	3.86	0.161	3.79	0.150	3.70	0.133	3.59	0.111	3.53	0.094	3.46	0.088	3.41	0.115	3.32	0.207
-30.3	4.15	0.202	4.06	0.200	3.93	0.189	3.77	0.166	3.67	0.143	3.58	0.128	3.50	0.142	3.39	0.227
-24.8	4.45	0.205	4.35	0.216	4.21	0.224	4.01	0.219	3.87	0.200	3.72	0.182	3.61	0.185	3.46	0.250
-20.2	4.64	0.193	4.55	0.209	4.41	0.229	4.21	0.243	4.05	0.238	3.86	0.223	3.72	0.228	3.55	0.283
-15.3	4.83	0.181	4.75	0.193	4.62	0.218	4.43	0.245	4.26	0.265	4.04	0.269	3.87	0.280	3.64	0.333
-10.4	4.96	0.166	4.89	0.177	4.78	0.199	4.60	0.233	4.44	0.265	4.21	0.291	4.02	0.321	3.79	0.376
- 5.6	5.08	0.156	5.02	0.162	4.91	0.178	4.76	0.212	4.61	0.251	4.40	0.298	4.20	0.353	3.89	0.433
- 1.2	5.15	0.153	5.09	0.153	5.00	0.164	4.86	0.193	4.73	0.231	4.53	0.291	4.34	0.363	4.01	0.467
3.6	5.22	0.153	5.16	0.144	5.07	0.149	4.95	0.174	4.84	0.209	4.66	0.272	4.47	0.358	4.15	0.486
8.8	5.27	0.171	5.22	0.149	5.14	0.138	5.03	0.156	4.93	0.187	4.77	0.246	4.61	0.338	4.31	0.493
14.4	5.32	0.193	5.26	0.159	5.18	0.133	5.08	0.140	5.00	0.166	4.86	0.222	4.72	0.318	4.44	0.491
19.9	5.37	0.242	5.29	0.186	5.21	0.136	5.12	0.127	5.05	0.147	4.93	0.197	4.81	0.291	4.56	0.476
25.5	5.42	0.324	5.33	0.233	5.24	0.154	5.14	0.123	5.07	0.132	4.97	0.176	4.87	0.265	4.64	0.462

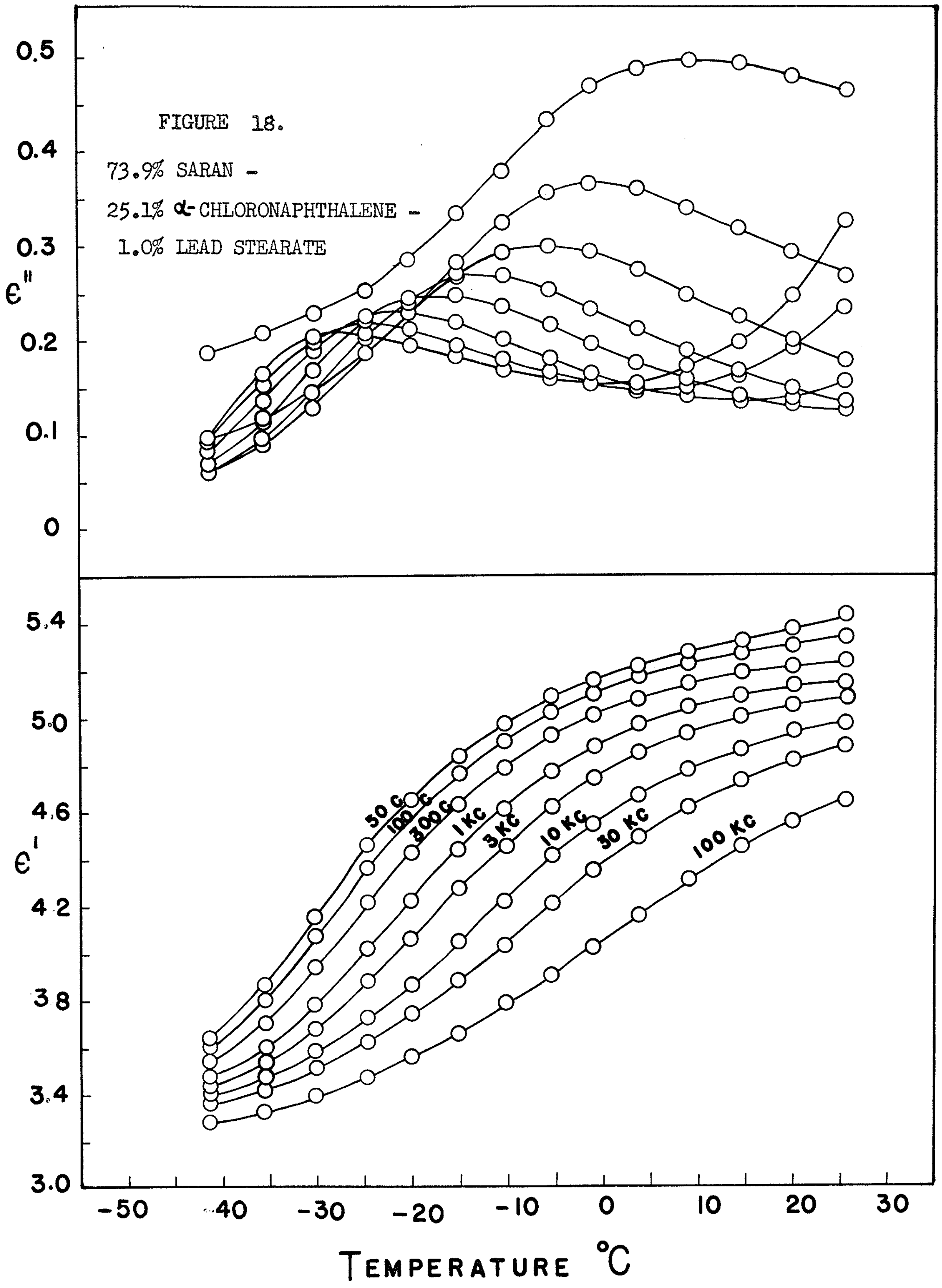


FIGURE 18.

73.9% SARAN -

25.1% α-CHLORONAPHTHALENE -

1.0% LEAD STEARATE

DISCUSSION

Experimental Results

The calculated values of loss factor and dielectric constant are given in Tables 1 to 21. Graphs of loss factor and dielectric constant against temperature for the unplasticized polymers and for Saran (M.W. 10,000) plasticized with α-Chloronaphthalene are given in Figures 10 to 18. Since very little difference exists between the curves for the pure polymer and those for the hexachlorobenzene and nujol plasticized samples they are not included. In Table 22 are given the values of the temperature at which the peak in the loss factor occurs for the different frequencies and compositions. Figure 19 shows the variation of log $\frac{1}{\tau}$ with $\frac{1}{T}$ for the unplasticized polymers and the α-Chloronaphthalene compositions from which the thermodynamic data are calculated. Table 23 lists the calculated values of ΔH^*, ΔS^*, T_x (the value of T at $\tau = 1$) and the densities (calculated from the physical dimensions of the disc) for all compositions.

The Dielectric Dispersion Curves

On comparison of the dielectric constant and loss factor curves with those of previous investigations (F3, F7, F9, F10, F11, F12, F13, M3, S2) the general aspect of the curves is quite similar. On closer inspection of the curves, however, a number of interesting sidelights appear. The maximum values attained by the dielectric constant and loss factor curves are possibly lower than would be expected from the highly polar nature of polyvinylidene chloride. Two explanations can be put forward for this behaviour, both of which depend on the crystalline nature of the polymer.

TABLE 22

Temperatures in °A at which f_{max} occurs

Substance	50c.	100c.	300c.	1kc.	3kc.	10kc.	30kc.	100kc.
Polyvinylidene Chloride	294.1	297.0	301.4	306.4	311.3	318.7	325.5	334.7
Saran (M.W. 100,000)	298.9	301.2	304.6	309.5	315.0	321.2	327.8	337.2
Saran (M.W. 10,000)	296.4	298.4	302.6	307.2	312.9	318.9	325.7	335.2
Saran (M.W. 10,000) with								
1.0% Lead Stearate	291.2	293.2	296.4	301.6	306.6	312.9	320.2	328.8
3.0% Mineral Oil★	289.0	291.4	295.1	299.3	304.6	311.4	317.9	326.9
6.0% Mineral Oil★	289.4	291.5	295.4	299.5	304.4	310.5	317.3	325.7
10.0% Mineral Oil★	295.9	297.5	300.6	305.2	309.9	314.5	322.2	332.2
14.9% Mineral Oil★	296.1	297.7	301.2	305.5	310.5	316.5	322.8	331.7
1.0% Hexachlorobenzene★	289.5	292.6	296.1	299.7	305.2	309.8	317.5	325.7
4.4% Hexachlorobenzene★	286.0	287.9	291.5	296.3	301.3	307.5	314.3	322.7
7.9% Hexachlorobenzene★	288.4	290.5	294.9	298.5	303.7	309.5	316.0	325.3
12.4% Hexachlorobenzene★	288.6	290.8	293.9	299.0	303.3	310.2	316.7	325.2
19.8% Hexachlorobenzene★	288.0	290.4	293.8	298.2	302.8	308.9	315.3	325.8
24.7% Hexachlorobenzene★	288.0	290.6	294.2	298.7	303.7	310.2	316.4	324.3
49.5% Hexachlorobenzene★	286.4	288.2	292.6	298.0	302.6	307.9	313.8	320.5
74.2% Hexachlorobenzene★	289.0	291.0	294.2	299.7	304.3	309.7	317.2	323.7
3.1% α-Chloronaphthalene★	285.2	287.2	290.6	296.3	300.9	306.5	313.3	322.1
6.0% α-Chloronaphthalene★	279.7	281.6	284.4	290.0	294.8	300.9	307.9	317.0
10.0% α-Chloronaphthalene★	270.9	273.2	276.5	281.0	286.4	292.2	299.0	307.2
15.0% α-Chloronaphthalene★	261.5	263.7	267.4	271.5	276.3	281.9	288.7	300.5
25.1% α-Chloronaphthalene★	244.2	247.2	251.2	255.2	260.2	266.7	271.7	281.7

★ also contain 1% Lead Stearate

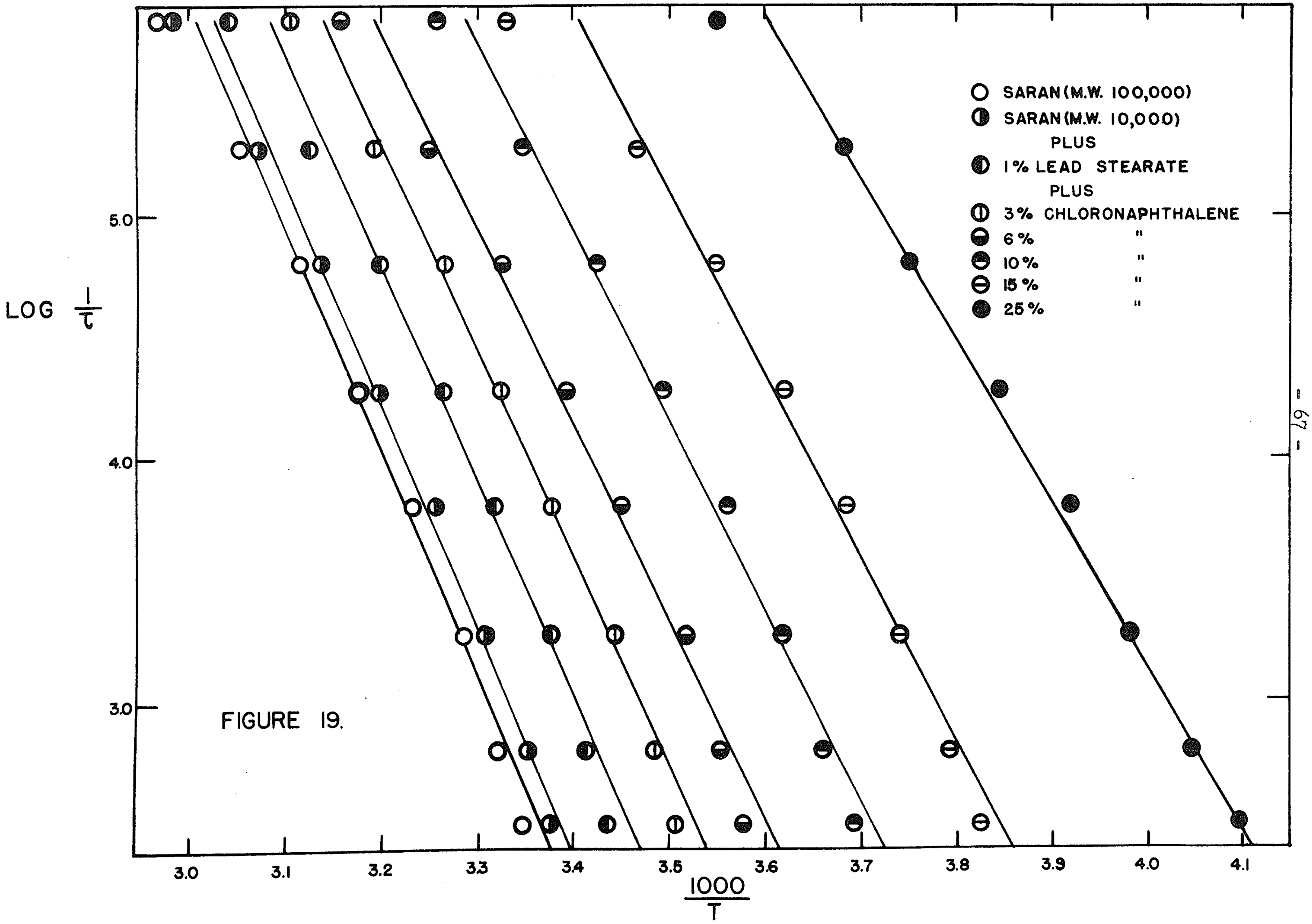

○ SARAN (M.W. 100,000)
◐ SARAN (M.W. 10,000)
PLUS
◐ 1% LEAD STEARATE
PLUS
◐ 3% CHLORONAPHTHALENE
◒ 6% "
◒ 10% "
⊖ 15% "
● 25% "
LOG 1/τ
5.0
4.0
3.0
1000/T
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1

FIGURE 19.

TABLE 23

Activation Enthalpies (ΔH^*), Activation Entropies (ΔS^*), extrapolated temperature for $\tau = 1$ (T_x) and calculated densities (d) for all samples.

Substance	ΔH^* kcal./mole	ΔS^* cal./°C/mole	T_x °A	d grams/cc.
Polyvinylidene Chloride	38.5	83.9	269.8	1.29
Saran (M.W. 100,000)	41.9	93.7	275.3	1.73
Saran (M.W. 10,000)	40.8	90.9	272.6	1.74
Saran (M.W. 10,000) with				
1.0% Lead Stearate	40.1	91.2	267.6	1.75
3.0% Mineral Oil*	39.6	90.7	265.7	1.69
6.0% Mineral Oil*	41.4	96.4	267.0	1.64
10.0% Mineral Oil*	45.0	105.9	273.8	1.58
14.9% Mineral Oil*	43.7	101.2	273.5	1.51
1.0% Hexachlorobenzene*	42.6	100.2	268.1	1.74
4.4% Hexachlorobenzene*	39.5	91.8	263.0	1.74
7.9% Hexachlorobenzene*	41.3	96.6	266.2	1.76
12.4% Hexachlorobenzene*	40.6	94.1	265.8	1.78
19.8% Hexachlorobenzene*	41.2	96.5	265.7	1.81
24.7% Hexachlorobenzene*	40.5	93.8	265.5	1.80
49.5% Hexachlorobenzene*	41.0	96.3	264.6	1.89
74.2% Hexachlorobenzene*	41.4	96.7	266.7	1.93
3.1% α-Chloronaphthalene*	39.6	92.2	262.5	1.75
6.0% α-Chloronaphthalene*	37.8	88.7	256.5	1.70
10.0% α-Chloronaphthalene*	36.1	86.9	248.5	1.70
15.0% α-Chloronaphthalene*	34.2	84.5	239.5	1.68
25.1% α-Chloronaphthalene*	29.9	76.0	223.1	1.64

* also contain 1% Lead Stearate

Saran is one of the most crystalline of the vinyl polymers, which is due to the highly polar nature of the dipole, and the crystallinity is, possibly, a form of association which results in a decrease in the dielectric constant from that expected. Since the dispersion region occurs in a temperature range below the softening point of the polymer (where the polymer is still quite hard and brittle) it is quite possible that although there is dipole freedom, the actual displacement of the dipoles may be relatively small and consequently the dielectric constant would be rather small.

Another point of interest is that the value of ϵ''_{max} appears to increase with temperature. Since the density decreases with increasing temperature the behaviour expected is a decrease in the value of ϵ''_{max} as the temperature is increased due to the decrease in the number of dipoles per unit volume. Also the value of the loss factor at the higher frequencies and lower temperatures does not appear to be approaching zero as are the values at the lower frequencies. The circular arc plot gives a better indication of what is happening. Figure 20 is a Cole and Cole plot for Saran (M.W. 100,000) at 31.5°C. The low frequency part of the curve appears to be quite normal but a deviation is noted at the high frequencies. The curve appears quite similar to that found for solid DBr (Pl) which is given in Figure 21 and shows the resultant curve for two dispersion regions which overlap. The author has also separated them into two separate dispersion regions, both of which show a distribution of relaxation times. In the case of the Saran there are not enough points to calculate the secondary curve, but the principle curve shows a very great distribution of relaxation times, the value of h (cf. Fig. 5) being in the neighbourhood of 0.56 and the values

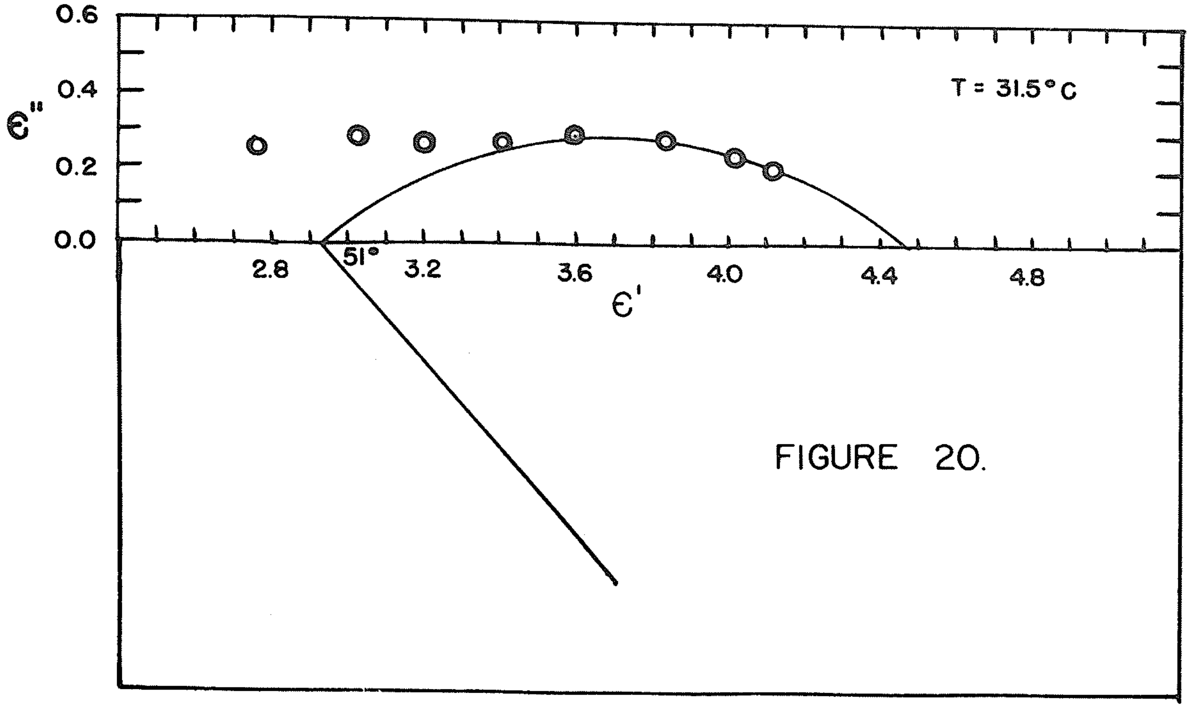


FIGURE 20.

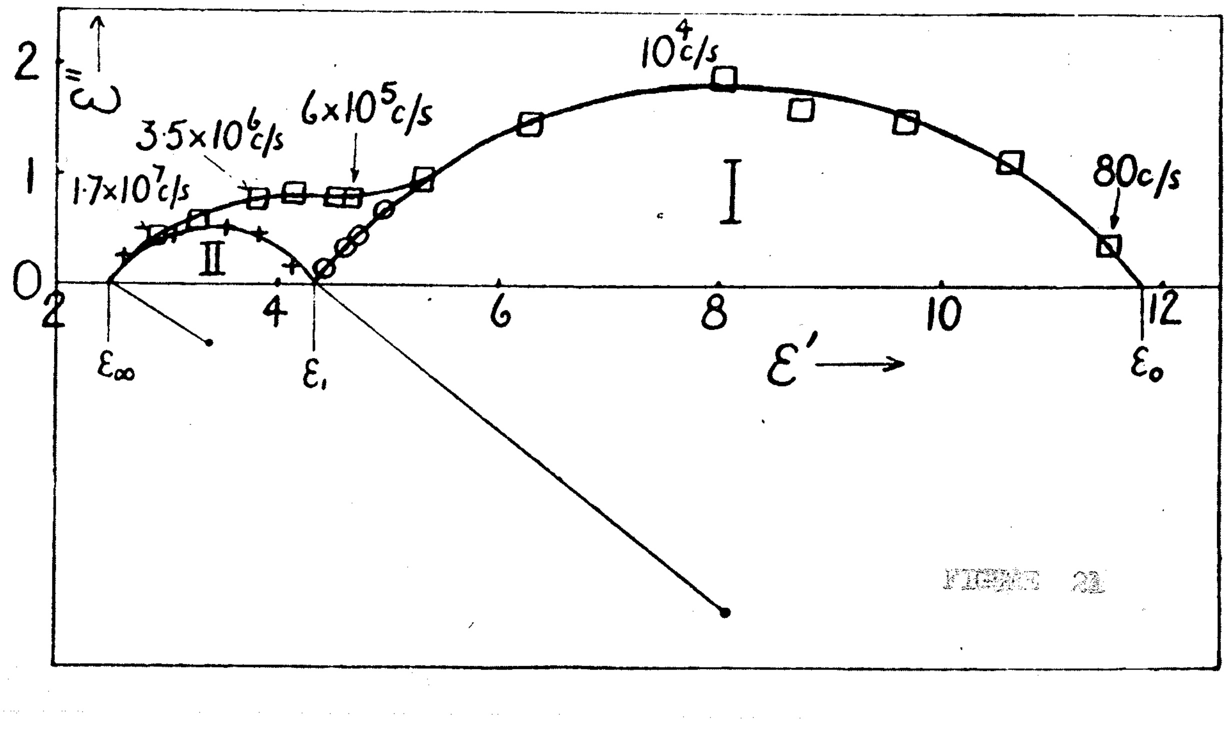


FIGURE 21

of ϵ_0 and ϵ_∞ being respectively 4.49 and 2.91.

There are a number of indications pointing to the crystalline regions as the cause of the secondary, lower temperature dispersion region. In his investigations of polyvinyl chloride Fuoss (F12, F3) found a low temperature dispersion region which was quite broad. The loss factor peaks for this region were shifted to lower temperatures with addition of plasticizer while at the same time the value of ϵ''_{max} decreased until the maximum disappeared. Fuoss (F14) attributed this dispersion region to the presence of crystalline areas in the polymer. In the case of the present investigation on polyvinylidene chloride the dispersion region occurs above and below room temperature so that it facilitated the investigation if the study was made in two sections - one above and one below room temperature. Due to slight distortions in the sample (usually less than 1%) in the first section it was necessary to normalize the data from the second section to that from the first. This could usually be done by expressing the change as a change in the geometry of the sample, so that data at all frequencies would be normalized by the same factor. However, difficulty was observed in some cases, the data at high frequencies were not continuous after normalization. This phenomenon did not appear in the case of Saran plasticized with α-Chloronaphthalene, however, it did to a minor extent with mineral oil and to a very marked extent with hexachlorobenzene. Figure 22 shows the effect for Saran plasticized with 75% hexachlorobenzene. In this run, the section above room temperature was completed first and then the section below room temperature. There is a very marked jump in the 100kc. data and the effect becomes less pronounced as the frequency is decreased

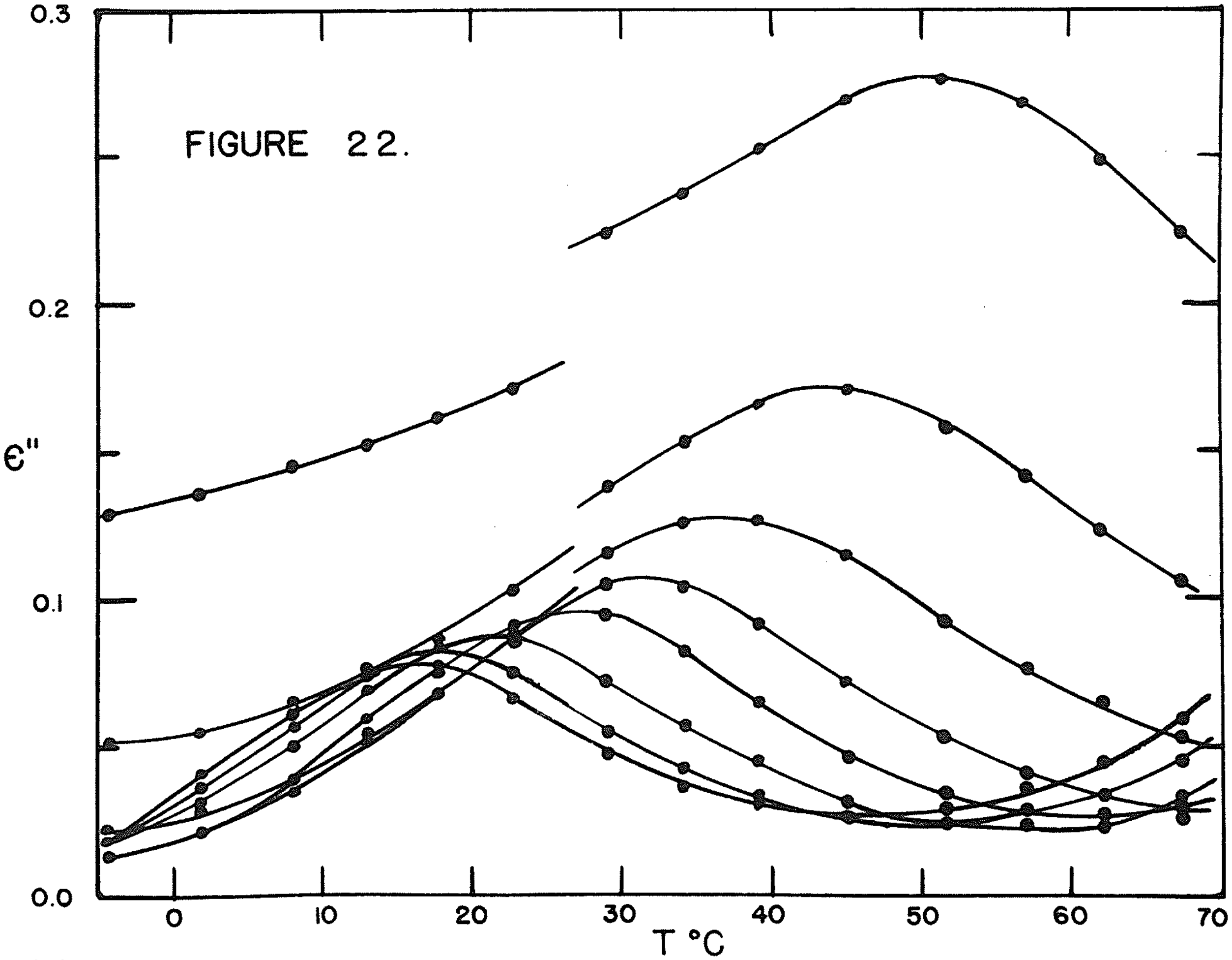


FIGURE 22.

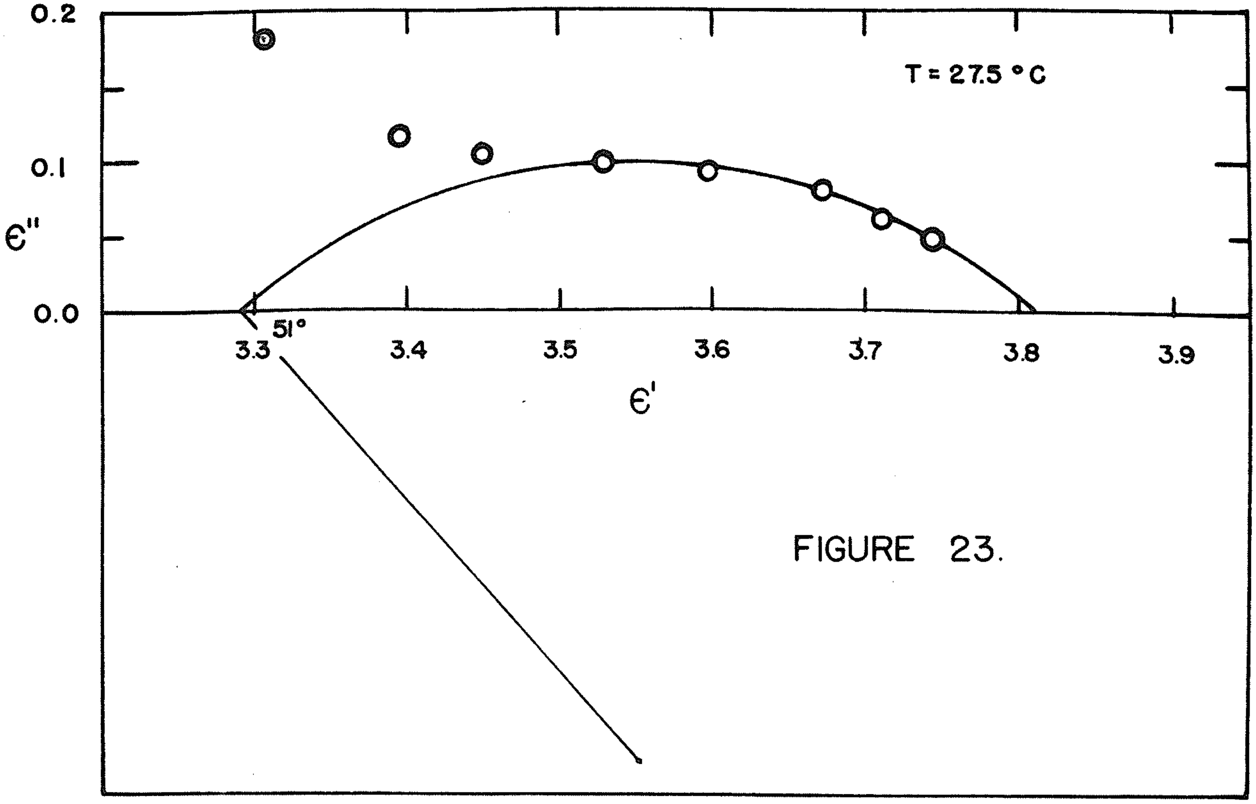


FIGURE 23.

and at 3,000 c/s is not noticeable. A sample containing 20% hexachlorobenzene does not show this effect while a sample containing 25% hexachlorobenzene does exhibit this behaviour. In the former case, the low temperature section had been completed first while in the latter case the low temperature section was done last. In practically every case where the high temperature section was completed first, this phenomenon is evident. The value of ϵ'' at a given temperature is found to decrease after being heated and then cooled. It is quite plausible that this effect is due to a partial melting of some of the crystallites present, with a subsequent decrease in the number of dipoles contributing to the low temperature dispersion region. The nature of hexachlorobenzene might possibly be conducive to the crystallization of the polymer as the effect is most pronounced in the more concentrated samples. Examination of the circular arc plot for the 75% hexachlorobenzene sample, Figure 23, shows that at the high frequency end of the graph the value of ϵ'' is higher than it is at the centre of the circular arc. This might indicate that a greater number of dipoles are in the crystalline state.

Absolute Reaction Rates

Free energies, enthalpies and entropies of activation were calculated after the method of Kauzmann (K2). The value of the activation enthalpy for each sample was found by the least squares method using weighted points, the weighting factor being determined by the sensitivity of the apparatus at the various frequencies. The 50, 100 and 300 cycle points since they are at one end of the range were each given a weight of three, the remaining points were each given a weight of four except for the 100kc. point, which, due to interference from a secondary loss mechanism, and the reduced sensitivity of the apparatus at this point, was given a weight of unity. The values so calculated are given in Table 23.

The values of the enthalpies of activation for the pure polymers are quite low as might be expected from measurements of Boyer and Spencer (B2) who found that polyvinylidene chloride exhibited a very low second order transition temperature indicating a high degree of internal mobility.

In order to study the effects of different types of plasticizers on dielectric relaxation, nujol, a straight chain hydrocarbon was taken as an example of an oil type, non-solvent, plasticizer and two chlorinated aromatic compounds were chosen as solvent types.

It is seen that mineral oil and hexachlorobenzene have little or no effect on the activation enthalpy, entropy and free energy for the relaxation process. In going from zero percent to 75% hexachlorobenzene, the values have remained remarkably constant within experimental error. Although the values for the mineral oil appear to be increasing, it is thought that this is due to a larger experimental error due to incompatibility of the mineral oil and the polyvinylidene chloride and the subsequent "sweating out" of the mineral oil. The reason for the constancy is believed to be due to the fact that neither of these two compounds is dissolved by the polymer and the samples are merely mechanical mixtures of the two substances, hence the polymer would behave as it would in the absence of plasticizer.

However, if there is a genuine increase in the activation free energies, enthalpies and entropies in the case of mineral oil it could be explained by the following picture. If the mineral oil and polymer are quite intimately mixed then there will be large areas where the polymer dipoles are adjacent to the mineral oil molecules. Since these two compounds are not mutually soluble there must be a repulsion between them and the internal freedom of the polyvinylidene dipoles will be decreased in these regions (i.e. the activation energy would be increased). If the fraction of dipoles in these regions is large then an increase in the activation enthalpy would be found. This effect is not observed in the case of hexachlorobenzene, since the high halogen content of this compound creates an atmosphere around the dipole similar to that of the polymer dipole group.

The results obtained from the α-Chloronaphthalene compositions create much more interest. Since this compound is reasonably soluble in polyvinylidene chloride polymers (H1) the results appear to be less erratic due to the uniformity of composition. A definite decrease in the activation free energy, enthalpy and entropy is observed with increasing amounts of this plasticizer.

There are relatively few papers on this particular subject and hence little data is available and few relationships put forth for the variation of the "thermokinetic" properties with plasticizer concentration. Boyer and Spencer (B3) found empirically that the enthalpy and entropy of activation for polyvinyl chloride plasticized with tricresyl phosphate (data of Davies, Miller and Busse (D1) as recalculated by Kauzmann (K2))

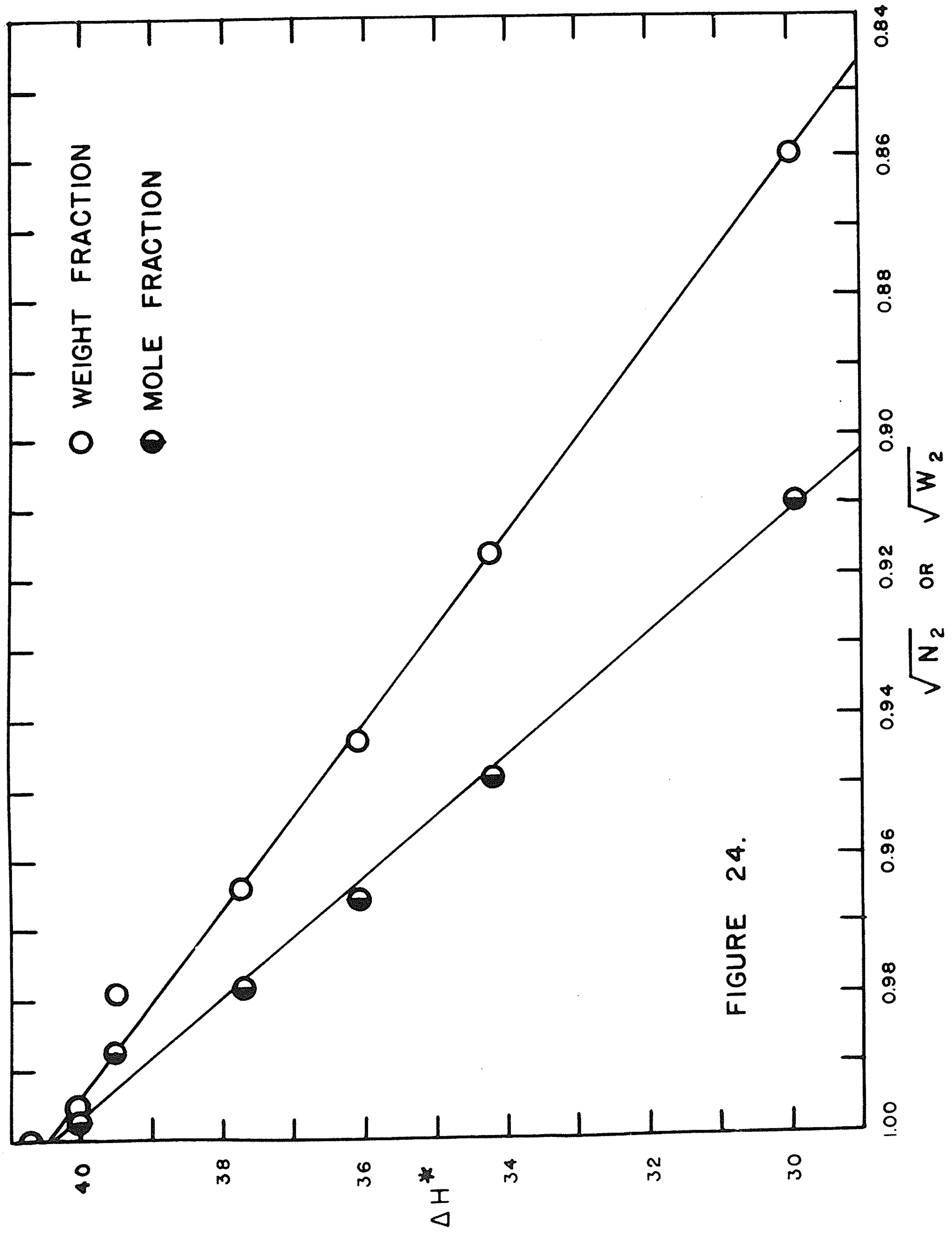

○ WEIGHT FRACTION
◐ MOLE FRACTION
ΔH*
40
38
36
34
32
30
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
$\sqrt{N_2}$ OR $\sqrt{W_2}$

FIGURE 24.

was linear with the square root of the weight fraction of plasticizer. The results for polyvinylidene chloride plasticized with α-Chloronaphthalene show that ΔH^* is linear with the square root of the weight fraction of polymer and also with the square root of the mole fraction of polymer (Fig. 24). (N.B. in the calculation of the mole fraction the monomer molecular weight was used instead of the polymer molecular weight). A more general relationship is presented which shows that on a molecular basis a number of plasticizers appear to be equally efficient. The logarithms of the enthalpies and entropies of activation (recalculated by Kauzmann (K2)) for polyvinyl chloride plasticized with tetralin (F8), diphenyl (F3) and tricresyl phosphate (D1) are found to be linear with the mole fraction of plasticizer or polymer and, what is more startling, appear to fall on the same straight line (Fig. 25). The polyvinyl chloride used by Fuoss was very similar to that used by Davies, Miller and Busse and displayed, within experimental error, the same enthalpy of activation. The variation of these entities ($\log \Delta H^*$ and $\log \Delta S^*$) with mole fraction for the system polyvinylidene chloride α-Chloronaphthalene follows a linear relationship also (Fig. 26) but with a slope different from that in the case of polyvinyl chloride.

From these observations the following relations are suggested:

$$\Delta H^* = \Delta H_0^* \cdot e^{-K_1 n_1} \qquad \text{A.}$$

$$\Delta S^* = \Delta S_0^* \cdot e^{-K_2 n_1} \qquad \text{B.}$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation respectively at mole fraction of plasticizer n_1. ΔH_0^* and ΔS_0^* are the values for the pure polymer (i.e. where $n_1 = 0$) and K_1 and K_2 are the slopes from the

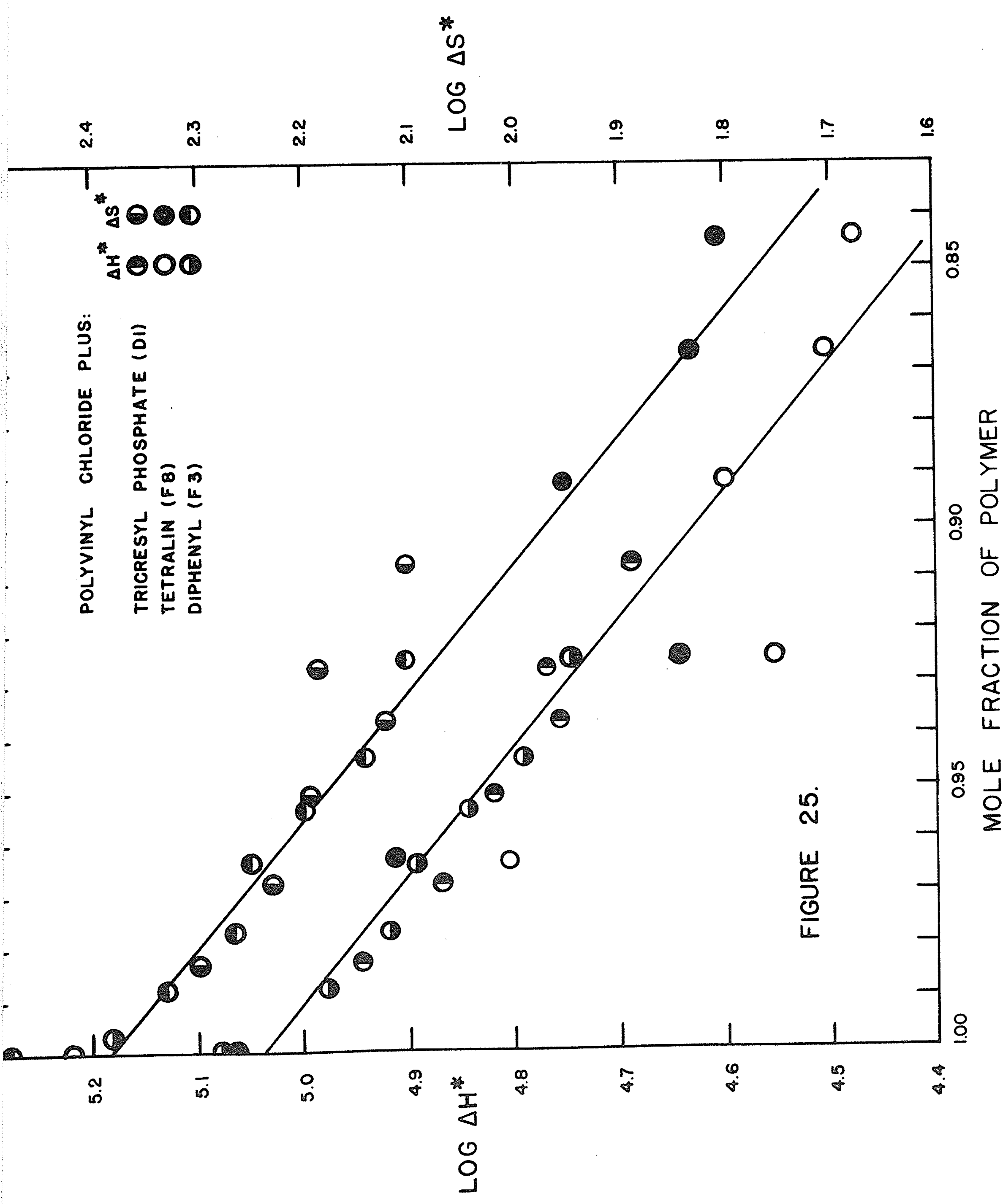
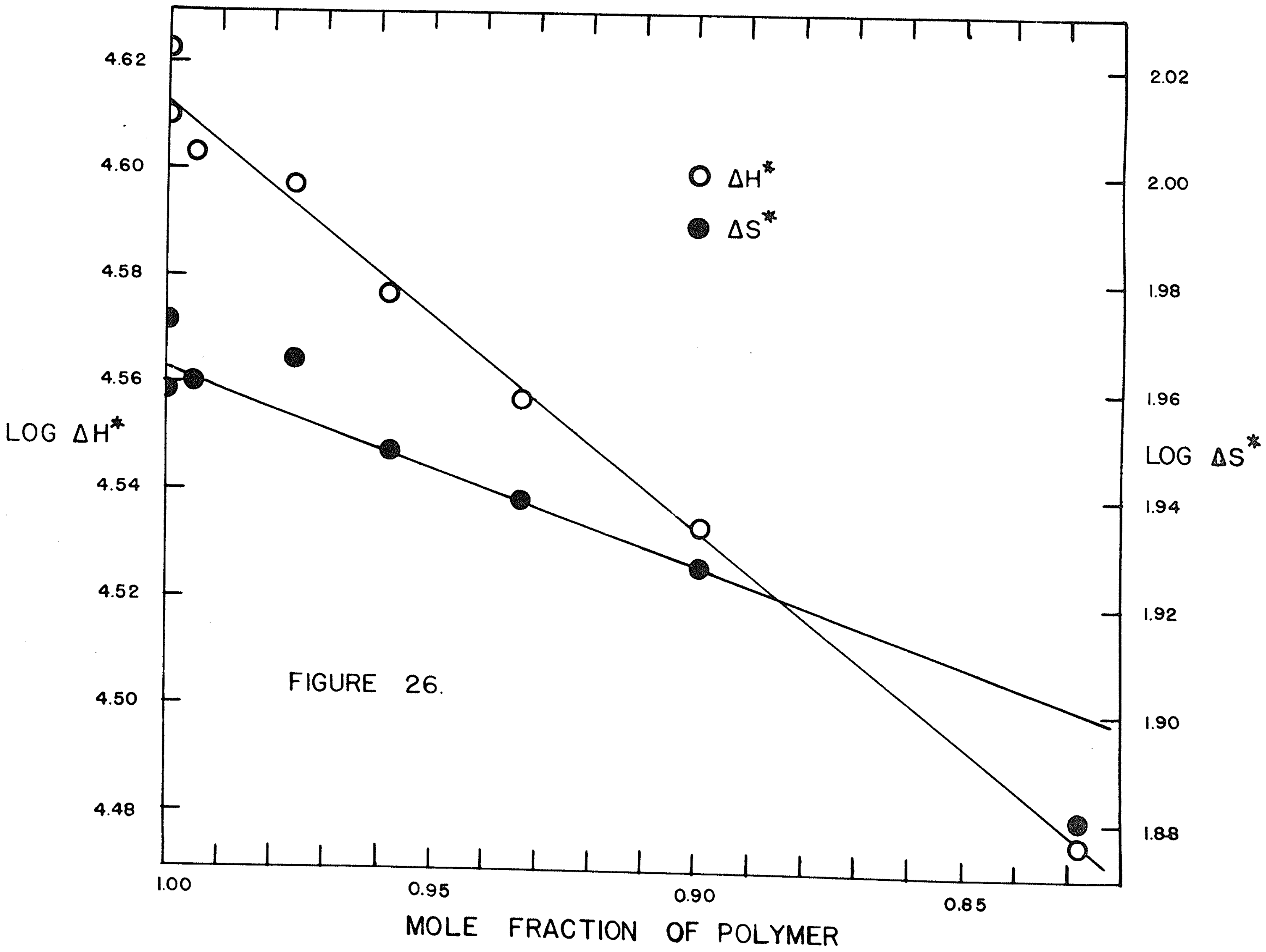

POLYVINYL CHLORIDE PLUS:
ΔH* ΔS*
TRICRESYL PHOSPHATE (DI) ◐ ◐
TETRALIN (F8) ○ ●
DIPHENYL (F3) ◐ ◐
LOG ΔS*
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
LOG ΔH*
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
1.00
0.95
0.90
0.85
MOLE FRACTION OF POLYMER

FIGURE 25.



4.62
4.60
4.58
4.56
4.54
4.52
4.50
4.48
LOG ΔH*
2.02
2.00
1.98
1.96
1.94
1.92
1.90
1.88
LOG ΔS*
ΔH*
ΔS*
1.00
0.95
0.90
0.85
MOLE FRACTION OF POLYMER

FIGURE 26.

log plots.

Expressed as differential equations:

$$\frac{d\Delta H^*}{\Delta H^*} = -K_1 dn_1$$

and

$$\frac{d\Delta S^*}{\Delta S^*} = -K_2 dn_1$$

that is, the fractional decrease in the enthalpy and entropy of activation is proportional to the decrease in the mole fraction of polymer (i.e. the increase in the mole fraction of plasticizer).

Up to this point the only data used has been that of Fuoss and Davies, Miller and Busse (loc. cit.). There are two other sets of data available for polyvinyl chloride; polyvinyl chloride plasticized with tricresyl phosphate and dioctyl phthalate by Dyson (D2) and polyvinyl chloride plasticized with dimethylthianthrene by Fitzgerald and Miller (F9). In Figure 27 these data are shown compared to the solid line found statistically from the previously mentioned data. Dyson's data for dioctyl phthalate appears to be reasonably straight, up to a mole fraction of plasticizer of about 0.12, the line being roughly parallel to the line found from the data of Fuoss and Davies, Miller and Busse. At higher concentrations there is very little change in ΔH^* which may mean that the solubility of the dioctyl phthalate in polyvinyl chloride has been exceeded. The graphs for polyvinyl chloride-tricresyl phosphate (Dyson) and polyvinyl chloride dimethylthianthrene differ from the others in that the slopes of the lines are not as great. A disconcerting fact is that the tricresyl phosphate compositions of Davies, Miller and Busse appear to differ from the tricresyl phosphate compositions of Dyson. In the loss factor-temperature

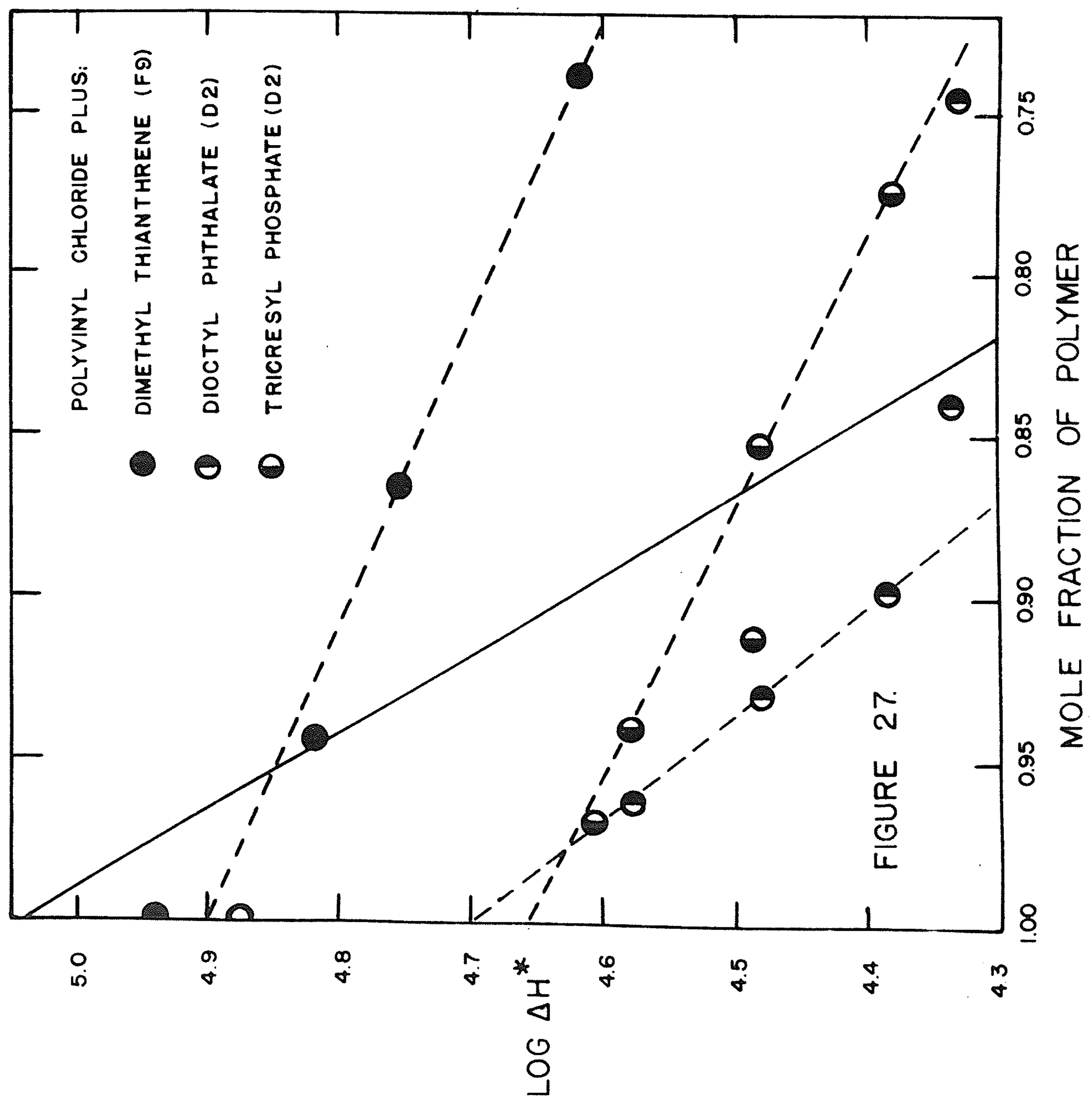

POLYVINYL CHLORIDE PLUS:
● DIMETHYL THIANTHRENE (F9)
◐ DIOCTYL PHTHALATE (D2)
◑ TRICRESYL PHOSPHATE (D2)
LOG ΔH*
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
1.00
0.95
0.90
0.85
0.80
0.75
MOLE FRACTION OF POLYMER

FIGURE 27.

graphs for the dimethylthianthrene compositions of Fitzgerald and Miller a side hump appears on the loss factor maxima, which may be an indication of a miscibility gap in the solid solutions or incomplete compounding of the mixtures. These same reasons may account for the departure of Dyson's tricresyl phosphate compositions from the expected behaviour, however, since the loss factor-temperature graphs for these compositions were not published, this supposition cannot be supported.

For polyvinyl chloride plasticized with tetralin, diphenyl and tricresyl phosphate the following equations were determined by the least squares method for the variation of ΔH^* and ΔS^* with composition.

$$\log \Delta H^* = 2.038 - 4.093\, n_1$$

$$\text{or} \qquad \Delta H^* = 109.1\, e^{-9.426\, n_1}$$

where ΔH^* is in kilocalories and n_1 is the mole fraction of plasticizer.

$$\log \Delta S^* = 2.403 - 4.235\, n_1$$

$$\text{or} \qquad \Delta S^* = 252.9\, e^{-9.753\, n_1}$$

For polyvinylidene chloride plasticized with α-Chloronaphthalene the following equations for ΔH^* and ΔS^* were found by the least squares method:

$$\log \Delta H^* = 1.6101 - 0.7772\, n_1$$

$$\text{or} \qquad \Delta H^* = 40.75\, e^{-1.790\, n_1}$$

where ΔH^* is in kilocalories.

$$\log \Delta S^* = 1.9680 - 0.3786\, n_1$$

$$\text{or} \qquad \Delta S^* = 92.9\, e^{-0.8719\, n_1}$$

Given below is a comparison between the observed values of ΔH^{*} and ΔS^{*} and those obtained from equations A. and B.

Substance	ΔH^{*}obs.	ΔH^{*}calc.	ΔS^{*}obs.	ΔS^{*}calc.
	kcal./mole		cal./°C/mole	
Saran (M.W. 100,000)	41.9	40.8	93.7	92.1
Saran (M.W. 10,000)	40.8	40.8	90.9	92.1
Saran (M.W. 10,000)*	40.1	40.4	91.2	91.7
Saran + 3.1% α-Chloronaphthalene*	39.6	39.0	92.2	90.2
Saran + 6.0% α-Chloronaphthalene*	37.8	37.8	88.7	88.8
Saran + 10.0% α-Chloronaphthalene*	36.1	36.1	86.9	86.9
Saran + 15.0% α-Chloronaphthalene*	34.2	34.0	84.5	84.3
Saran + 25.1% α-Chloronaphthalene*	29.9	30.0	76.0	79.3

* also contain 1% Lead Stearate

In Table 24 the values of ΔF^{*} for plasticized polyvinylidene chloride calculated from the equation

$$\Delta F^{*} = \Delta H^{*} - T\Delta S^{*}$$

$$= \Delta H_0^{*}\, e^{-K_1 n_1} - T\Delta S_0^{*}\, e^{-K_2 n_1} \qquad \text{C.}$$

are shown in comparison to the experimental values. These results are also shown in Figure 28. The agreement is fairly good except at the extremes in composition. The most highly plasticized composition shows a divergence from the calculated values on the ΔH^{*} and ΔS^{*} graphs also and, moreover, exhibits rather different behaviour on the loss factor and dielectric constant graphs. In the case of the unplasticized polymers, the effect appears to be due to the influence of the molecular weight which is

TABLE 24

Comparison between the observed values of ΔF^* and those calculated by means of equation C.

Freq.	ΔF^*obs.	ΔF^*calc.	ΔF^*obs.	ΔF^*calc.
	Saran (M.W. 100,000)		Saran (M.W. 10,000)	
50c.	14.08	13.23	13.96	13.46
100c.	13.78	13.02	13.64	13.27
300c.	13.27	12.70	13.18	12.89
1kc.	12.76	12.25	12.66	12.46
3kc.	12.31	11.74	12.22	11.94
10kc.	11.79	11.17	11.70	11.39
30kc.	11.33	10.57	11.26	10.76
100kc.	10.87	9.70	10.80	9.88
	Saran (M.W. 10,000)[*]		Saran + 3.1% α-Chloronaphthalene[*]	
50c.	13.70	13.68	13.41	13.31
100c.	13.40	13.50	13.11	13.13
300c.	12.90	13.21	12.64	12.82
1kc.	12.42	12.73	12.19	12.31
3kc.	11.97	12.27	11.73	11.89
10kc.	11.48	11.69	11.23	11.39
30kc.	11.06	11.02	10.81	10.78
100kc.	10.59	10.24	10.36	9.98

[*] also contains 1% Lead Stearate

TABLE 24 (Continued)

Freq.	ΔF^*obs.	ΔF^*calc.	ΔF^*obs.	ΔF^*calc.
	Saran + 6.0% α-Chloronaphthalene☆		Saran + 10.0% α-Chloronaphthalene☆	
50c.	13.14	12.97	12.71	12.61
100c.	12.85	12.80	12.45	12.41
300c.	12.36	12.55	12.00	12.12
1kc.	11.92	12.05	11.53	11.73
3kc.	11.48	11.63	11.14	11.26
10kc.	11.01	11.09	10.68	10.76
30kc.	10.61	10.46	10.29	10.17
100kc.	10.18	9.66	9.85	9.46
	Saran + 15.0% α-Chloronaphthalene☆		Saran + 25.1% α-Chloronaphthalene☆	
50c.	12.25	11.96	11.41	10.59
100c.	11.99	11.77	11.21	10.35
300c.	11.59	11.46	10.85	10.04
1kc.	11.12	11.11	10.42	9.72
3kc.	10.73	10.71	10.07	9.32
10kc.	10.28	10.24	9.70	8.81
30kc.	9.91	9.66	9.30	8.41
100kc.	9.62	8.67	8.98	7.62

☆ also contains 1% Lead Stearate

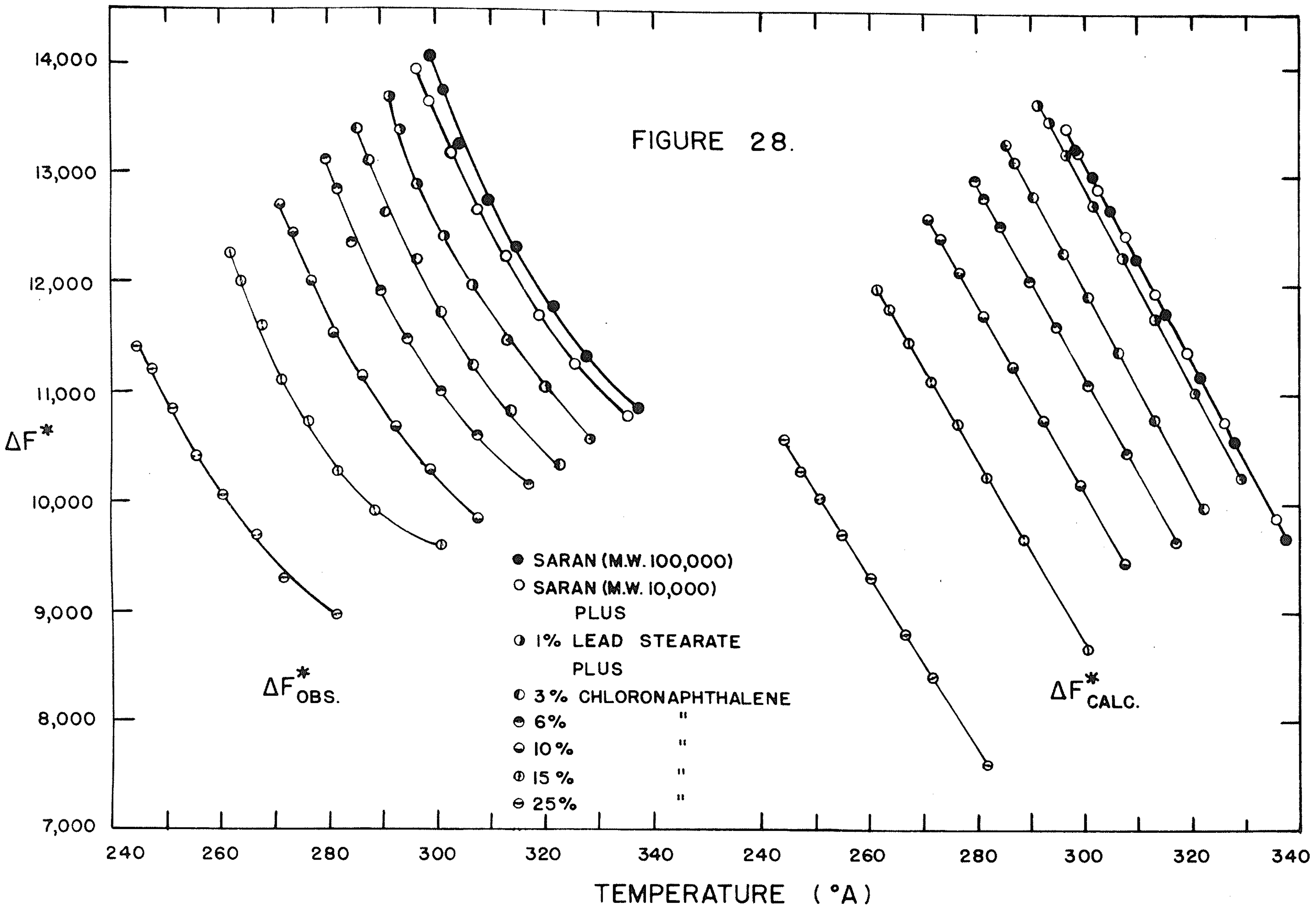


FIGURE 28.

ΔF*
14,000
13,000
12,000
11,000
10,000
9,000
8,000
7,000
240
260
280
300
320
340
TEMPERATURE (°A)
ΔF*OBS.
ΔF*CALC.
● SARAN (M.W. 100,000)
○ SARAN (M.W. 10,000)
PLUS
1% LEAD STEARATE
PLUS
3% CHLORONAPHTHALENE
6% "
10% "
15% "
25% "

possibly a logarithmic dependence. The polyvinylidene chloride prepared in the laboratory gives all indications of being a low molecular weight sample since ΔH^*, ΔF^*, ΔS^* and T_x (the temperature at which $\tau = 1$) are all considerably lower than for the Saran (M.W. 10,000) and Saran (M.W. 100,000) samples.

A further test of the aforementioned equations is the calculation of the temperature at which a given relaxation time will be exhibited at different concentrations. The equation

$$\Delta F^* = \Delta H_0^* \; e^{-K_1 n_1} - T\Delta S_0^* \; e^{-K_2 n_1}$$

can be simplified if, as an approximation, we assume $K_1 \approx K_2$ (which indeed has been found in the case of polyvinylidene chloride and polyvinyl chloride) then the equation can be written

$$\Delta F^* = (\Delta H_0^* - T\Delta S_0^*) \; e^{-Kn_1}$$

where K is some value between K_1 and K_2. From the law of absolute reaction rates

$$\Delta F^* = -RT \ln \frac{h}{kT\tau} = RT \ln \frac{kT\tau}{h}$$

and hence

$$RT \ln \frac{kT\tau}{h} = (\Delta H_0^* - T\Delta S_0^*) \; e^{-Kn_1}$$

or logarithmically

$$\ln RT \ln \frac{kT\tau}{h} = \ln (\Delta H_0^* - T\Delta S_0^*) - Kn_1$$

Having specified the value of τ, then over a small temperature range (of possibly 30C°) the first term on the right hand side is virtually constant and the variation of the $\ln \frac{kT\tau}{h}$ term with temperature is very small, hence a plot of log T against the mole fraction should be a straight line. Figure 29 is a plot of this type for plasticized Saran at $\tau = 1$ and the results appear to indicate that the relation is acceptable for this system.

Further support is lent to this theory from the data of Fuoss et al (M4) on polyvinyl chloride. In this work, Fuoss determined the 60 and 6000 cycle loss factor maxima at 60°C of polyvinyl chloride plasticized with fourteen separate plasticizers. Hence at a given temperature all compositions having a maximum at the same frequency should have the same mole fraction. In Table 24a are listed the plasticizers, their molecular weight and the value of the mole fractions which produce 60 and 6000 cycle loss factor maxima at 60°C.

TABLE 24a

Plasticizer	Molecular Weight	Mole Fraction of Polymer at:	
		60c.	6000c.
tetralin	132	0.948	0.920
diphenyl	154	0.946	0.912
diphenylmethane	168	0.959	0.935
diphenylmethylmethane	182	0.958	0.933
dibenzyl	182	0.958	0.933
amylnaphthalene	198	0.953	0.923
styrene dimer	208	0.964	0.943
dibenzyl ketone	210	0.959	0.934
1, 2 diphenoxyethane	214	0.956	-
dibenzyl maleate	296	0.965	0.944
dibenzyl succinate	298	0.966	0.947
dibenzyl phthalate	346	0.959	0.933
dibenzyl sebacate	382	0.975	0.962
dioctyl phthalate	390	0.971	0.957

Considering the nature of the problem it is thought that the agreement is quite good.

Resistance Measurements

Resistance measurements were taken to correct the ϵ'' values according to the method of Fuoss (F15), where the correction to be subtracted from the loss factor to allow for d.c. conductance. $\epsilon''_{d.c.}$ is given as

$$\epsilon''_{d.c.} = \frac{18 \times 10^{11} \times K_o}{f}$$

where K_o is the specific conductance as measured on a d.c. bridge and f is the frequency. However, the highest conductance measured involved a correction of about 0.02 in the loss factor and this at the high temperature end of the 50 cycle loss curve, consequently the resistance data is unimportant from this standpoint.

Saran displays a rather great ability to pick up electrostatic charges, causing powdered Saran to adhere to glass surfaces to resist removal from these surfaces. This particular property of Saran is believed to enhance the adsorption of moisture on the surfaces of the sample. Since the thicknesses of the discs were of the order of 0.02 to 0.03 inches, adsorption of moisture on this surface would cause a leakage path, therefore, a number of readings were taken on one sample of saran plasticized with

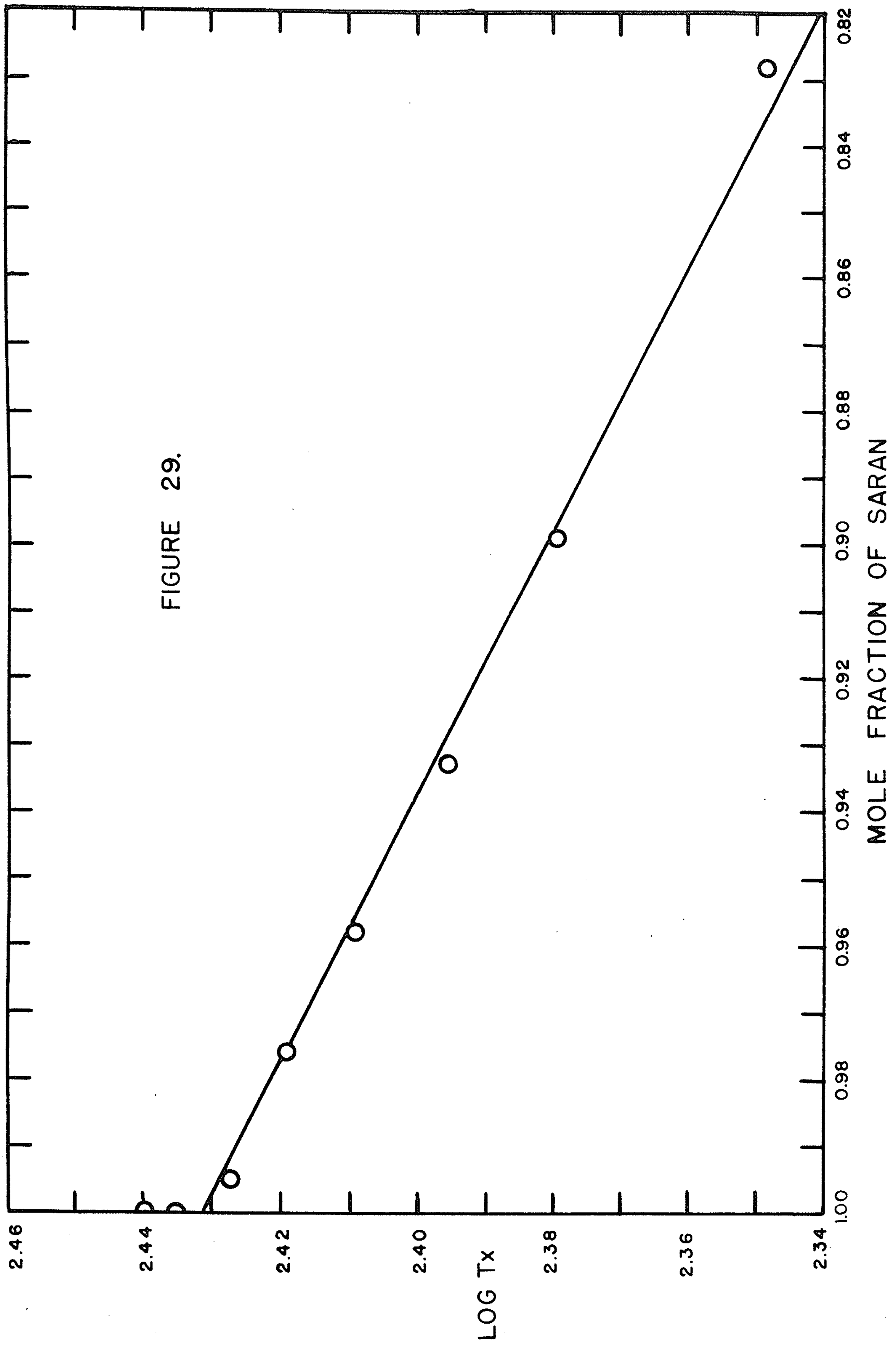


FIGURE 29.

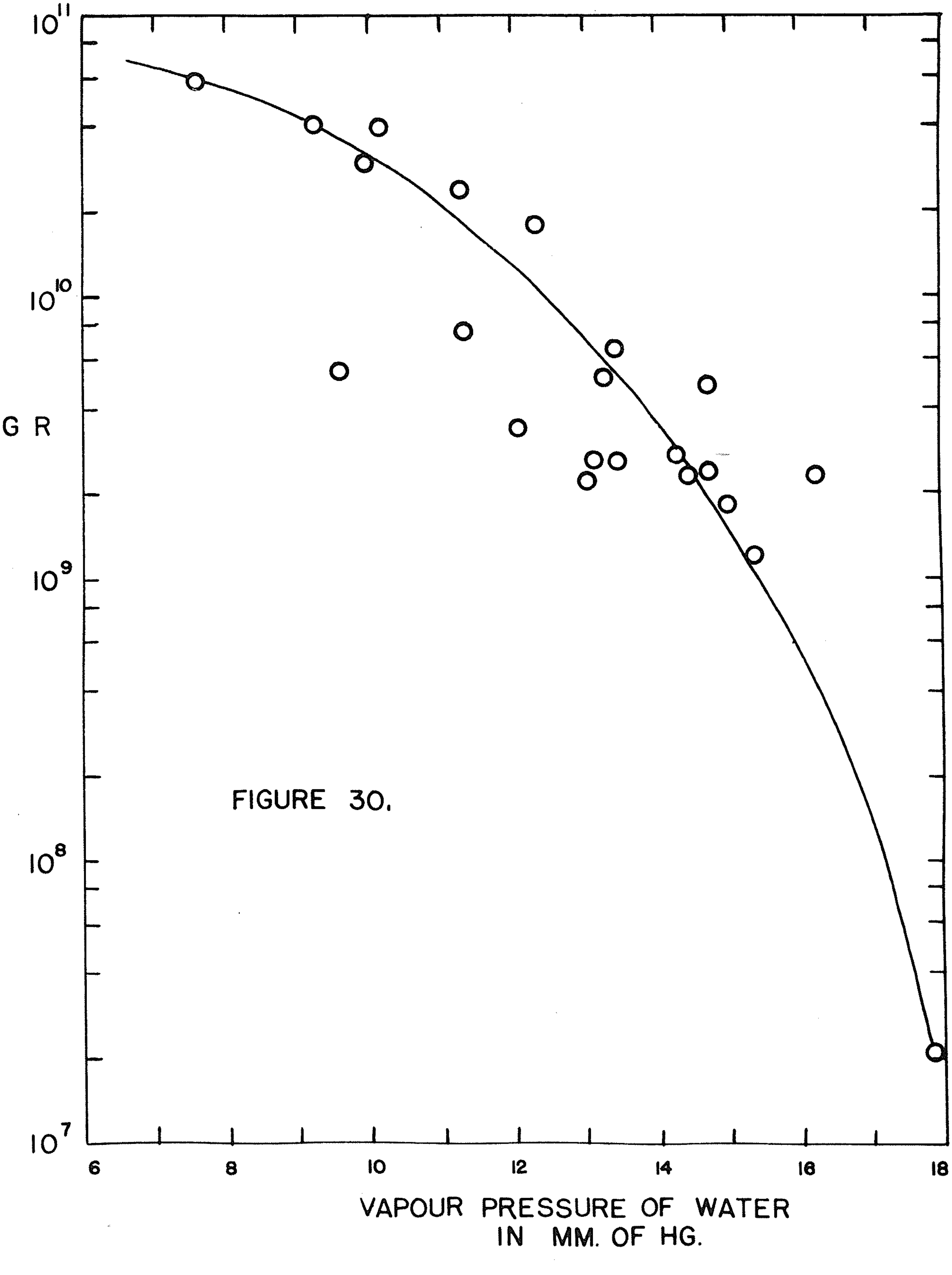
LOG Tx
2.46
2.44
2.42
2.40
2.38
2.36
2.34
MOLE FRACTION OF SARAN
1.00
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82

about 3% hexachlorobenzene at different relative humidities to ascertain if there was an effect. Figure 30, where the resistance of the sample is plotted against the partial pressure of water vapour in the air (as determined by a wet and dry bulb thermometer), gives an indication that the maximum resistance that can be measured depends on the relative humidity at the time of the measurement. The values were all taken at room temperature (circumambient between 74° and 82°F.), the scatter in the data being caused by the latter fact coupled with the inaccuracy of the particular wet and dry bulb thermometer used. The data do, however, give a qualitative picture of the situation.

The specific resistance values do have an intrinsic interest, however. If it is found that the logarithm of the specific resistance is linear with the reciprocal absolute temperature (Fig. 31) then an enthalpy of activation can be found for the process of d.c. conductance. Due to the aforementioned humidity effect (especially at low plasticizer concentrations) some of the plots are not very extensive and hence the results derived from them are not too precise. Table 25 gives a list of specific resistances at different temperatures for the pure polymers and the samples plasticized with α-Chloronaphthalene. The enthalpies of activation were determined by the least squares method and are given in Table 26. They were determined from the following equation

$$\ln \rho = \frac{\Delta H^{*}}{RT} + \text{constant}$$

where ρ is the specific resistance, ΔH^{*} is the activation enthalpy, R is the gas constant and T the absolute temperature. Very little variation in



10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
OG R
6
8
10
12
14
16
18
VAPOUR PRESSURE OF WATER IN MM. OF HG.

FIGURE 30.

TABLE 25

Specific resistances of Saran and plasticized Saran

Temperature °C	Specific Resistance ohm-cm x 10^{-12}	Temperature °C	Specific Resistance ohm-cm x 10^{-12}
Saran (M.W. 100,000)		Saran (M.W. 10,000)	
58.7	17.0	57.9	16.2
64.0	8.52	63.1	11.8
69.7	4.82	68.7	7.44
74.1	3.93	74.0	4.73
81.3	1.67	79.6	2.76
Saran (M.W. 10,000)★		Saran + 3.1% α-Chloronaphthalene★	
54.0	24.8	47.8	30.4
59.0	18.7	53.5	22.5
64.4	11.6	58.8	13.7
69.8	7.38	65.8	6.66
75.1	4.52		
Saran + 6.0% α-Chloronaphthalene★		Saran + 10.0% α-Chloronaphthalene★	
41.4	24.9	35.2	14.5
47.5	16.9	40.3	11.8
52.8	9.65	45.8	7.77
57.8	6.43	51.3	4.97
63.1	3.74		
Saran + 15.0% α-Chloronaphthalene★		Saran + 25.1% α-Chloronaphthalene★	
11.0	126.7	-5.6	85.9
25.2	21.3	-1.2	47.7
30.1	12.7	3.6	25.3
34.6	7.91	8.8	13.4
39.8	4.42	14.4	7.64
45.2	2.64	19.9	4.20
49.6	1.67	25.5	2.04

★ contain 1% Lead Stearate

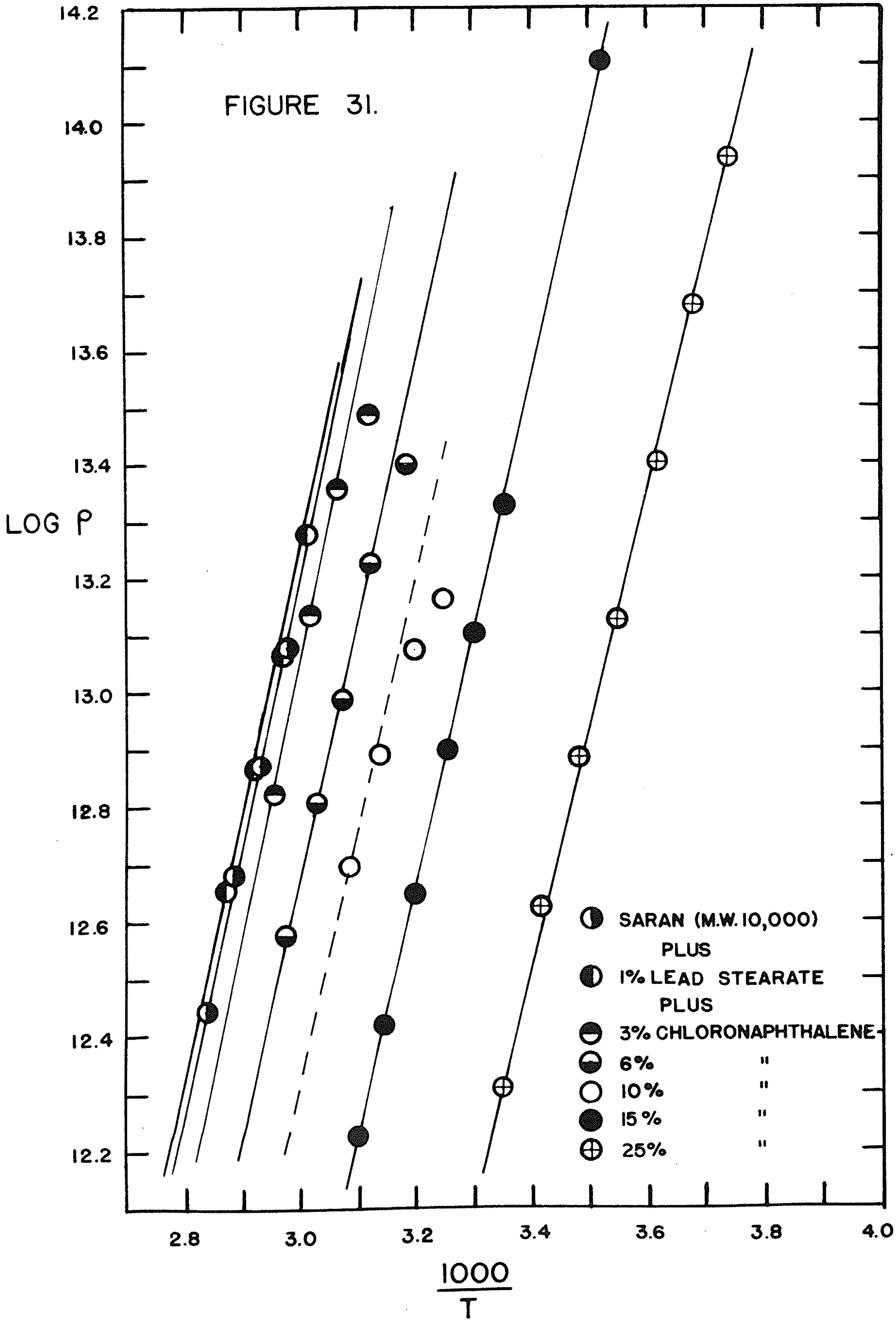


FIGURE 31.
LOG P
14.2
14.0
13.8
13.6
13.4
13.2
13.0
12.8
12.6
12.4
12.2
2.8
3.0
3.2
3.4
3.6
3.8
4.0
1000/T
SARAN (M.W. 10,000)
PLUS
1% LEAD STEARATE
PLUS
3% CHLORONAPHTHALENE
6% "
10% "
15% "
25% "

ΔH^* is noted in going from pure polymer to the most highly plasticized sample, most of the values being in the vicinity of 20 kilocalories.

TABLE 26

Activation Enthalpies for d.c. conductance

Substance	ΔH^* kcal./mole
Saran (M.W. 100,000)	23.0
Saran (M.W. 10,000)	20.7
Saran (M.W. 10,000)*	20.1
Saran + 3.1% α-Chloronaphthalene*	22.1
Saran + 6.0% α-Chloronaphthalene*	20.5
Saran + 15.0% α-Chloronaphthalene*	20.3
Saran + 25.1% α-Chloronaphthalene*	18.8

* also contain 1% Lead Stearate

According to the Debye theory, the relaxation time for dielectric relaxation should be related to the liquid viscosity by the relation

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

where τ is the relaxation time, η is the viscosity, a is the radius of the dipole particle, k is the Boltzmann constant and T the absolute temperature. In a few cases (e.g. Kobeko et al (K3)) found that log log plots of viscosity against dielectric relaxation times yielded straight lines with unit slope. They also found that a similar plot of viscosity against d.c. conductance gave the same result. Thus there might possibly be a relation between the dielectric relaxation rate and the d.c. conductance, that is, they should have the same enthalpy of activation which, judging from the results in Tables 23 and 26, does not hold in this case (as it has not in the majority of cases).

Reduction of Dielectric Data

In the treatment of dielectric data a recent contribution has been the reduction of dielectric data by Ferry et al (F4, F5, F6). By this method data at different frequencies and temperatures can be reduced by a set of equations to give a single composite curve for the loss factor and for the dielectric constant. The equations

$$\epsilon'_p = \epsilon' \frac{T\rho_0}{T_0\rho} + \epsilon_\infty \left(1 - \frac{T\rho_0}{T_0\rho}\right)$$

$$\epsilon''_p = \epsilon'' \frac{T\rho_0}{T_0\rho}$$

$$\omega_p = \omega b_T$$

can be applied if certain conditions prevail (i.e. the shapes of individual curves of ϵ' and ϵ'' against $\log\omega$ must coincide with horizontal shifting and the same values of b_T must superpose both the ϵ' and ϵ'' data). However, these equations are not generally applicable since the maximum values of ($\epsilon' - \epsilon_\infty$) and ϵ'' decrease faster with increasing temperature than proportional to ρ/T. In order to circumvent this the reduced variables $(\epsilon' - \epsilon_\infty) / (\epsilon_0 - \epsilon_\infty)$ and $\epsilon'' / (\epsilon_0 - \epsilon_\infty)$ were adopted in place of ϵ' and ϵ''. However, there are still some polymer systems for which even the reduced variables at different temperatures would not superpose. These systems are characterized by the fact that the maximum value of ϵ'' in frequency dispersion increases with temperature in some polyvinyl chloride systems (F3, F8) and also in styrene-acrylonitrile copolymers (E2). This effect can be attributed possibly to the melting of crystallites which are known to be present in the aforementioned polymer systems. This same phenomenon is exhibited in the case of the polyvinylidene chloride studied and hence this method is not applicable to the present work.

It is thought that the theory of Ferry et al is not quite in accord with the theory of absolute reaction rates since the enthalpy of activation derived from the variation of b_T with temperature vary by as much as a factor of three (in the case of the polymethyl acrylate of Mead and Fuoss (M3)). According to the theory of absolute reaction rates the value of ΔH^* should be almost constant. A slight curvature might be introduced in the log $\frac{1}{\tau}$ vs. 1/T plots by the omission of the log $\frac{kT}{h}$ term in this type of plot, however, it is doubtful whether the slight curvature usually introduced would cause a very large variation in ΔH^*. In the reductions performed by Ferry et al a basic assumption has been made that all relaxation times have the same temperature dependence. Since only segments of the ϵ' and ϵ'' curves are matched up, it is difficult to tell whether the shift is due to a difference in the activation energy as postulated by Ferry or whether it is due to a change in the breadth of the relaxation rate spectrum with temperature as found by Kauzmann (K2).

It is possible that the use of a different method of reduction of the dielectric data would bridge the gap between these two approaches. In the present work it is suggested that instead of choosing the factor b_T empirically, the shift in the loss factor peaks, taken from the plot of $\log \frac{1}{\tau}$ vs. $1/T$, should be used to superpose the data, then the values of ΔH^* from both methods would agree. Once the shift is accomplished then a set of equations could be derived empirically to superpose the values of ϵ' and ϵ''. Ferry, Williams and Fitzgerald (F6) effected a reduction of the data of Funt and Sutherland (F7) for polyvinyl acetal to a temperature of 80°C (a temperature near the lower extremity of the region investigated). A proposed improvement on their theory involves choosing a temperature in the middle of the dispersion region. Figure 32 shows the data for polyvinyl acetal reduced by the method of Ferry et al to a temperature of 80°C. As a comparison, Figure 33 shows a reduction of the same data to 95°C following the modification set forth above. After shifting the loss factor peaks, the following equations were used to reduce the data to the composite curves shown in the diagram.

$$\epsilon'_p = \epsilon' \frac{T}{T_o}$$

$$\epsilon''_p = \epsilon'' \frac{T}{T_o}$$

The deviations in this plot occur at the temperatures at the extreme ends of the absorption region and could possibly be explained on the basis of a change in the breadth of the relaxation rate distribution.

Having accomplished this, a Cole-Cole plot can be used to determine the distribution of relaxation times at the temperature to which the

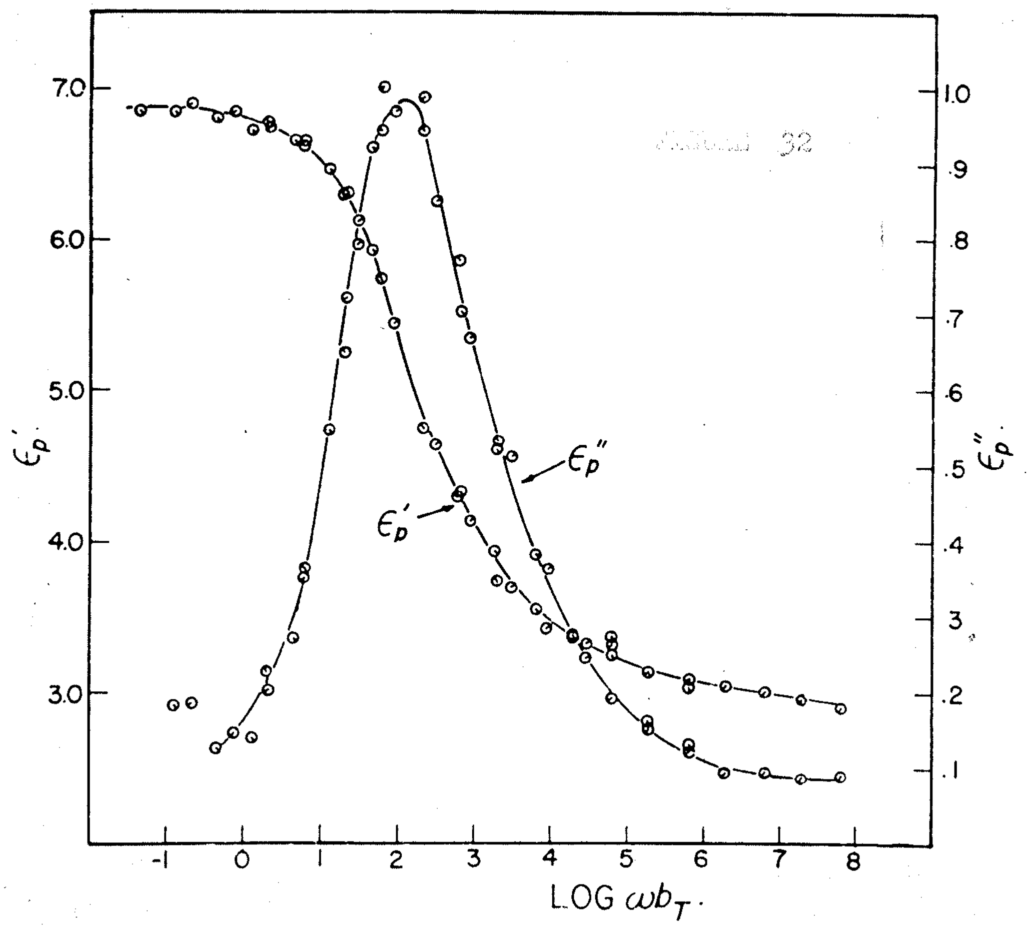


FIGURE 32

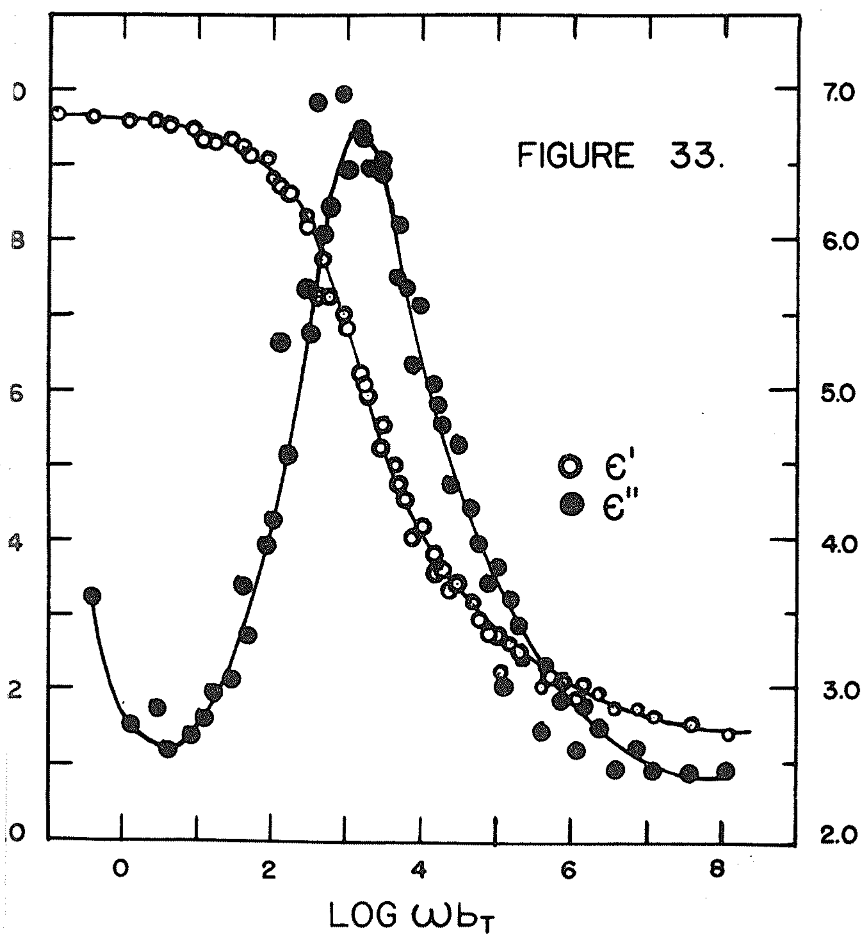


FIGURE 33.

data is reduced. The equation given by Cole and Cole for the complex dielectric constant where there is a distribution of relaxation times

$$\epsilon - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (j\omega\tau)^{1-h}}$$

can be separated into real and imaginary parts as given in Bottcher (B1 P. 370)

$$\epsilon' - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty)\ \frac{1 + (\omega\tau)^n \operatorname{Cos} \frac{n\pi}{2}}{1 + 2(\omega\tau)^n \operatorname{Cos} \frac{n\pi}{2} + (\omega\tau)^{2n}}$$

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)\ \frac{(\omega\tau)^n \sin \frac{n\pi}{2}}{1 + 2\ (\omega\tau)^n \operatorname{Cos} \frac{n\pi}{2} + (\omega\tau)^{2n}}$$

where n = 1 - h and all other symbols are the same as previously defined. In the application of this equation to the already reduced data, ϵ' and ϵ'' are actually ϵ'_p and ϵ''_p. Hence knowing the value of τ at the temperature to which the data is reduced and the values of ϵ_0, ϵ_∞ and n (or 1 - h) (found from the Cole-Cole plot) the values of ϵ'_p and ϵ''_p can be calculated for the plot of the reduced data. Then, working back through the reduction equations and the equation for the variation of log $\frac{1}{\tau}$ vs. 1/T, the dielectric data for any temperature and frequency can be calculated. This would appear to be the ideal way for expressing the dielectric data. That is, in order to express the experimental results of a dielectric investigation, all that is necessary are the values of ϵ_0, ϵ_∞, n, T_0 and the equation relating log $\frac{1}{\tau}$ and 1/T as well as the equations used in the reduction of the data. Hence, the value of the method of reducing data is increased and is in complete harmony with the theory of absolute reaction rates. Of further benefit is the convenience with which the results of a dielectric investigation could be expressed, compressing graphs and tables of data into a few equations.

SUMMARY

SUMMARY

The dielectric constants and loss factors of polyvinylidene chloride (commercial Saran A with molecular weights of 10,000 and 100,000, and a polymer produced in the laboratory) at 50, 100, 300, 1000, 3000, 10,000, 30,000 and 100,000 cycles per second have been investigated along with Saran A with incorporated amounts of mineral oil, hexachlorobenzene or α-Chloronaphthalene. Free energies, enthalpies and entropies of activation were calculated and a relation was developed for their variation with concentration which was found to be applicable to other polymer systems.

A method was developed using a series of more or less empirical equations to express the variation of loss factor and dielectric constant with temperature and frequency of similar dielectric investigations in a more convenient way. The method is applicable to systems which give a circular arc on a Cole and Cole plot together with the limitations imposed in the method of Ferry et al.

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