DIELECTRIC RELAXATION AND INFRARED STUDIES OF HYDROGEN BONDING

A Thesis Submitted To

Lakehead University
Thunder Bay, Ontario, Canada

by

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in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

1985

ProQuest LLC.
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ISBN 0-315-31674-8

TO MY PARENTS

ABSTRACT

Dielectric relaxation and infrared study of a number of associating (H-bonding) compounds in glassy media, mainly polystyrene, have been carried out. The dielectric measurements by a General Radio 1621 Precision Capacitance bridge and infrared measurements by a Beckman spectrophotometer IR4250 have been described. The experimental dielectric data as a function of frequency at different temperatures were subjected to analysis by a series of computer programs written in APL and BASIC languages. The activation energy barriers opposing the dielectric relaxation processes were obtained by the application of the Eyring rate equation.

An infrared study of various sterically hindered alcohols in polystyrene have been carried out. It is shown that a decrease in temperature leads to an increase in the degree of polymerization. The effect of steric factors on the degree of polymerization at a given temperature has also been discussed.

Dielectric studies of sterically hindered alcohols, mainly in polystyrene matrix, have yielded, in some cases, completely separated molecular and intramolecular processes due to the H-bonded species. All alcohols gave a process owing to the H-bonded species with the exception of the most sterically hindered di-tert-butyl carbinol, tricyclohexyl carbinol and diphenyl methyl carbinol. The presence of H-bonded species was indentified by the infrared spectrum of the sample. In addition to sterically hindered alcohols, some simple small alcohols and water were also studied in a polystyrene matrix and in some other glassy media. The process owing to the H-bonded species was found to occur in the similar temperature region as was observed for sterically hindered alcohols. The energy barriers of the process related with H-bonded species for all the alcohols and water in a polystyrene were of a similar order of magnitude. A possible mechanism for the process related to H-bonded species was discussed.

Dielectric studies on alcohol and amine systems in a polystyrene matrix have been carried out. It has been discussed that alcohols interact with amines, thus increase the dipole moment of the complexes which leads to an increase in the dielectric loss factor of the system. However, in many cases the dielectric process due to the complex, formed by alcohol-amine interaction, was overlapped with the absorption owing to the H-bonded species of the alcohol and/or to the molecular process of amine.

ACKNOWLEDGEMENTS

The work described in this thesis was carried out at Lakehead University, Thunder Bay, Ontario, Canada, in 1983-85.

I wish to express my sincere gratitude to my research supervisor, Professor S. Walker, for his guidance and assistance throughout the course of this work. I am very indebted to him for his constant inspiration and for being available at any time for discussion.

I am thankful to my research colleagues Mr. M.E. Huque, Miss J.C.N. Chao, Mr. M.S. Ahmed and Mr. H. Mandal for stimulating discussions and keeping the friendly atmosphere in the laboratory. I also thank my department fellow Mr. H. Mirza.

I would also like to thank Mr. B.K. Morgan for his indispensable technical assistance and to Dr. T.J. Griffith of the Instrumentation Laboratory for allowing me to use the infrared spectrophotometer.

I am very grateful to Miss Ellen M. McDonald, for her constant encouragement, sharing my work and drawing most of figures, during the preparation of this thesis.

Thanks are also due to Mrs. J. Parnell for her hard work in typing this thesis.

I gratefully acknowledge the financial assistance from Lakehead University through my teaching assistantship and NSERC for their research grant.

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CHAPTER I

GENERAL INTRODUCTION AND BASIC THEORY

INTRODUCTION

A H-bond exists if one hydrogen atom H is bonded to more than one other atom, for instance, to two atoms named X and Y. In this case, X and Y are connected with each other along H. If the two bonds of H to X and Y have different strengths the stronger bond will be written X-H and termed a normal XH-bond, but the weaker bond will be written H····Y and termed a hydrogen bond (abbreviated H-bond). The H-bond can be of two types (a) intramolecular H-bond, is one belonging to the same molecule, e.g. in salicylaldehyde and (b) intermolecular H-bond, formed between the molecules, e.g. in alcohols, water, carboxylic acids etc.

The H-bond is an intermediate range intermolecular interaction between an electron-deficient hydrogen and a region of high electron density. H-bond plays a vital role in the structure of DNA (1) and the secondary and tertiary structure of proteins (2). Another very important intermolecularly H-bonding compound is water which is closely related to alcohols.

Infrared and nuclear magnetic resonance spectroscopy have provided a sensitive means of detecting H-bond formation. However, dielectric relaxation remains one of the attractive methods which offers a way of studying the phenomenon of H-bonding in great detail (3,4).

In recent years, the dielectric absorption studies of non H-bonding polar solutes dispersed in a polymer-matrix such as polystyrene, polypropylene and polyethylene matrix have received some attention in the literature. It has been found to yield reasonably reliable intramolecular energy barriers (5,6). One of the great advantages of polymer-matrix technique is that for a molecule with a flexible polar group, where both molecular and intramolecular processes overlap at microwave frequency around room temperature, the relaxation time for the former can be increased to such an extent either it may be considerably slowed down or may even be eliminated owing to a highly viscous surrounding medium, so either or both of the processes may be studied independently. Such a technique appeared more straightforward in comparison to the dielectric solution approach, since in solution studies complications are frequently met owing to overlap of different types of processes which for their separation require Budó analyses which in a number of cases is now known to be unsatisfactory (6). Moreover, the frequency and temperature ranges accessible to the solution studies are fairly limited, and hence relaxation parameters cannot be obtained with reasonable accuracy. However, these limitations may be overcome in the polymer-matrix techniques, since different instruments can be used to cover a wide frequency range of investigations over a broad temperature range (i.e. from liquid nitrogen temperature [∿80 K] to the glass transition temperature of the matrix system).

One of the most commonly used polymer solvents is polystyrene. Polystyrene is used as the solvent for a matrix, which contains the cavities within which the solute molecules can be trapped (5,7). Since the polystyrene is almost a non-polar solvent, studies in which polar molecules are monomolecularly dispersed in the matrix are simplified by the very low loss of polystyrene. Samples of polystyrene have low losses which are less than 1.0×10^{-3} over the frequency range 100 Hz to 1 GHz.

In addition to polystyrene, two other molecular glass-forming solvent systems, o-terphenyl and polyphenyl ether (trade name, Santovac), have been used by the polymer matrix technique. o-Terphenyl is virtually a non-polar solvent which melts at 328.7 K and the liquid may be cooled to a glass with an apparent glass transition at ∿243 K (8). Polyphenyl ether is a six-ring meta-linked bis(m(m-phenoxy phenoxy)phenyl) ether with a glass transition at about 270 K (8). Polyphenyl ether differs from o-terphenyl in that it is more polar since it contains polar ether linkages.

The work presented in this thesis is aimed at gaining basic information on the dielectric relaxation behaviour of intermolecularly H-bonding compounds, mainly alcohols, in a polystyrene matrix. Some of the infrared measurements are also made to assist in interpreting dielectric results of alcohols in a polystyrene matrix.

BASIC THEORY

A. Dielectric Theory

Dielectric materials differ from conductors in that they have no free charges that can move through the material under the influence of electric field. In non-polar dielectrics all the electrons are bound, and the only motion possible in the presence of an electric field is a very small displacement of positive and negative charges in opposite directions. A non-polar dielectric material in which charge displacement has taken place is said to be polarized, and its molecules possess induced dipole moments. The total polarization of a material is made up of different components and can be represented by the Clausius-Mossotti-Debye theories (9) as:

$$\begin{aligned} P_T &= P_E + P_A + P_O \\ &= \frac{4\pi N}{3}\left(\alpha_E + \alpha_A + \frac{\mu^2}{3kT}\right) \\ &= \frac{\varepsilon_o - 1}{\varepsilon_o + 2} \cdot \frac{M}{d} \qquad \text{(I-1)} \end{aligned}$$

where α is the polarizability, N is Avogadro's number, k is the Boltzmann constant, μ is the dielectric dipole moment, T is the absolute temperature, M is the gram molecular weight, d is the density (g ml^{-1}), and ε_o is the static dielectric constant of the material. The subscripts, E, A and O in P indicate the electronic, atomic and orientation polarization components, respectively, of the total polarization, P_T.

The quantity $(\varepsilon_o-1)M/(\varepsilon_o+2)d$ is known as the molar polarization. From Equation I-1, the following conclusions can be made. For a non-polar material the molar polarizability should be a constant independent of the temperature and pressure. An increase in the density leads to an increase in permittivity For a polar substance the molar polarization falls with increasing temperature, because the thermal agitation decreases the dipolar polarization. If a plot of molar polarization versus the reciprocal of temperature is made, a straight line is obtained whose slope yields the dipole moment.

The Clausius-Mossotti-Debye theories are applicable to gases but are often inadequate when applied to polar liquids due to the invalidity of the Lorentz field used in these theories as a measure of the local field in a dipolar dielectric.

In order to give a theory which would extend the relation between permittivityand dipole moment to liquids and solids, Onsager (10) developed a theory on the assumption that there exists a cavity which is a sphere in a homogeneous medium of static dielectric constant, ε_o, as:

$$\frac{(\varepsilon_o - \varepsilon_\infty)(2\varepsilon_o + \varepsilon_\infty)}{\varepsilon_o(\varepsilon_\infty+2)^2} \qquad \frac{M}{d} = \frac{4\pi N\mu^2}{9kT} \qquad \text{(I-2)}$$

where ε_∞ is the very high frequency or optical dielectric constant. At a very high frequency when the orientation polarization vanishes Equation I-1 becomes:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} (\alpha_E + \alpha_A) \qquad \text{(I-3)}$$

A combination of Equation I-1 and Equation I-3 gives the Debye equation:

$$\frac{3(\varepsilon_o-\varepsilon_\infty)}{(\varepsilon_o+2)(\varepsilon_\infty+2)} \cdot \frac{M}{d} = \frac{4\pi N\mu^2}{9kT} \qquad \text{(I-4)}$$

From Equation I-2 and Equation I-4 we can obtain a relationship of dipole moment between the Onsager and the Debye equation as follows:

$$\frac{\mu^2 \text{ (Onsager)}}{\mu^2 \text{ (Debye)}} = \frac{(2\varepsilon_o+\varepsilon_\infty)(\varepsilon_o+2)}{3\varepsilon_o(\varepsilon_\infty+2)} \qquad \text{(I-5)}$$

For gases at low pressures the Onsager equation reduces to the Debye equation when ε_o and ε_∞ are practically identical.

When an insulating material is placed in an electric field it becomes polarized, owing to the relative displacement of positive and negative charges in the material. The ratio of field strength without any dielectric material to that in the presence of the dielectric is called the static dielectric constant (relative permittivity), ε_o, of the material. If a dielectric material is placed in an electric field; which alternates at low frequency the polarization will also follow it. As the frequency is increased the P_O component of P_T will have difficulty in following the alternating field this will result in a decrease in total permittivity. It is this decrease in polarization and permittivity and the resultant absorption of energy which describes the dielectric dispersion. The phase difference between the applied field and the dipole reorientation causes a dissipation of energy known as Joule heating which is measured by the dielectric loss (ε'') defined below as:

$$\varepsilon'' = \varepsilon' \tan\delta \tag{I-6}$$

where ε' is the real component of the complex term of the dielectric constant and $\tan\delta$ is the loss tangent or energy dissipation factor.

The complex quantity of the dielectric constant in the dispersion region is given by:

$$\varepsilon^* = \varepsilon' - i\varepsilon'', \text{ where } i = \sqrt{-1} \qquad \text{(I-7)}$$

The relationship between ε', ε" and δ is illustrated by the diagram:

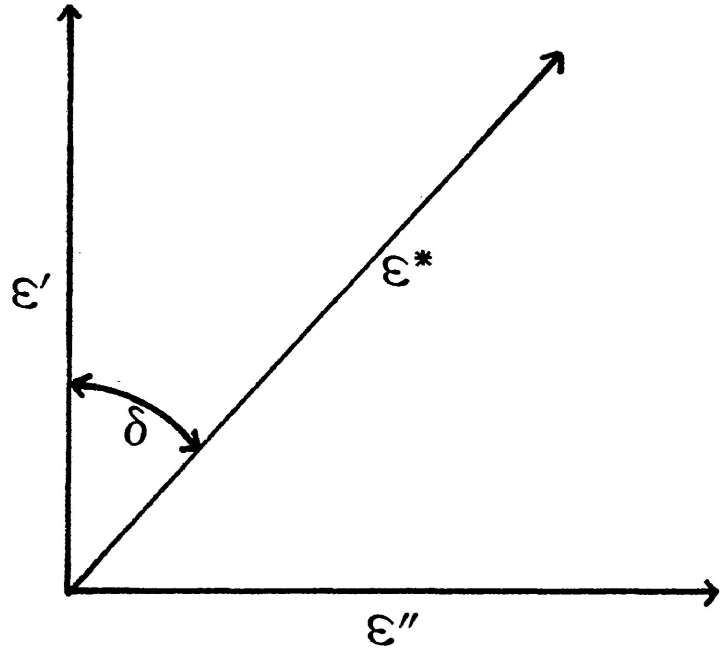

Figure I-1: Loss tangent curve

The absorption region associated with the different mechanisms of polarization occurs in different parts of the electromagnetic spectrum, as shown in Figure I-2. For example, electronic polarization is a process which arises from the displacement of a molecule's electrons in an applied field. The electronic polarization process occurs with a frequency

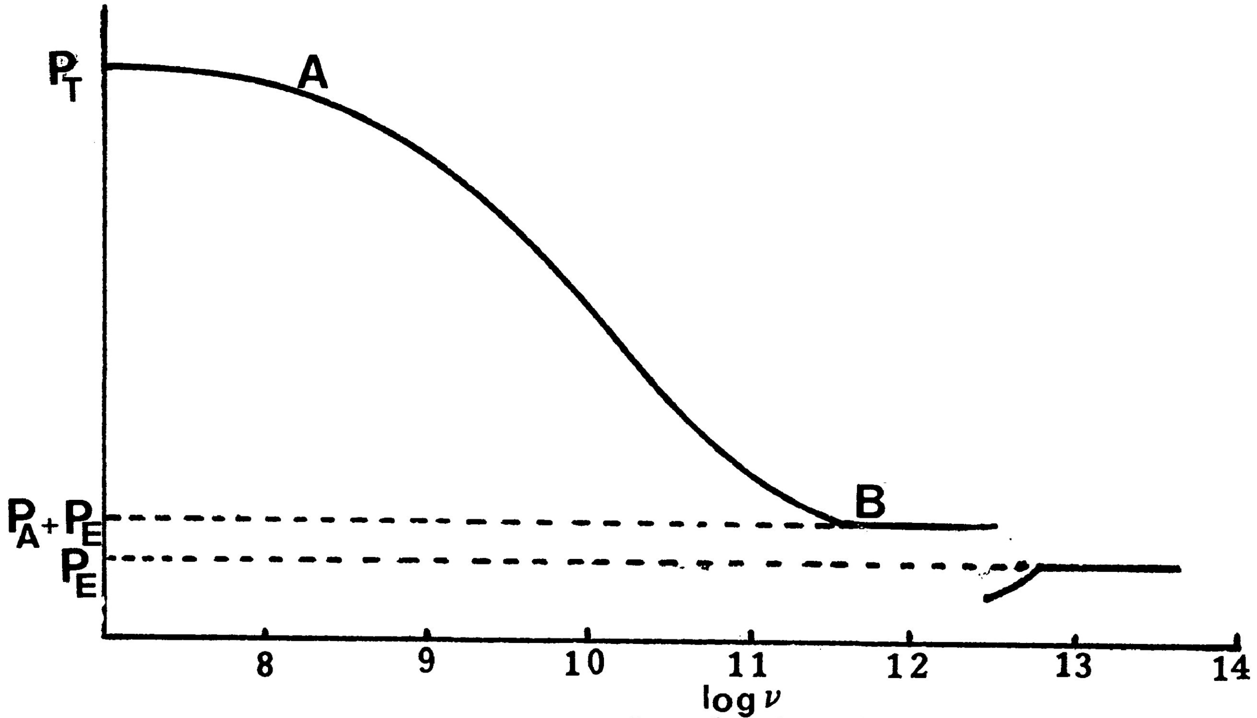

FIGURE I-2: Total polarization versus log frequency curve.

of about 10^{15} Hz which corresponds to frequencies in the ultraviolet region. Atomic polarization arises from the displacement of atoms relative to one another in the molecule, and occurs at frequencies of 10^{12} to 10^{14} Hz, corresponding to the infrared region of the electromagnetic spectrum. The time required for the orientation polarization response depends in part on the frictional resistance of the medium to the change in molecular orientation. In a highly viscous medium a molecule will encounter more frictional drag as it rotates than in a low viscous medium. This will result in a longer period of time for molecular reorientation in a more viscous medium. Small molecules in liquids of low viscosity reorientate themselves in a period of 10^{-11} s to 10^{-12} s with frequencies of

10^{11} to 10^{12} Hz. These frequencies correspond to the microwave region.

Dielectric relaxation is the expontential decay with time of the polarization in a dielectric when an external field is removed. The relaxation time, τ, is defined as the time (t) in which the polarization is reduced to 1/e times its original value (P_O), therefore:

$$P(t) = P_O \exp(-t/\tau) \qquad \text{(I-8)}$$

where, P_O = specific polarization in a static field,

$P(t)$ = specific polarization at time t in an electromagnetic field.

The frequency dependence of ε' and ε'' in the region of dielectric absorption for a system characterized by a single discrete relaxation time is given by the Debye equation:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_O - \varepsilon_\infty}{1 + i\omega\tau} \qquad \text{(I-9)}$$

where ω is the angular frequency.

On separation into real and imaginary parts, Equation I-9 becomes:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{1+\omega^2\tau^2} \qquad \text{(I-10)}$$

$$\varepsilon'' = \frac{(\varepsilon_0-\varepsilon_\infty)\,\omega\tau}{1+\omega^2\tau^2} \qquad \text{(I-11)}$$

Elimination of $\omega\tau$ from these equations gives:

$$(\varepsilon' - \frac{\varepsilon_0-\varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_0-\varepsilon_\infty}{2})^2 \qquad \text{(I-12)}$$

This is the equation of a circle. The locus of ε' and ε'' in an Argand diagram is a semi-circle of radius $(\varepsilon_0-\varepsilon_\infty)/2$ with the centre lying on the abscissa, and is known as the Cole-Cole plot (11).

For many molecules, the dielectric absorption is not characterized by a single discrete relaxation time. Cole and Cole (11) considered the case of a symmetrical distribution about the mean relaxation time, τ_0, and obtained:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0-\varepsilon_\infty}{1+(i\omega\tau_0)^{1-\alpha}} \qquad \text{(I-13)}$$

where α, measured in units of $\pi/2$ radians, is the distribution parameter, and may have values between 0 and 1. When $\alpha = 0$ the Debye equation is obtained.

A number of other functions have been considered for non-Debye type absorption curves. Davidson and Cole (12) have formulated a function which describes right-skewed arcs. The equation is given by:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{(1+i\omega\tau)^{\beta_1}} \qquad \text{(I-14)}$$

where β_1 is the asymmetric distribution co-efficient. If β_1 is 1 then the Debye equation is obtained.

Fuoss and Kirkwood (13) also developed a theory regarding the distribution of relaxation times. These workers found that the dielectric loss of some polymers could be represented by the expression:

$$\varepsilon'' = \varepsilon''_{\text{max}} \operatorname{sech}\{\beta \ln (\omega/\omega_{\text{max}})\} \qquad \text{(I-15)}$$

The mean relaxation time characterizing the dipole motion giving rise to the absorption is represented by $\tau = 1/\omega_{\text{max}} = 1/2\pi\nu_{\text{max}}$, where ν_{max} (Hz) is the frequency at which the maximum loss factor, ε_{max}, is observed. β is itself a significant empirical parameter as its inverse measures the width of the absorption relative to the Debye process ($\beta = 1$), and ν_{max} are usually evaluated from the linear relationship:

$$\cosh^{-1}\left(\frac{\varepsilon''_{max}}{\varepsilon''}\right) = 2.303\beta(\log\nu_{max}-\log\nu) \qquad (I\text{-}16)$$

The Fuoss-Kirkwood β value may be related to the Cole-Cole α value by an equation given by Poley (14).

$$\beta\sqrt{2} = (1-\alpha)/\cos\{1-\alpha)\pi/4\} \qquad (I\text{-}17)$$

For molecules which contain a rotatable polar group, dielectric absorption may often be characterized by two discrete relaxation times corresponding to molecular and intramolecular rotations. Budó (15) considered that for multiple discrete relaxation processes the complex dielectric constant could be represented by the superimposition of overlapping Debye absorptions. Use of Budó equation to evaluate relaxation parameters has been described by Crossley, Tay and Walker (16).

A number of models have been suggested to account for the mechanism of the molecular relaxation processes. Debye (9) has suggested a simple relaxation mechanism and according to his theory, each dipole has two equilibrium positions separated by an energy barrier, ΔE. In such a situation the dipoles will oscillate within the potential minima, and sometimes acquire enough energy to jump the barrier.

The Eyring rate theory (17) is often applied to the reorientation of an electric dipole between two equilibrium positions. According to this treatment if ΔG_E is the free energy of activation for the dipole to reach the top of the barrier opposing reorientation, then the number of times such a reorientation occurs per second is given by the expression:

$$1/\tau = (\kappa kT/h)\ \exp(-\Delta G_E/RT) \qquad \text{(I-18)}$$

where T is the absolute temperature, h is the Planck's constant, R is the universal gas constant, k is the Boltzmann's constant, and κ is the transmission co-efficient normally taken to be 1; this corresponds with the case that each time the dipolar molecule is excited to the top of the energy barrier it continues to move in the same direction to the adjacent minimum position. Thus, the process is one of relaxation between two equilibrium positions but it is commonly referred to as rotation.

Since

$$\Delta G_E = \Delta H_E - T\Delta S_E$$

where ΔH_E is the heat of activation and ΔS_E is the entropy of activation for this dipole relaxation process. Thus:

$$\tau = (h/kT)\exp(\Delta H_E/RT)\exp(-\Delta S_E/R) \qquad \text{(I-19)}$$

which on taking logarithms and rearrangement gives:

$$\ln\tau T = (\Delta H_E/RT) + \ln(h/k)-(\Delta S_E/R) \qquad \text{(I-20)}$$

Thus, it is evident from the above equations that a plot of $\ln(\tau T)$ versus $1/T$ is a straight line. The slope and intercept of the line therefore yields the ΔH_E and ΔS_E, respectively, the observed relaxation process.

B. Infrared

The formation of H-bonds (X-H····Y) gives rise to the following prominent effects in the infrared spectra of the systems:

(i) the stretching mode (ν_{X-H}) and its harmonics are shifted to lower wavenumbers.

(ii) the stretching mode (ν_{X-H}) and its harmonics are broadened.

(iii) the integrated intensity of the fundamental is increased, sometimes by factors of up to ten or more, while the corresponding overtones decrease slightly in intensity.

(iv) both the wavenumber and intensity of stretching mode (ν_{X-H}) may be altered radically by a temperature change of several degrees.

(v) similarly, the wavenumber and intensity of stretching mode (ν_{X-H}) are concentration dependent.

(vi) the absorption of stretching mode (ν_{X-H}) may be altered either by an acidic or basic solvent.

A brief outline of the basic features are given here. However, detailed discussion on basic theories given in the literature (18-20).

For a diatomic molecule X-H, a close replica of a harmonic oscillator, the quantum mechanical solution for λ yields the following equation for the vibrational frequency (ω cm^{-1} units):

$$\Delta E/h = c\omega = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}} \qquad \text{(I-21)}$$

where h is constant, c is the velocity of light and μ is the reduced mass. The force constant k may be regarded as a measure of the stiffness of the springlike X-H bond.

The lowering of the ν_{X-H} frequency was first attributed to the weakening of the X-H bond on the formation of the H-bond. This hypothesis is supported by the observed lengthening of X-H bond by 0.1 to 0.2 Å in an H-bonded crystal (21,22). Semiempirical calculations (23), however, have shown that the force constant of the X-H bond decreases but not sufficiently to account for the totality of the frequency shift. Another significant factor modifying the frequency has been found to be the change in anharmonicity of the stretching vibration while forming the H-bonded complex (24).

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CHAPTER II

EXPERIMENTAL PROCEDURE

INTRODUCTION

When a material of dielectric constant ε completely fills the space between the two plates of an ideal capacitor, the dielectric constant is defined by the simple ratio:

$$\varepsilon = \frac{C}{C_o} \qquad \text{(II-1)}$$

where C is the capacitance when the space is filled with the material, and C_o is the capacitance measured when there is a perfect vacuum between the plates. When a sinusoidal potential of amplitude E and frequency ω rad s^{-1} is applied to the capacitor, the current, I, flowing through the circuit is given by:

$$I = E\omega C = E\omega C_o \ (\varepsilon' - i\varepsilon'') \qquad \text{(II-2)}$$

In this equation the real component $E\omega C_o\varepsilon'$, known as charging current, is 90° out of phase with the applied potential and therefore, does not involve any electrical work. The imaginary component, $E\omega C_o\varepsilon''$, known as the loss current, is, however, in phase with the applied potential and is related to the energy dissipated as heat since it causes some electrical work to be done by the dot product, $EI = E^2\omega C_o\varepsilon''$. If we define δ as the angle between the total current and the charging current axis, i.e. the angle by which the charging current fails to become 90° out of phase with the potential then:

$$\tan\delta = \frac{\text{Loss current}}{\text{charging current}}$$

$$= \frac{E\omega\ C_o \varepsilon''}{E\omega\ C_o \varepsilon'}$$

$$= \frac{\varepsilon''}{\varepsilon'}$$

where ε' is the observed dielectric constant according to Equation II-1 and ε'' is known as the loss factor. These are the basic principles of the dielectric measurements.

CHEMICALS

Chemicals which are used in the present work were purchased from chemical sources except water which was highly pure and deionized. Most of the chemicals were of high purity. However, some of the chemicals, such as, methanol, tert-butanol, tert-amyl alcohol and 1-propanol were refluxed with drying agents like CaH_2, $CaSO_4$ and lime and then distilled over the 4 Å molecular sieves. All chemicals were stored in a vacuumed dissicator and used whenever needed with extreme care to avoid any moisture. The names of the chemicals and their sources are listed below:

Chemicals	Source
Deuterium oxide	Aldrich Chemical Co.
Methanol	Fisher Scientific Co.
Ethanol	Consolidate Alcohols Ltd., Toronto.
1-Propanol	Fisher Scientific Co.
tert-Amyl alcohol	Fisher Scientific Co.
2-Adamantanol	Aldrich Chemical Co.
Di-tert-butyl carbinol	Wiley Organics
Diethyl isopropyl carbinol	ICN, K&K Inc.
Diisopropyl methyl carbinol	ICN, K&K Inc.
tert-Butyl ethyl methyl carbinol	ICN, K&K, Inc.
Isopropyl ethyl methyl carbinol	Aldrich Chemical Co.

Chemicals	Sources
tert-Butyl isopropyl carbinol	ICN, K&K Inc.
Dimethyl-tert-butyl carbinol	Wiley Organics
Dimethyl isopropyl carbinol	ICN, K&K Inc.
tert-Butyl methyl carbinol	Aldrich Chemical Co.
Tricyclohexyl carbinol	Aldrich Chemical Co.
Diphenyl methyl carbinol	Aldrich Chemical Co.
Dimethyl benzyl carbinol	ICN, K&K Inc.
Dimethyl phenyl carbinol	Aldrich Chemical Co.
Pyridine	Aldrich Chemical Co.
Pyrazine	Aldrich Chemical Co.
Isoquinoline	Aldrich Chemical Co.
4-Phenyl pyridine	Aldrich Chemcial Co.
Polystyrene (M.W. 250,000-300,000)	Polysciences Inc. (Lot #10256)
o-Terphenyl	Merck
Santovac	Monsanto Co., Missouri, U.S.A.

A. Dielectric Measurements

Dielectric measurements were carried out on the samples placed in capacitance cells and by measuring the capacitance, C, and conductance, G, of the samples, using a General Radio bridge in the frequency range 10 to 10^5 Hz.

Sample Preparation for Dielectric Measurements

Liquid samples were used in the co-axial cells. The solution of desired concentration was prepared by adding a given quantity of solute to the solvent (e.g. o-terphenyl and Santovac®). The solutions were heated slightly and shaken a few times until it was certain that the solution was homogeneous.

For a chemical system, the sample was cooled to near liquid nitrogen temperature [∿80 K] and slowly heated to the glass transition temperature while capacitance and conductance at selected temperature were taken periodically. From the resultant plot of loss factor, ε'', versus temperature, T(K), at the fixed frequencies, suspected areas of dielectric absorption were identified. The system was then heated again to melt the sample and cooled quickly to some temperature well below the temperature at which the absorption process was expected to begin from the lowest frequency of the measurement. Full frequency dielectric measurements at specific temperatures were then carried out so as to obtain as broad a $\log\nu_{max}$ range as possible. The temperature was recorded to an accuracy of ±0.1 K with the help of a Newport 264-3 platinum resistance thermometer.

In the case of solutions of H-bonding solutes trapped in atactic polystyrene, the samples were prepared by employing the procedure similar to that described by Davies and Swain (1). The desired amount of solute with polystyrene pellets (nearly 2.5 grams) were dissolved in ∿10 ml of 1,2-trans dichloro ethylene, in a porcelain crucible. The mixture was stirred thoroughly, until it was dissolved completely, followed by evaporation in a drying oven at about 353 K. The plastic mass was then placed in a stainless steel die, and after heating the die to ∿383 K, applying the pressure of 5 tons and then cooling the die to room temperature, a disk was obtained which was trimmed to the size. The average thickness and weight of the disk was noted. The molar concentration of the solute in the matrix was calculated according to the formula given by Tay and Walker (2) as:

$$\text{concentration} = \frac{\text{wt. of solute used}}{\text{mol. wt. of solute}} \times \frac{\text{wt. of disk}}{\text{wt. of PS + Solute}} \times \frac{1000}{\text{Vol. of disk}}$$

The polystyrene disk was clamped between the two electrodes of the parallel plate capacitance cell and the dielectric measurement carried out in the previously described way.

The conductance or dissipation factor and capacitance were measured with the General Radio bridge. The product of the frequency and dissipation factor gives loss tangent value, tanδ. With these values obtained experimentally and the following relations, it was possible to determine dielectric loss values for the parallel plate capacitance cell.

$$\varepsilon'' = \varepsilon' \tan\delta \qquad \text{(II-3)}$$

$$\varepsilon' = \frac{Cd}{0.08842A} \qquad \text{(II-4)}$$

$$\varepsilon'' = \frac{\varepsilon' G}{\omega C} \qquad \text{(II-5)}$$

where C is the capacitance of the cell with the sample in picofarads, d is the spacing of the capacitance plates (in cm), A is the effective area of the plates (in cm²), G is the conductance of the system in micromhos.

The effective area of the electrode plates, A, had been determined by measuring the capacitance of the cell containing a standard quartz disk having a diameter of 2.0 inch and a thickness measuring 0.0538 inch (supplied by the Rutherford Research Products Co., New Jersey, U.S.A.) with a dielectric constant of 3.819.

The co-axial cells were also calibrated, to determine relevant constants, with purified cyclohexane at room temperature.

The Capacitance Cells

The cells, designed by Mr. B.K. Morgan of this laboratory, were described earlier by previous workers. However, the cells which were used for this work are illustrated in the following figures (reproduced by the courtsey of D.L. Gourlay (3)). Figure II-1 and Figure II-2 shows a three-terminal coaxial cell and parallel-plate capacitance cell, respectively. A three-terminal coaxial cell was used for dielectric measurements of the samples (which are liquid at room temperature) in o-terphenyl and Santovac®. The three-terminal circular parallel-plate capacitance cell (Figure II-2) was used for dielectric measurements of samples dispersed in polystyrene matrices in the form of solid disks.

The capacitance cells, regardless of design, were encased in essentially the same type of air-tight aluminum chamber. Each cell was cooled from the top by conduction through a flat-bottomed, styrofoam insulated, liquid nitrogen container. Heating balance was accomplished through a temperature control circuit consisting of a thermocouple, and a thermoelectric temperature controlled model 3814021133 unit (accuracy ∿±0.1 K) using nichrome wire heating element surrounding the cell.

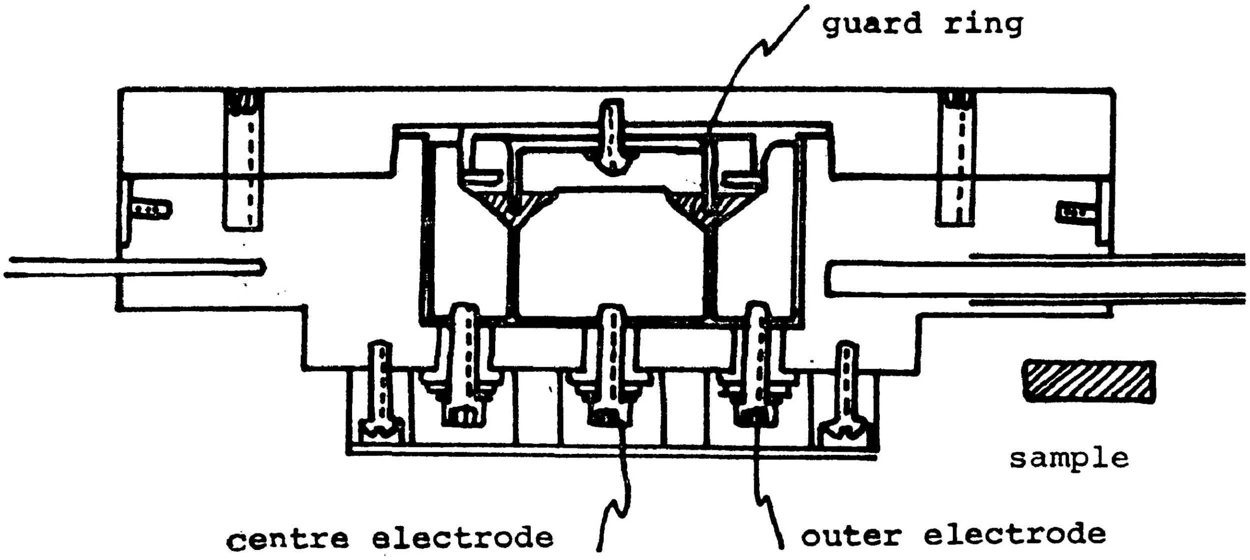

FIGURE II-1: Three-terminal coaxial cell

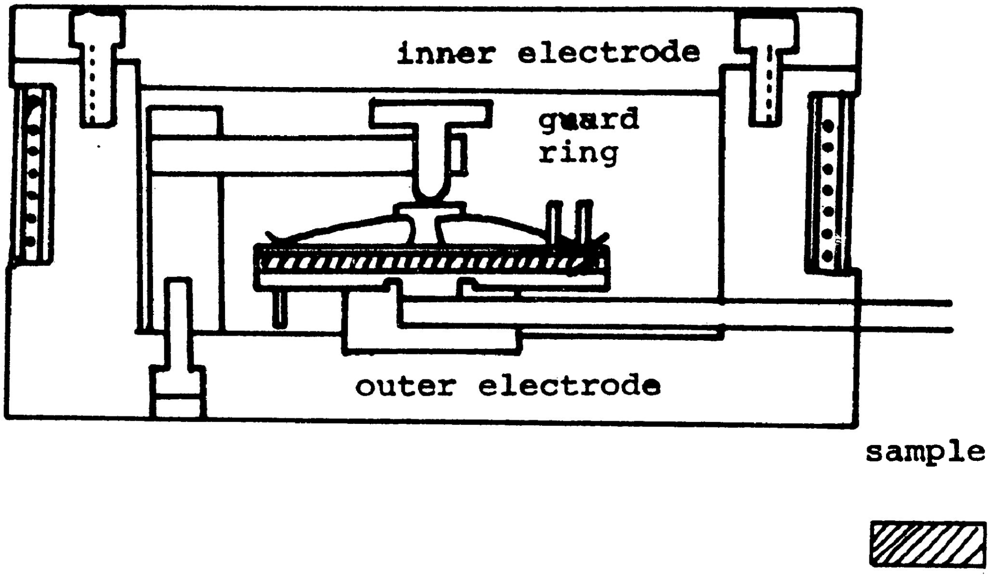

FIGURE II-2: Parallel-plate capacitance cell

The General Radio Bridge

The GR 1621 Precision Capacitance Measurement system is manufactured by the General Radio Company, Concord, Massachusetts, U.S.A. The GR1621 system consists of the GR1616 Precision capacitance bridge with GR1316 Oscillator and the GR1238 Detector. This GR1621 system measures the capacitance and conductance of a capacitor very precisely in the frequency range 10 - 10^5 Hz. After a warm-up period the frequency stability is typically within ±0.001% for a few minutes. The resolution limit of capacitance from this system is 0.1 aF (10^{-7} picofarad) to a maximum of 10 μF (10 microfarad) with internal standards, or farther with external standards.

This GR bridge measures the capacitance and conductance of the capacitor, which can be related to the components of the complex permittivity by the following equations (4):

$$\varepsilon' = C/C_o \qquad \text{(II-6)}$$

and

$$\varepsilon'' = G/\omega C_o \qquad \text{(II-7)}$$

where G is the conductance of the system and the other forms have their usual meaning. Actual measurements were made by bringing the bridge into balance as indicated by null-detector for solutions studied in different three-terminal coaxial and parallel-plate capacitance cells.

Analysis of Experimental Data

The experimental data, obtained by dielectric measurements, were analysed by a series of computer programs. The programs were written in the APL language. The dielectric loss of the sample solution was calculated using a Radio Shack TRS-80, pocket computer (BASIC language).

$$\Delta\varepsilon''_{solute} = \varepsilon''_{solution} - \varepsilon''_{solvent}$$

For each measurement of temperature, the data of dielectric loss factor as a function of frequency were analysed by the computer according to the Fuoss-Kirkwood equation (5) the linear form of which is:

$$\cosh^{-1} \frac{\varepsilon''_{max}}{\varepsilon''} = 2.303\ \beta(\log\nu_{max} - \log\nu) \qquad \text{(II-8)}$$

by a procedure employed by Davies and Swain (1). By interaction the computer program finds that the value of ε''_{max} provides the best linear fit to the plot of $\cosh^{-1}(\varepsilon''_{max}/\varepsilon'')$ against $\log\nu$; the slope of this straight line gives the β-value and ν_{max} is obtained from the slope and intercept.

The energy barrier which must be surmounted in the motion of the dipole was evaluated in terms of the Eyring enthalpy of activation, ΔH_E by using the Eyring rate expression equation (II-9), a procedure commonly used in dielectric work (1,6):

$$\tau = \frac{h}{kT} \exp(\frac{\Delta H_E}{RT}) \exp(\frac{-\Delta S_E}{R})$$

which can be rearranged to the linear form as:

$$\ln(T\tau) = \frac{\Delta H_E}{RT} - (\frac{\Delta S_E}{R}) + \ln(\frac{h}{k}) \qquad \text{(II-9)}$$

The plot of log(Tτ) against 1/T yielded a straight line, and from the slope and intercept of this line the value of the enthalpy of activation, ΔH_E, and the entropy of activation, ΔS_E, respectively were evaluated with the help of a computer program. The computer program also calculates relaxation times, τ, and free energies of activation, ΔG_E, at different temperatures by employing the Equation (II-10) and Equation (II-11), respectively:

$$\tau = \frac{h}{kT} e^{-\Delta G/RT} \qquad \text{(II-10)}$$

$$\Delta G_E = \Delta H_E - T\Delta S_E \qquad \text{(II-11)}$$

Standard statistical techniques (7) provide a means of estimating errors in fitting a straight line ot a set of graph points. The FUOSSK computer program calculates errors in $\log\nu_{max}$ and β for the 90%, 95%, 98% and 99% confidence intervals. The 95% confidence interval was chosen as a good representation of experimental error, typical value for $\log_{10}(\nu_{max})$ being ±0.05 to 0.15.

The same technique was adopted to calculate the 95% confidence intervals for both ΔH_E and ΔS_E.

B. Infrared Measurements

The low temperature infrared spectra were obtained in the range 3100-4000 cm^{-1} using a Beckman spectrophotometer, IR4250. Thin films (∿0.02 mm to 0,5 mm) of polystyrene containing a compound were prepared in the same way as the polystyrene disk for dielectric measurements with the difference in the amount of the sample. Beckman's variable temperature unit, VLT-2, equipped with the sodium chloride windows was used to hold the samples. Temperature of the cell (VLT-2) was controlled by Beckman's automatic temperature controller, CTC-250. The operational temperature range for the VLT-2 unit was 113-333 K. Liquid nitrogen was used as a coolant and the temperature of the cell is believed to be accurate to ±1 K. During the sample preparation and measurement, extreme care was taken to avoid the moisture.

The VLT-2 with a polystyrene sample at desired temperature was placed in the sample beam holder of the IR Spectrophotometer and the reference beam holder had approximately the same thickness of polystyrene film to cancel the absorption due to the polystyrene. In order to place the spectra of one sample at different temperatures in one chart, the pen was set at different points on the % transmission axis (at 4000 cm^{-1}). The scan speed of most of the samples was 300 cm^{-1}/minute.

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CHAPTER III

INFRARED STUDIES OF SOME STRONGLY STERICALLY HINDERED ALCOHOLS IN POLYSTYRENE

INTRODUCTION

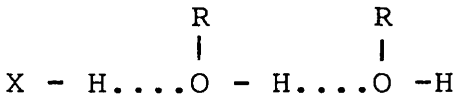
The hydrogen bond has been studied by several physical techniques (1). However, infrared spectroscopy remains the most straightforward and convenient method for detection of the hydrogen bond. Although there are several classes of compounds which form the hydrogen bond, the alcohols have received considerable attention. The infrared spectrum of a normal alcohol, in an appropriate dilute solution and at ambient temperature, exhibits at least three absorption peaks (related to the O-H stretching vibrations). A band which appears near 3600 cm^{-1} is termed as the "monomer band", and the peak which is observed near 3500 cm^{-1} is assumed to arise from the presence of "dimers; a band(s) which is (are) below 3500 cm^{-1} is (are) often termed a "Polymer band(s)" (2). The infrared peaks associated with O-H stretching of an alcohol are affected by the concentration, type of the solvent, pressure and the temperature. Apparently, this reaction is due to the sensitivity of hydrogen-bonded equilibrium. Under these circumstances, the peak which is most affected by the above conditions is the polymer peak.

About 35 years ago, Coggeshall (3) showed the effect of concentration on the O-H stretching frequencies of benzyl alcohol in carbon tetrachloride. The infrared spectrum of this alcohol is shown at 6 different concentrations. The lowest concentration used was 0.0486 mole/liter. Besides a peak at 3610 cm^{-1}, which is present at all the concentrations, there is a relatively broad peak at about 3500 cm^{-1}. As the concentration increases, the band at 3500 cm^{-1} shifts to a lower wave number and at certain concentrations it becomes quite asymmetrical and gives the impression that it is made up of two individual peaks. When the concentration reaches its highest value, 0.278 mol/liter, a broad and relatively large band appears which centres near 3340 cm^{-1}. It is indicated that the peak which appears at about 3610 cm^{-1} is due to O-H stretching of the free monomer, while the band which appears near 3500 cm^{-1} may be attributed to dimers, and a band at about 3340 cm^{-1} is due to the polymer.

Bellamy et al (4), following Allerhand and Schleyer (5), studied the effect of solvents on the hydrogen bonded systems. Methanol and phenol self-dimerization together with their complex with diethyl ether were studied in several solvents. The data for self-dimerization of alcohols in different solvents at ambient temperature are extracted from the work of the above authors.

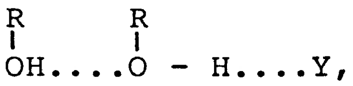
Solvent	Methanol Monomer νOH cm^{-1}	Methanol Self-dimer νOH cm^{-1}	Phenol Monomer νOH cm^{-1}	Phenol Self-dimer νOH cm^{-1}
Hexane	3653	3552	3621	3500
Carbon tetrachloride	3642	3534	3611	3481
Chloroform	3632	3481	3599	3454
Benzene	3613	3502	3558	3454
Toluene	3608	3502	3552	3455
Mesitylene	3598	3504	3536	3441

It is concluded that the formation of an OH•••O bond involves changes in the character of both the terminal atoms. The hydroxyl group oxygen becomes more basic, whilst any hydrogen attached to the acceptor oxygen becomes more acidic. They thus believe that a very substantial part of the frequency shifts shown by such systems in different solvents, can be assigned to specific dipolar association at one end or other of the hydrogen bridge. With alcohol self-dimers the point of solvent attachment can be at either end of the dimer system



$\mathrm{X - H....\overset{\overset{R}{|}}{O} - H....\overset{\overset{R}{|}}{O} -H}$

or



$\mathrm{\overset{\overset{R}{|}}{O}H....\overset{\overset{R}{|}}{O} - H....Y}$, where XH is a proton donor solvent (e.g. chloroform) and Y is a proton acceptor (e.g. the π-electrons of toluene).

The effect of temperature on the O-H stretching frequencies of alcohols has been studied by Sandorfy and co-workers (6,7). They studied fundamental and first overtone spectra of methanol, ethanol, isopropanol, and tert-butanol and their deuterated analogues. Infrared spectrum of methanol, in the mixture of freon solution, at 233 K, exhibits a peak at 3655 cm^{-1} for the free monomer. The associated bands appear near 3510, 3400 and 3332 cm^{-1}. At lower temperatures a strong, low frequency band dominates the spectrum. At 173 K the maximum for this strong band is near 3240 cm^{-1}: at 133 K it is at 3225 cm^{-1}, and at 83 K it has reached 3157 cm^{-1}. The associated bands have not been assigned to particular species, rather a general approach is taken as the species causing the associated bands of higher frequencies are referred to as "oligomers", and the bands due to OH groups, the oxygen of which acts both as a proton donor and acceptor, are referred to as "polymer" bands. It is, thus, indicated that at lower temperatures the "polymers" are the dominant species and grow larger as temperature decreases. For isopropanol and tert-butanol, at the concentration used, 0.2 M, the associated bands remain very weak until about 233 K. However, below this temperature the associated bands grow in intensity, and at 92 K the polymer band centres at 3231 and 3255 cm^{-1} for isopropanol and tert-butanol, respectively. The downward shift of the frequencies accompanying the decrease in temperature has been attributed to gradual decrease in the average O....O distance with slowing down of thermal motion, making the hydrogen bond gradually stronger and more specific. It is also observed that the half width of polymer band from 233 K to 93 K diminishes from 192 to 95 cm^{-1} for isopropanol.

The infrared spectra of alcohols in liquid solution usually give three bands. The bands due to associated species are broad; therefore to assign them accurately to certain species is often difficult. However, the matrix isolation technique permits the identification of discrete absorptions due to the various multimer species present because the peaks due to multimers are sharp (8). Barnes and Hallam (9,10) have studied methanol, and ethanol and their deuterated analogues in an inert argon matrix at 20 K. The methanol monomer absorbs at 3667 cm^{-1}, and the open chain dimer gives a band at 3541, 3533, 3528 and 3519 cm^{-1}. The open chain trimer absorbs at 3505, 3495 and 3482 cm^{-1}, while the open tetramer gives peaks at 3458, 3446 and 3435 cm^{-1}. The cyclic tetramer absorbs at 3379 and 3359 cm^{-1}, and the high polymers give peaks at 3297, 3254 and ∿3200 cm^{-1}. In the case of ethanol two rotamers have also been detected: monomer (gauche) absorbs at 3662 cm^{-1} and monomer (trans) shows an absorption at 3658 cm^{-1}. The bands which correspond to the open chain-dimer are 3534, 3531, 3527, and 3522 cm^{-1}. The open trimer absorbs at 3506, while tetramer shows bands at 3453 and 3437 cm^{-1}. The cyclic tetramer is assumed to give absorption at about 3368 cm^{-1} and the high polymer at 3270 and $\sim$3210 cm^{-1}.

Besides concentration, temperature and type of solvents, the structure of alcohols and the steric effect in the vicinity of an OH group can also limit the polymerization through hydrogen bonding. Substituting bulkier groups in the vicinity of an OH group will hinder the approach of another OH group to form a hydrogen bond. Thus, it is expected that in sterically hindered alcohols the association will be limited perhaps to a few hydrogen bonds. Patterson and Hammaker (11) have shown that di-tert-butyl carbinol in carbon tetrachloride, from 263 K to 298 K, forms only linear dimers. In addition, Becker et al (12), have studied 2,4-dimethyl-3-ethyl-3-pentanol in carbon tetrachloride, from 272 K to 331.5 K. Their result shows that this alcohol is in monomer-dimer equilibrium, obviously due to severe steric factors.

Kolodziej and Malarski (13) carried out the study of di-tert-butyl carbinol in n-heptane and carbon tetrachloride solutions. Dielectric studies were also carried out, and it is concluded that di-tert-butyl carbinol is in monomer $\rightleftharpoons$ open-dimer $\rightleftharpoons$ cyclic-dimer equilibrium, and that at lower temperatures the cyclic aggregates are more favourable.

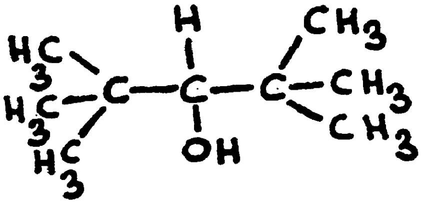
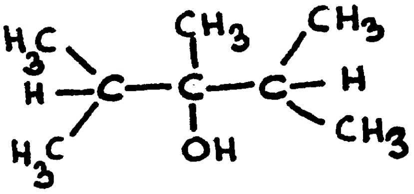
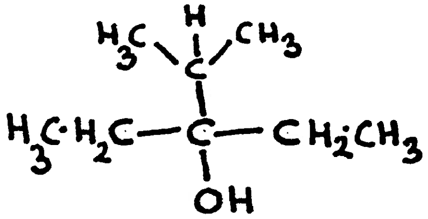
Bourdéron, Péron and Sandorfy (14), carried out the study of some sterically hindered alcohols at temperatures ranging from 83 K to 293 K. 2,6-Dimethyl phenol at a concentration of 0.095 M showed only free OH band at room temperature. At lower temperatures a shoulder which centered at about 3380 cm^{-1} is assigned to "oligomer" ("oligomer" is considered a generic name for dimer, trimer and tetramer) and a peak which centered at 3300 cm^{-1} is believed to arise from the presence of a "polymer" (higher than a tetramer). The first overtone spectrum gave the better way of finding different associated species. 2,6-Di-isopropyl phenol, which is most sterically hindered among alcohols studied, gave one absorption at 3474 cm^{-1} attributed to the presence of a cyclic-trimer. It is shown that in one solvent mixture (CF_2BrCF_2Br + CCl_3F) at a fixed concentration this alcohol showed an absorption at 3376 cm^{-1} whereas in another solvent (CCl_3F + methyl cyclohexane) the band was observed at 3325 cm^{-1}. Thus, it is indicated that the solvent has great influence on the position of the absorption. The band at 3325 cm^{-1} was said to belong to the polymer. 2,2,4-Trimethyl-3-pentanol (or tert-butyl isopropyl carbinol) at 82 K showed a sharp polymer band at 3340 cm^{-1}, but the band showed a shoulder at about 3390 cm^{-1}. A weak band at 3500 cm^{-1} was also observed. The 3390 cm^{-1} shoulder and 3500 cm^{-1} band are indicated to belong to the "oligomer".

From the brief survey of the literature, it appears that the infrared spectrum (fundamental) of alcohols, associated with OH stretching, is fairly successful in pinpointing certain associated species which others fail to do. Thus, we made an attempt to study the infrared spectrum of some sterically hindered alcohols in a polystyrene matrix. These alcohols were chosen because, at optimum temperature and in dilute solution, their polymerization through the hydrogen bond is very limited. The polystyrene which is a solid and an inert medium, does not have any interference from absorption in the range of our interest (4000-3100 cm^{-1}). Thus, polystyrene may serve as a suitable matrix as Hallam (15) describes, "A suitable matrix must, at the temperature of the experiment, be a solid which is inert, rigid with respect to diffusion and transparent in the spectral region of interest". Another reason for studying the infrared spectra of these sterically hindered alcohols is to provide a guideline for this work for interpreting the dielectric relaxation study of the same molecules in the same medium and at identical temperatures and concentrations. An account of the dielectric relaxation study of these alcohols will follow this chapter.

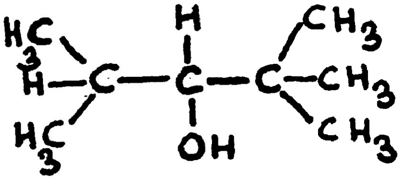
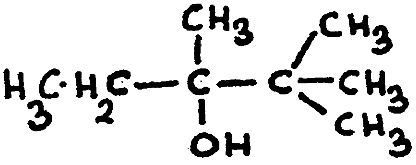
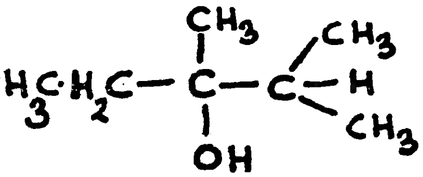
EXPERIMENTAL RESULTS

The alcohols which have been studied are divided into three classes according to the type of substituents and/or length of the carbon chain. However, all of them are regarded as the derivatives of methanol. Besides the compound listed below, ethanol has been studied also.

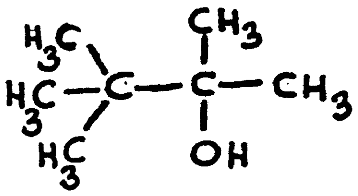
TYPE "A"

NUMBER	NAME	STRUCTURAL FORMULAE
1	Di-tert-butyl carbinol (DTBC)	
2	Di-isopropyl methyl carbinol (DIMC)	
3	Diethyl isopropyl carbinol (DEIC)	

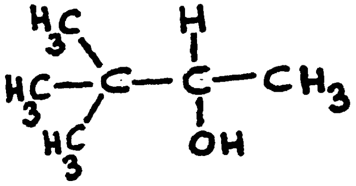
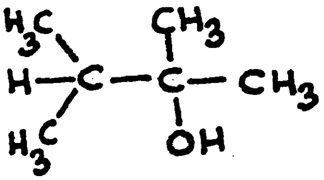
TYPE "A" continued...

NUMBER	NAME	STRUCTURAL FORMULAE
4	tert-Butyl isopropyl carbinol (TBIC)	
5	tert-Butyl ethyl methyl carbinol (TBIC)	
6	Isopropyl ethyl methyl carbinol (IEMC)	

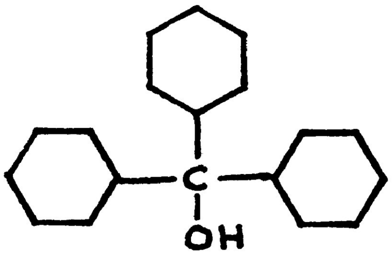
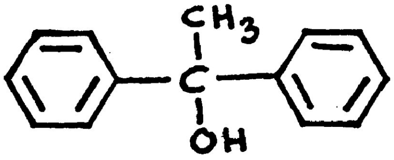
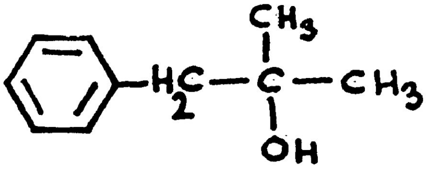
TYPE "B"

7	Dimethyl-tert-butyl carbinol (DMTBC)	

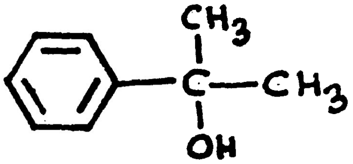
TYPE "B" continued...

NUMBER	NAME	STRUCTURAL FORMULAE
8	tert-Butyl methyl carbinol (TBMC)	
9	Dimethyl-isopropyl carbinol (DMIC)	

TYPE "C"

NUMBER	NAME	STRUCTURAL FORMULAE
10	Tri cyclohexyl carbinol (TCHC)	
11	Diphenyl methyl carbinol (DPMC)	
12	Dimethyl benzyl carbinol (DMBC)	

TYPE "C" continued...

NUMBER	NAME	STRUCTURAL FORMULAE
13	Dimethyl phenyl carbinol (DMPC)	

All compounds were obtained commercially. In some cases they were further purified by recrystallization, and in the cases of liquid they were dried using 4 Å molecular sieves and filtered before use.

The experimental detail on the infrared measurements and sample preparation are given in the experimental section of this thesis.

DISCUSSION

Ethanol, which we shall regard as a non-sterically hindered alcohol, is studied in a polystyrene matrix (see Figure III-1). At 113 K, a sharp peak at 3580 cm^{-1} is observed. Hallam (10) observed a peak for the ethanol monomer in argon matrix at around 3657 cm^{-1}, and Bellamy et al (4) have studied methanol in hexane, which is an inert medium, and obtained a peak for monomer methanol at 3653 cm^{-1}. However, when toluene, which is close to polystyrene in unit structure, was used as a solvent, the monomer methanol was observed at 3608 cm^{-1}. It indicates that when we change from a completely inert solvent to a π-electron containing solvent, the monomer stretching frequency shifts by about 50 cm^{-1}. The peak at 3580 cm^{-1} of ethanol in polystyrene, therefore, may be ascribed to the O-H stretching of the monomeric ethanol. There is an indication of a band at $\sim$3430 cm^{-1} which is more likely due to the presence of a dimer and/or trimer. A shoulder at 3350 cm^{-1} may be assigned to a cyclic tetramer which has been observed by Hallam (10) at 3368 cm^{-1} for ethanol in argon matrix. A band at 3280 cm^{-1} and a shoulder at 3230 cm^{-1} correspond to a high polymer as Hallam has also reported. At 153 K similar peaks and shoulders appear with the difference that now the 3430 cm^{-1} band has shifted to $\sim$3450 cm^{-1}. At 193 K the bands and shoulder below 3400 cm^{-1}

become less intense relative to the band at 3450 cm^{-1}. At 203 K, 213 K and 233 K, ethanol shows a very broad "associated band" (dimer, trimer, tetramer and/or polymer) with an indication of a peak centering at ∿3460 cm^{-1} which is probably dimeric ethanol. At 273 K and 293 K there is an extremely weak and broad band centering at about 3470 cm^{-1}. When the temperature reaches 313 K, there is only a monomer band at 3590 cm^{-1}. The similarities between the study of ethanol in an argon matrix (10) and the polystyrene matrix enables some of the species present in the polystyrene matrix at a particular temperature to be identified.

TYPE "A"

1. Di-tert-butyl carbinol (DTBC)

DTBC has previously been studied in n-heptane and carbon tetrachloride (11,13) with the conclusion that DTBC forms only a dimer (cyclic and/or open). We studied this compound at two different concentrations, 0.70 M and 0.07 M, from 113 K to 293 K (Figures III-2a and III-2b). At higher concentration, 0.70 M, and at 113 K there is a sharp peak at 3610 cm^{-1}, and a relatively broad asymmetric peak at 3230 cm^{-1}. At 300 K and from very dilute solution of DTBC in CCl_4 to pure liquid (film), Kolodziej and Malarski (13) have obtained a monomer peak at 3652 cm^{-1} and a dimer band at ∿3530 cm^{-1}. Bellamy et al (4) have indicated for methanol that in going from CCl_4 to toluene, which is close to polystyrene (one unit) in π-electron density, the monomer and the dimer frequencies are both lowered by about 35 cm^{-1}. Our frequencies for DTBC in polystyrene at 3610 cm^{-1} and 3490 cm^{-1} are about 40 cm^{-1} lower than the monomer and dimer frequencies in CCl_4. Thus, for DTBC in polystyrene, the peaks at 3610 cm^{-1} and 3490 cm^{-1} may reasonably be assigned to a monomer and dimer, respectively. A band at 3230 cm^{-1} which is relatively broad and asymmetric, would be seen to arise from the presence of a high polymer (i.e. higher than a tetramer). At 153 K, besides a monomer, 3610 cm^{-1}, and a dimer, 3490 cm^{-1}, band, we also observed a band at about 3220 cm^{-1} which appears to have a shoulder at about 3270 cm^{-1}. The 3220 cm^{-1} band and 3270 cm^{-1} shoulder can probably be attributed to the presence of high polymers. At 193 K, again we obtain monomer and dimer bands, but now both the bands have shifted to higher frequencies by 5 cm^{-1} (i.e. the monomer appears at 3615 cm^{-1} and the dimer at 3495 cm^{-1}). Besides these two peaks, there is now a clear indication of a peak at about 3360 cm^{-1} which according to Barnes and Hallam (11) may be due to a cyclic tetramer. A broad band at about 3235 cm^{-1} is probably due to the presence of a high polymer. Increasing the temperature from 193 K to 213 K results in sudden loss of peaks at $\sim$3230 cm^{-1} and 3360 cm^{-1}. At 213 K we observed only two peaks, one at

3615 cm^{-1} and the other at 3500 cm^{-1}. The former peak, as indicated earlier, is more likely due to the O-H stretching of the monomers whereas the latter is probably attributed to the presence of the dimer (open and/or cyclic). At 233 K, 273 K and 293 K, we again observe monomer, 3620 cm^{-1}, and dimer, 3500 cm^{-1}, peaks. The infrared spectrum of DTBC at 0.07 M has the same features except in this case the band intensities are reduced considerably (see Figure III-2b).

2. Di-isopropyl methyl carbinol (DIMC)

DIMC is studied at only one concentration, 0.75 M, and from 113 K to 293 K in a polystyrene matrix (see Figure III-3). At 113 K there is a sharp peak at 3605 cm^{-1}, a weak band at 3470 cm^{-1}, a broad band at about 3350 cm^{-1}, and a sign of a peak at 3230 cm^{-1}. A peak at 3605 cm^{-1} is more likely due to an O-H stretching of the monomer. The band at 3470 cm^{-1} is probably due to the dimer (cyclic and/or open). The band at ∿3350 cm^{-1} may be assigned to a cyclic tetramer and at 3230 cm^{-1} to the high polymer (16). At 153 K and 193 K all features of the spectrum are the same except that now 3350 cm^{-1} and 3230 cm^{-1} are well resolved and conspicuous. At 213 K, unlike DTBC, we do not obtain only two peaks but evidence of three peaks - a sharp peak at 3610 cm^{-1}, a relatively broad band at about 3490 cm^{-1} and a sign of a shoulder at 3360 cm^{-1}. The peaks at 3610 cm^{-1} and 3490 cm^{-1} are more likely due to the presence of the momomer and the dimer, respectively. A shoulder at 3360 cm^{-1} may probably be attributed to a tetramer (cyclic). At 233 K, 273 K and 293 K same peaks appear as at 213 K but increasing the temperature makes the 3360 cm^{-1} shoulder rather weak.

3. Diethyl isopropyl carbinol (DEIC)

DEIC was scanned at 0.73 M in polystyrene from 113 K to 293 K (see Figure III-4). At 113 K a sharp peak at 3580 cm^{-1}, an indication of a shoulder at about 3470 cm^{-1}, the appearance of another shoulder at about 3360 cm^{-1}, and a very broad band which appears to centre at 3220 cm^{-1} were observed. As before, a peak at 3580 cm^{-1} and a shoulder at about 3470 cm^{-1} are probably the outcome of a monomer and a dimer (open and/or cyclic), respectively. A shoulder at 3360 cm^{-1} may again be attributed to the presence of a tetramer (probably cyclic). The broad peaks at $\sim$3220 cm^{-1} is believed to arise from the presence of a high polymer which may form at lower temperatures even in the most sterically hindered alcohol (in our case DTBC). The "associated band" (due to dimer, trimer, tetramer and/or high polymer) at 153 K and 193 K has grown so much in intensity that the assignment is almost impossible. However, a careful look at this band at both the temperatures reveals that there is an extremely weak shoulder at about 3470 cm^{-1}, probably due to the presence of a dimer. At 213 K, the situation is quite clear. A sharp peak at 3585 cm^{-1} and a relatively broad band at 3480 cm^{-1} appeared due to a monomer and a dimer, respectively. Besides a monomer and a dimer band, there is a sign of a shoulder at about 3400 cm^{-1} which suggests the presence of a trimer and/or a tetramer. A small and broad band at 3240 cm^{-1} indicates the presence of the higher polymer. At 233 K, 273 K and 293 K we get only a monomer and a dimer band at 3585 cm^{-1} and 3480 cm^{-1}, respectively.

4. tert-Butyl isopropyl carbinol (TBIC)

TBIC is studied in polystyrene at only one concentration, 0.70 M, and at temperatures from 113 K to 293 K (see Figure III-5). At 113 K TBIC gives a sharp peak at 3605 cm^{-1} and a very broad band which centres around 3230 cm^{-1}. A careful inspection of this broad band shows that there is one shoulder at about 3470 cm^{-1} and at 3370 cm^{-1} possibly due to a dimer/trimer and tetramer, respectively. The band at 3605 cm^{-1}, as discussed earlier, is due to the monomer and the broad band at 3230 cm^{-1} to the high polymer. The "associated band" at 153 K, 193 K and 213 K has grown so much in intensity that their correct assignment to certain species is not possible. However, it seems that at these temperatures the polymerized species, higher than the dimer, are very dominant. At 233 K and 273 K only two peaks appear, one at 3605 cm^{-1} and the other at 3495 cm^{-1} which are the most probable candidates for the monomer and dimer, respectively. At 293 K the monomer band is observed at 3610 cm^{-1} and a weak dimer band at 3500 cm^{-1}.

5. tert-Butyl ethyl methyl carbinol (TBEMC)

TBEMC is studied at 0.75 M, from 113 K to 293 K (see Figure III-6). At 113 K, 153 K and 193 K, besides a monomer peak at 3600 cm^{-1} and an indication of a possible dimer band at 3480 cm^{-1}, the associated band grows too intense, thus making its attribution to certain species almost impossible. However, at 213 K, 233 K and 273 K there is a sharp monomer peak at 3600 cm^{-1} and a conspicuous dimer band at about 3500 cm^{-1}. At all these temperatures, 213 K, 233 K and 273 K, however, a very weak and not readily discernible peak seems to appear at about 3230 cm^{-1}, probably due to a high polymer. At 293 K only a monomer, 3600 cm^{-1}, and a dimer, 3500 cm^{-1}, band appear.

6. Isopropyl ethyl methyl carbinol (IEMC)

This compound is studied in polystyrene at 1.00 M from 113 K to 293 K (see Figure III-7). At 113 K and 153 K it gives a sharp peak at about 3580 cm^{-1}, a shoulder at about 3360 cm^{-1} and a broad band at 3220 cm^{-1}. The peak at 3580 cm^{-1} possesses all the characteristics of a monomer O-H stretching peak; therefore, the most likely candidate for this peak is the monomer. A shoulder at about 3360 cm^{-1} and a broad band at $\sim$3220 cm^{-1} correspond to the cyclic tetramer and the high polymer of ethanol in an argon matrix (10). Owing to a tremendous increase in intensity of "associated band" at 193 K and 213 K, the monomer band becomes very weak and appears at $\sim$3575 cm^{-1}. However, the assignment to associated species cannot be made owing to the enhanced intensity of the "associated band ". Thus it is evident that from 113 K to 213 K IEMC is polymerized into a larger species than the dimer. At 233 K, IEMC gives a monomer band at 3580 cm^{-1}, a dimer band at 3470 cm^{-1} and an indication of a shoulder at 3350 cm^{-1} for tetramer (probably cyclic). At 273 K and 293 K only monomer, 3590 cm^{-1} and dimer, 3480 cm^{-1} bands are observed.

TYPE "B"

7. Dimethyl-tert-butyl carbinol (DMTBC)

DMTBC is scanned in polystyrene at one concentration, 0.93 M, from 113 K to 293 K (see Figure III-8). At 113 K and 153 K it shows four conspicuous absorptions; a sharp peak at 3585 cm^{-1}, another sharp peak at 3465 cm^{-1}, an indication of a band at about 3380 cm^{-1} and a weak peak at 3220 cm^{-1}. A peak at 3585 cm^{-1} seems, most likely, a consequence of O-H stretching in an unbonded molecule (i.e. a monomer). Another sharp peak at 3465 cm^{-1} seems to arise from the presence of a dimer (cyclic and/or open). A shoulder at 3380 cm^{-1} and a weak peak at 3220 cm^{-1} corresponds, respectively, to a cyclic tetramer and a high polymer of ethanol in an argon matrix (10). When the temperature reaches 193 K, a peak, which appeared at 3220 cm^{-1}, vanished. However, bands at 3585 cm^{-1}, 3470 cm^{-1} and 3380 cm^{-1} are still present. At 203 K and 213 K peaks at 3585 cm^{-1}, 3475 cm^{-1} and a shoulder at about 3360 cm^{-1}, appear which are due to a monomer, dimer, and probably, a tetramer (cyclic). It is worth noting that, as the temperature increases from 113 K to 213 K, the polymerized species larger than the dimer decreases tremendously. At 233 K hardly any distinguishable peak at about $\sim$3360 cm^{-1} is present. However, the asymmetry of the dimer band, 3490 cm^{-1}, indicates that there is a polymerized species (probably tetramer) at about $\sim$3380 cm^{-1} in extremely low concentration. At 273 K and 293 K only monomer, 3590 cm^{-1}, and dimer, 3480 cm^{-1}, bands are present.

8. tert-Butyl methyl carbinol (TBMC)

The infrared spectrum of TBMC in polystyrene at 0.93 M which has been examined from 113 K to 293 K, has shown at least four absorption bands related to O-H stretching (see Figure III-9). At 113 K and 153 K there is one sharp peak at 3585 cm^{-1}, a distinct shoulder at ∿3450 cm^{-1}, another shoulder at about 3330 cm^{-1} and a peak at 3220 cm^{-1}. A peak at 3585 cm^{-1} may be attributed to the O-H stretching of the monomer and a shoulder at about 3450 cm^{-1} may be due to the presence of a dimer and/or a trimer. A shoulder at about 3330 cm^{-1} may be an outcome of the presence of a tetramer while a sharp band at 3220 cm^{-1} is believed to arise from a high polymer. As the temperature goes up from 153 K to 193 K, the ∿3450 cm^{-1} shoulder disappears, and the shoulder at about 3350 cm^{-1} remains. The monomer band now appears at 3590 cm^{-1} and a high polymer band shows up at 3230 cm^{-1} which is now broader relative to two lower temperatures (viz. 113 K and 153 K). At 213 K the monomer band appears at 3595 cm^{-1} and another absorption at about 3450 cm^{-1} may be due to the dimer and/or the trimer. The 3220 cm^{-1} band, on the other hand, has disappeared at this temperature. However, the shoulder at ∿3370 cm^{-1}, probably due to a tetramer, is still present. Increasing the temperature from 213 K to 233 K makes a slight difference in the spectrum. The monomer band now appears 3595 cm^{-1}, and the "associated band" (dimer, trimer, tetramer and so on) gives a weak shoulder at about 3460 cm^{-1}. At 273 K and 293 K the monomer band appears at 3600 cm^{-1} and the "associated band" seems to centre at 3480 cm^{-1}. However, the "associated band" is very asymmetrical, thus giving an indication that besides the dimer at 3480 cm^{-1}, it also receives some contribution from the polymer (probably the tetramer).

9. Dimethyl isopropyl carbinol (DMIC)

DMIC has also been studied at 0.93 M from 113 K to 293 K (see Figure III-10). At the lowest temperature, 113 K, it shows a sharp peak at 3570 cm^{-1}, a shoulder at ∿3460 cm^{-1}, another shoulder at ∿3360 cm^{-1} and a sharp peak at 3220 cm^{-1}. As with TBMC, the peak at 3570 cm^{-1} and a shoulder at ∿3460 cm^{-1} may arise from a monomer and dimer and/or trimer, respectively. A shoulder at ∿3360 cm^{-1} and a peak at 3220 cm^{-1} correspond to a cyclic tetramer and a high polymer, respectively, of ethanol in an argon matrix (10). The spectra at 153 K and 193 K have almost similar features as the spectrum at 113 K, except that at the former two temperatures the shoulder at ∿3460 cm^{-1} has disappeared. At 213 K the monomer band is at 3575 cm^{-1} and the 3220 cm^{-1} band becomes broad and flat and appears to be disappearing. However, the shoulder at ∿3380 cm^{-1} still exists. At 233 K and 273 K there is no high polymer band at 3220 cm^{-1}.

However, a broad, weak band which shows some asymmetry at the lower wave number side, appears at about 3475 cm^{-1}. A 3475 cm^{-1} band is believed to arise from dimer (cyclic and/or open) whereas the asymmetry in this band may be assumed to be an indication of extremely low concentration of the polymer being higher than the dimer. At 293 K only the monomer, 3590 cm^{-1}, and dimer, 3480 cm^{-1}, band are apparent.

TYPE "C"

10. Tricyclohexyl carbinol (TCHC)

TCHC is studied in polystyrene at 0.31 M from 113 K to 293 K (see Figure III-11). At 113 K and 153 K, TCHC showed an absorption split into a doublet at 3600 cm^{-1} and 3580 cm^{-1}. The "associated band" shows a shoulder at about 3355 cm^{-1} and a peak at about 3220 cm^{-1}. TCHC had previously been studied in CCl_4 solution at different concentrations and at ambient temperature (16). The dilute solution of TCHC in carbon tetrachloride showed an incompletely resolved doublet with an absorption maximum at 3632 cm^{-1} and a shoulder at 3614 cm^{-1}. In a concentrated solution an additional band at 3525 cm^{-1} has also been observed. The doublet was assigned to various orientations of the OH group in the monomer TCHC and the band at 3525 cm^{-1} to the dimer. The analogy of the split peak of TCHC in polystyrene with a TCHC doublet in carbon tetrachloride permits us to reasonably assign the split peak to two different orientations of the OH group in the monomer. The difference of ∿32 cm^{-1} from CCl_4 to polystyrene solution may be understood from the fact that when we move from CCl_4 to toluene, which is close to one polystyrene unit, there is a difference of about ∿34 cm^{-1} in the monomer stretching frequency (4). A shoulder at about 3355 cm^{-1}, as in other cases, may arise from the presence of a tetramer (probably cyclic). The 3220 cm^{-1} band is believed to arise from a high polymer. The "associated band" at 193 K and 213 K grew so much that its correct assignment was quite difficult. At 233 K, 273 K and 293 K there is only one absorption, with the doublet now centering at ∿3610 cm^{-1} and 3590 cm^{-1}, obviously due to the monomer.

11. Diphenyl methyl carbinol (DPMC)

The infrared spectrum of DPMC in polystyrene at 0.25 M from 113 K to 293 K showed, at the most, three absorptions associated with the OH group of the alcohol (see Figure III-12). At 113 K and 153 K there is one sharp peak at 3560 cm^{-1}, a sign of a shoulder at about 3370 cm^{-1} and a peak at 3220 cm^{-1}. Most likely the peak at 3560 cm^{-1} is an outcome of the OH stretching of the monomer. A shoulder at about 3370 cm^{-1}, as in others, may be due to tetramer (cyclic), whereas a peak at 3220 cm^{-1} belongs to the high polymer. At 193 K the "associated band" has grown so much in intensity that the correct assignment is not possible. At 213 K, 233 K, 273 K and 293 K there is no sign of a high polymer. However, a band, 3460 - 3470 cm^{-1}, at all the four temperatures is observed and assumed to arise from the dimer (cyclic/open).

12. Dimethyl benzyl carbinol (DMBC)

The infrared spectrum of DMBC is measured in polystyrene at 0.92 M from 113 K to 293 K (see Figure III-13). At 113 K a sharp peak appears at 3560 cm^{-1}, a broad band which shows the sign of two peaks, one centering at ∿3420 cm^{-1} and another at ∿3350 cm^{-1}, and a shoulder at 3220 cm^{-1}. A peak at 3560 cm^{-1} seems to arise from the presence of a monomer, whereas the sign of a peak at ∿3420 cm^{-1} may be due to a dimer/trimer and/or an open tetramer. Another sign of a peak at ∿3350 cm^{-1} may be attributed to a cyclic tetramer. A peak at 3220 cm^{-1}, as discussed earlier, is probably due to a high polymer. Increasing the temperature from 113 K to 153 K does not lead to much change in the spectrum except that now the two peaks at ∿3420 cm^{-1} and ∿3350 cm^{-1} are not well resolved. At 193 K a monomer peak appears at 3570 cm^{-1}. A band which centres at ∿3440 cm^{-1} and a shoulder at ∿3350 cm^{-1} may arise from the dimer and/or trimer and cyclic tetramer, respectively. At

203 K, 213 K and 233 K the same features are obtained as at 193 K. At 273 K and 293 K a monomer band appears at 3575 cm^{-1} while a band, probably due to a dimer, centres at ∿3450 cm^{-1} with apparent asymmetry towards the low frequency side.

13. Dimethyl phenyl carbinol (DMPC)

DMPC is scanned in polystyrene at 1.30 M from 113 K to 293 K (see Figure III-14). At 113 K, and 153 K a very weak peak seems to centre at about 3560 cm^{-1}, an inconspicuous shoulder at about 3360 cm^{-1}, and a broad band at about 3220 cm^{-1}. The analogy of these peaks with DPMC indicates that they can be attributed to the monomer, tetramer (cyclic) and high polymer respectively. At 193 K the "associated band" is too strong and squared off, so to attribute it to certain species is not possible. However, a very weak shoulder for the monomer at about 3560 cm^{-1} seems to appear. At 213 K and 233 K, besides a monomer band, a very broad band centres at about 3360 cm^{-1} with an inconspicuous asymmetry towards the high frequency side. Thus, it seems that this broad band is a composite band for the dimer, tetramer and probably trimer which could not be resolved into individual peaks. At 273 K and 293 K the same situation persists with the difference that in this case the band seems to centre at 3380 cm^{-1}.

CONCLUSION

From the foregoing discussion it is evident that in sterically hindered alcohols in polystyrene matrix, we get, at least, four kinds of species, namely, monomer, dimer, tetramer and high polymer though at the moment we cannot say with great confidence that in all the alcohols, the dimer peak is well resolved from other high polymeric species. It is also clear that at the lowest temperature, here 113 K, and at the concentrations used here all our alcohols show a high polymer, 3220 cm^{-1}, band. Most of the alcohols at 233 K and at the concentrations used always give a monomer and a dimer band and never a high polymer, 3220 cm^{-1}, band. The infrared spectra of the three groups, A, B and C, indicate the relative magnitude of steric hindrance in the vicinity of the OH group at given temperatures and concentrations as:

A. Di-tert-butyl carbinol > Diethyl isopropyl carbinol > Diisopropyl methyl carbinol > tert-Butyl ethyl methyl carbinol ≈ Isopropyl ethyl methyl carbinol > tert-Butyl isopropyl carbinol.

B. Dimethyl-tert-butyl carbinol > Dimethyl isopropyl carbinol ≈ tert-Butyl methyl carbinol.

C. Tricyclohexyl carbinol $\approx$ Diphenyl methyl carbinol > Dimethyl benzyl carbinol > Dimethyl phenyl carbinol.

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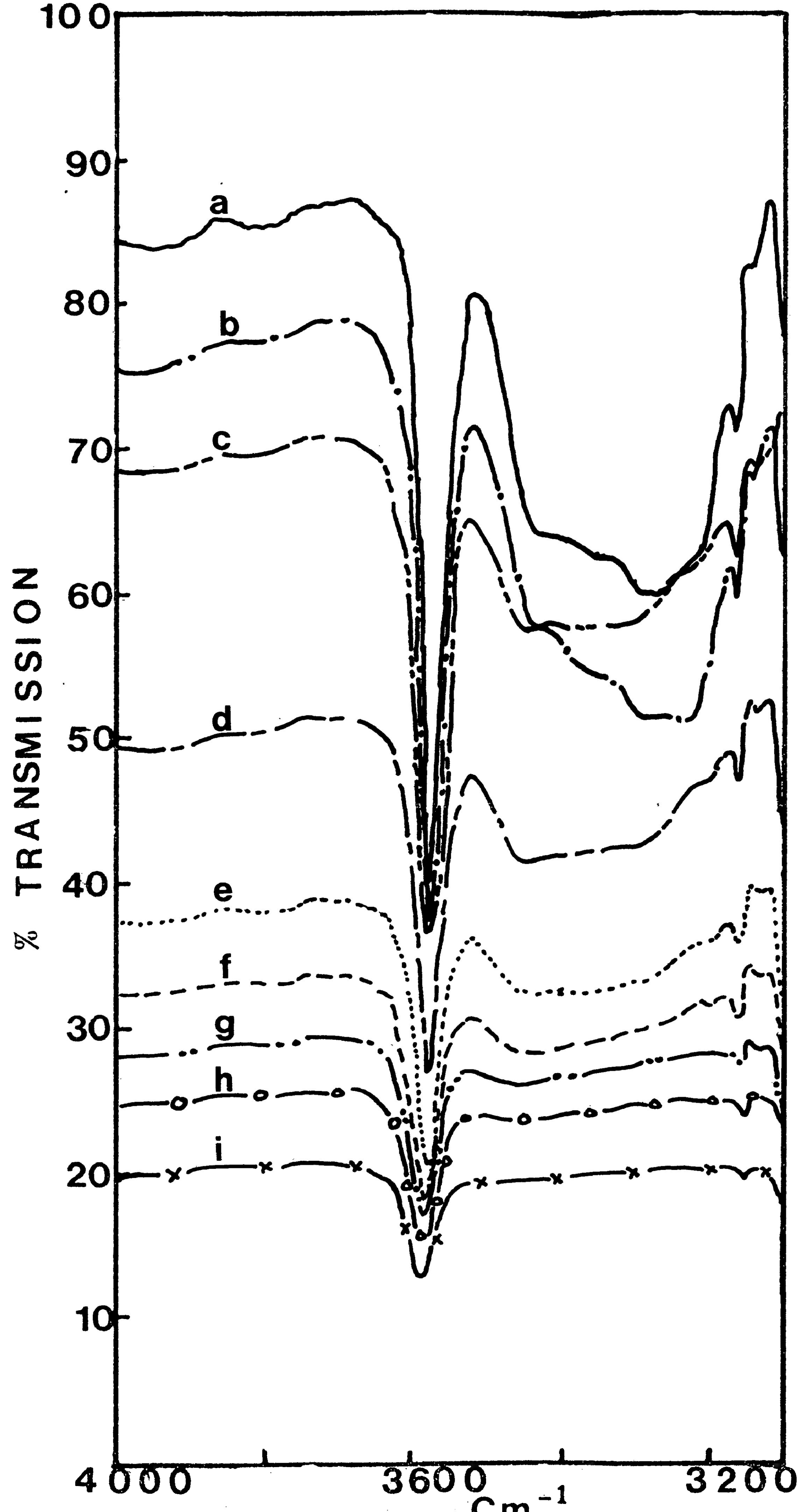


FIGURE III-1: Infrared spectrum of ethanol in polystyrene (thickness = 0.31 mm and concentration = 2.30 M) at a= 113 K; b = 153 K; C = 193 K; d = 203 K; e = 213 K; f= 233 K; g = 273 K; h = 293 K and i = 313 K.

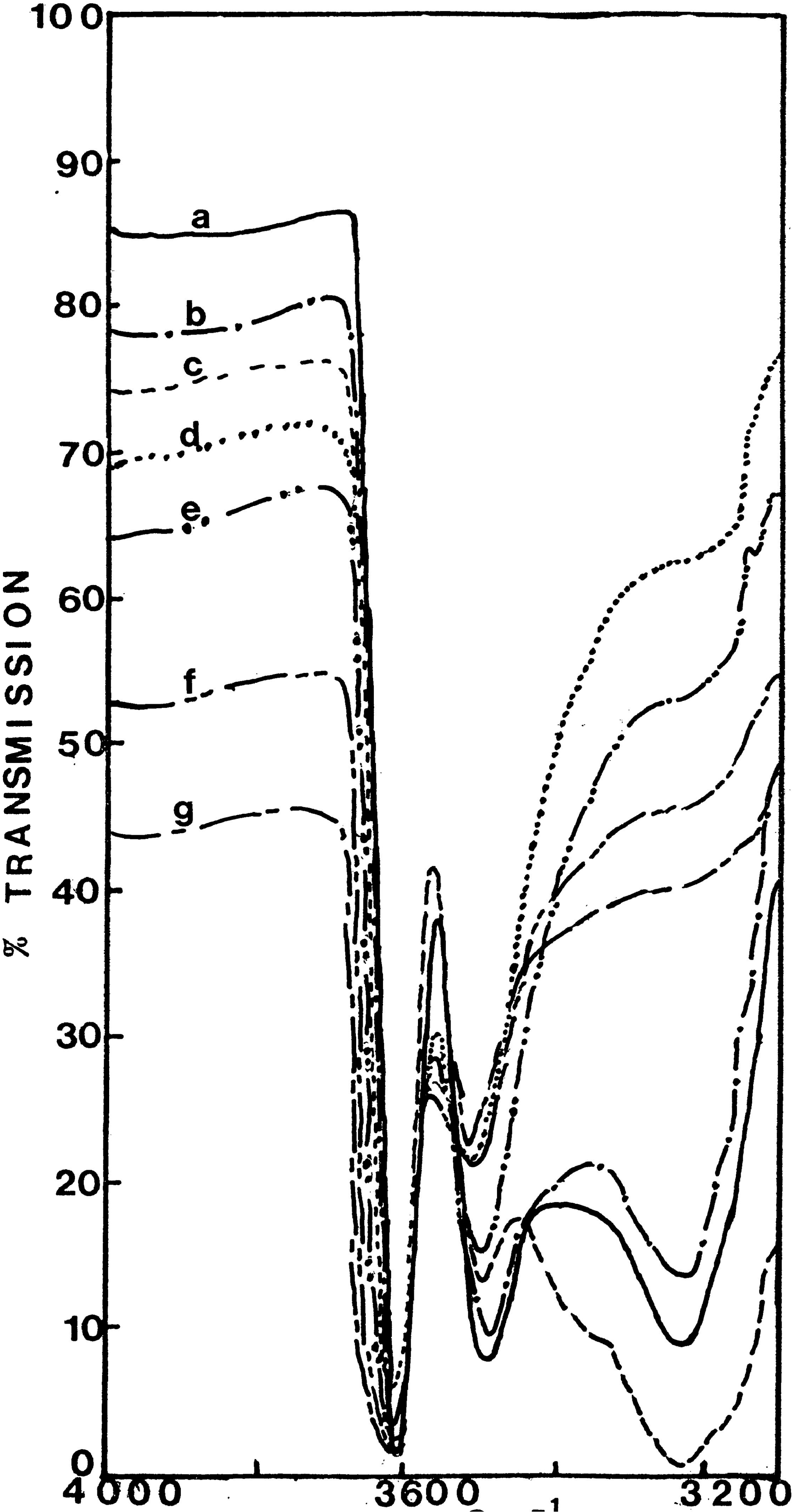


FIGURE III-2a: Infrared spectrum of di-tert-butyl carbinol in polystyrene (thickness = 0.30 mm and concentration = 0.70 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

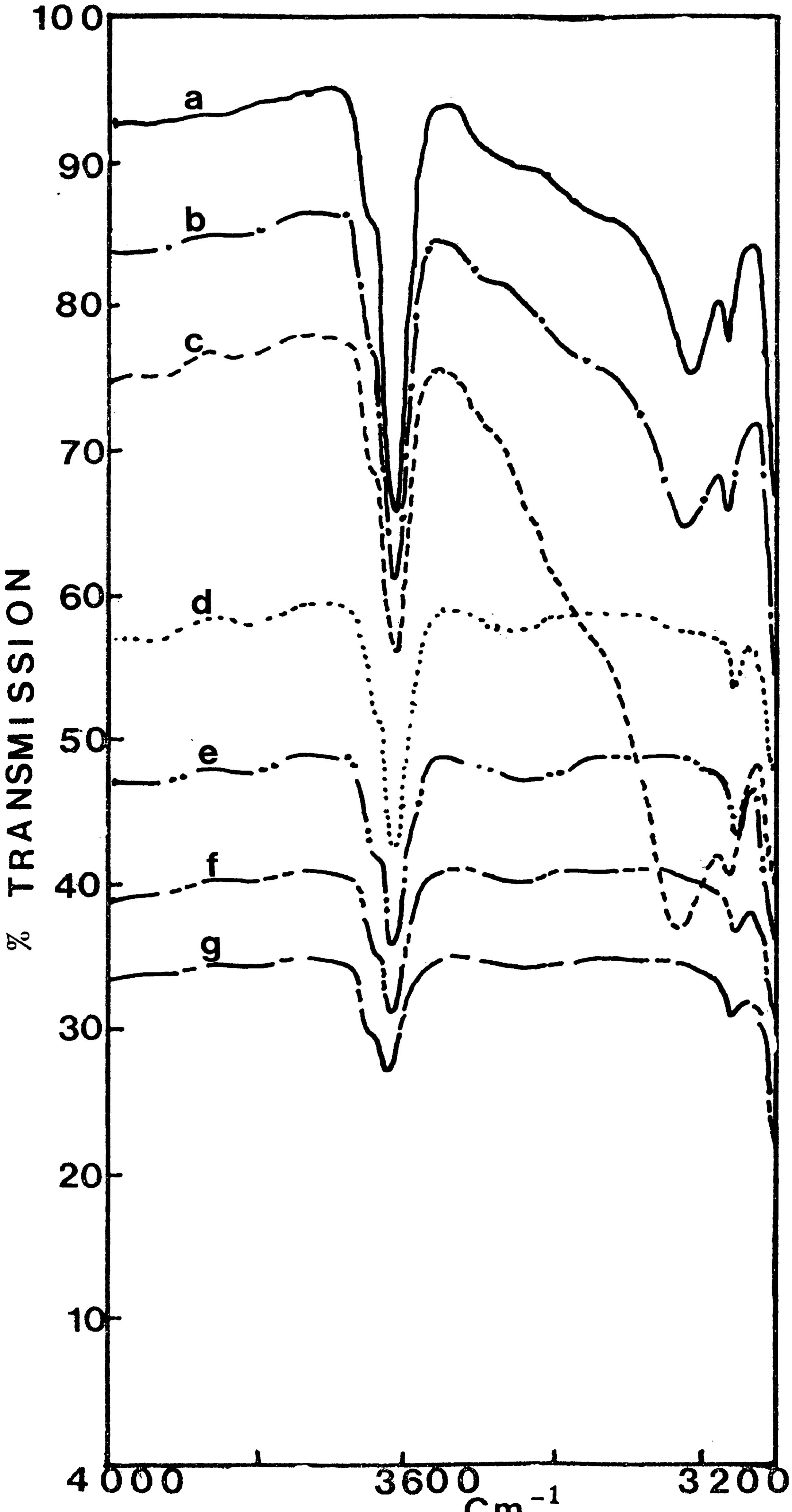


FIGURE III-2b: Infrared spectrum of di-tert-butyl carbinol in polystyrene (thickness = 0.15 mm and concentration = 0.07 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

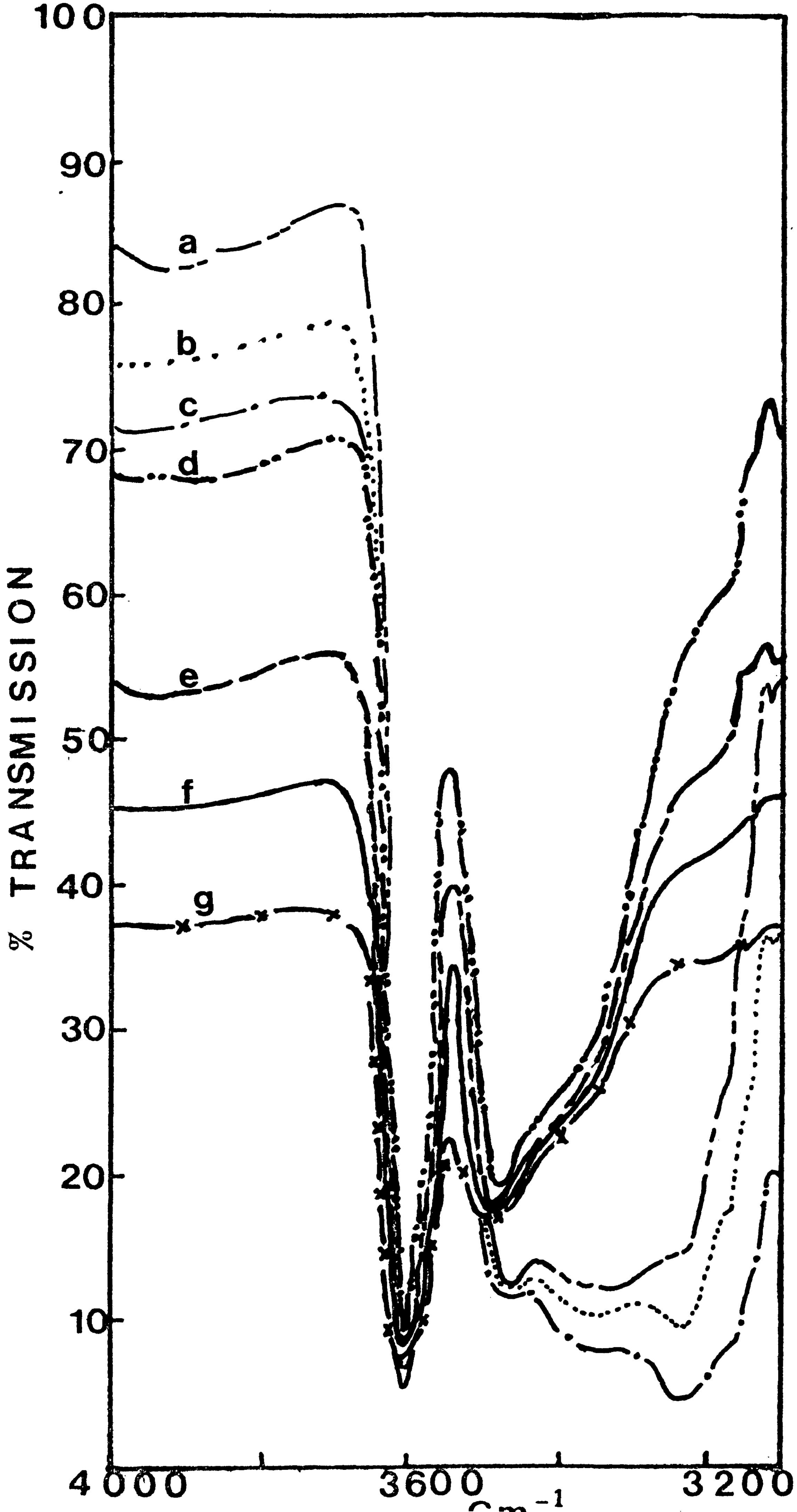


FIGURE III-3: Infrared spectrum of diisopropyl methyl carbinol in polystyrene (thickness = 0.30 mm and concentration = 0.75 M) at a = 113 K; b = 153 K, c = 193 K, d = 213 K, e = 233 K; f = 273 K and g = 293 K.

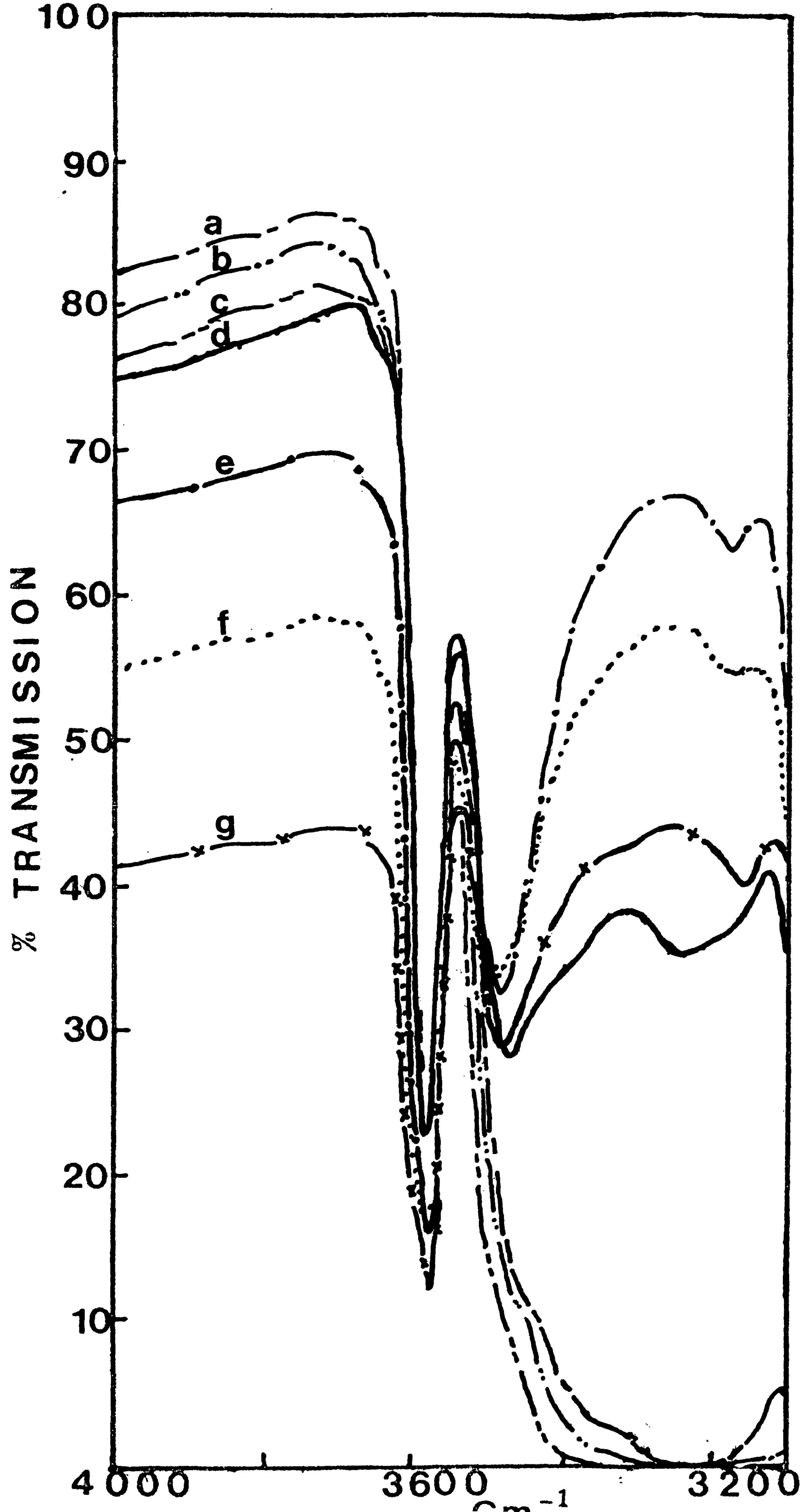


FIGURE III-4: Infrared spectrum of diethyl isopropyl carbinol in polystyrene (thickness = 0.15 mm and concentration = 0.73 M) at a = 113 K; b = 153 K; c = 193 K, d = 213 K; e = 233 K; f = 273 K and g = 293 K.

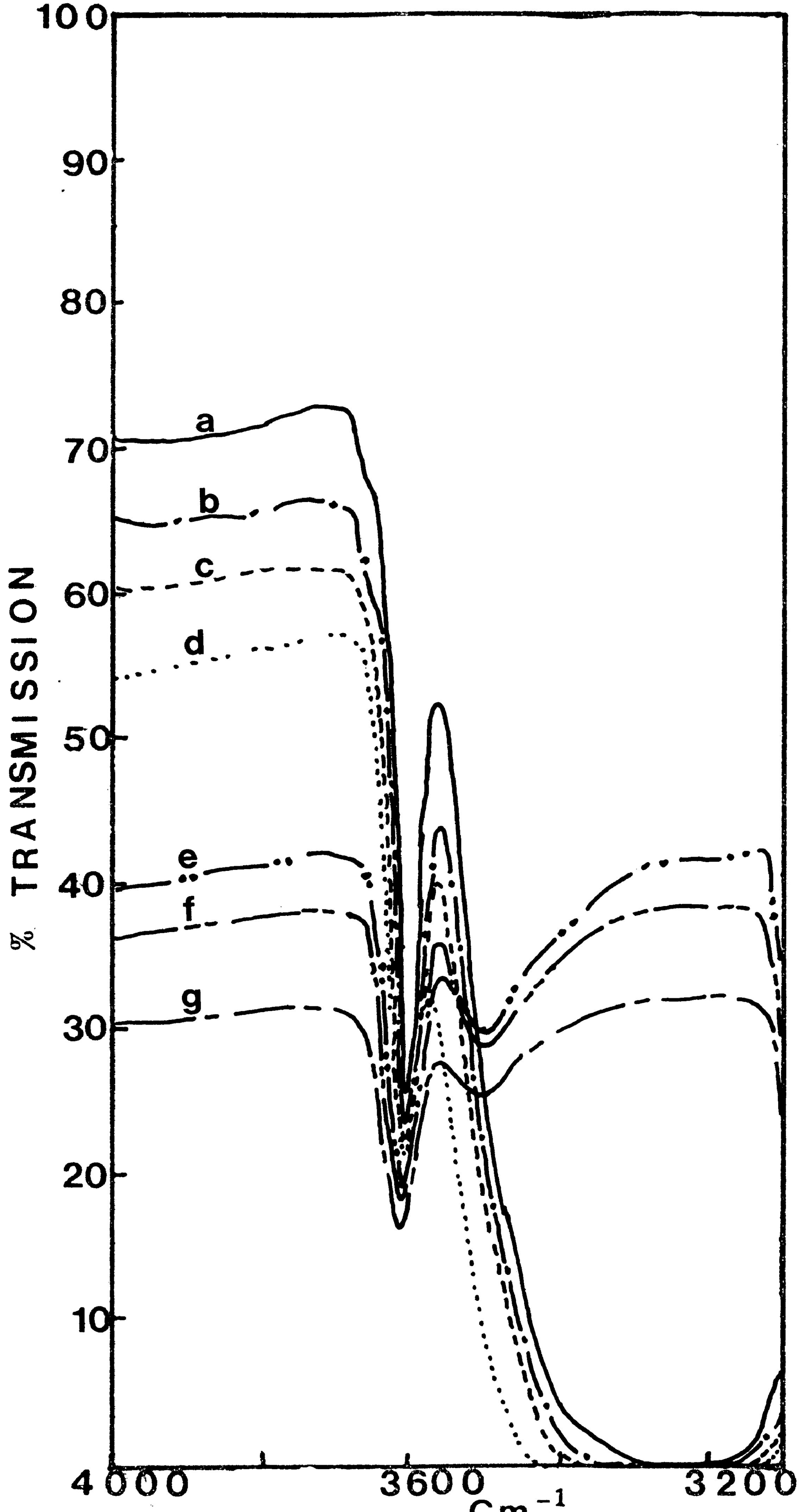


FIGURE III-5: Infrared spectrum of tert-butyl isopropyl carbinol in polystyrene (thickness = 0.10 mm and concentration = 0.70 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

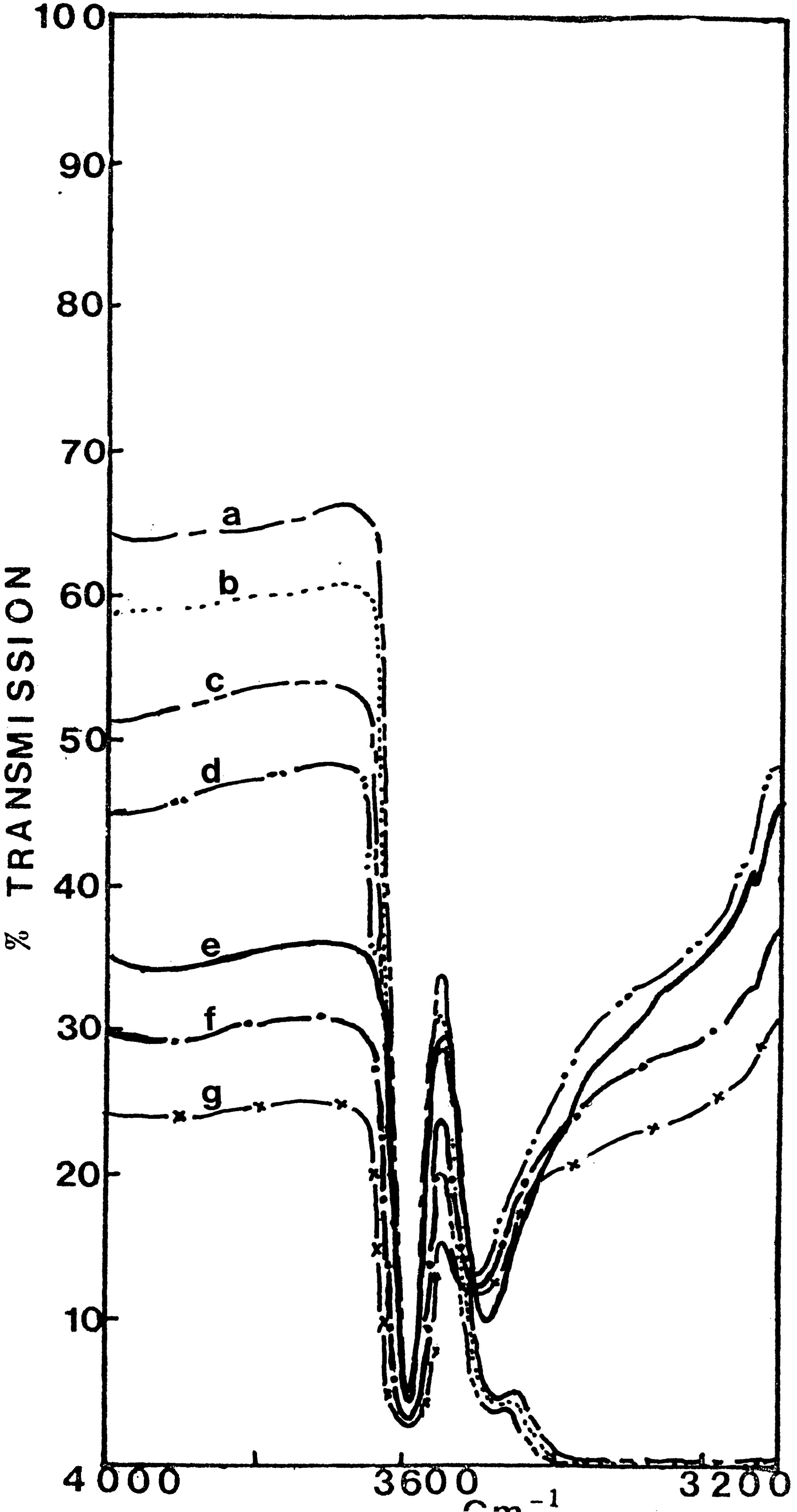


FIGURE III-6: Infrared spectrum of tert-butyl ethyl methyl carbinol in polystyrene (thickness = 0.30 mm and concentration = 0.75 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

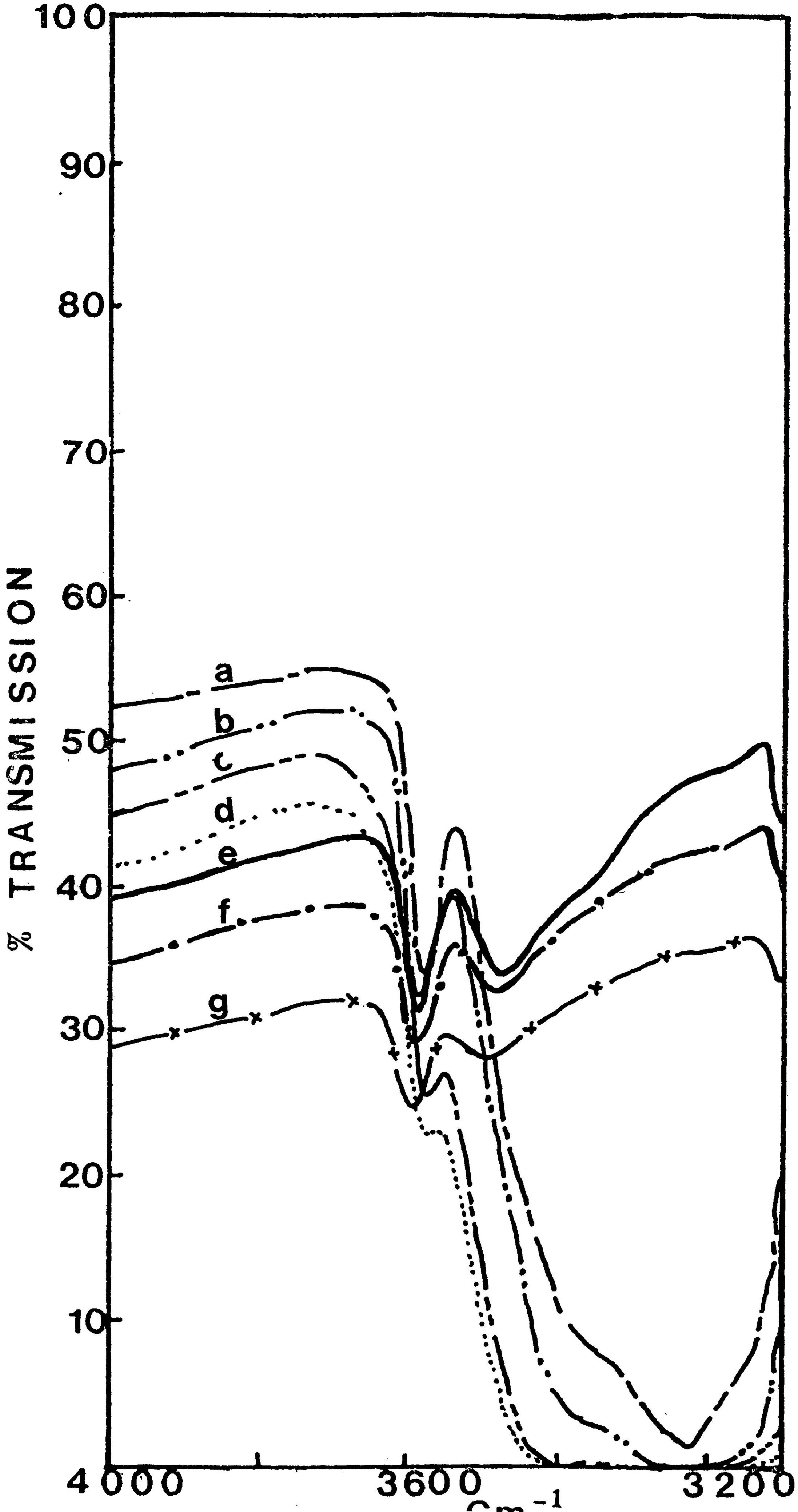


FIGURE III-7: Infrared spectrum of isopropyl ethyl methyl carbinol in polystyrene (thickness = 0.07 mm and concentration = 1.00 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

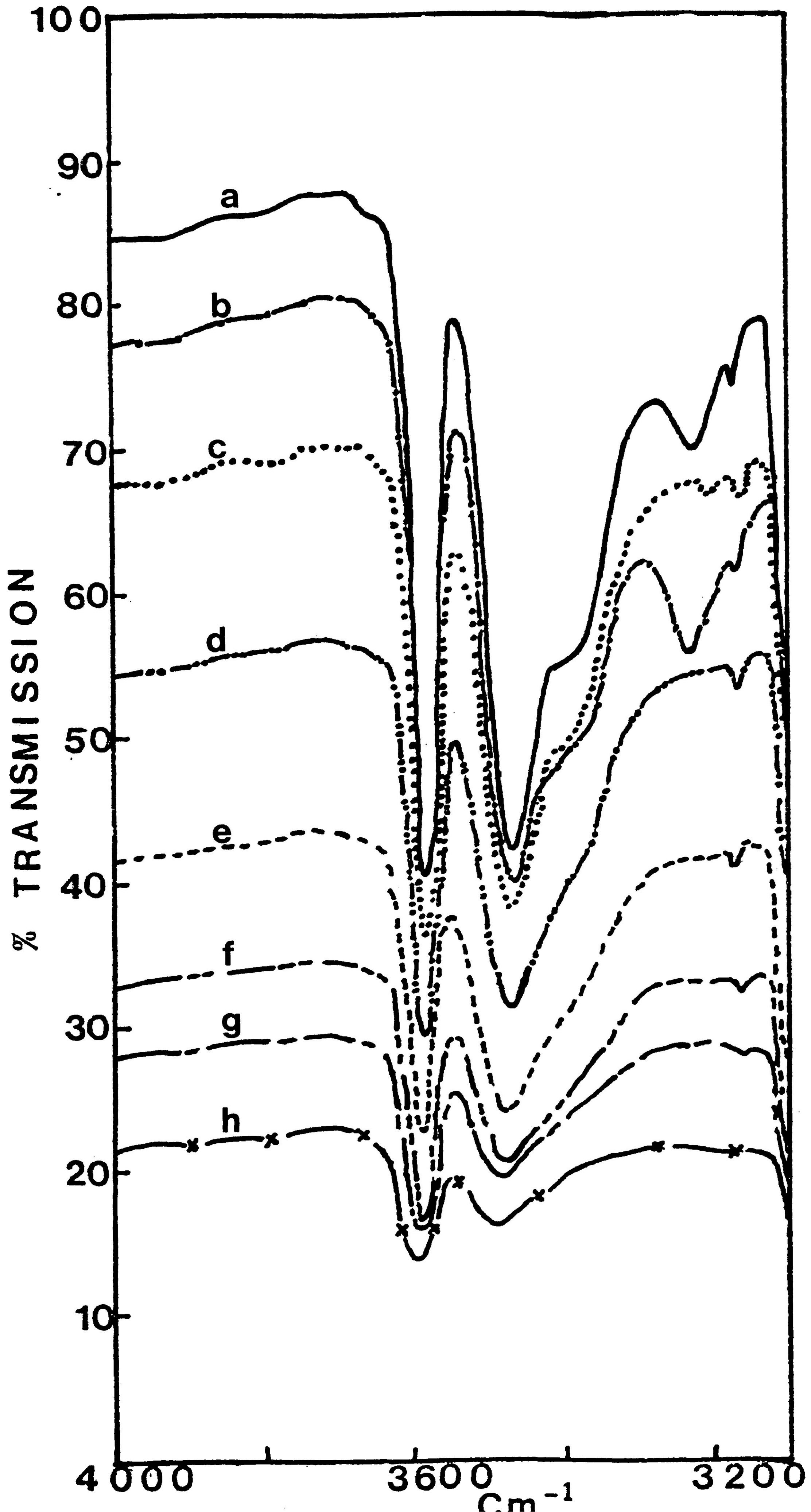


FIGURE III-8: Infrared spectrum of dimethyl-tert-butyl carbinol in polystyrene (thickness = 0.07 mm and concentration = 0.93 M) at a = 113 K; b = 153 K; c = 193 K; d = 203 K; e = 213 K; f = 233 K; g = 273 K and h = 293 K.

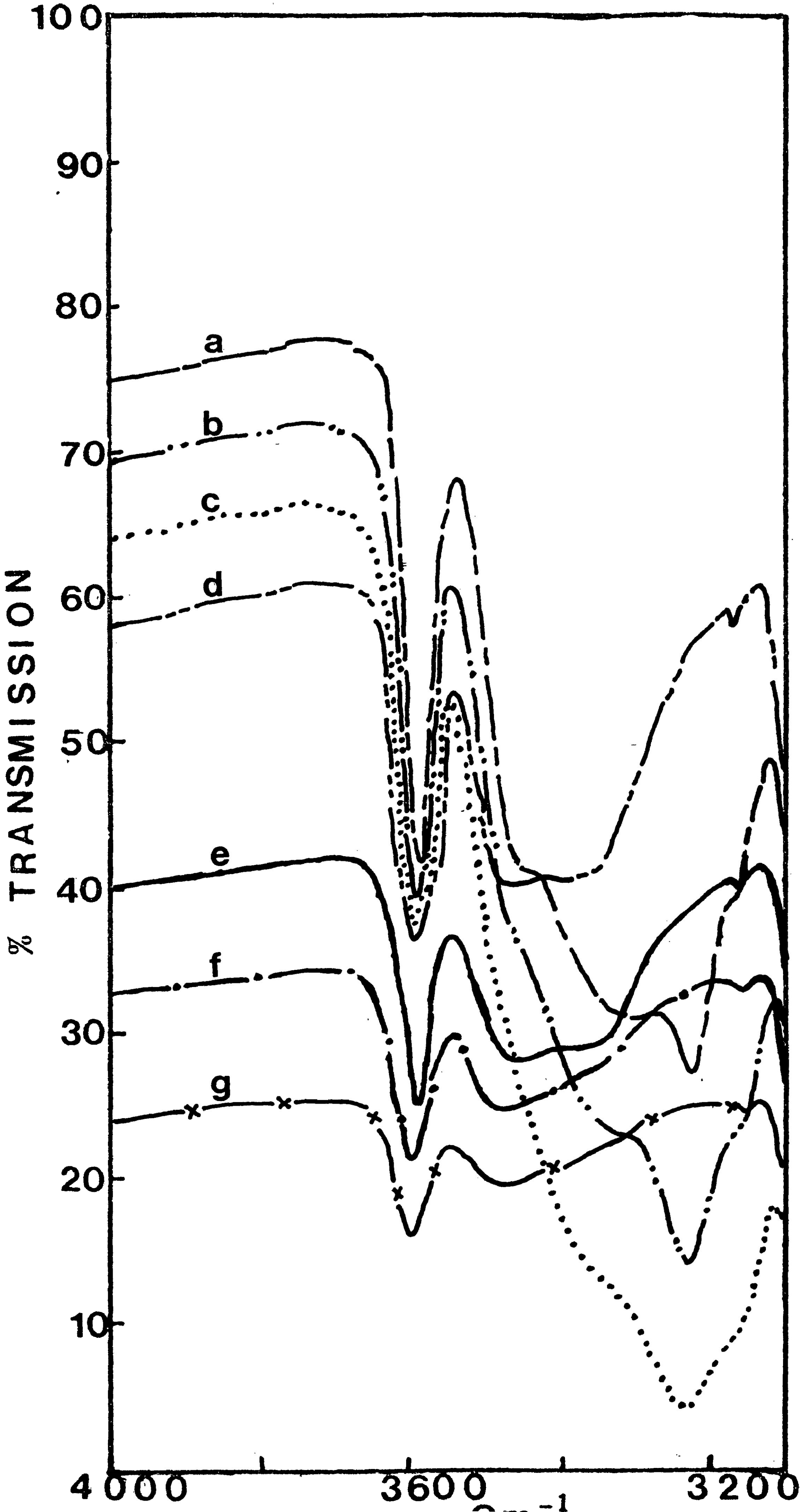


FIGURE III-9: Infrared spectrum of tert-butyl methyl carbinol in polystyrene (thickness = 0.07 mm and concentration = 0.93 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

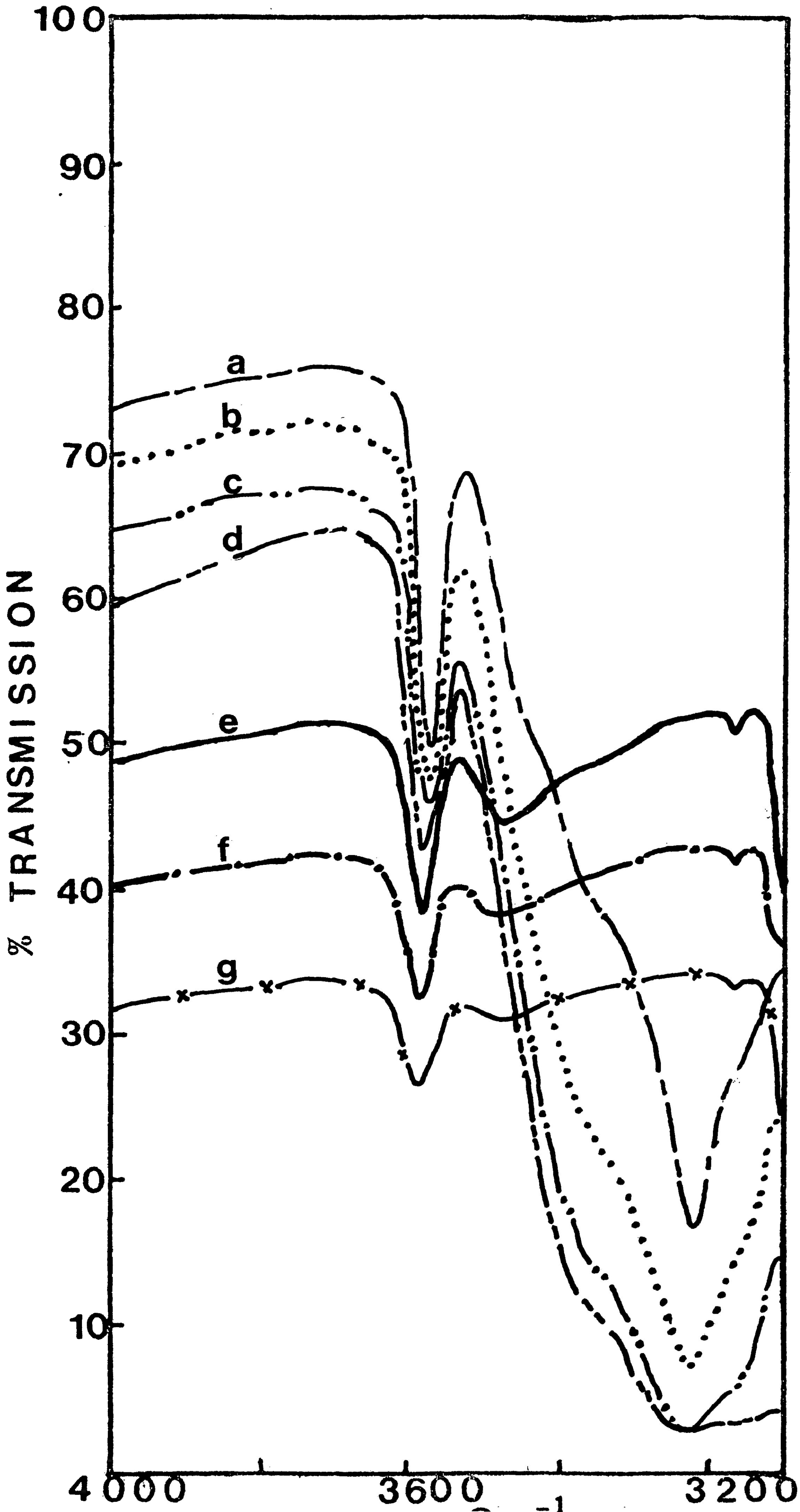


FIGURE III-10: Infrared spectrum of dimethyl isopropyl carbinol in polystyrene (thickness = 0.06 mm and concentration = 0.93 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

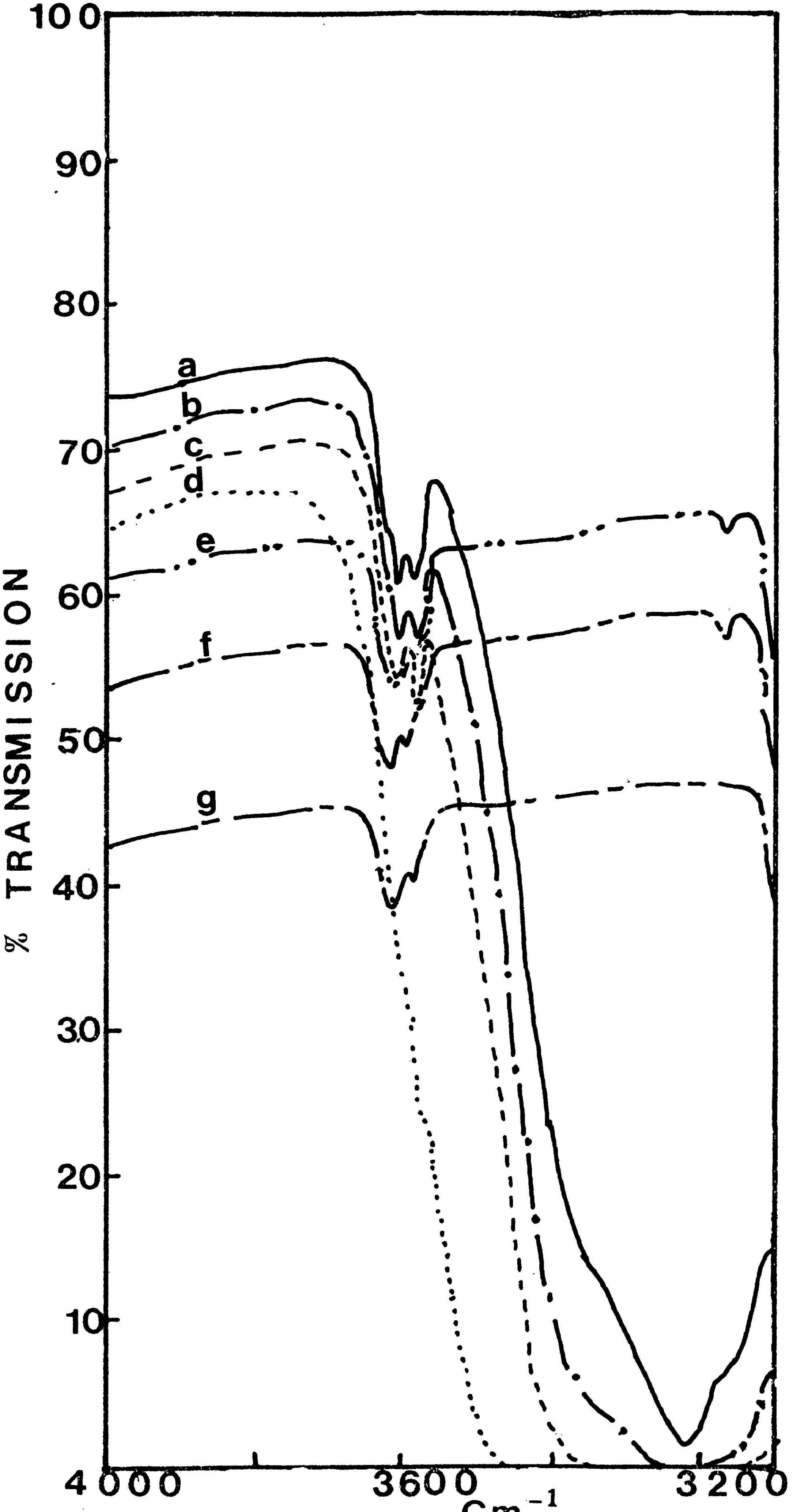


FIGURE III-11: Infrared spectrum of tricyclohexyl carbinol in polystyrene (thickness = 0.08 mm and concentration = 0.31 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and g = 293 K.

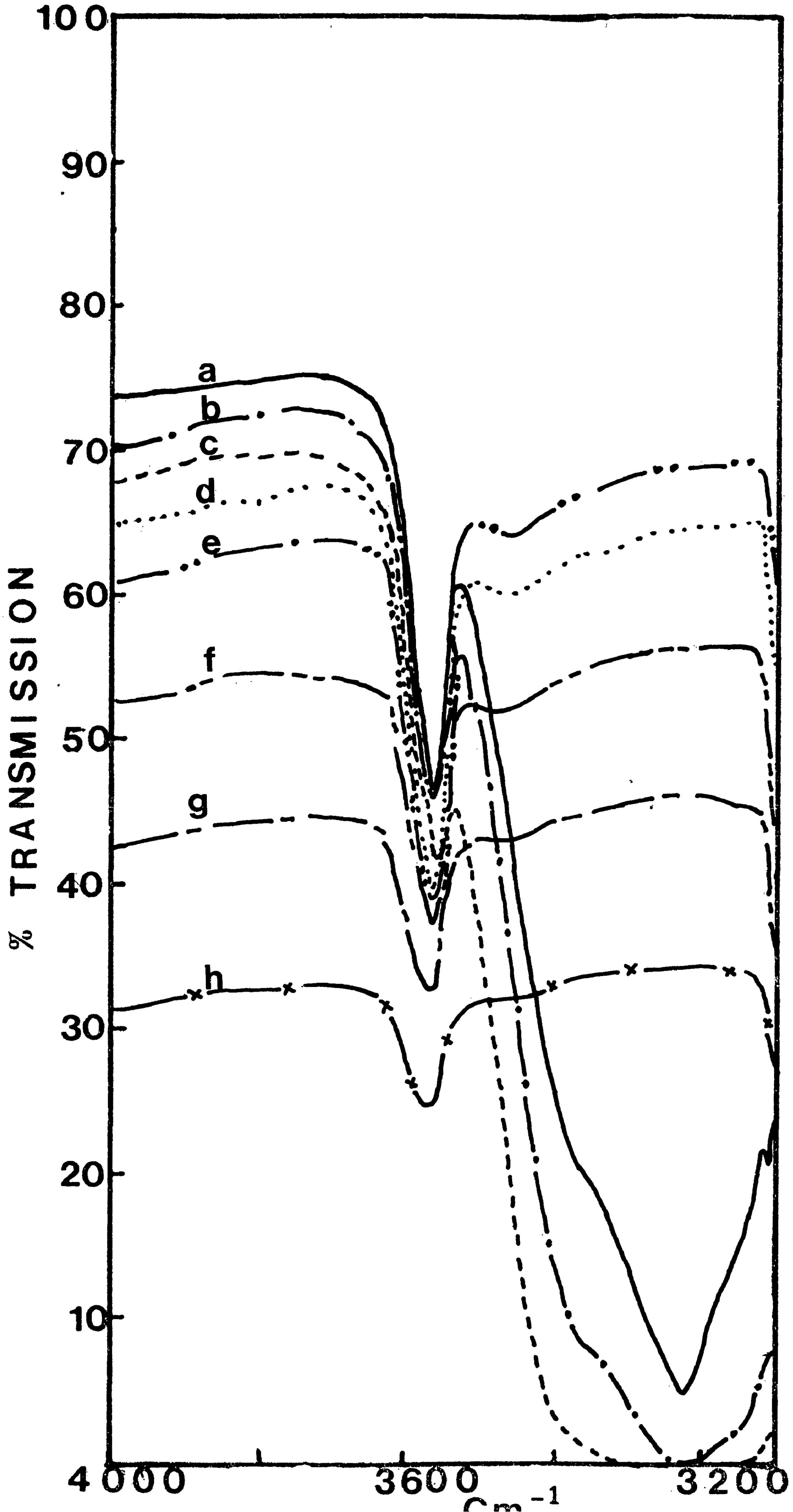


FIGURE III-12: Infrared spectrum of diphenyl methyl carbinol in polystyrene (thickness = 0.08 mm and concentration = 0.25 M) at a = 113 K; b = 153 K; c = 193 K; d = 203 K; e = 213 K; f = 233 K g = 273 K and h = 293 K.

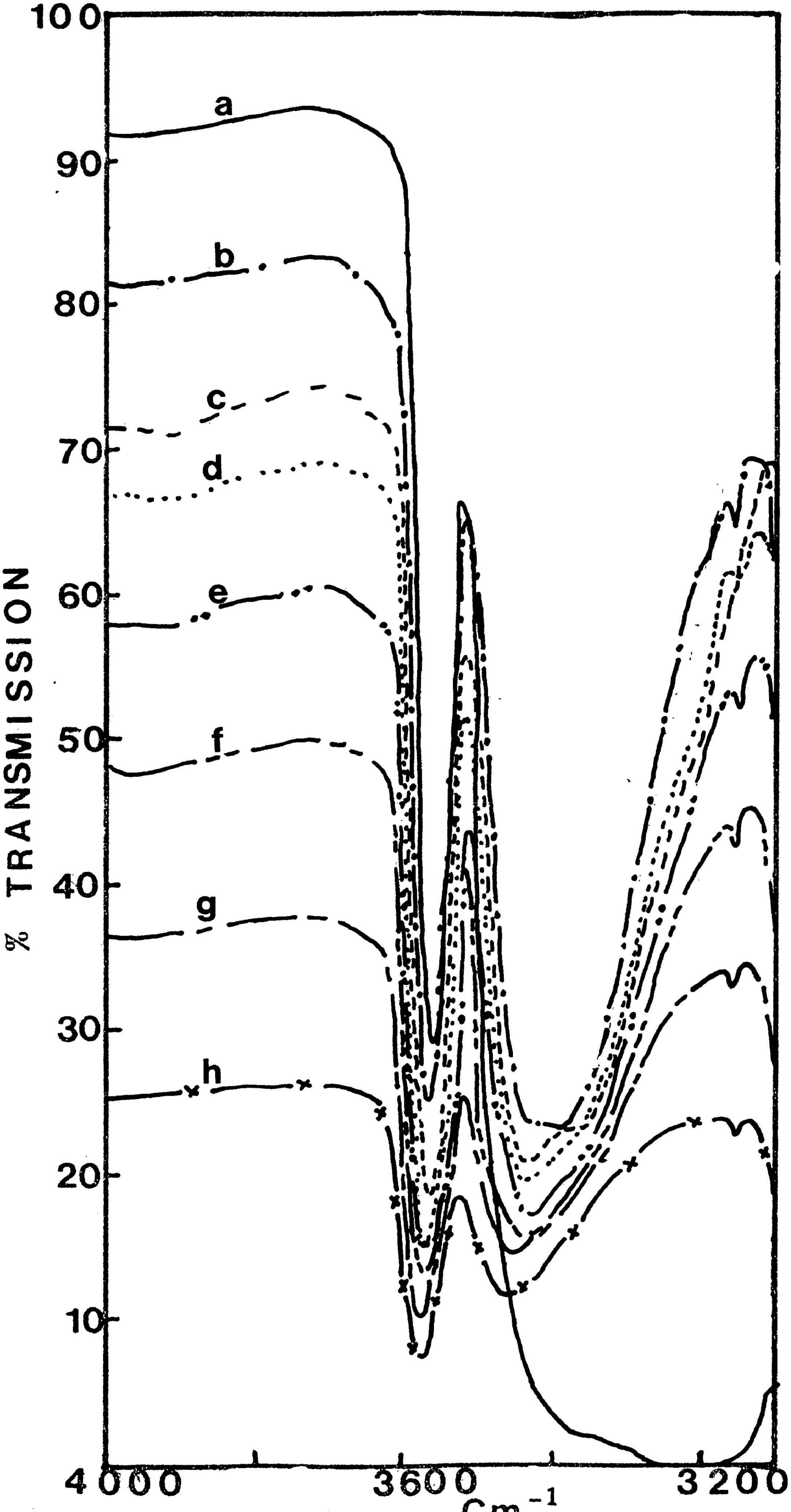


FIGURE III-13: Infrared spectrum of dimethyl benzyl carbinol in polystyrene (thickness = 0.15 mm and concentration = 0.92 M at a = 113 K; b = 153 K; c = 193 K; d = 203 K; e = 213 K; f = 233 K; g = 273 K and h = 293 K.

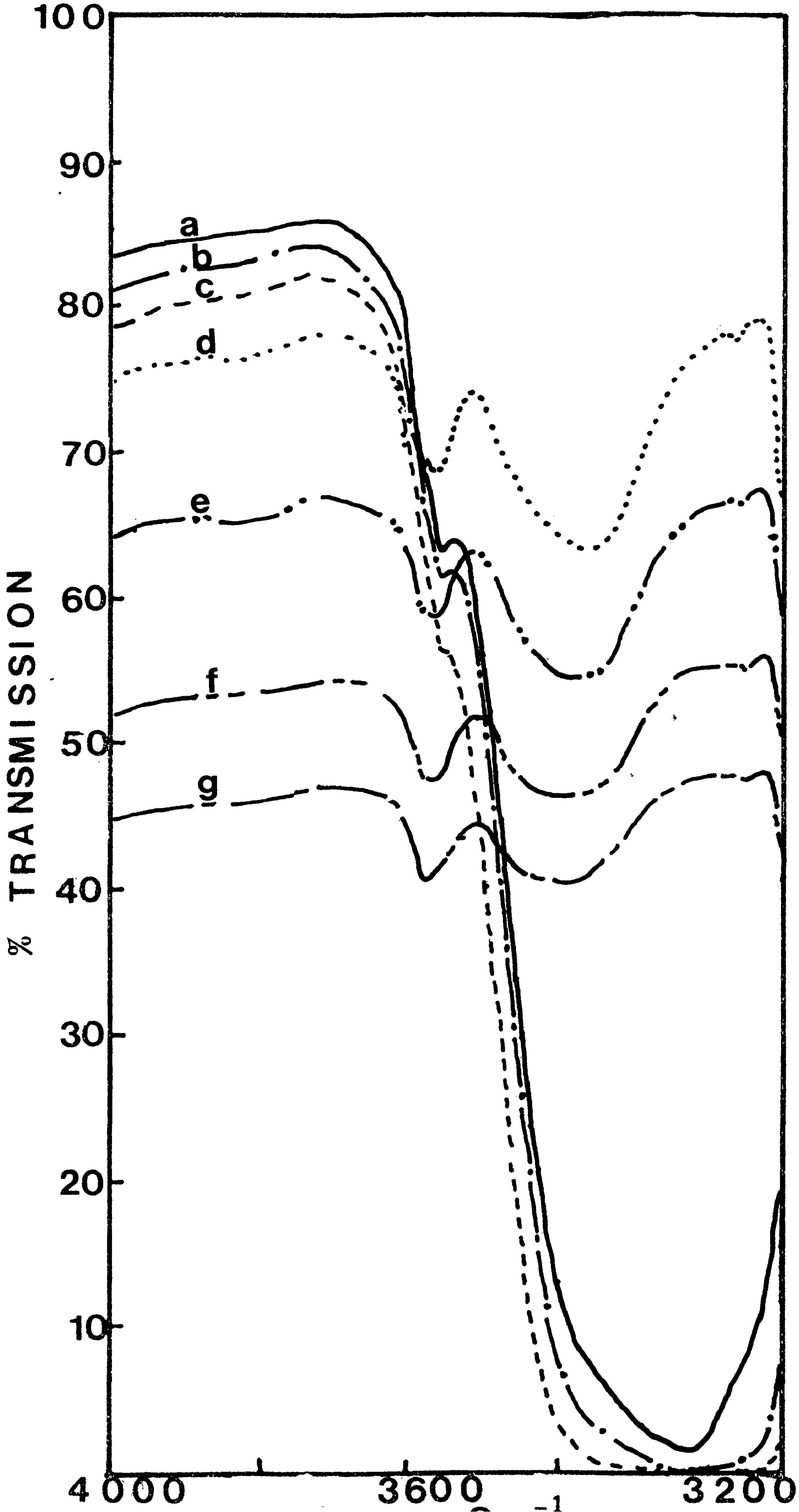


FIGURE III-14: Infrared spectrum of dimethyl phenyl carbinol in polystyrene (thickness = 0.02 mm and concentration = 1.30 M) at a = 113 K; b = 153 K; c = 193 K; d = 213 K; e = 233 K; f = 273 K and h = 293 K.

CHAPTER IV

DIELECTRIC RELAXATION STUDIES OF STRONGLY STERICALLY HINDERED ALCOHOLS MAINLY IN POLYSTYRENE

INTRODUCTION

From the dielectric studies (1,2) of numerous long chain molecules of the type $CH_3-(CH_2)_n-CH_2X$ (where X = OH, SH and Br) in a polystyrene matrix, it was apparent that the molecular process occurred in the temperature range ∿200-270 K for the frequencies of $10-10^5$ Hz. However, in the case of 1-alkanols the ΔH_E values did not form a consistent pattern and correlate with the corresponding 1-thiols and 1-bromoalkanes (2). It was suggested that the difference might be accounted for by significant intermolecular H-bonding in the case of the 1-alkanols. The alcohols chosen for the present study would be expected to yield a molecular process around 100 K. Thus, any additional process in the 200-270 K region would be available for more precise study. This was one of the major aspects of our present investigation.

Dielectric relaxation studies on liquid normal alcohols have revealed that the dielectric dispersion may be characterized by three relaxation regions (3-6). The high frequency dispersion is attributed to an OH-group reorientation whereas the intermediate dispersion is suggested to be a contribution from a molecular rotation, and end group of linear polymer and/or a smaller polymer reorientation. The low frequency dispersion is a dominant process and characterized by a simple Debye nature. The mechanism of the low frequency dispersion has been the subject of countless investigations and various interpretations (4,5,7-11).

Johari and Dannhauser (12) have carried out a dielectric study of some sterically hindered octanols in the pure liquid state. They have concluded that the octanol isomers in which the environment about the OH-group is sterically hindered by an alkyl group on the same or on the next carbon atom tend to associate into the ring dimers, while those isomers whose OH-group is less severely hindered associate into the linear chains. The enthalpy per mole of H-bond formation in ring dimers was found to be 19 kJ mol^{-1}. Kunst et al (13) measured dielectric permittivity and infrared spectra of very dilute solutions of 3-ethyl-3-pentanol, (triethyl carbinol) which is a sterically hindered isomer of 1-heptanol, in carbon tetrachloride at temperatures between 288 and 318 K. They proposed that this alcohol exists in a monomer-dimer-tetramer equilibrium. The heats of association of the dimer and the tetramer are found to be 20 and 65 kJ mol^{-1}, respectively.

Sterically hindered alcohols, whose degree of association is more limited, would potentially seem to be the simplest type of alcohol for study and may more readily give insight into the nature of multiple relaxation processes of alcohols. In the present study we have chosen some sterically hindered alcohols which have appreciable steric hindrance surrounding the OH-group. A dielectric study of these alcohols in a polystyrene matrix at low concentrations offered a possible means of separating absorption processes such as molecular relaxation and intramolecular rotation and that owing to the presence of intermolecularly H-bonded species. The infrared measurements in the same medium at similar temperatures to those employed in the higher temperature dielectric absorption work were utilized to interpret the dielectric data.

EXPERIMENTAL RESULTS

Dielectric measurements were carried out using a General Radio 1621 Percision Capacitance bridge (over $10\text{-}10^5$ Hz). Polystyrene samples were placed in a three-terminal, circular, parrallel-plate capacitor and glassy o-terphenyl and Santovac samples in a three-terminal, stainless-steel, coaxial capacitor. The capacitors were mounted in temperature-controlled chambers and were operational from ca. 80 to 400 K. Details of sample preparation and measuarement techniques are given in Chapter II.

Figures IV-5, IV-6, IV-7 and IV-9 show the plots of $\log T\tau$ versus 1/T. Figures IV-1, IV-8, IV-10, IV-11, IV-12, IV-13, IV-14, IV-15 and IV-16 show the plots of dielectric loss $(=\varepsilon''_{obs}-\varepsilon''_{solv})$ versus T/K at fixed frequencies. Figures IV-2, IV-3 and IV-4 show the sample plots of ε'' versus $\log\nu$ in polystyrene.

DISCUSSION

Dimethyl isopropyl carbinol

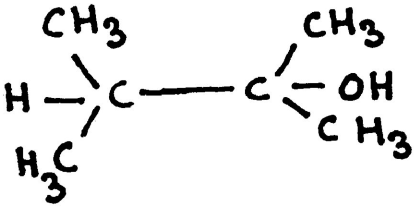
This alcohol yielded three distinct processes as is evident from the ε'' versus T plot at 1.01 kHz (Figure IV-1). A process observed in the temperature range 82-101 K had a ΔH_E of 15 kJ mol^{-1} and a relaxation time of 1.7×10^{-5} s at 100 K. These values are in fair agreement with those obtained for the molecular motion of the slightly larger molecules, 1-fluoro-1,1,2,2-tetrachloroethane in polystyrene (c.f. ΔH_E = 14 kJ mol^{-1} and $\tau = 7.0\times10^{-5}$ s at 100 K)(14). The lower β values of 0.15-0.18 also support molecular rotation as being the process. The second absorption was studied in the range 140-173 K. The high value of β, 0.32-0.50, suggests that this process may be attributed to intramolecular motion as is indicated for 1-bromoalkanes in a polystyrene matrix (1). The ΔH_E 28 kJ mol^{-1} cannot be reconciled with the OH-group rotation about the C-O bond because the energy barriers for the OH-group rotation about the C-O bond in sterically hindered tri-tert-butyl carbinol and phenyl-di-tert-butyl carbinol in benzene solution are only 2 and 5 kJ mol^{-1} respectively (15). Thus, it seems that the intramolecular motion involves rotations about the C-C bonds which consequently rotate the OH-dipole. The third absorption is a broad peak and was studied in the temperature range 234-278 K which cannot be assigned to rotation of the isolated molecule or intramolecular motion. The infrared spectrum of this compound at the same concentration in a polystyrene matrix at 233 K and 273 K (Figure III-10) shows only two distinct bands in the 4000-3100 cm^{-1} region. At both the temperatures one sharp band occurs at 3580 cm^{-1} and other relatively weak bands at about 3475 cm^{-1}. The 3475 cm^{-1} band shows some asymmetry on the lower wave number side. Bellamy et al (16), have shown that the OH-stretching frequency of monomeric methanol changes from 3642 cm^{-1} to 3608 cm^{-1} and the frequency of dimeric methanol from 3534 cm^{-1} to 3502 cm^{-1} by changing the solvent from carbon tetrachloride to toluene (see Table IV-2). The polystyrene unit structure is close to that of toluene.

From the data in Table IV-2 it is apparent that the OH-stretching frequency of methanol varies considerably in different media and at different degrees of polymerization. Further, the OH-stretching frequency of the monomeric form depends also on the alkyl part of the alcohol. For example, the monomer form of methanol in carbon tetrachloride has an OH-stretching frequency of 3642 cm^{-1}, and this is to be contrasted with a value of 3620 cm^{-1} for triethyl carbinol in the same solvent (13). The infrared spectrum of 0.2 M solution of n-hexanol in carbon tetrachloride exhibits monomer, dimer and polymer bands at 3640, 3480 and 3345 cm^{-1} respectively. In fact, all the n-alcohols from C_3 to C_{18}

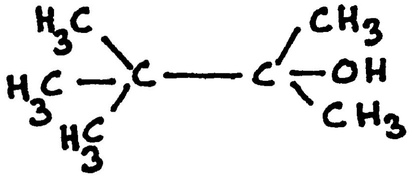
in C_nH_{2n+1}-OH exhibit almost identical behaviour (34). In addition, the open dimer H-bonded OH-stretching frequency of triethyl carbinol is at 3500 cm^{-1} (13) whereas that for methanol (also in carbon tetrachloride) is 3534 cm^{-1}. Altogether, these facts and those in Table IV-2 indicate that there is appreciable variation in the positions (wave numbers) of the monomer, dimer and polymer bands according to both the solvent media and the nature of the alkyl portion of the alcohol molecule. In view of the solvent effect, the 3580 cm^{-1} band of dimethyl isopropyl carbinol in polystyrene can be attributed to the OH stretching of the monomer (17). Again, by taking into account the solvent effect, a band at $\sim$3480 cm^{-1} may be assigned to the presence of a dimer. The asymmetry in the dimer band on the lower wave number side suggests a contribution from a more polymerized alcohol. Thus, the dielectric absorption in the temperature range 234-278 K, in the light of our infrared study and the fact that we have isolated the molecular and intramolecular process, leads to the interpretation that the highest temperature process is to be sought in the presence of the H-bonded species. A ΔH_E value of 51 kJ mol^{-1} was obtained for this process.

<u>Dimethyl-tert-butyl carbinol</u>

The ε" versus T plot of this alcohol at 1.01 kHz shows three distinct processes (Figure IV-1). An absorption which when studied in the temperature range 79-93 K gives a ΔH_E of 14 kJ mol^{-1}. The shape and the size of dimethyl-tert-butyl carbinol are similar to the shape and size of 1-fluoro-1,1,2,2-tetrachloroethane. The latter has an energy barrier for molecular rotation in polystyrene of 14 kJ mol^{-1} which is the same for the former. Thus, the absorption studied in the 79-93 K region can be attributed to molecular rotation which is further supported by the lower β values of 0.16-0.17. The second absorption was examined in the temperature range 208-218 K. The structure of dimethyl isopropyl carbinol and dimethyl-tert-butyl carbinol may be regarded as that of a substituted ethane, i.e.



and



respectively. It is clear from the structures of the two alcohols that the rotation about the C-C bond in the case of dimethyl-tert-butyl carbinol would involve a higher energy barrier than dimethyl isopropyl carbinol, since the additional methyl group results in larger steric hindrance. The observed ΔH_E values are 28 and 42 kJ mol^{-1}, and these are to be compared with the V_3 (energy barrier of internal rotation from vibrational spectroscopy) values for 1,1,1,2-tetrachloroethane and pentachloroethane of 42 and 60 kJ mol^{-1} for rotation about the C-C bond (18). Thus, in the case of 1,1,1,2-tetrachloroethane, the insertion of an additional chlorine increases the barrier by 18 kJ mol^{-1} while the progression from dimethyl isopropyl carbinol to dimethyl-tert-butyl carbinol leads to an increase of 14 kJ mol^{-1}. It would be anticipated that the larger dipole (C-Cl) would lead to a larger increase in the barrier. Thus, it seems that the ΔH_E value of 42 kJ mol^{-1} for the 208-218 K process of dimethyl-tert-butyl carbinol is reasonable for an intramolecular rotation involving the C-C bond. The third process which was studied in the temperature range range, 246-270 K, cannot be attributed to molecular or intramolecular rotation. The infrared spectrum of this alcohol in a polystyrene matrix at the same concentration as used for dielectric measurements and in the wide temperature range, 113-293 K, is shown in Figure III-8 where it can be seen that, at both 233 K and 273 K, two distinct bands are present. One band, which is sharper and centres at 3590 cm^{-1}, may be attributed to the OH-stretching of the monomer and another band at $\sim$3480 cm^{-1} may be attributed to the presence of the dimer. In addition, there is an overlapping band $\sim$3400 cm^{-1} which is most likely a contribution from a more polymerized species (see Table IV-2). Hence, in the light of infrared measurements in the same medium, concentration and temperature range, the dielectric absorption in the temperature range 246-270 K can be assigned to the presence of the H-bonded species. The ΔH_E for this process is found to be 65 kJ mol^{-1} which corresponds with the heat of association of the tetramer of triethyl carbinol (or 3-ethyl-3-pentanol) in carbon tetrachloride (13) and for the dissociation of the cyclic tetramer of tert-butanol in cyclohexane (19).

tert-Butyl methyl carbinol

This alcohol showed only two well resolved absorptions as evident from the ε" versus T plot (Figure IV-1). The low temperature process was studied between 81-95 K. The ΔH_E = 15 kJ mol^{-1} and $\tau = 1.1\times10^{-5}$ s at 100 K are in very good agreement with the molecular rotation for the same size isomer, dimethyl isopropyl carbinol (c.f. ΔH_E = 15 kJ mol^{-1} and $\tau = 1.7\times10^{-5}$ s at 100 K). The low β, 0.14-0.15, also supports the proposal that the 81-95 K process of tert-butyl methyl carbinol most probably arises from the molecular rotation.

Another process observed in the temperature range, 239-265 K, cannot be assigned to molecular rotation. A fairly low β value, 0.16-0.26, and such a broad absorption peak do not suggest that the high temperature process is related to intramolecular motion. The only possible candidate for this process seems to be the H-bonded species. The ΔH_E value is found to be 73 kJ mol^{-1} which is somewhat larger than the ones previously discussed for the high temperature process. The infrared spectrum of tert-butyl carbinol in a polystyrene matrix at 233 K and 273 K exhibits two clear cut bands (see Figure III-9). One band which appears at $\sim$3600 cm^{-1} arises from the OH-stretching of the monomer. The other band, which is very broad, and which, at 233 K and 273 K, has indications of two peaks at 3480 and 3360 cm^{-1}, seems to arise from the presence of oligomers (e.g. dimer, trimer and tetramer). Thus, from the infrared measurements, it would seem that the absorption studied in the 239-265 K region resulted from the presence of the H-bonded species.

Di-tert-butyl carbinol

Di-tert-butyl carbinol is studied in three different glassy media, namely, polystyrene, glassy o-terphenyl and Santovac [bis(m(m-phenoxy phenoxy)phenyl)ether]. In polystyrene this alcohol showed only one absorption in the temperature range, 80-280 K (Figure IV-8). Di-tert-butyl carbinol may be regarded as a methyl substituted derivative of 3-pentanol while the non-associating (non H-bonding) analogue of 3-pentanol is 3-bromopentane. The 3-bromopentane, which has been studied in a polystyrene matrix (20), showed only one absorption in the temperature range 122-139 K. It is demonstrated that the processes obtained in 3-bromopentane, where the C-Br dipole occupies a central position is a contribution from both molecular and intramolecular rotation. The half width, $\Delta T_{\frac{1}{2}}$, (the width of a peak at half height in ε'' versus T plot at a fixed frequency of 1.01 kHz) of the dielectric absorption peak for di-tert-butyl carbinol is 108 K which is approximately twice as wide as that obtained for the intramolecular rotation in 1-bromoalkanes. The infrared spectrum of di-tert-butyl carbinol in a polystyrene matrix in the temperature range 113-293 K, (Figure III-2a) showed a very sharp band at 3615 cm^{-1} at all the temperatures. Another band, which is also observed at all the temperatures, occurs at $\sim$3495 cm^{-1}. The lowest wave number band is at $\sim$3220 cm^{-1} is broad and appears only at the lowest temperatures of 113 K and 153 K. Kolodziej and Malarski (21) reported that the infrared spectrum of di-tert-butyl carbinol in carbon tetrachloride exhibited a monomer band at 3653 cm^{-1} and a dimer band at 3531 cm^{-1}. These may be compared with our values of 3615 cm^{-1} and 3495 cm^{-1} where the difference may be attributed to the different solvent media. The lower temperature band at 3220 cm^{-1} may be attributed to a high polymer band (see Table IV-2). In short, the infrared spectrum of di-tert-butyl carbinol in the full temperature range, 113-293 K, and the concentration employed, 0.70 M, shows the presence of the monomer, dimer and high polymer. However, it must be emphasized that between 213 and 293 K at the employed concentration, there is only the monomer and dimer present. This case is unique among all sterically hindered alcohols we have examined.

The dielectric absorption of di-tert-butyl carbinol as exhibited in Figure IV-8 by analogy with 3-bromopentane, seems to arise from molecular and intramolecular motions. As is evident from the infrared spectrum in Figure III-2a, di-tert-butyl carbinol shows an appreciable amount of dimer at all the temperatures. If we assume the dimer to be an open dimer (23), then a process due to one H-bond breaking with a $\Delta H_E \sim 18$ kJ mol^{-1} may well appear in the same temperature region as for molecular and intramolecular motions. Unlike other alcohols included in this study, di-tert-butyl carbinol does not show any sign of a dielectric process in the temperature region, 200-270 K. From the infrared study, it is clear that in this temperature range the only associated species is a dimer. Thus, we conclude that the presence of a dimer itself does not lead to dielectric absorption in the temperature range, 200-270 K.

To investigate further the dielectric behaviour of di-tert-butyl carbinol, it has also been examined in glassy o-terphenyl and Santovac. In glassy o-terphenyl two processes were obtained (Figure IV-10): an absorption studied in the range 86-108 K, seems to arise from molecular and/or intramolecular motion; another process in the temperature range, 165-214 K, gave a ΔH_E value of 22 kJ mol^{-1}. tert-Butanol in glassy o-terphenyl (24) yielded an almost indentical ΔH_E value of 21 kJ mol^{-1}. These values are of the order of magnitude reported in the literature (17,23,25-29) for the breaking of one H-bond. Consequently, it seemed worthwhile to study di-tert-butyl carbinol in Santovac. A similar ΔH_E value (24 ±5 kJ mol^{-1}) was obtained.

Diethyl isopropyl carbinol

This alcohol shows one sharp process in the temperature range, 158-195 K, and a sign of a shoulder above 200 K (Figure IV-12). The half width, $\Delta T_{\frac{1}{2}}$, of a 158-195 K peak is 48 K which falls in the range, 40-58 K, obtained for intramolecular rotation in 1-bromoalkanes (1). The β value, 0.29-0.41, is high and suggests an intramolecular process. The

ΔH_E of 34 kJ mol^{-1} seems reasonable for the hindered intramolecular rotation. The infrared spectrum of diethyl isopropyl carbinol in polystyrene at 213 K and 233 K is obtained (see Figure III-4). At both these temperatures, a band at 3585 cm^{-1} and another band at $\sim$3480 cm^{-1} arise from the monomer and the dimer, respectively. At 213 K there is a broad peak at 3240 cm^{-1} ascribable to a high polymer (22). At 233 K, there is a shoulder at about 3350 cm^{-1} which can probably be attributed to a smaller polymerized species. A sign of a weak shoulder above 200 K in the ε'' versus T plot may be related to the presence of a very low concentration of an H-bonded species which is larger than a dimer.

Di-isopropyl methyl carbinol

A dielectric loss versus temperature plot of this alcohol (Figure IV-12) shows an absorption in the temperature range 123-152 K and a shoulder at above 200 K. Di-isopropyl methyl carbinol is a methyl substituted derivative of 3-pentanol the non-associating corresponding compound of which is 3-bromopentane which gives an absorption, arising from molecular and intramolecular rotation, in the temperature range, 122-139 K. Owing to the similarity in the structure of di-isopropyl carbinol and 3-bromopentane, the observed absorption in the former seems to be a contribution from the molecular and the intramolecular motion. The infrared spectrum of the alcohol in a polystyrene matrix at 213 K, 233 K, 273 K and 293 K shows bands due to (a) the monomer at 3610 cm^{-1}, (b) the dimer at 3480-3500 cm^{-1} and (c) a shoulder due to a species larger than the dimer at ∿3360 cm^{-1} (Figure III-3). Thus, with the results previously discussed in mind, a shoulder above 200 K in the ε'' versus T plot seems to arise from the presence of the H-bonded species which is larger than the dimer.

tert-Butyl ethyl methyl carbinol

The dielectric measurements on this alcohol in a polystyrene matrix showed two absorption peaks (Figure IV-12). A low temperature absorption peak (studied in the range, 91-104 K) had a half width of 100 K which is approximately the same as that obtained for di-tert-butyl carbinol (c.f. 108 K). This bears out that the lower temperature peak in tert-butyl ethyl methyl carbinol is a contribution from both the molecular and the intramolecular rotation with the possibility of some contribution from the breaking of one H-bond of a dimer. Another absorption was studied in the temperature range, 224-263 K. The infrared spectrum of tert-butyl ethyl methyl carbinol in a polystyrene matrix at 233 K and 273 K (Figure III-6) showed a band at 3600 cm^{-1} owing to the monomer OH-stretching

Another band obtained at both temperatures was observed at 3495 cm^{-1} which may be attributed to a dimer. An inconspicuous shoulder, which can be assigend to a polymerized species at about 3340 cm^{-1} was observed at both temperatures. Thus, the dielectric absorption in the 224-263 K region may be related to the presence of a polymerized H-bonded species. The ΔH_E for the 224-263 K absorption peak is 56 kJ mol^{-1}. This value is close to the ΔH_E kJ mol^{-1} obtained for dimethyl isopropyl carbinol.

Isopropyl ethyl methyl carbinol

The dielectric measurements on this alcohol in a polystyrene matrix show one very strong absorption studied in the temperature range, 137-166 K and a shoulder above 200 K (Figure IV-12). The half-width of the low temperature, 137-166 K, process is 72 K. This is greater than the half-width obtained for an intramolecular process in dimethyl isopropyl carbinol (c.f. 44 K). Isopropyl ethyl methyl carbinol is a little larger in size than dimethyl isopropyl carbinol which yields separate molecular and intramolecular process as in the temperature ranges, 80-101 K and 140-173 K. The larger size of the former alcohol would shift the molecular process to a higher temperature. Thus, two separate molecular and intramolecular processes may merge and appear as one absorption peak in the ε" versus T plot. The infrared spectrum of isopropyl ethyl methyl carbinol in a polystyrene matrix at 233 K and 273 K (Figure III-7) shows a band at 3590 cm^{-1} for the monomer and another band at 3480 cm^{-1}, due to the presence of the dimer. At both temperatures there is a very weak shoulder at about 3400 cm^{-1}, for an H-bonded species which is larger than the dimer. A shoulder above 200 K in ε" versus T plot of isopropyl ethyl methyl carbinol seems likely to arise from the presence of the H-bonded species.

tert-Butyl isopropyl carbinol

This alcohol in a polystyrene matrix yielded two well resolved peaks (Figure IV-13). An absorption which was observed in the temperature range 85-108 K gave a $\tau = 2.3\times10^{-4}$ s at 100 K. tert-Butyl isopropyl carbinol is quite similar in structure yet smaller in size than di-tert-butyl carbinol. An absorption obtained for the merged molecular and intramolecular rotation in di-tert-butyl carbinol in a polystyrene matrix yielded a mean relaxation time 3.5×10^{-4} s at 100 K which corresponds with the mean relaxation time 2.3×10^{-4} s at 100 K for tert-butyl isopropyl carbinol in polystyrene. It seems likely that the 85-108 K absorption is a contribution from the molecular and the intramolecular rotation. The infrared spectrum of tert-butyl isopropyl carbinol in a polystyrene matrix at 193 K and 213 K showed the presence of highly polymerized H-bonded species (see Figure III-5). The dielectric absorption obtained for this alcohol in 204-228 K region, compared to other sterically hindered alcohols, is characterized by appreciably high dielectric loss. Since the infrared spectrum of tert-butyl isopropyl carbinol in the temperature region 193-213 K shows the presence of highly polymerized H-bonded species which bears out that the dielectric absorption in 204-228 K region is due to the highly polymerized H-bonded species. The enthalpy of activation for this high temperature (204-228 K) process was found to be 84 kJ mol^{-1} which is virtually the same value as obtained for its isomer, 2,2-dimethyl-1-hexanol in the pure liquid state (c.f. E_a = 84 kJ mol^{-1}) (8).

Tricyclohexyl carbinol

Tricyclohexyl carbinol in a polystyrene matrix exhibited only one absorption in the temperature range 231-273 K (Figure IV-14). The ΔH_E value of 55 kJ mol^{-1} is obtained for this process. Infrared spectrum of tricyclohexyl carbinol in polystyrene at the same concentration as used for dielectric measurements (i.e. 0.31 M) and at 233 K, 273 K, and 293 K does not show any H-bonded species (see Figure III-11), obviously due to severe steric factors about the OH-group. Meakins (38) obtained an energy barrier of 18 kJ mol^{-1} for the OH-group rotation in crystalline tricyclohexyl carbinol. The ΔH_E value of 55 kJ mol^{-1} for tricyclohexyl carbinol in polystyrene does not conform to the OH-group rotation. The β value obtained for tricyclohexyl carbinol is 0.22-0.24 which, compared to the one obtained for chair-to-chair transformation of cyclohexyl chloride (40) in polystyrene (c.f. 0.51-0.65) is too low. Tricyclohexyl phosphine in a polystyrene matrix, which possesses approximately the same size as tricyclohexyl carbinol, yielded a ΔH_E of 72 kJ mol^{-1} for the molecular rotation (39). The ΔH_E for chair-to-chair flipping for cyclohexyl chloride and bromide in polystyrene is found to be 42 and 43 kJ mol^{-1}, respectively. Thus, neither only molecular nor intramolecular chair-to-chair fliping of tricyclohexyl carbinol can explain the observed value of ΔH_E. Thus, it appears likely that the absorption obtained for tricyclohexyl carbinol in polystyrene in the temperature range 231-273 K is due to the contribution from both the molecular as well as the intramolecular chair-to-chair fliping.

Diphenyl methyl carbinol

This alcohol shows only one absorption peak in the temperature range 219-257 K (Figure IV-15). The infrared spectrum of diphenyl methyl carbinol in polystyrene at 213 K, 233 K and 273 K, shows the presence of a monomer and a dimer (see Figure III-12). As discussed in the case of di-tert-butyl carbinol in a polystyrene matrix, the dimer does not give a dielectric absorption in the 200-270 K region. The half-width, $\Delta T_{\frac{1}{2}}$, for the observed process in diphenyl methyl carbinol is 100 K (at 1.01 kHz) which does not conform to an intramolecular rotation (1). Diphenyl methyl carbinol yielded a ΔH_E of 63 kJ mol^{-1} and relaxation time, τ, 7.5x10^{-2} s at 200 K. These values are in fair agreement with the values obtained for approximately the same size of rigid molecule diphenyl sulfone in polystyrene (c.f. ΔH_E = 62 kJ mol^{-1} and τ = 1.7x10^{-3} s at 200 K) (41). Hence, it seems likely that the dielectric absorption obtained for diphenyl methyl carbinol in polystyrene is due to the molecular rotation.

Dimethyl phenyl carbinol

Dielectric measurements on this alcohol in polystyrene showed two well resolved peaks in the ε'' versus T plot at the fixed frequencies (Figure IV-16). An absorption which is obtained in the temperature range 82-104 K yielded a ΔH_E of 12 kJ mol^{-1}. Bromobenzene in polystyrene, which is a fairly similar sized and shaped molecule to that of dimethyl phenyl carbinol, gives a ΔH_E of 13 kJ mol^{-1} for the molecular rotation (42). Similarities in size and shape and ΔH_E values of bromobenzene and dimethyl phenyl carbinol bear out that the process obtained for the latter in the temperature range 82-104 K is most likely due to the molecular rotation. This is again borne out by the lower β, 0.15-0.18. Another absorption which is obtained in the temperature range 205-230 K yields a ΔH_E of 62 kJ mol^{-1} typical of that obtained for some other sterically hindered alcohols in polystyrene. As it is apparent from the infrared study of dimethyl phenyl carbinol in polystyrene (see Figure III-14) that at 193 K, 213 K and 233 K, the polymerized species exist (larger than the dimer) which would account for the dielectric absorption of dimethyl phenyl carbinol in polystyrene in the temperature range 205-230 K.

CONCLUSION

It is clearly demonstrated that for some alcohols in a polystyrene matrix (a) the relaxation processes due to the molecular, intramolecular and to the presence of the H-bonded species have been resolved, whereas, (b) in some others the processes due to the molecular and the intramolecular rotation are merged together, yet are separated from the process relating to the presence of an H-bonded species. In contrast to this, clear-cut separation of the processes in dilute liquid solutions of the alcohols has not been achieved (6,30,31). The infrared measurements on these sterically hindered alcohols in polystyrene at fairly low concentrations indicate that in our temperature range, 113-293 K, all these alcohols possess H-bonded species, e.g. dimer, tetramer and high polymers, etc. and their amount varies with temperature. With the exception of di-tert-butyl carbinol, diphenyl methyl carbinol and tricyclohexyl carbinol, the dielectric process due to the presence of an H-bonded species always occurs in the temperature range ∿200-270 K. However, for di-tert-butyl carbinol our infrared and dielectric studies have shown the presence of dimers does not lead to dielectric absorption in the ∿200-270 K region.

If reorientation of a particular type of a stable polymerized species were responsible for the 200-270 K absorption, one might expect, for example, the τ at 200 K and ΔH_E values of tert-butyl ethyl methyl carbinol to be greater than those of dimethyl-tert-butyl carbinol or tert-butyl methyl carbinol, but this is not the case (e.g. the ΔH_E values are 56, 65, and 73 kJ mol^{-1}, respectively). Further, the variation in ΔH_E values given in Table IV-2 would seem a very small one if each of the molecules had a variety of different polymerized species where each of the polymerized species relaxed as a whole unit. For the liquid long chain alcohols a major factor, invoked to explain the low frequency process, has been one which involved the breaking of H-bonds (3-7,10,11). For sterically hindered alcohols our ΔH_E values in polystyrene bear considerable similarity to those found for the τ_1 process (first dispersion or low frequency dispersion) of sterically hindered liquid alcohols as quoted by Böttcher and Bordewijk (32):

Alcohol	2-Heptanol	3-Heptanol	4-Heptanol
ΔH_E (kJ mol^{-1})	47	63	63

Alcohol	2-Octanol	3-Octanol	4-Octanol
ΔH_E (kJ mol^{-1})	50	67	66

Alcohol	6-Methyl-3-heptanol	5-Methyl-3-heptanol
ΔH_E (kJ mol^{-1})	76	86

If a dissociation process is one of the major factors in accounting for the ΔH_E values in liquid alcohols, then it would seem likely that it also operates for the dissociation of our sterically hindered alcohols in a polystyrene matrix. Our ΔH_E values for the ∿200-270 K process(es) are of a similar order of magnitude, and since (a) the strength of one H-bond would appear to be about 18 ±2 kJ mol^{-1} (12,25,27-29,33) and since (b) our experimental error is about ±6 kJ mol^{-1}, it would seem that a dissociation process involving on average the breaking of about three and occasionally four H-bonds (dimethyl phenyl carbinol) is taking place. Certainly, the results for di-tert-butyl carbinol in polystyrene where there is no absorption in the 200-270 K region and only one (or at most two if a cyclic dimer were present) intermolecular H-bond to be broken, bear out that the most likely process in this region for the other similar sterically hindered alcohols is a dissociation process involving the breaking of a greater number of H-bonds.

The fact that a range of ΔH_E values exists for those sterically hindered alcohols and the fact that the literature on the liquid alcohols indicates that steric factors influence the ΔH_E values of the τ_1 process would suggest that a mechanism involving solely H-bond breaking may well be too simplistic.

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TABLE IV-1: Dielectric Relaxation Parameters of Some Sterically Hindered Alcohols

Alcohol (mole/litre)	Medium	ΔT(K)	Relaxation time τ(s) 100 K	150 K	200 K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
Dimethyl isopropyl-carbinol (0.93)	P.S.*	82-101	1.7×10^{-5}	2.3×10^{-8}		15±1	10±13
		140-173		6.4×10^{-4}	1.8×10^{-6}	28±2	8±14
		234-278			2.7×10^{-1}	51±4	24±18
Dimethyl-tert-butyl carbinol (0.93)	P.S.	79-93	4.4×10^{-6}	9.2×10^{-9}		14±1	10±18
		208-218		9.2×10^{-9}	4.0×10^{-3}	42±12	13±60
		246-270			2.1×10^{0}	65±6	78±22
tert-Butyl methyl carbinol (0.93)	P.S.	81-95	1.1×10^{-5}	1.5×10^{-8}		15±2	13±19
		239-265			4.7×10^{0}	73±3	110±14
Di-tert-butyl carbinol (0.70)	P.S.	90-115	3.5×10^{-4}	3.6×10^{-7}		16±2	-8±15
Di-tert-butyl carbinol (0.40)	GOTP**	86-103	9.5×10^{-5}	7.0×10^{-7}		11±0.5	-46±6
		165-204		6.6×10^{-3}	6.1×10^{-5}	22±2	-52±11
Di-tert-butyl carbinol	SV***	99-118	1.8×10^{-3}	7.8×10^{-8}		24±5	57±45
Diethyl isopropyl carbinol (0.73)	P.S.	158-195		1.2×10^{-4}	8.3×10^{-6}	34±1	25±6
Diisopropyl methyl carbinol (0.75)	P.S.	130-152	6.9×10^{-1}	3.0×10^{-5}		27±2	25±16
tert-Butyl ethyl methyl carbinol (0.75)	P.S.	91-104	4.1×10^{-5}	3.1×10^{-9}		23±1	74±16
		224-263			9.2×10^{-2}	56±6	60±23
Isopropyl ethyl methyl carbinol (1.00)	P.S.	137-166		2.3×10^{-4}	3.0×10^{-7}	32±2	42±12
tert-Butyl isopropyl carbinol (0.70)	P.S.	85-108	2.3×10^{-4}	3.4×10^{-6}		10±1	-70±15
		204-228		2.7×10^{5}	9.5×10^{-3}	84±5	218±21
Tricyclohexyl carbinol (0.31)	P.S.	231-272			6.3×10^{-1}	55±3	39±12

TABLE IV:1 Continued...

Alcohol (mol/litre)	Medium	ΔT(K)	Relaxation time τ(s)			ΔH_E	ΔS_E
			100 K	150 K	200 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Tricyclohexyl phosphine[1]	P.S.	294-320			4.0×10^{2}	72±5	54±16
Diphenyl methyl carbinol (0.25)	P.S.	219-257			7.5×10^{-2}	63±3	93±14
Dimethyl phenyl	P.S.	82-104	6.7×10^{-5}	3.4×10^{-7}		12±2	-34±25
carbinol (1.30)		205-230		7.8×10^{2}	2.4×10^{-3}	62±2	118±11

NOTE: * P.S. means polystyrene
** GOTP means glassy o-terphenyl
*** SV means Santovac

[1] reproduced courtsey of Miss J. C. N. Chao, Ph.D. student (this laboratory)

TABLE IV-2:

O-H Stretching Frequencies (cm^{-1}) obtained for methanol in different media and at different degrees of polymerization

Type of H-bonded Species	Vapour	Argon Matrix	Nitrogen Matrix	CH_2Cl_2 Solution	CCl_4 Solution	Toluene Solution	Benzene Solution	Mesitylene Solution
Monomer	3682[a]	3667[b]	3660[c]	3637[d]	3642[e]	3608[e]	3613[e]	3598
Dimer (Open chain)	3590	3528		3494	3534	3502	3502	3404
Dimer (Cyclic)			3490					
Trimer (Open chain)		3495						
Trimer (Cyclic)			3445					
Tetramer (Open chain)		3446	3290					
Tetramer (Cyclic)	3380	3359						
High Polymer		3254	3200					

References: a (35); b (22); c (36); d (37); e (16).

TABLE IV-3: Fuoss-Kirkwood Analysis Parameters for some Sterically Hindered Alcohols in Glassy Media

T(K)	$10^6\tau$(s)	$\log\nu_{max}$	$\bar{\beta}$	$10^3\varepsilon''_{max}$
Dimethyl isopropyl carbinol (P.S.)				
82.6	1019.7	2.19	0.16	4.70
84.8	519.2	2.49	0.15	4.86
87.0	365.7	2.64	0.18	5.19
90.5	118.8	3.13	0.17	5.37
93.0	64.3	3.39	0.18	5.76
95.0	41.8	3.58	0.17	5.86
97.0	34.7	3.66	0.18	6.07
101.0	14.5	4.04	0.16	6.32
Dimethyl isopropyl carbinol				
141.0	3169.5	1.70	0.33	12.20
143.5	1979.9	1.91	0.33	12.00
147.8	933.9	2.23	0.36	11.90
151.7	444.1	2.55	0.39	11.70
155.4	250.0	2.80	0.42	11.50
158.9	145.5	3.04	0.45	11.30
166.6	65.5	3.39	0.50	10.80
173.5	31.1	3.71	0.49	10.20
Dimethyl isopropyl carbinol				
234.7	3151.1	1.70	0.14	1.70
236.4	2472.0	1.81	0.15	1.70
238.4	1427.9	2.05	0.18	1.60
239.9	1298.4	2.09	0.16	1.60
254.3	632.7	2.40	0.16	1.50
250.9	388.2	2.61	0.17	1.50
256.8	244.2	2.81	0.19	1.40
264.4	106.4	3.18	0.20	1.30
270.6	63.2	3.40	0.22	1.20
278.3	44.1	3.56	0.24	1.10
Dimethyl-tert-butyl carbinol (P.S.)				
79.0	475.4	2.52	0.17	12.40
82.7	236.7	2.83	0.16	12.80
85.2	114.6	3.14	0.16	13.20
87.7	58.3	3.44	0.16	13.60
89.6	34.7	3.67	0.16	13.90
91.8	23.2	3.84	0.16	14.10
93.3	15.1	4.02	0.16	14.40

TABLE IV-3: continued...

Dimethyl-tert-butyl carbinol				
208.9	1287.7	2.09	0.23	2.00
211.9	982.6	2.21	0.22	1.90
215.5	587.8	2.43	0.22	1.90
218.0	470.0	2.53	0.21	1.80
Dimethyl-tert-butyl carbinol				
246.2	1053.9	2.18	0.18	2.10
249.1	835.0	2.28	0.19	2.10
251.9	481.0	2.52	0.21	2.10
255.4	353.9	2.65	0.22	2.00
258.6	224.5	2.85	0.24	2.00
261.9	130.6	3.09	0.23	1.90
265.7	101.0	3.20	0.23	1.80
270.0	64.1	3.39	0.24	1.80
tert-Butyl methyl carbinol (P.S.)				
81.8	726.2	2.34	0.15	10.10
84.7	344.1	2.67	0.15	10.50
89.0	139.5	3.06	0.14	10.90
92.0	55.1	3.46	0.14	11.30
93.4	38.7	3.61	0.14	11.50
95.1	27.9	3.76	0.14	11.68
tert-Butyl methyl carbinol				
239.2	3016.7	1.72	0.16	2.57
242.6	1803.6	1.95	0.17	2.50
246.2	929.1	2.23	0.18	2.39
249.0	688.1	2.36	0.17	2.30
251.9	477.0	2.52	0.18	2.20
254.6	280.6	2.75	0.19	2.10
257.6	200.5	2.90	0.20	2.00
264.8	78.8	3.31	0.19	1.90
Di-tert-butyl carbinol (P.S.)				
90.8	2188.9	1.86	0.13	6.40
93.2	1537.3	2.02	0.12	6.70
97.0	874.0	2.26	0.12	7.10
99.7	424.8	2.57	0.13	7.40
106.4	101.0	3.20	0.08	8.00
109.4	58.9	3.43	0.09	8.30
113.0	27.4	3.76	0.08	8.51
114.8	26.5	3.78	0.09	8.70

TABLE IV-3: continued...

Di-tert-butyl Carbinol (GOTP)

86.7	882.7	2.26	0.15	2.40
89.4	508.0	2.50	0.15	2.50
92.1	328.0	2.69	0.16	2.60
94.0	251.9	2.80	0.16	2.60
96.9	153.9	3.01	0.15	2.60
99.8	101.4	3.20	0.16	2.70
102.7	61.8	3.41	0.15	2.80

Di-tert-butyl carbinol

165.0	1127.0	2.15	0.11	2.60
169.7	831.0	2.28	0.12	2.60
173.8	524.1	2.48	0.13	2.60
177.9	308.1	2.71	0.14	2.60
182.9	277.8	2.84	0.15	2.70
187.8	175.5	2.96	0.17	2.70
194.2	98.0	3.21	0.17	2.60
204.5	41.1	3.59	0.18	2.70

Di-tert-butyl carbinol (SV)

99.0	1871.2	1.93	0.16	2.70
101.0	1253.4	2.10	0.15	2.80
104.6	527.0	2.48	0.14	2.80
107.9	307.2	2.71	0.14	3.00
111.6	118.1	3.13	0.13	3.10
115.5	28.9	3.74	0.11	3.10
117.6	13.7	4.07	0.11	3.20

Diethyl isopropyl carbinol (P.S.)

158.9	2200.5	1.86	0.29	16.50
162.6	1200.9	2.12	0.30	16.70
166.2	598.1	2.43	0.33	16.70
170.3	315.1	2.70	0.35	16.60
174.3	185.7	2.93	0.37	16.60
178.6	104.5	3.18	0.39	16.50
184.3	52.3	3.48	0.41	16.50
190.0	27.5	3.76	0.40	16.20
195.5	13.7	4.07	0.41	16.00

Diisopropyl methyl carbinol (P.S.)

130.0	927.3	2.23	0.19	7.10
133.6	434.3	2.56	0.19	7.40
138.3	231.0	2.84	0.19	7.60
142.3	97.1	3.21	0.18	7.90
146.2	51.5	3.49	0.17	8.00
152.2	22.0	3.86	0.17	8.40

TABLE IV-3: continued...

tert-Butyl ethyl methyl carbinol (P.S.)

91.7	515.9	2.49	0.13	5.50
94.0	250.5	2.80	0.11	5.70
97.0	89.3	3.25	0.10	5.90
100.2	42.0	3.58	0.12	6.30
101.6	25.9	3.79	0.12	6.40
102.6	21.8	3.86	0.12	6.40
104.5	10.8	4.17	0.11	6.60

tert-Butyl ethyl methyl carbinol

224.2	2072.2	1.89	0.16	4.20
225.9	1541.4	2.01	0.16	4.10
229.0	936.6	2.23	0.16	4.00
232.8	650.7	2.39	0.15	3.90
236.6	413.8	2.59	0.16	3.80
239.6	334.6	2.68	0.20	3.76
243.2	268.9	2.77	0.18	3.60
247.3	129.7	3.09	0.18	3.50
251.6	74.4	3.33	0.19	3.30
257.3	47.0	3.53	0.21	3.30
259.7	26.9	3.77	0.21	3.20
262.4	21.5	3.87	0.21	3.20

Isopropyl ethyl methyl carbinol (P.S.)

137.5	2318.7	1.84	0.17	10.40
140.4	1614.0	1.99	0.17	10.50
143.7	778.9	2.31	0.17	10.60
147.5	371.4	2.63	0.18	10.80
151.4	173.2	2.96	0.19	10.90
155.0	102.5	3.19	0.21	11.10
158.8	45.6	3.54	0.21	11.30
162.7	27.6	3.76	0.22	11.40
166.6	18.3	3.94	0.26	11.70

tert-Butyl isopropyl carbinol (P.S.)

85.5	1859.3	1.93	0.14	3.60
88.4	1323.7	2.08	0.14	3.80
91.0	924.2	2.23	0.12	3.90
94.4	405.9	2.59	0.13	4.10
104.8	129.1	3.09	0.17	4.60
108.5	93.7	3.23	0.16	4.70

TABLE IV-3: continued...

tert-Butyl isopropyl carbinol

203.8	3715.8	1.63	0.14	9.80
207.0	1744.0	1.96	0.14	9.70
210.6	714.0	2.35	0.14	9.50
214.7	285.1	2.75	0.14	9.30
218.9	94.2	3.23	0.15	9.10
223.0	41.3	3.59	0.16	8.90
225.7	26.0	3.79	0.16	8.80
227.9	20.7	3.89	0.17	8.70

Tricyclohexyl carbinol (P.S.)

231.2	6826.4	1.37	0.23	4.90
238.4	2149.6	1.87	0.25	5.00
240.2	1868.7	1.93	0.25	5.00
243.3	1252.0	2.10	0.22	5.00
246.4	1018.4	2.19	0.24	5.00
252.3	542.5	2.47	0.25	5.00
256.6	345.2	2.66	0.24	5.10
260.7	221.1	2.86	0.24	5.10
266.1	119.3	3.13	0.24	5.10
271.9	64.3	3.39	0.24	5.10

Diphenyl methyl carbinol (P.S.)

219.7	2584.2	1.79	0.18	2.40
223.5	1313.8	2.08	0.18	2.40
227.6	606.4	2.42	0.17	2.50
231.9	392.6	2.61	0.17	2.50
235.4	195.4	2.91	0.18	2.50
240.2	112.7	3.15	0.18	2.51
244.2	71.2	3.35	0.20	2.50
257.3	13.9	4.06	0.25	2.70

Dimethyl phenyl carbinol (P.S.)

82.3	1438.0	2.04	0.18	5.40
85.4	983.6	2.21	0.17	5.60
90.0	519.6	2.49	0.15	5.80
92.6	276.3	2.76	0.15	6.10
96.4	137.1	3.06	0.15	6.30
99.7	59.8	3.43	0.15	6.60
103.0	35.3	3.65	0.16	6.90

TABLE IV-3: continued....

Dimethyl phenyl carbinol

205.0	873.2	2.26	0.14	13.20
206.8	630.5	2.40	0.14	13.40
209.8	443.8	2.55	0.13	13.80
212.0	301.5	2.72	0.16	14.30
214.2	207.2	2.89	0.15	14.50
217.2	117.2	3.13	0.16	15.10
220.8	62.5	3.41	0.17	15.80
223.7	41.1	3.59	0.17	16.30
227.0	25.0	3.80	0.18	16.90
229.8	16.7	3.98	0.19	17.40

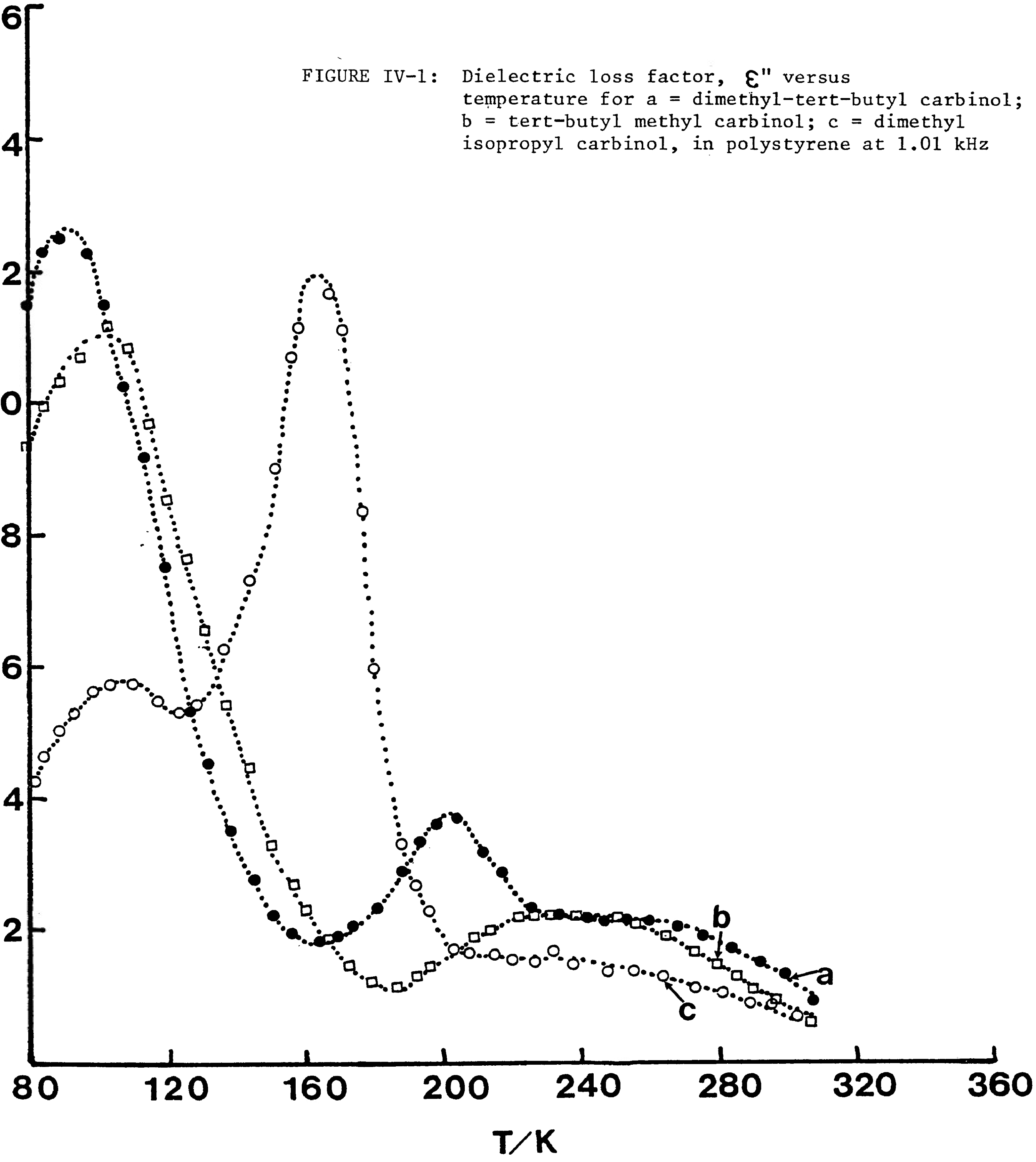


FIGURE IV-1: Dielectric loss factor, ε" versus temperature for a = dimethyl-tert-butyl carbinol; b = tert-butyl methyl carbinol; c = dimethyl isopropyl carbinol, in polystyrene at 1.01 kHz

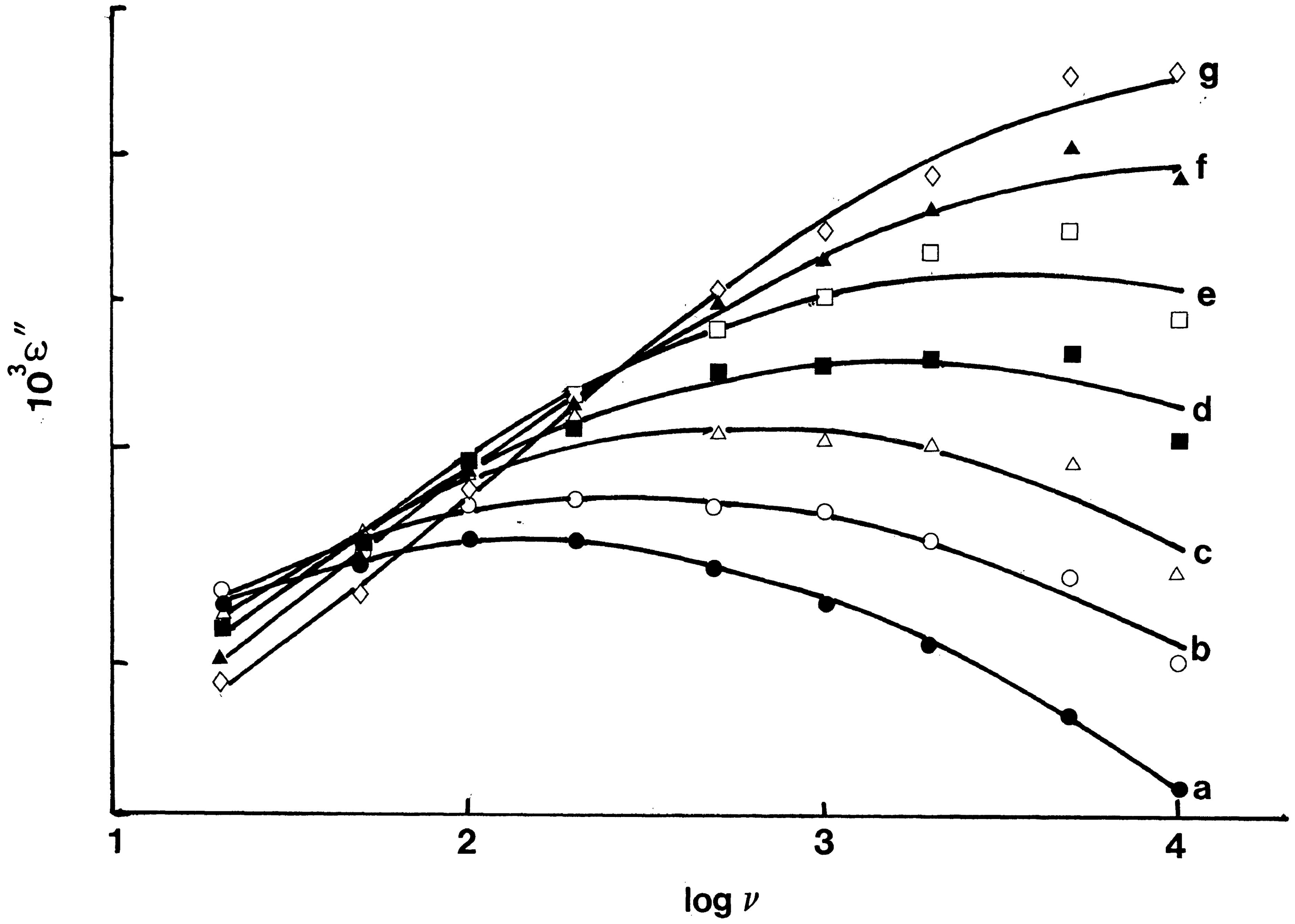


FIGURE IV-2: Dielectric loss factor, ε'' versus log ν for dimethyl isopropyl carbinol in polystyrene at a = 82.6 K; b = 84.8 K; c = 87.6 K; d = 90.5 K; e = 93.0 K; f = 97.0 K and g = 101.0 K.

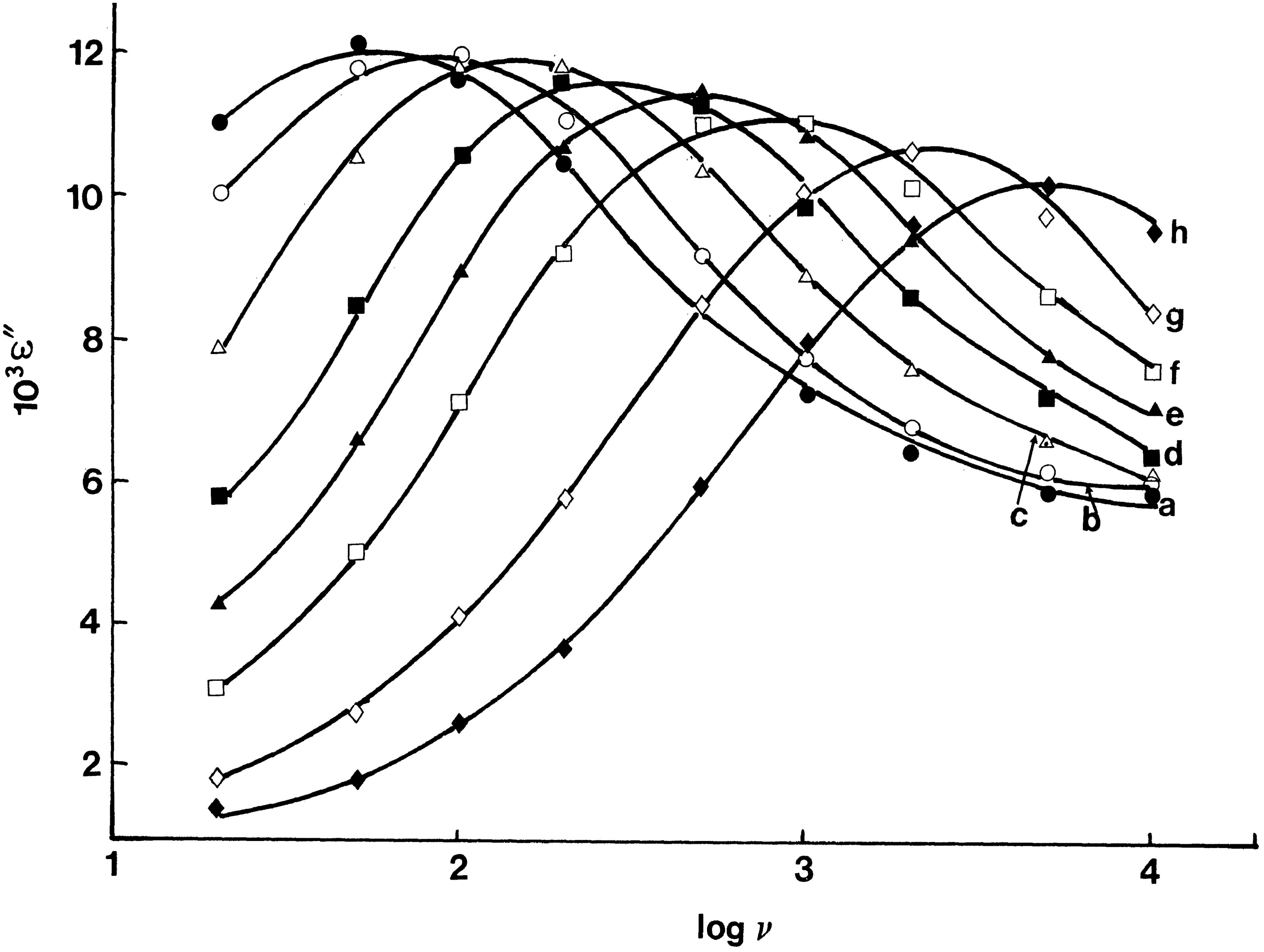


FIGURE IV-3: Dielectric loss factor, ε'' versus log ν for dimethyl isopropyl carbinol in polystyrene at a = 141.0 K; b = 143.5 K; c = 147.8 K; d = 151.7 K; e = 155.4 K; f = 158.0 K; g = 166.6 K and h = 173.5 K.

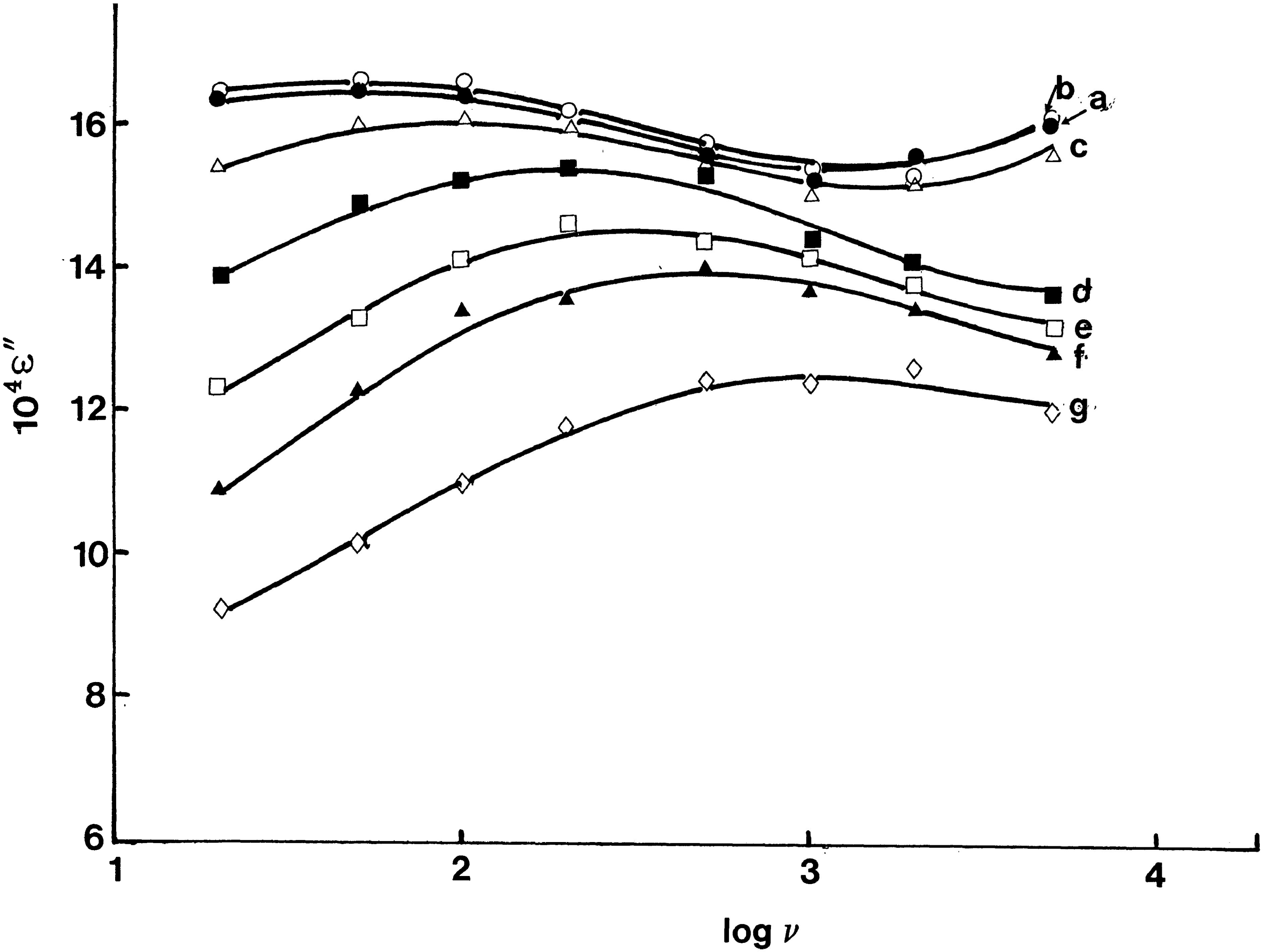


FIGURE IV-4: Dielectric loss factor, ε'' versus log ν for dimethyl isopropyl carbinol in polystyrene at a = 234.7 K; b = 236.4 K; c = 238.4 K; d = 245.3 K; e = 250.9 K; f = 256.8 K and g = 264.4 K.

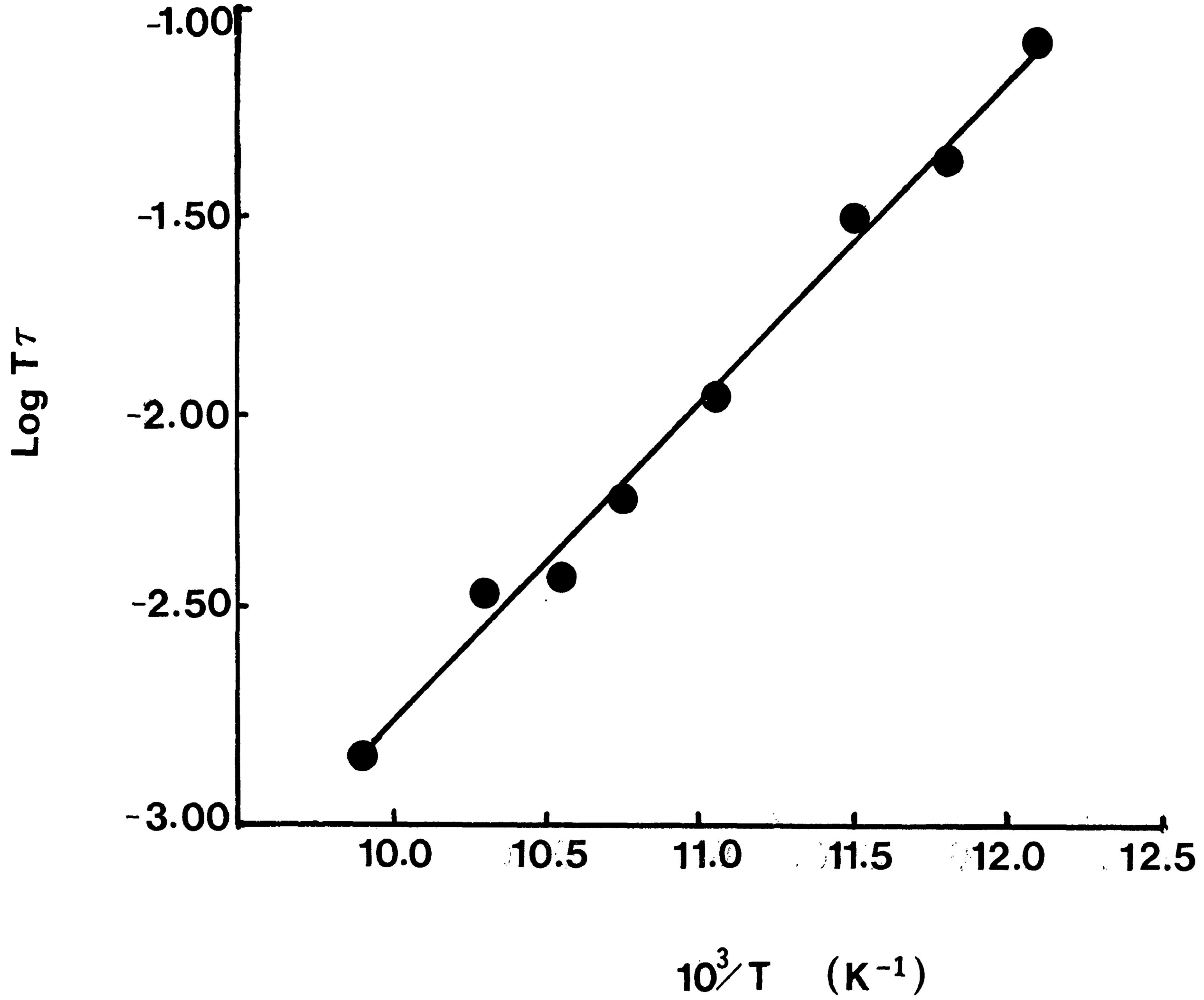


FIGURE IV-5: Eyring rate plot of log Tτ versus 1/T for the lowest temperature of dimethyl isopropyl carbinol in polystyrene.

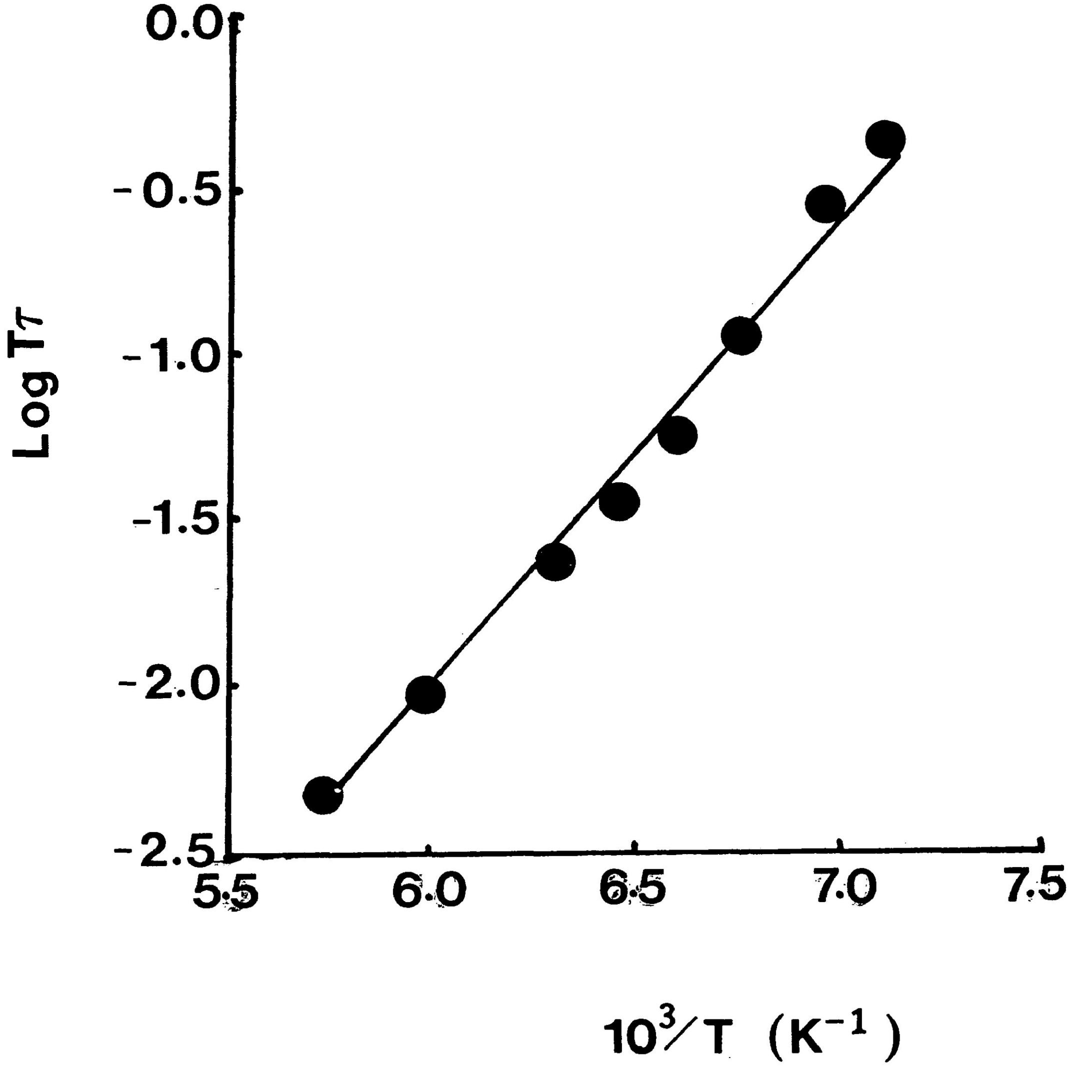


FIGURE IV-6: Eyring rate plot of log Tτ versus 1/T for intermediate process of dimethyl isopropyl carbinol in polystyrene.

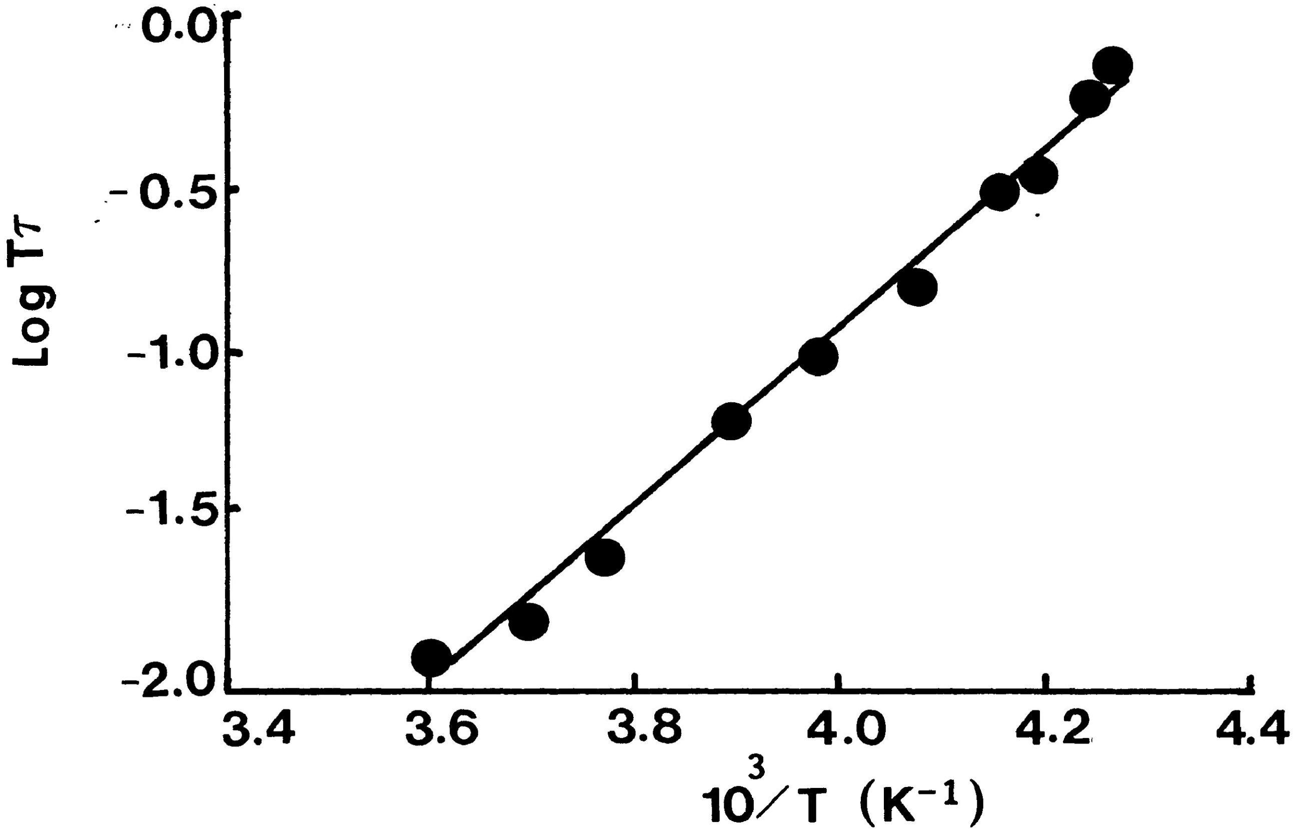


FIGURE IV-7: Eyring rate plot of log Tτ versus 1/T for high temperature process of dimethyl isopropyl carbinol in polystyrene.

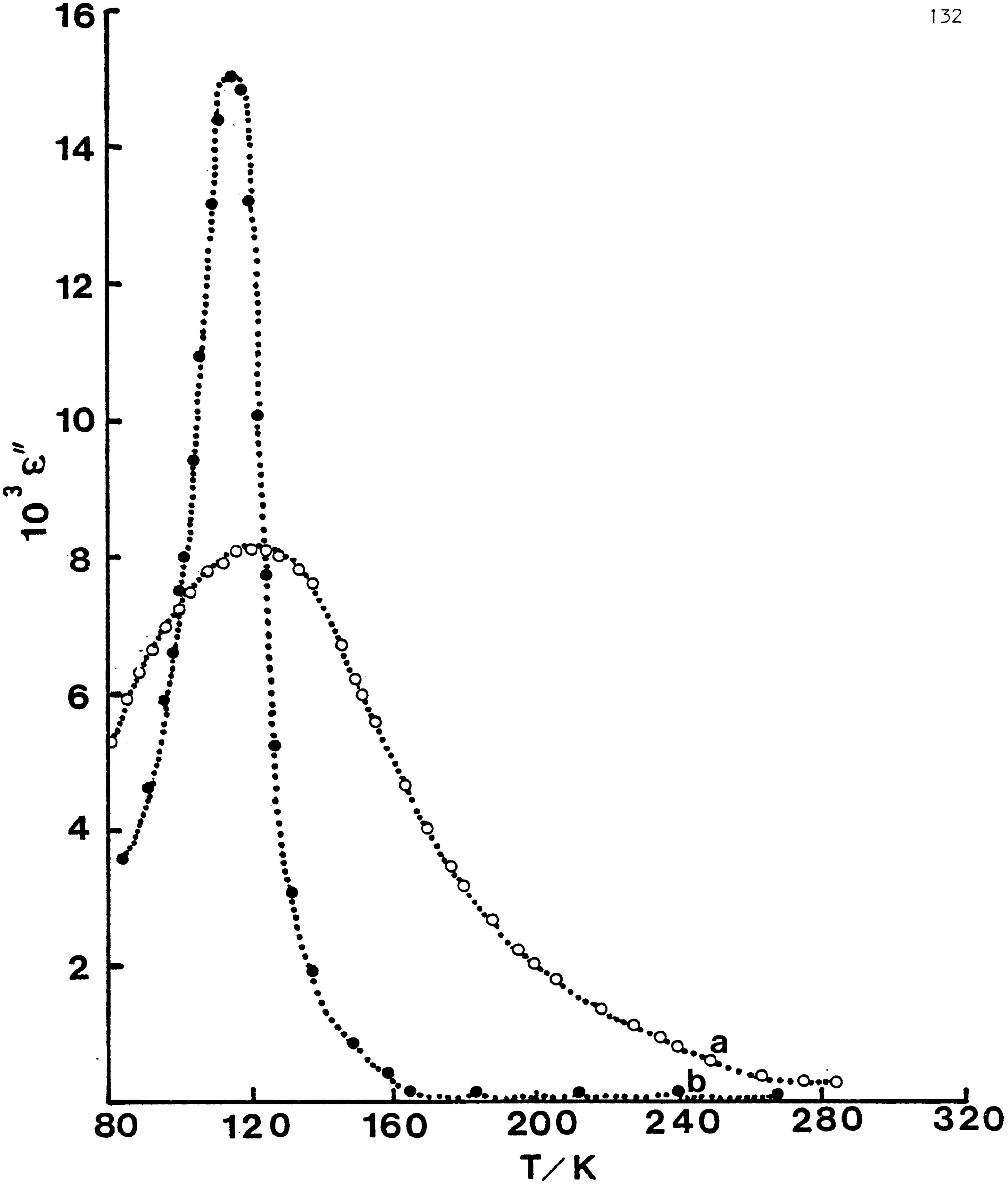


FIGURE IV-8: Dielectric loss factor, ε" versus temperature for a = di-tert-butyl carbinol; b = 3-bromopentane in polystyrene at 1.01 kHz.

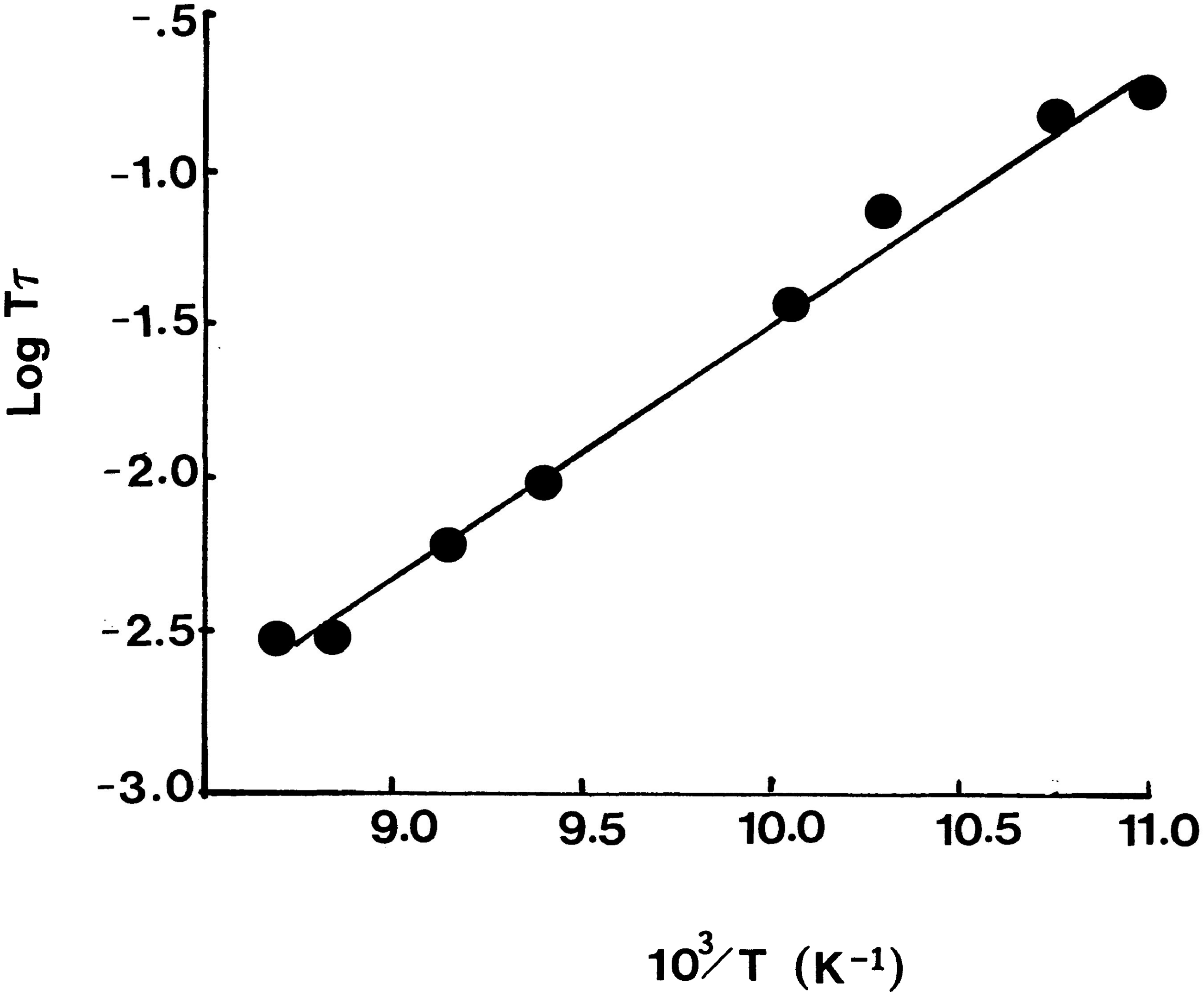


FIGURE IV-9: Eyring rate plot of log Tτ versus 1/T for di-tert-butyl carbinol in polystyrene.

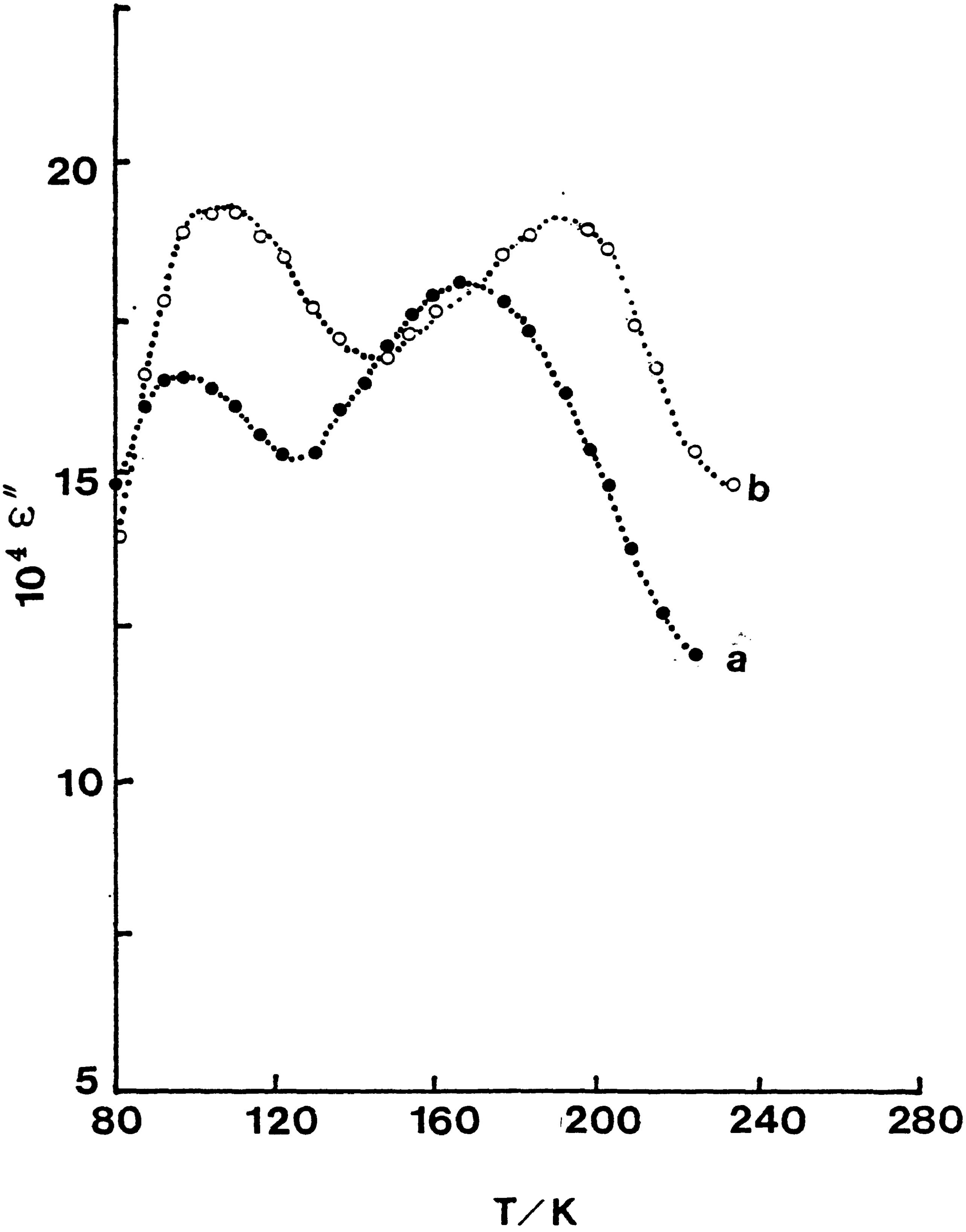


FIGURE IV-10: Dielectric loss factor, ε'' versus temperature for di-tert-butyl carbinol in glassy o-terphenyl at a = 50.2 Hz and b = 1.01 kHz.

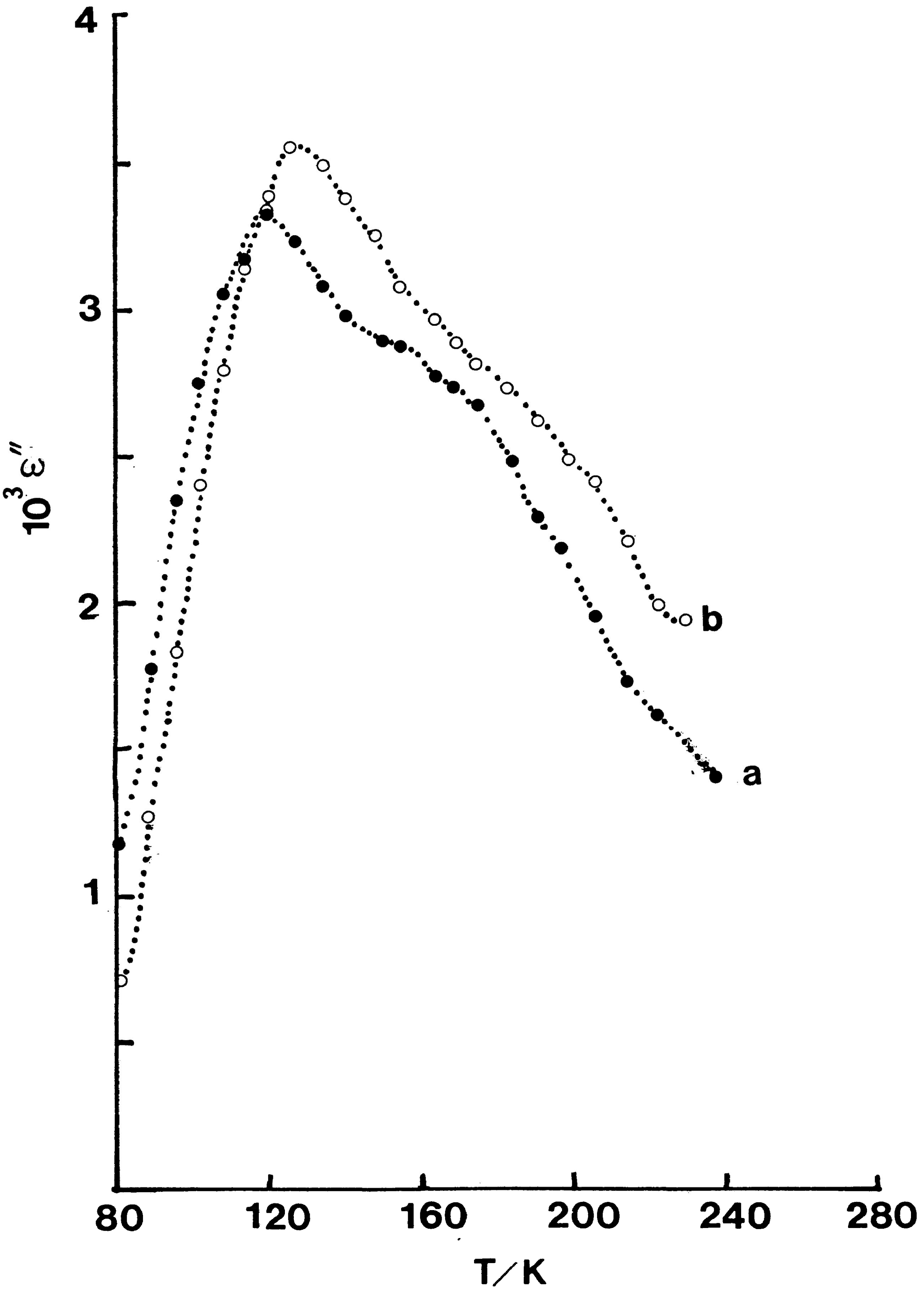
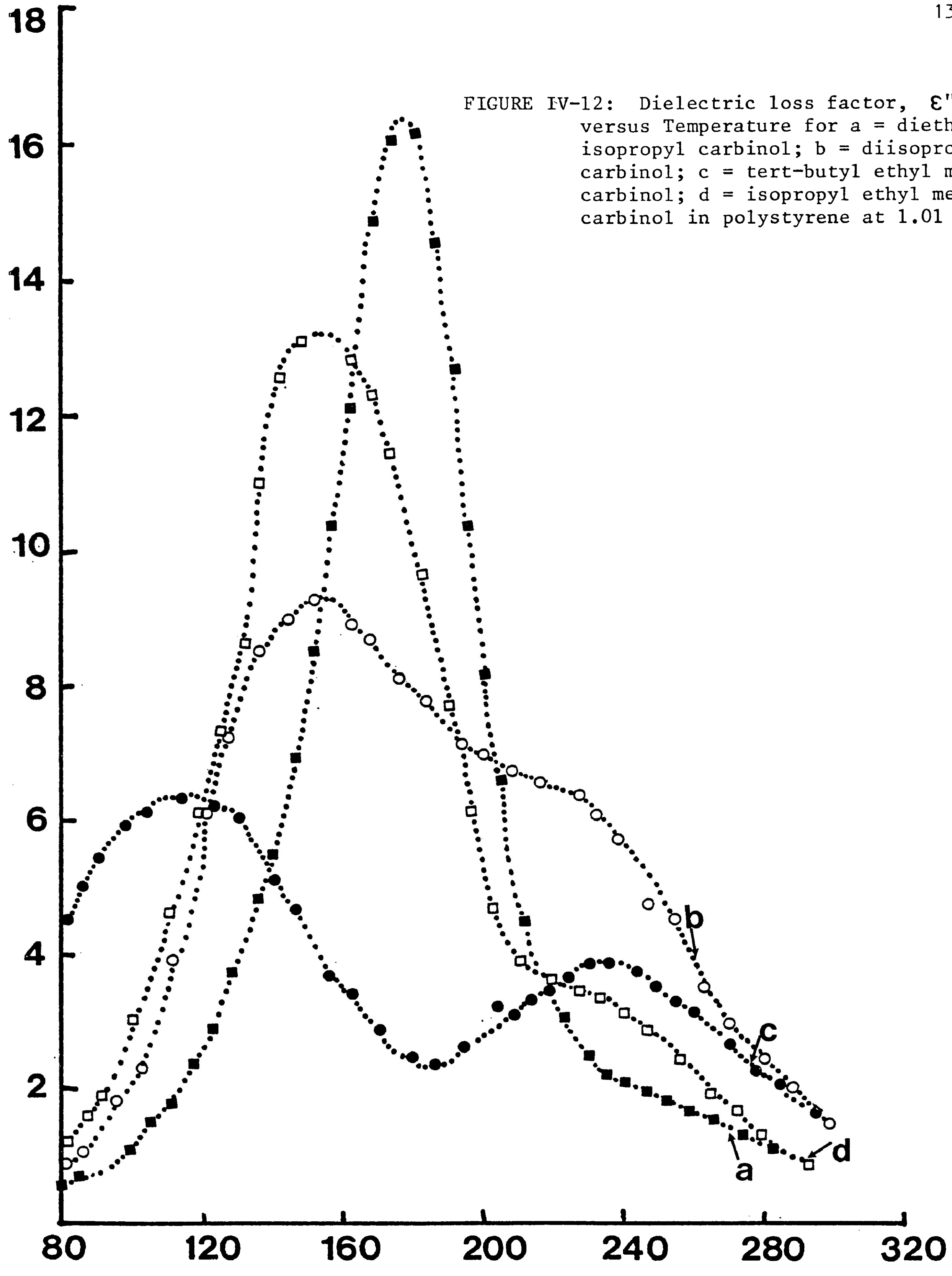


FIGURE IV-11: Dielectric loss factor, ε" versus temperature for di-tert-butyl carbinol in Santovac at a = 1.01 kHz and b = 10.2 kHz

FIGURE IV-12: Dielectric loss factor, ε" versus Temperature for a = diethyl isopropyl carbinol; b = diisopropyl methyl carbinol; c = tert-butyl ethyl methyl carbinol; d = isopropyl ethyl methyl carbinol in polystyrene at 1.01 kHz.



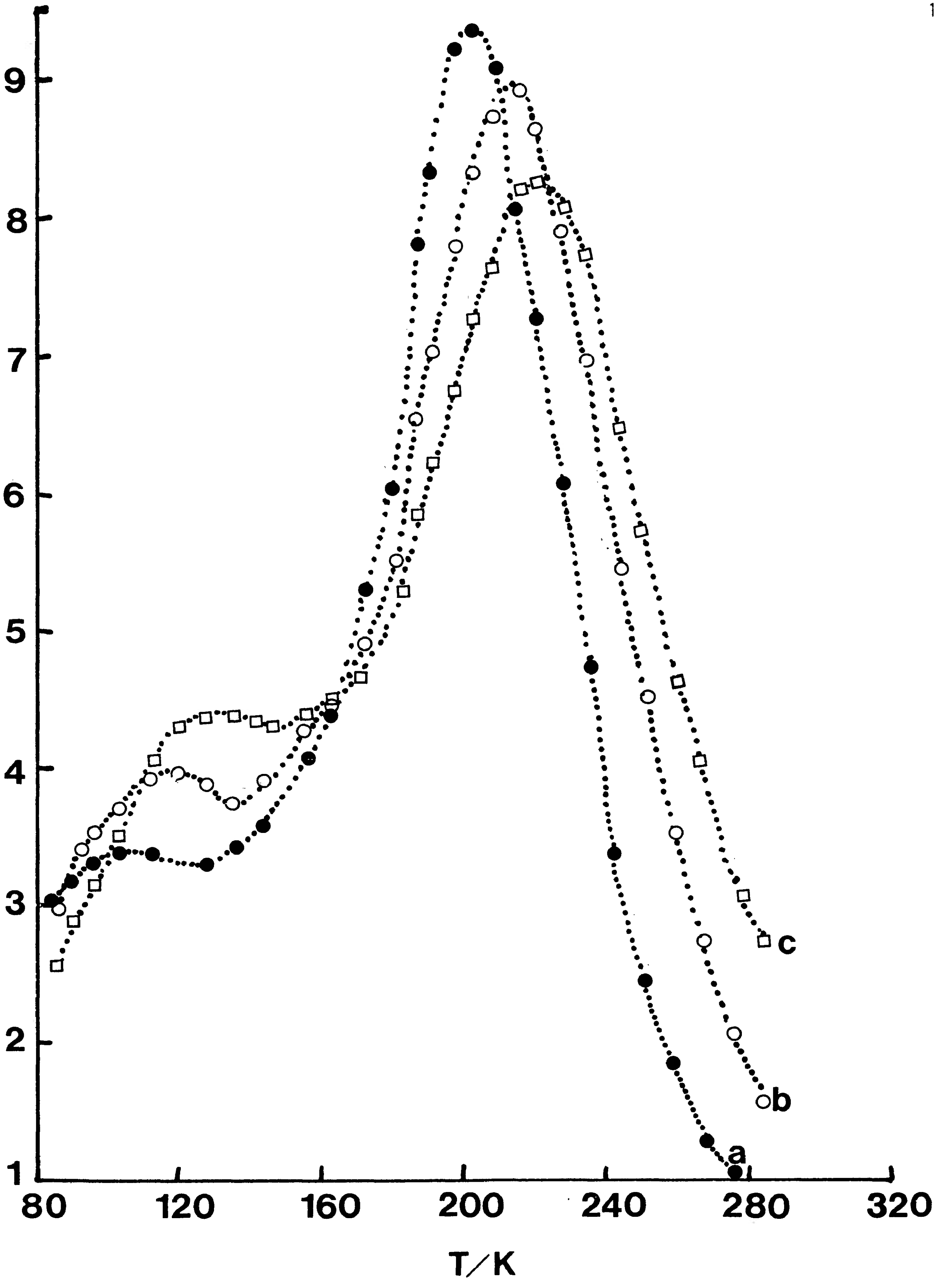


FIGURE IV-13: Dielectric loss factor, ε" versus Temperature for tert-butyl isopropyl carbinol in polystyrene at a = 50.2 Hz; b = 1.01 kHz and c = 10.2 kHz.

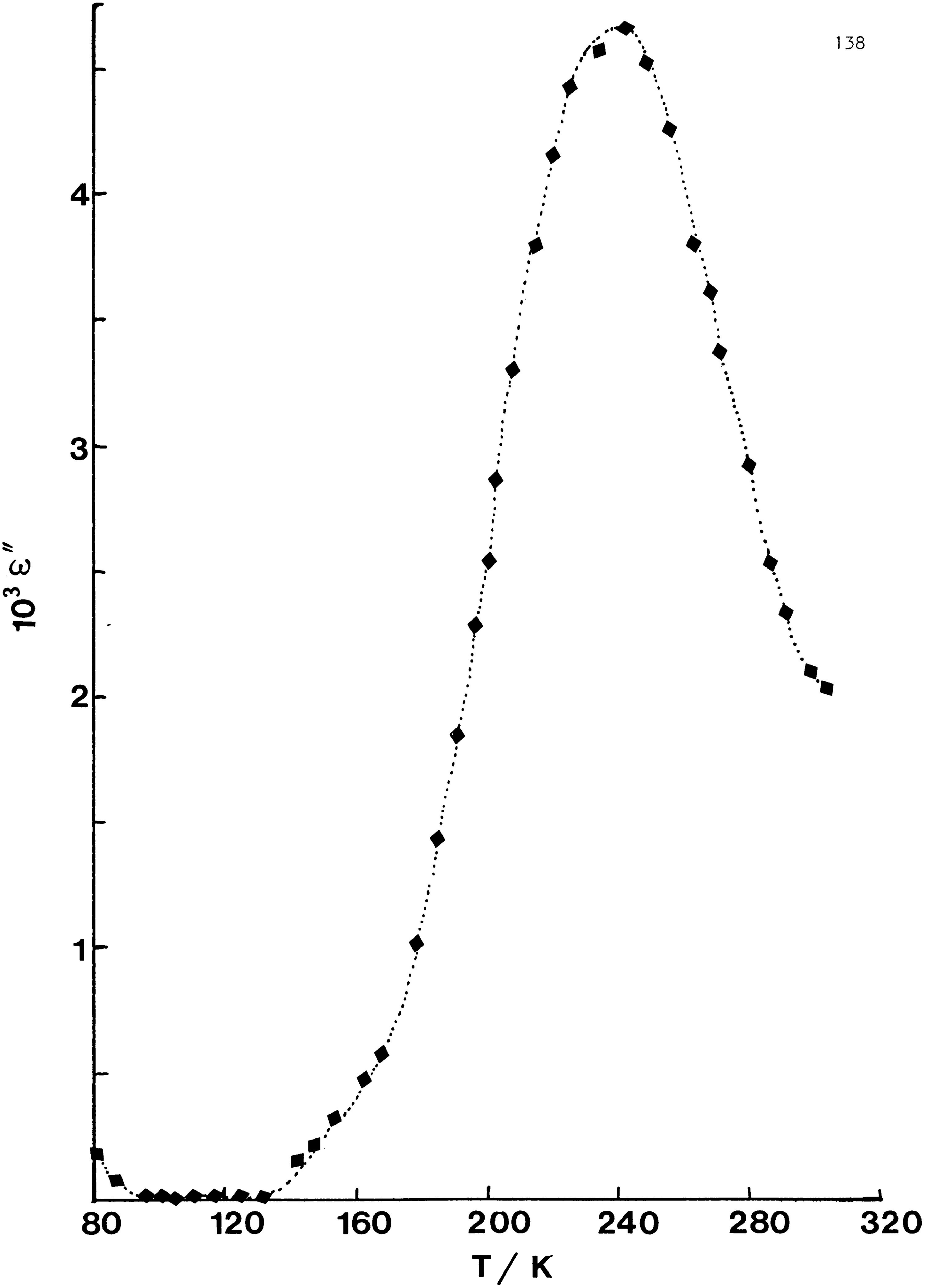


FIGURE IV-14: Dielectric loss factor, ε'' versus Temperature for tricyclohexyl carbinol in polystyrene at 50.2 Hz.

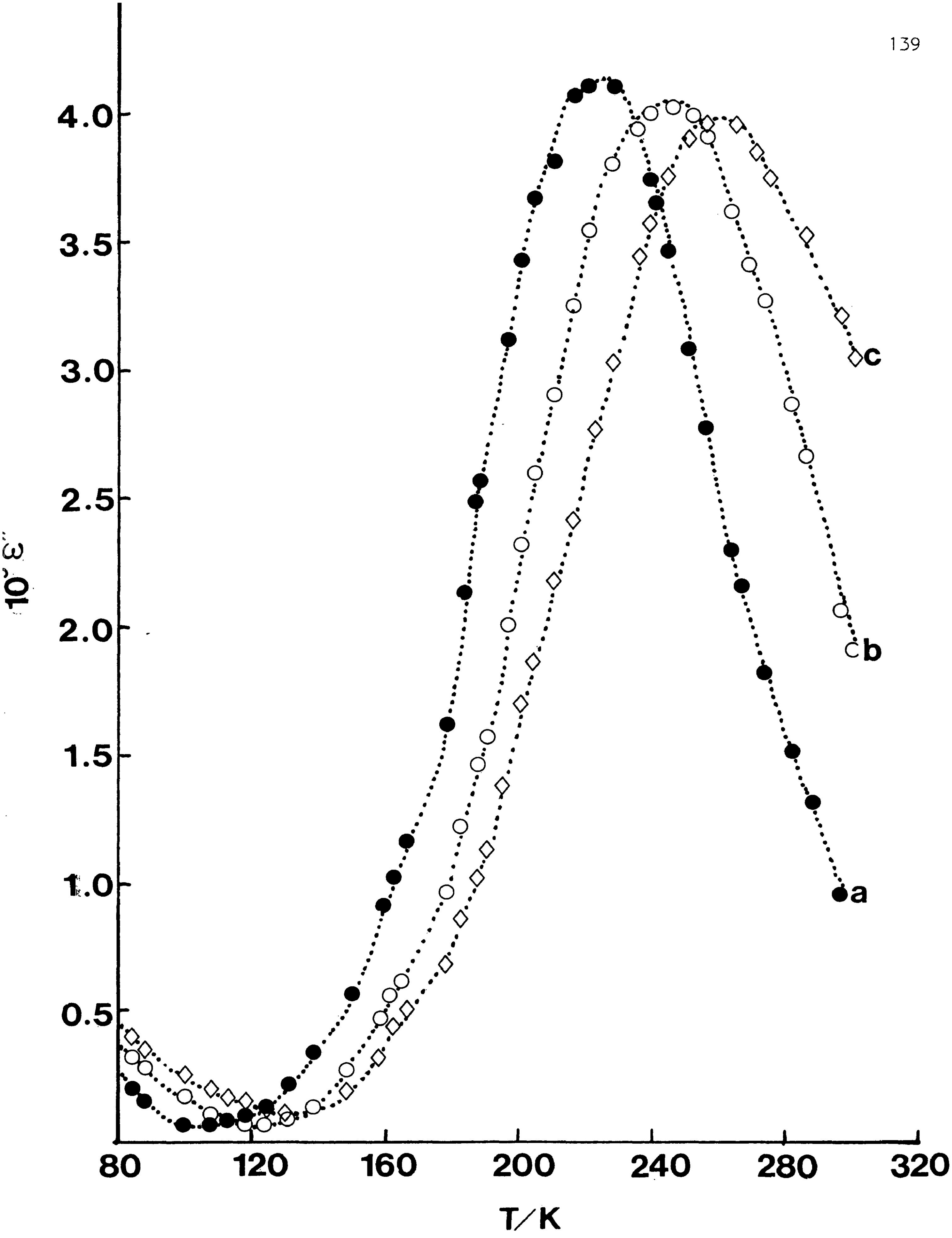


FIGURE IV-15: Dielectric loss factor, ε'' versus Temperature for diphenyl methyl carbinol in polystyrene at a = 50.2 Hz; b = 1.01 kHz and c = 10.2 kHz.

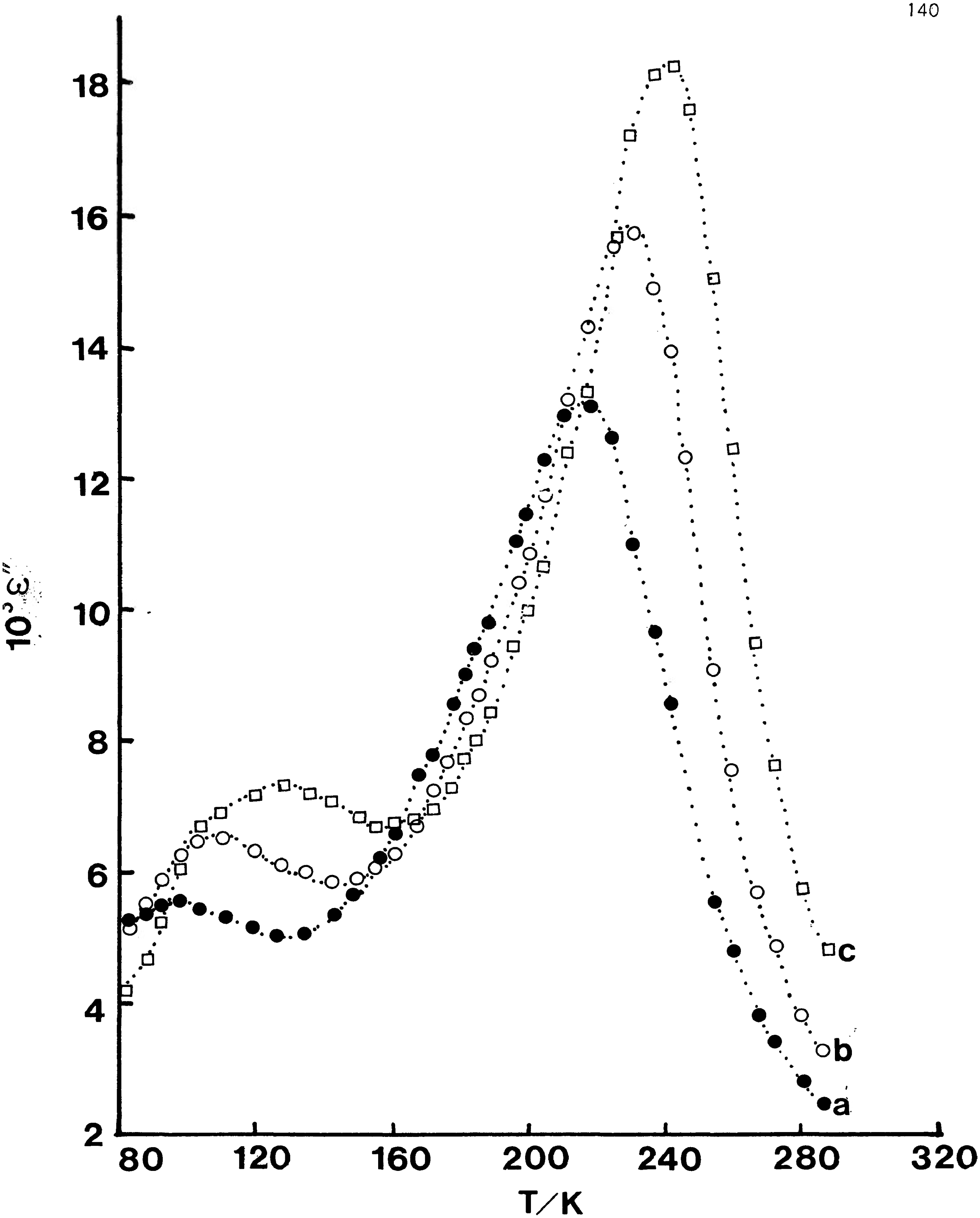


FIGURE IV-16: Dielectric loss factor, ε" versus Temperature for dimethyl phenyl carbinol in polystyrene at a = 50.2 Hz; b = 1.01 kHz and c = 10.2 kHz.

CHAPTER V

DIELECTRIC RELAXATION STUDIES OF SOME SMALL ALCOHOLS AND WATER IN GLASSY MEDIA

INTRODUCTION

The dielectric study of alcohols in the pure liquid state (1-5) and in liquid solutions (6-10), over a wide temperature and frequency range has shown that the dielectric dispersion may be characterized by three relaxation times, namely, τ_1, τ_2, and τ_3. The τ_3 process, obtained at the highest frequency is virtually insensitive to the effect of medium and molecular size, has sometimes been assigned to OH-group rotation (3,7) while the τ_2 process is attributed to contributions from OR-group rotation, molecular rotation and/or from small multimers (3,4,11). The τ_1 process is the dominating process, and appears at the lowest frequency, would still be generally regarded as not adequately explained, has been accounted for in terms of several models.

Garg and Smyth (3) ascribed the τ_1 process to the breaking of an H-bond immediately followed by rotation of the partially liberated molecule. In their model it was proposed that, since the enthalpy of activation for the τ_1 process is close to the strength of one H-bond, the breaking of an H-bond is a dominant step. However, this model was criticized by Dannhauser and co-workers (4,5,12). From a dielectric study of isomeric octanols the latter (4,5) concluded that the H-bond breaking is not the rate determining step: rather it is a prerequisite for the occurrence of dielectric relaxation. Another model to explain the τ_1 process and its Debye nature was advanced by Böttcher and associates (13,14). The mixture of 1- and 4-heptanol in the pure liquid state exhibited a zero distribution of relaxation times, and to account for this, they assumed that a cyclic, nonplanar, and highly polar tetramer is responsible for the τ_1 process. Higasi and co-workers (15,16) explained the first dispersion (τ_1 process) in the alcohols as one involving a rate process for the breaking of an end H-bond and subsequent dipole inversion arising from co-operative rotation of the OH-group of the multimer chain.

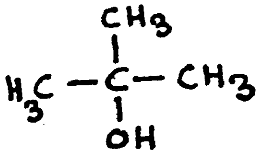
Recent dielectric studies by Huque and Walker (17) on long chain 1-alkanols and thiols in a polystyrene matrix have shown two well resolved dielectric peaks. An ε'' versus T plot at a fixed frequency showed a process which occurred at lower temperatures and was assigned to the intramolecular motion, while the higher temperature process in 1-alkanols was shown to be related to molecular rotation which was influenced by the presence of some intermolecular H-bonding.

It has been shown by Huque and Walker (17) that alcohols such as 1-pentanol and 1-hexanol in a polystyrene matrix exhibit an absorption due to molecular and/or intramolecular motion in temperature region approximately 80-110 K in our frequency range ($10-10^5$ Hz). The alcohols we have chosen in the present study are smaller than 1-hexanol, thus it is to be expected that the contribution to the dielectric absorption from molecular and/or intramolecular process of monomer would not occur in the temperature range 200-270 K. Hence, if any process(es) occurs in the 200-270 K region then it would not involve contribution from the molecular and/or intramolecular motion of the alcohols. In addition to small alcohols water and heavy water are also studied in glassy media so as to determine any resemblence in their dielectric behaviour. Dielectric relaxation studies of alcohols in glassy media offer a fresh approach over the dielectric studies of liquid alcohols where it is not feasible to isolate three separate absorption peaks characterized by relaxation times, τ_1, τ_2 and τ_3 (16,11,18). In order to interpret present dielectric results, the infrared spectra of some of the alcohols are also obtained in glassy media.

EXPERIMENTAL RESULTS

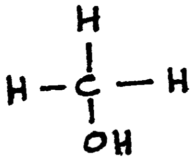
Compounds included in this chapter are listed as follows:

tert-Butanol



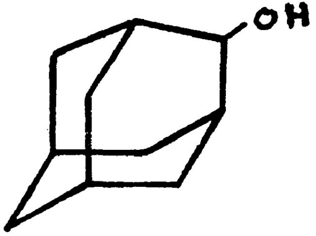
$H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$

Methanol

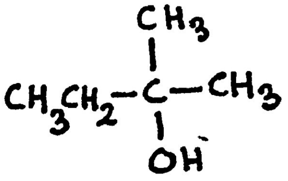


$H-\overset{H}{\underset{OH}{C}}-H$

2-Adamantanol

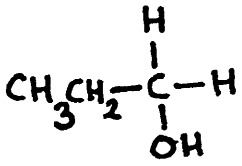


tert-Amyl alcohol



$CH_3CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3$

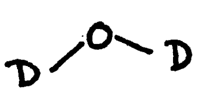
1-Propanol



$CH_3CH_2-\overset{H}{\underset{OH}{C}}-H$

Water

Heavy water



All alcohols except 2-adamantanol used here were of sufficient purity, and they were further purified by refluxing with suitable drying agents and distilling over 4 Å molecular sieves. 2-Adamantanol was of 99% purity and used without further purification.

Figures V-1, V-4, V-8 and V-12 show typical ε'' versus T plots. Plots of ε'' versus $\log\nu$ are shown in Figures V-5, V-6, V-9, V-10, V-12 and V-13. Some representative plots of $\log\tau T$ versus $1/T$ are illustrated in Figures V-7, V-14, V-15, V-18 and V-20. The infrared spectra of tert-butanol in thin film of glassy o-terphenyl and polystyrene at different temperatures are given in Figures V-2 and V-3.

DISCUSSION

tert-Butanol

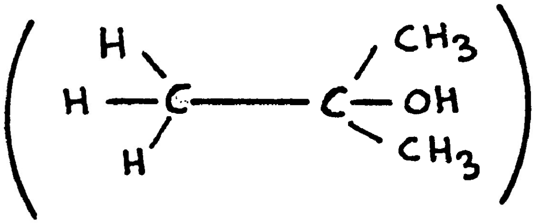
tert-Butanol has been studied in glassy o-terphenyl at one concentration (0.59 M) and in polystyrene at five concentrations.

tert-Butanol in glassy o-terphenyl, 0.59 M, yielded only one absorption (Figure V-1) in the temperature range 120-152 K which is a similar temperature range to that for tert-butanol in carbon tetrachloride (19). The ΔH_E and τ values at 100 K for tert-butanol in glassy o-terphenyl are 21 kJ mol^{-1} and 3.5×10^{-1} s, respectively. The ΔH_E 21 kJ mol^{-1} cannot be reconciled with the OH-group rotation about the C-O bond because the energy barriers for the OH-group rotation about the C-O bond in sterically hindered tri-tert-butyl carbinol and phenyl-di-tert-butyl carbinol in benzene solution are only 2 and 5 kJ mol^{-1} respectively (20). The tert-butanol is comparable in size and shape with tert-butyl chloride, tert-butyl bromide and 2-methyl-2-nitropropane. The ΔH_E values for molecular rotation in the pure solid state for these molecules are virtually identical, being 5.4, 6.3 and 6.7 kJ mol^{-1}, respectively (21). Thus, the ΔH_E of 21 kJ mol^{-1} for tert-butanol in glassy o-terphenyl cannot be assigned to molecular rotation.

The infrared spectrum of a thin film of tert-butanol in glassy-o-terphenyl at 0.59 M in the temperature range 123-193 K is given in Figure V-2, and at all the temperatures there are three peaks. A peak, which is extremely weak, centres at 3585 cm^{-1} and does not change its intensity and position with increasing temperature while the two peaks occurring below 3300 cm^{-1} change their shape, position and relative intensity with the temperature. Allerhand and Schleyer (22) and Bellamy et al (23) have shown that the monomer stretching frequency of an alcohol depends on the solvents. With the solvent effects on the OH-stretching frequency of an alcohol in mind, the 3585 cm^{-1} peak can be ascribed to the monomer OH-stretching (24). The two peaks below 3300 cm^{-1}, which tend to merge with the increase of the temperature, in view of the literature data (25-28) can be assigned to the presence of the polymerized species. Thus, in the temperature region (120-152 K) of the dielectric absorption of tert-butanol in glassy o-terphenyl, the presence of polymerized H-bonded species would seem to lead to the absorption.

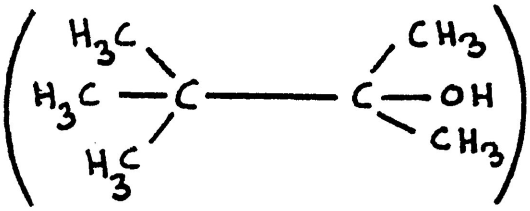
The infrared spectrum of the tert-butanol in a polystyrene matrix at 3.31 M, in the temperature range 193-293 K, was determined (Figure V-3). At all the temperatures, a sharp peak appears between 3570-3580 cm^{-1}. Bellamy et al (23) have shown that the monomer stretching frequency of methanol shifts to 34 cm^{-1} towards the lower wave number side by changing the solvent from carbon tetrachloride to toluene. The π-electron cloud of toluene may well be expected to have a similar interacting capacity with the OH-proton to that of the monomer phenyl unit in polystyrene. The monomer stretching frequency of tert-butanol in carbon tetrachloride is observed at 3617 cm^{-1} (29). A peak between 3570-3580 cm^{-1} for tert-butanol in polystyrene has shifted by 37-47 cm^{-1} relative to the monomer peak observed in carbon tetrachloride. The difference in $\sim$37 cm^{-1} by changing the solvent from carbon tetrachloride to polystyrene is approximately the same as that observed for methanol by changing the solvent from carbon tetrachloride to toluene. Hence, it seems that the 3570-3580 cm^{-1} peak of tert-butanol in polystyrene is due to the monomer. The band which appears between 3440-3450 cm^{-1} is probably due to a dimer and/or a trimer. A band below 3400 cm^{-1} broadens with increase in temperature. At 193 K it is around 3320 cm^{-1} whereas at 233 K it is found to be at $\sim$3340 cm^{-1} while at 293 K there is hardly any sign of this band. In the light of a matrix isolation study (28) of methanol and ethanol in an argon matrix, the band which appears below 3400 cm^{-1} can probably be assigned to some type(s) of relatively small polymerized species.

The dielectric study of tert-butanol at five different concentrations in a polystyrene matrix exhibited an absorption in the temperature range ∿200-270 K (Figure V-4). It is evident from Figure V-4 that, besides absorption in the ∿200-270 K region, there appears to be the tail of an absorption peak near 80 K at all five concentrations. As discussed earlier, the molecular process and the process due to OH-group rotation would either occur near or below the liquid nitrogen temperature. Another possibility of intramolecular rotation could be the rotation about the C-C bond which consequently turns the OH-dipole. It has been shown for the substituted haloethanes that increasing the steric factor about the C-C bond increases the barrier of rotation considerably (30). tert-Butanol may be considered as a substituted ethane



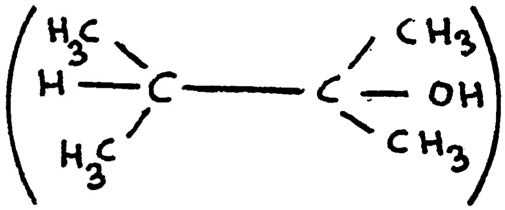
with fewer steric factors than

a) dimethyl-tert-butyl carbinol



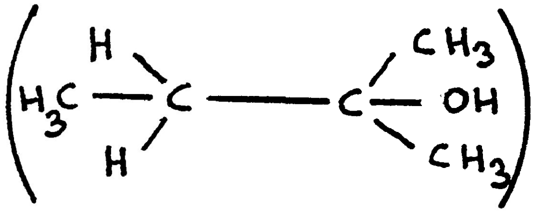
,

b) dimethyl isopropyl carbinol



,

and c) tert-amyl alcohol



(to be discussed later) whose ΔH_E values are 42, 28 and 20 kJ mol^{-1}, respectively. For the intramolecular rotation of tert-butanol, absorption should occur even below the absorption obtained for the intramolecular rotation of the tert-amyl alcohol, ΔT = 100-134 K. In fact, the only candidate for the absorption peak in the temperature range 200-270 K is, thus, the H-bonded species, the presence of which has been indicated by the infrared study of tert-butanol in a polystyrene matrix. It is apparent from the ε'' versus T plot (Figure V-4) that at almost all the concentrations studied the $\sim$200-270 K absorption gives indications of two partially resolved peaks. It is shown by the infrared spectrum that tert-butanol in a polystyrene matrix possesses a variety of H-bonded species in the temperature region of the dielectric absorption. The two partially resolved peaks may arise from the presence of two different types of H-bonded species. Nevertheless, the enthalpy of activation 61 ±11 kJ mol^{-1} may well be a characteristic of the dominant relaxation process.

Methanol and 2-Adamantanol

Methanol was studied in polystyrene at three different concentrations, and the absorption was found in the ∿200-270 K range (Figure V-8). As discussed earlier in the case of tert-butanol in a polystyrene matrix, the dielectric absorption due to the free molecule and to the OH-group rotation would occur below liquid nitrogen temperature. Mehanol, being smaller in size and having fewer steric factors about the OH-group than the tert-butanol, should exhibit these processes at even lower temperatures. Hence, the absorption, which is observed in the temperature region ∿200-270 K, is related to the presence of H-bonded species. At all the three concentrations, the absorption in the ∿200-270 K region seems to involve contributions from two processes, possibly owing to the presence of two kinds of polymerized species. Again the ΔH_E of 61 ±11 kJ mol^{-1} would seem typical of the dominant relaxation processes.

The dielectric absorption of 2-adamantanol in a polystyrene matrix has been carried out. Two well resolved absorptions were obtained (Figure V-11). The absorption, which occurs in the temperature range 80-95 K, is termed LTP (low temperature process) and yielded a ΔH_E of 14 kJ mol^{-1}. The high temperature process (HTP) was found in the temperature range ∿200-260 K. 1-Adamantanamine, which is of a similar size to 2-adamantanol, in a polystyrene matrix, yielded a ΔH_E 15 kJ mol^{-1} for molecular rotation (31). Hence, the LTP of 2-adamantanol may be attributed to molecular rotation. The HTP which is observed in the temperature range 224-267 K is not symmetrical and has a ΔH_E=54 kJ mol^{-1} which is to be attributed to the presence of H-bonded species as is the case for methanol where the ΔH_E values range between 54 and 61 kJ mol^{-1} for the three methanol cases at different concentration.

tert-Amyl Alcohol and 1-Propanol

Dielectric studies of tert-amyl alcohol at four different concentrations and 1-propanol at one concentration in polystyrene matrices yielded two peaks in each case (Figures V-12, V-17). The LTP was found in the vicinity of liquid nitrogen temperature. The HTP occurs in the 200-260 K region and corresponds with those found for tert-butanol and methanol. 1-Propanol possesses the same number of carbons in the chain (i.e. three) as tert-amyl alcohol but has different steric factors around the OH-group. The ΔH_E of LTP in tert-amyl alcohol is independent of the concentration and is 20 kJ mol^{-1}. This indicates that all these concentrations the nature of LTP is the same. tert-Amyl chloride, which is a corresponding nonassociating molecule, has a similar size and shape to tert-amyl alcohol. In the polystyrene matrix, the tert-amyl chloride exhibited only one absorption in the temperature range 116-151 K with a ΔH_E 24 kJ mol^{-1}. The ΔH_E of tert-amyl chloride is in fair agreement with the ΔH_E for LTP in tert-amyl alcohol (i.e. 20 kJ mol^{-1}). As indicated by Ahmed and Walker (32), for 1-bromoalkanes in a polystyrene matrix, the intramolecular processes are characterized by a higher β. An appreciably high β, 0.29-0.54, for tert-amyl chloride suggests that the process is an intramolecular one. tert-Amyl alcohol for its LTP has also a β value larger than that to be expected from a molecular process. Altogether, the correspondence of the ΔH_E and β values of tert-amyl alcohol and tert-amyl chloride suggests that the LTP of tert-amyl alcohol is most likely due to intramolecular rotation. 1-Propanol, which is slightly smaller in molecular volume than tert-amyl alcohol, in view of the type of argument, is not expected to yield a molecular absorption process above $\sim$80 K. The ΔH_E for the LTP of 1-propanol was found to be 15 kJ mol^{-1}. This value is reasonable for intramolecular rotation. The non H-bonding tert-amyl chloride, which is the same size as tert-amyl alcohol but slightly larger than 1-propanol, does not possess any absorption above 160 K. Thus, the peak observed in tert-amyl alcohol and 1-propanol in the temperature region ∿200-260 K cannot be assigned to either molecular or intramolecular rotations. The only candidate for the ∿200-260 K process would seem to be the H-bonded species. As in the case of tert-butanol and methanol in polystyrene, tert-amyl alcohol and 1-propanol also possess asymmetry in the ∿200-260 K absorption peak. However, the asymmetry in the tert-amyl alcohol is not so apparent as is the case of 1-propanol. Thus, the absorption in the 200-260 K region may be a contribution from two (or more) processes involving different kinds of H-bonded species where the magnitude of the ΔH_E value is about 61 ±11 kJ mol^{-1}.

Water and Heavy Water

A dielectric study of water in three glassy media, namely, glassy o-terphenyl, Santovac and polystyrene, and of heavy water in polystyrene has been carried out. A very low concentration of water (i.e. 0.11 M) in glassy o-terphenyl yielded a dielectric absorption in the temperature range 180-226 K (Figure V-18) with a ΔH_E of 45 kJ mol^{-1} (33). The β range for water in glassy o-terphenyl for the process is found to be 0.38-0.67 which is too high a value for the molecular process. Further, owing to the small size of the water molecule the molecular and intramolecular processes are expected to occur below 80 K in our frequency range (i.e. $10\text{-}10^5$ Hz). Santovac is a glassy forming viscous liquid. Water in Santovac (0.7% by weight) also yielded an absorption in the temperature range 180-212 K (Figure V-20) with a ΔH_E of 43 kJ mol^{-1} (33). The Fuoss-Kirkwood β range for water in Santovac is found to be 0.59-0.86 which does not conform to the molecular process. Since the activation energy of water in glassy o-terphenyl and Santovac is virtually identical, hence, it appears that the nature of the relaxation process is the same in both cases. The ΔH_E value $\sim$44 kJ mol^{-1} has been observed for some forms of ice (e.g. ice VI)(34) which corresponds with the ΔH_E values obtained for water in glassy o-terphenyl and Santovac. Further, the ΔH_E $\sim$44 kJ mol^{-1} for ice is suggested to be related to the H-bond structure of ice (34).

A dielectric study of water and heavy water in polystyrene at very low concentrations yielded only one absorption peak in each case with an apparent asymmetry in the peak (Figure V-21). Absorption observed in water in the temperature range 219-256 K gives a ΔH_E of 55 kJ mol^{-1}. Heavy water exhibited absorption in the temperature range 222-261 K with a ΔH_E of 49 kJ mol^{-1}. Since molecular and intramolecular rotation cannot account for the observed process of water/ heavy water in polystyrene, therefore, it appears more likely that the H-bonded species are responsible for the dielectric absorption in both water and heavy water.

Lang and Lüdemann (35) have studied the pressure and the temperature dependence of longitudinal proton relaxation times in supercooled water. At atmospheric pressure an activation energy of 55 kJ mol^{-1} was obtained. It was indicated that at lower temperatures in supercooled water, a random H-bond network is fully developed. The energy barrier of 55 kJ mol^{-1} was suggested to arise from processes where, during reorientation of the molecules, several H-bonds have to be broken. Auty and Cole (36) have carried out a dielectric study of ice and solid D_20 and obtained a ΔH_E of 53 and 54 kJ mol^{-1}, respectively. The higher ΔH_E values for water and D_20 in solid form were suggested to correspond with the breaking of three H-bonds. The ΔH_E values of water and D_20 in polystyrene at low temperatures are in close agreement with those obtained by Auty and Cole. Later studies (37-41) of a variety of ices and water have shown that the dielectric relaxation mechanism in ice and water involves the breaking of H-bonds as one of the important steps.

Our results on water in different glassy media bear out that the dielectric absorption obtained in these three media involve H-bonded species. However, it is worth noting that the dielectric absorption for water in glassy o-terphenyl and Santovac occurs at lower temperatures than the polystyrene possibly owing to the influence of the medium on the H-bonded equilibria. Further, the activation energies obtained for water and heavy water in polystyrene are close to those obtained for alcohols (due to H-bonded species).

CONCLUSION

It is evident from the foregoing discussion that the dielectric absorption peak in tert-butanol in glassy o-terphenyl is due to the presence of the intermolecularly H-bonded species whose presence is clearly demonstrated from the infrared spectrum of tert-butanol in glassy o-terphenyl. However, tert-butanol in a polystyrene matrix seems a different case in that its dielectric absorption occurs at about 100 K higher than that found in tert-butanol in glassy o-terphenyl. Again the absorption is to be related to the presence of the H-bonded species. In general, for a given alcohol it appears that the H-bonded equilibria are medium dependent (see τ values in Table V-1) as indicated previously by other workers (42,43) and that this influences the rate process(es) detected by dielectric absorption studies. The influence of medium on H-bonded equilibria is also apparent from the studies of water in different media.

In contrast to the work on pure liquid alcohols, the present study has achieved in some cases separation of the intramolecular/molecular process from one related to the presence of intermolecularly H-bonded species. It is striking that when polystyrene is the dispersion medium, dielectric absorption for alcohols and water is found in the 200-270 region which yields a ΔH_E in the range 51 to 72 kJ mol^{-1}. On the whole, this is a similar range to that found for the sterically hindered alcohols in a polystyrene matrix (see Chapter IV). It is tempting to ascribe the absorption to a dissociation process involving the breaking on average of about three H-bonds since the strength of one H-bond is about 18 ±2 kJ mol^{-1} (12,24,44-48). In contrast, the ΔH_E value 21 kJ mol^{-1} for tert-butanol in glassy o-terphenyl can be assigned to the breaking on average of one H-bond.

Absorption which can be attributed solely to dissociation of H-bonds would seem too simplistic a model, and this is particularly borne out by the data in Figures V-4 and V-8 where some of these simple alcohols in a polystyrene matrix exhibit two absorption peaks in the 200-270 K region. In fact, our ΔH_E's in polystyrene are probably at best some mean type of value which may be used as an indicator as to the energy involved in the rate processes. The infrared evidence also bears out that we are dealing with a variety of species under our experimental conditions.

Of the mechanism considered in our introduction, present data are against the interpretation of our 200-270 K absorption observed when polystyrene is the dispersion medium in terms of:

i) sole relaxation of a highly polar tetramer (13,14);

ii) a mechanism (4,5,12) which does not involve H-bond breaking as a rate determining step;

iii) the attractive process invoked by Garg and Smyth (3) which involves the breaking of an H-bond followed by rotation of the partially liberated molecule since our ΔH_E values exhibit no correspondance with increasing size and in some cases two absorption peaks were observed.

Although our results for these small alcohols and water favour a dominant contribution from a dissociation process involving the breaking of H-bonds, it would seem that some additional factor(s) is involved.

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TABLE V-1. Relaxation Parameters for Some Small Alcohols

Compound (mole/litre)	Medium	ΔT (K)	Relaxation Times (s) 100 K	150 K	200 K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
tert-Butanol (0.59)	GOTP*	120-152	3.5×10^{-1}	5.4×10^{-5}		21 ±0.6	-18 ±4
tert-Butanol (0.58)	P.S.‡	253-270		1.6×10^{6}	1.8×10^{0}	67 ±15	88 ±58
tert-Butanol (1.69)	P.S.	226-263		2.9×10^{4}	2.1×10^{-1}	58 ±8	59 ±33
tert-Butanol (2.11)	P.S.	229-254		2.3×10^{6}	9.0×10^{-1}	72 ±8	120 ±33
tert-Butanol (2.64)	P.S.	239-273		1.1×10^{6}	4.3×10^{0}	61 ±9	49 ±36
tert-Butanol (3.31)	P.S.	203-225		9.6×10^{3}	6.0×10^{-3}	70 ±2	150 ±9
Methanol (1.45)	P.S.	240-265		6.9×10^{4}	3.0×10^{-1}	60 ±5	70 ±20
Methanol (4.00)	P.S.	210-238		4.1×10^{2}	5.9×10^{-3}	54 ±4	72 ±19
Methanol (7.05)	P.S.	240-260		1.8×10^{5}	6.3×10^{-1}	61 ±6	69 ±23
2-Adamantanol (0.30)	P.S.	80-95 224-267	5.9×10^{-6}	1.2×10^{-5} 1.1×10^{4}	 1.5×10^{-1}	14 ±2 54 ±4	9 ±21 46 ±16
tert-Amyl alcohol (0.02)	P.S.	214-246		1.9×10^{5}	5.9×10^{-2}	71 ±7	137 ±30

TABLE V-1: Continued...

Compound (mole/litre)	Medium	ΔT (K)	Relaxation Times (s)			ΔH_E	ΔS_E
			100 K	150 K	200 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
tert- Amylalcohol (0.12)	P.S.	102 - 130	$5.5x10^{-3}$	$1.1x10^{-6}$		20 ±1	10 ±10
		214-253		$9.6x10^{2}$	$.7x10^{-2}$	51 ±3	43 ±15
tert-Amyl alcohol (0.66)	P.S.	104-134	$8.7x10^{-3}$	$1.7x10^{-6}$		20 ±2	7 ±15
		201-233		$2.0x10^{2}$	$2.8x10^{-3}$	54 ±3	79 ±16
tert-Amyl alcohol (1.09)	P.S.	100-134	$1.0x10^{-2}$	$2.2x10^{-6}$		20 ±1	3 ±6
		193-231		$1.5x10^{2}$	$1.9x10^{-3}$	55 ±2	85 ±8
tert-Amyl chloride (1.00)	P.S.	116-151	$3.3x10^{-1}$	$1.1x10^{-5}$		24 ±3	19 ±24
1-Propanol (0.85)	P.S.	83-98	$1.3x10^{-5}$	$1.9x10^{-8}$		15 ±2	11 ±24
		229-265		$3.0x10^{4}$	$2\ 0x10^{-1}$	58 ±4	62 ±15
Water (0.11)	GOTP	180-226		7.6	$7.6x10^{-4}$	44 ±2	41 ±11
Water (0.70 wt %)	SV‡‡	180-212		3.2	$4.3x10^{-4}$	43 ±3	38 ±15

TABLE V-1: Continued...

Compound (mole/litre)	Medium	ΔT (K)	Relaxation Times (s)			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			100 K	150 K	200 K		
Water (0.79)	P.S.	219-256			$6.1x10^{-2}$	55 ±5	58 ±19
Heavy Water	P.S.	222-261			$4.8x10^{-2}$	49 ±3	31 ±14

* GOTP means glassy o-terphenyl
‡ P.S. means polystyrene
‡‡ SV means Santovac

TABLE V-2: Fuoss Kirkwood Analysis Parameters for some Small alcohols and water/heavy water in glassy media.

T(K)	$10^6\tau$(s)	$\log\nu_{max}$	β	$10^3\varepsilon''_{max}$
tert-Butanol (0.59 M) in GOTP				
120.3	4162.9	1.58	0.46	0.48
123.9	2099.3	1.88	0.44	0.49
126.9	1289.5	2.09	0.42	0.49
130.4	849.3	2.27	0.38	0.49
134.1	461.7	2.54	0.40	0.51
135.2	388.2	2.61	0.38	0.50
137.7	258.3	2.79	0.39	0.51
142.7	134.3	3.07	0.37	0.52
148.0	66.6	3.38	0.39	0.51
151.9	42.7	3.57	0.41	0.52
tert-Butanol (0.58 M) in P.S.				
253.0	335.5	2.68	0.24	0.62
257.1	188.2	2.93	0.23	0.59
260.8	99.4	3.20	0.28	0.60
265.8	68.7	3.36	0.29	0.54
269.7	42.4	3.57	0.29	0.55
tert-Butanol (1.69 M) in P.S.				
226.5	4324.8	1.57	0.17	1.31
232.4	1441.6	2.04	0.19	1.29
236.9	730.3	2.34	0.23	1.37
242.1	352.4	2.65	0.23	1.27
246.8	213.6	2.87	0.26	1.30
252.5	130.3	3.09	0.29	1.24
263.4	48.3	3.52	0.37	1.20
tert-Butanol (2.11 M) in P.S.				
229.5	2991.6	1.73	0.15	1.78
235.2	1084.0	2.17	0.15	1.73
240.3	523.6	2.48	0.18	1.72
248.3	179.4	2.95	0.21	1.65
254.3	60.8	3.42	0.20	1.58

TABLE V-2: continued...

tert-Butanol (2.64 M) in P.S.

239.3	10122.5	1.20	0.20	0.60
242.8	5472.9	1.46	0.21	0.60
256.2	923.6	2.24	0.26	0.60
260.4	601.2	2.42	0.25	0.50
264.8	544.0	2.47	0.22	0.50
273.1	152.8	3.02	0.52	0.80

tert-Butanol (3.31 M) in P.S.

203.2	3152.8	1.70	0.17	7.70
207.3	1240.7	2.11	0.18	7.60
211.3	598.0	2.43	0.18	7.40
215.5	266.3	2.78	0.18	7.20
219.4	132.6	3.08	0.18	7.00
222.2	84.6	3.27	0.18	6.90
225.0	48.4	3.52	0.18	6.80

Methanol (1.45 M) in P.S.

240.3	605.0	2.42	0.22	1.20
247.4	215.0	2.87	0.25	1.10
251.3	136.6	3.07	0.28	1.10
255.6	88.3	3.26	0.32	1.10
259.8	58.9	3.43	0.37	1.10
264.8	31.1	3.71	0.36	1.00

Methanol (4.00 M) in P.S.

210.4	1209.3	2.11	0.16	1.10
213.3	599.6	2.42	0.19	1.10
216.7	483.8	2.52	0.19	1.10
222.7	205.4	2.89	0.20	1.10
225.9	115.5	3.14	0.20	1.00
229.8	69.0	3.36	0.23	1.00
233.8	47.4	3.52	0.28	1.00
237.7	28.3	3.75	0.33	1.00

TABLE V-2: continued...

Methanol (7.05 M) in P.S.

240.1	1195.7	2.12	0.23	0.70
243.9	605.2	2.42	0.27	0.70
247.6	418.9	2.58	0.30	0.70
251.3	274.9	2.76	0.31	0.70
255.4	174.2	2.96	0.31	0.70
259.6	100.9	3.20	0.36	0.70

2-Adamantanol (0.30 M) in P.S.

80.5	484.3	2.52	0.22	8.03
83.5	248.2	2.81	0.23	8.25
86.4	95.4	3.22	0.22	8.55
87.6	67.3	3.37	0.22	8.65
92.9	27.2	3.77	0.22	8.96
94.8	15.4	4.01	0.24	9.16

2-Adamantanol (0.30 M) in P.S.

224.5	4701.9	1.53	0.17	1.60
229.2	1862.8	1.93	0.18	1.50
233.7	904.8	2.25	0.19	1.47
238.5	576.2	2.44	0.20	1.44
243.1	360.8	2.64	0.21	1.40
248.5	215.1	2.87	0.22	1.34
254.6	106.4	3.18	0.25	1.28
260.3	62.6	3.41	0.29	1.26
267.4	28.2	3.75	0.32	1.21

TABLE V-2: continued....

tert-Amyl alcohol (0.02 M) in P.S.

214.0	3130.3	1.71	0.14	1.90
217.5	1740.6	1.96	0.14	1.80
221.6	772.9	2.31	0.16	1.80
225.4	448.1	2.55	0.15	1.77
229.4	219.6	2.86	0.16	1.70
233.9	120.0	3.12	0.17	1.70
237.4	69.7	3.36	0.20	1.70
241.5	24.6	3.81	0.20	1.70
246.3	22.5	3.85	0.26	1.80

tert-Amyl alcohol (0.12 M) in P.S.

102.7	3510.0	1.66	0.30	1.10
104.2	1870.0	1.93	0.34	1.10
106.7	1089.5	2.16	0.32	1.10
110.4	492.9	2.51	0.40	1.20
114.6	190.5	2.92	0.40	1.10
118.8	91.9	3.24	0.39	1.10
122.5	49.7	3.51	0.38	1.10
126.4	27.9	3.76	0.39	1.10
130.2	17.4	3.96	0.41	1.10

tert-Amyl alcohol (0.12 M) in P.S.

214.7	3515.7	1.65	0.15	2.00
217.5	2056.2	1.89	0.16	2.00
220.7	1246.8	2.11	0.17	2.00
223.8	868.7	2.26	0.19	1.90
227.3	559.4	2.45	0.18	1.90
230.4	404.8	2.59	0.20	1.83
235.4	251.9	2.80	0.23	1.80
241.4	108.7	3.17	0.23	1.69
246.0	57.9	3.44	0.24	1.66
252.6	43.1	3.57	0.32	1.60

tert-Amyl alcohol (0.66 M) in P.S.

104.8	3759.9	1.63	0.23	3.60
109.6	804.4	2.30	0.30	3.70
113.2	346.0	2.66	0.34	3.70
116.8	188.4	2.93	0.37	3.80
119.5	138.5	3.06	0.38	3.80
122.5	81.3	3.29	0.38	3.80
125.7	51.2	3.49	0.37	3.80
128.2	34.4	3.66	0.36	3.80
131.2	22.7	3.85	0.34	3.80
134.1	11.8	4.13	0.30	3.80

TABLE V-2: Continued...

tert-Amyl alcohol (0.66 M) in P.S.

201.8	1905.9	1.92	0.17	4.80
205.4	1212.5	2.12	0.17	4.70
209.1	709.3	2.35	0.16	4.60
212.8	374.9	2.63	0.16	4.50
217.6	196.6	2.91	0.17	4.40
221.4	100.7	3.20	0.17	4.30
225.5	61.4	3.41	0.18	4.20
229.5	45.4	3.54	0.19	4.10
233.6	36.1	3.64	0.20	4.00

tert-Amyl alcohol (1.09 M) in P.S.

100.1	66137.1	0.38	0.48	10.10
104.3	5786.2	1.44	0.25	9.20
107.8	1812.7	1.94	0.30	9.40
110.7	858.4	2.27	0.33	9.40
113.8	458.1	2.54	0.35	9.40
117.6	227.9	2.84	0.38	9.60
122.1	108.6	3.17	0.29	9.60
125.7	61.1	3.42	0.39	9.60
129.7	33.8	3.67	0.38	9.60
133.7	16.4	3.99	0.36	9.60

tert-Amyl alcohol (1.09 M) in P.S.

193.8	6035.1	1.42	0.19	7.40
197.6	2495.1	1.80	0.21	7.30
201.7	1421.2	2.05	0.21	7.20
205.2	862.8	2.27	0.22	7.00
209.2	455.1	2.54	0.23	6.80
213.7	222.5	2.85	0.21	6.60
217.4	135.7	3.07	0.20	6.40
221.6	67.4	3.37	0.19	6.20
225.7	39.3	3.61	0.18	6.01
230.7	20.2	3.90	0.17	5.70

tert-Amyl chloride (1.00 M) in P.S.

116.7	6447.9	1.39	0.20	7.80
120.4	1740.4	1.96	0.34	7.70
123.7	691.8	2.36	0.40	7.60
127.4	333.8	2.68	0.44	7.30
131.6	179.5	2.95	0.50	7.20
135.6	105.5	3.18	0.53	7.10
139.8	57.2	3.44	0.54	6.90
150.8	11.9	4.13	0.47	6.50

TABLE VI-2: Continued...

1-Propanol (0.85 M) in P.S.

83.4	659.8	2.38	0.23	0.70
85.5	374.7	2.63	0.24	0.80
88.2	170.3	2.97	0.27	0.80
91.7	66.1	3.38	0.28	0.80
93.3	46.2	3.54	0.30	0.80
98.3	22.1	3.86	0.35	0.80

1-Propanol (0.85 M) in P.S.

228.9	2237.9	1.85	0.19	1.70
230.8	1851.9	1.93	0.19	1.60
234.3	963.0	2.22	0.21	1.60
237.5	577.8	2.44	0.22	1.60
241.4	379.7	2.62	0.23	1.50
244.8	262.6	2.78	0.24	1.50
248.8	181.9	2.94	0.25	1.50
253.0	102.9	3.19	0.28	1.40
258.8	60.7	3.42	0.31	1.30
264.7	46.3	3.54	0.42	1.30

Water (0.11 M) in GOTP

180.3	15111.5	1.02	0.57	3.50
184.3	9275.9	1.23	0.58	3.50
188.3	3963.4	1.60	0.63	3.50
191.0	2385.8	1.82	0.65	3.50
194.7	1499.6	2.03	0.67	3.50
198.5	950.1	2.22	0.68	3.50
206.8	334.0	2.68	0.67	3.60
210.5	214.6	2.87	0.64	3.60
214.5	135.9	3.07	0.59	3.50
218.2	85.1	3.27	0.54	3.60
222.1	48.4	3.52	0.45	3.50
226.0	22.3	3.85	0.38	3.70

Water (0.70 wt. %) in SV

180.4	9524.1	1.22	0.59	2.50
184.6	3870.8	1.61	0.65	2.40
188.4	2095.8	1.88	0.72	2.20
192.4	1114.9	2.15	0.72	2.50
195.9	738.5	2.33	0.81	2.30
199.6	427.4	2.57	0.83	2.50
203.4	255.4	2.79	0.86	2.70
207.0	191.0	2.92	0.85	2.50
211.9	106.1	3.18	0.83	2.70

TABLE V-2: Continued...

Water (0.79 M) in P.S.

219.2	2964.1	1.73	0.17	1.70
223.5	1925.2	1.92	0.17	1.70
227.4	1025.3	2.19	0.18	1.60
231.4	614.5	2.41	0.18	1.60
235.0	327.9	2.67	0.20	1.50
238.5	209.6	2.88	0.21	1.50
242.2	129.7	3.09	0.24	1.50
246.2	96.2	3.21	0.26	1.50
256.2	39.8	3.60	0.37	1.40

Heavy Water (0.59 M) in P.S.

222.4	2494.4	1.80	0.17	1.70
225.5	1294.4	2.09	0.18	1.70
228.4	1161.1	2.14	0.18	1.70
231.9	677.8	2.37	0.20	1.70
235.6	444.1	2.55	0.21	1.60
239.3	296.7	2.73	0.24	1.60
242.4	210.0	2.88	0.24	1.50
247.9	108.6	3.17	0.27	1.50
254.6	61.9	3.41	0.32	1.40
260.7	43.2	3.57	0.40	1.50

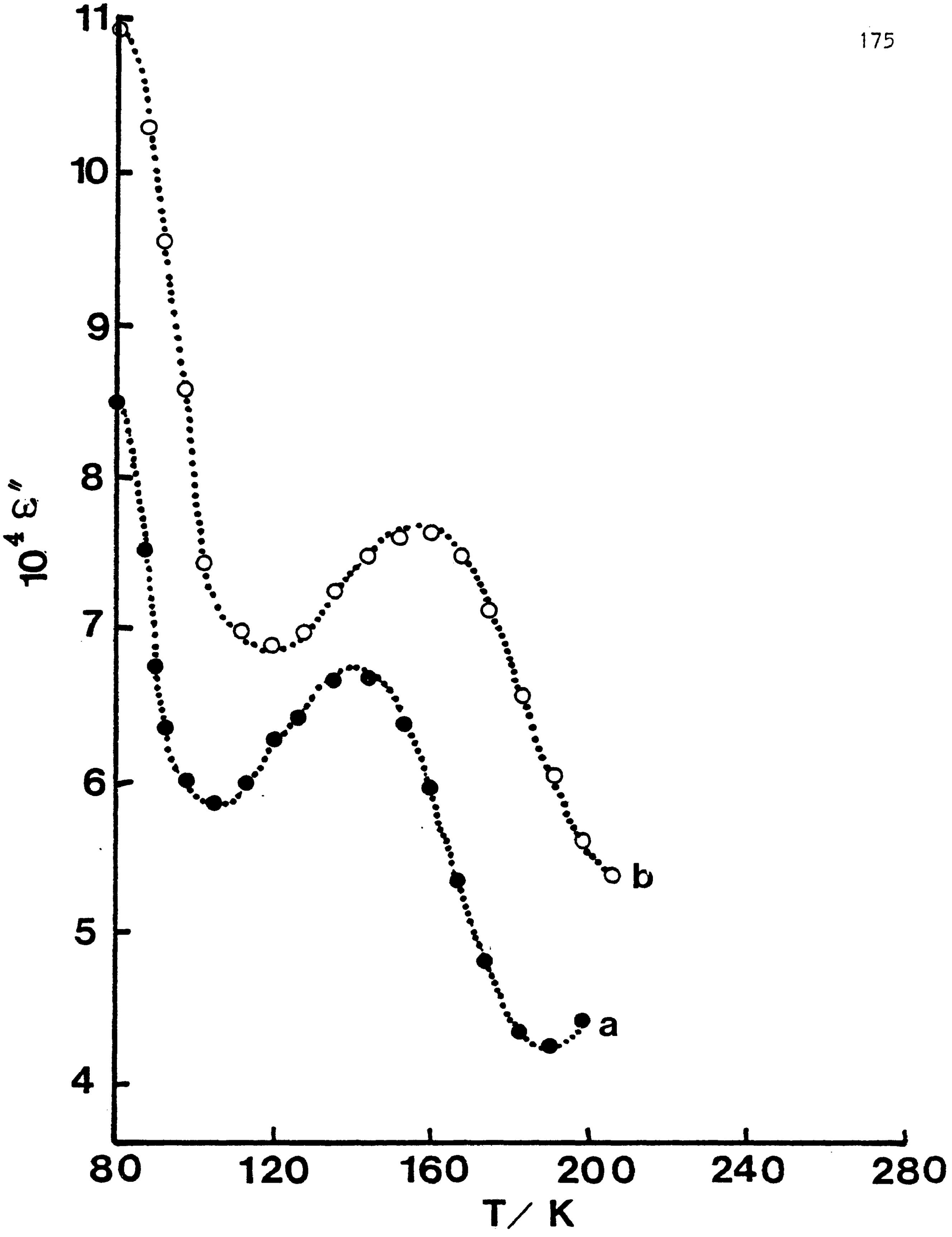


FIGURE V-1: Dielectric loss factor, ε'' versus Temperature for tert-butanol in glassy o-terphenyl at a = 50.2 Hz and b = 1.01 kHz.

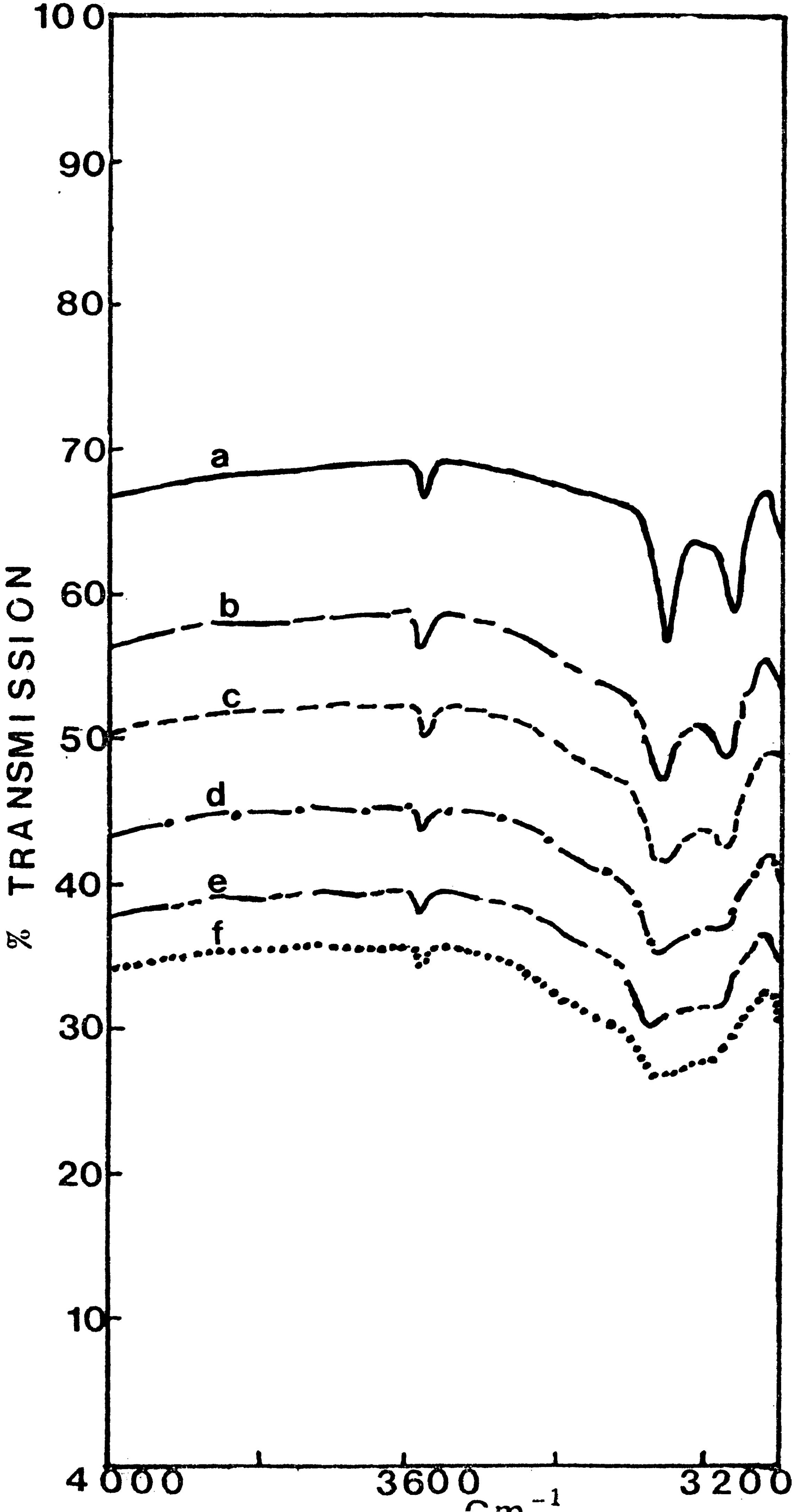


FIGURE V-2: Infrared spectrum of tert-butanol in glassy o-terphenyl (thin film and concentration = 0.59 M) at a = 123 K; b = 143 K; c = 153 K; d = 163 K; e = 176 K and f = 193 K.

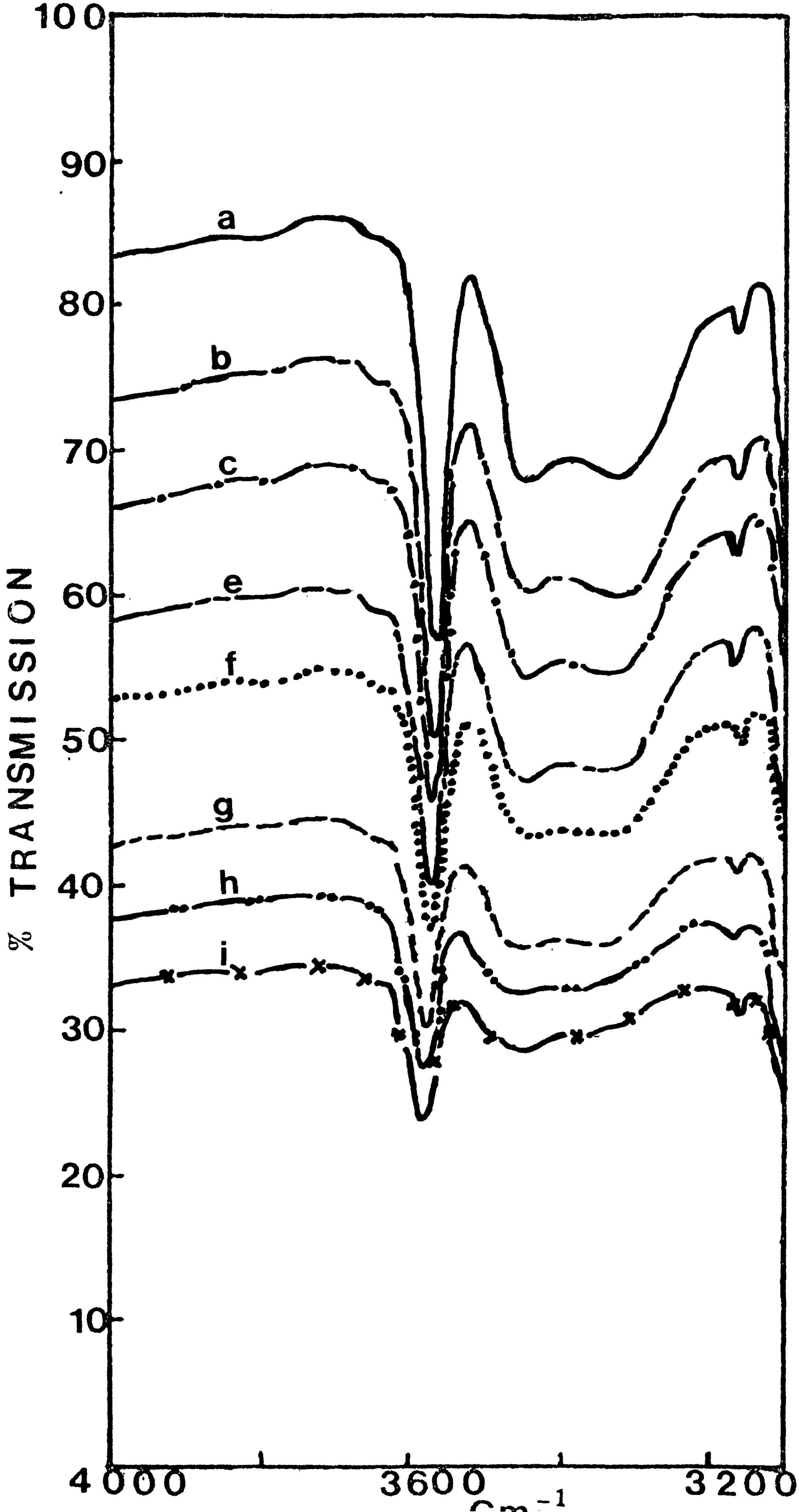


FIGURE V-3: Infrared spectrum of tert-butanol in polystyrene (thickness = 0.08 mm and concentration = 3.31 M) at a = 193 K; b = 203 K; c = 213 K; d = 223 K; e = 233 K; f = 233 K; g = 253 K; h = 273 K and i = 293 K.

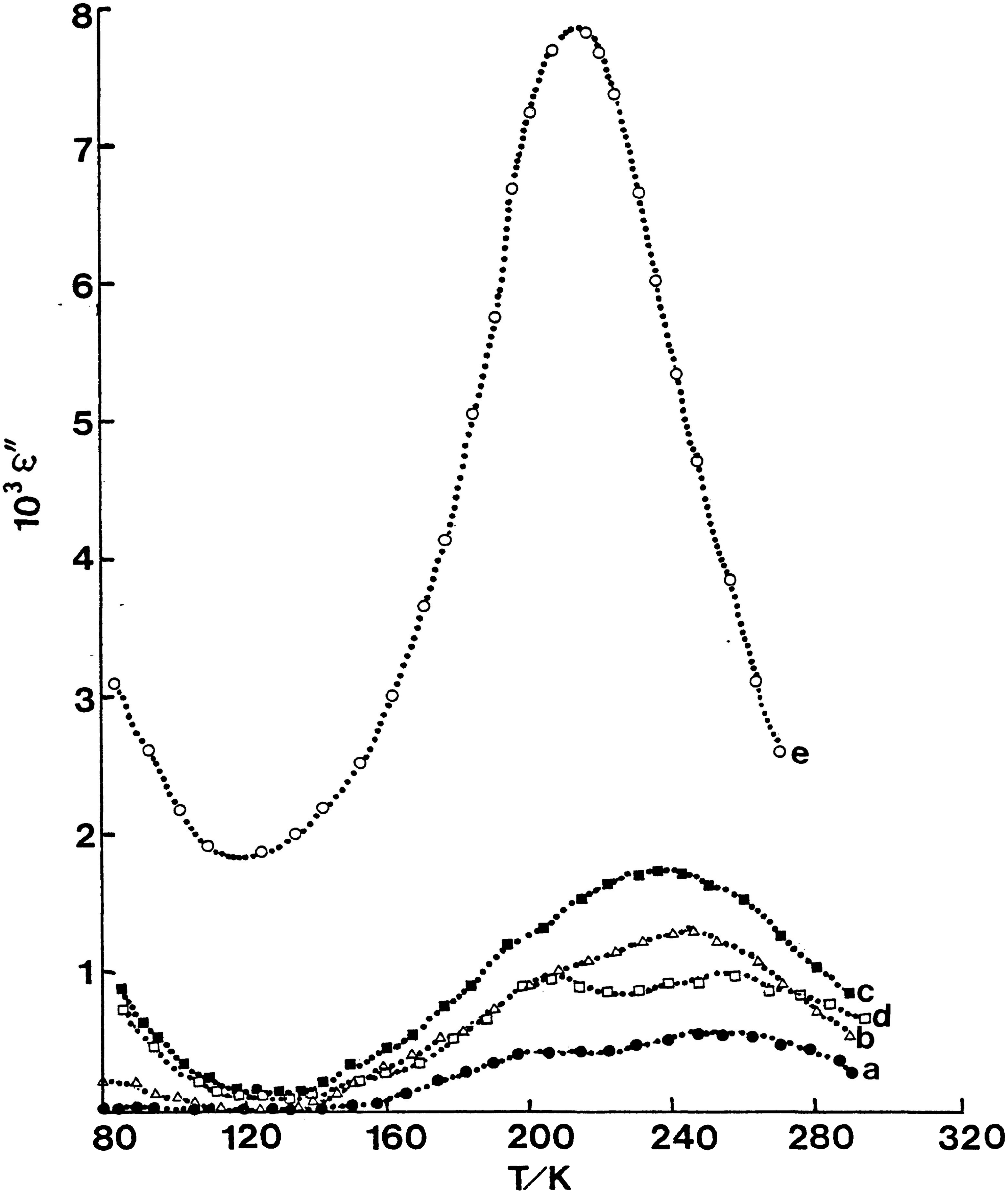


FIGURE V-4: Dielectric loss factor, ε'' versus temperature for a = 0.58 M, b = 1.69 M; c = 2.11 M; d = 2.64 M and c = 3.31 M of tert-butanol in polystyrene at 1.01 kHz.

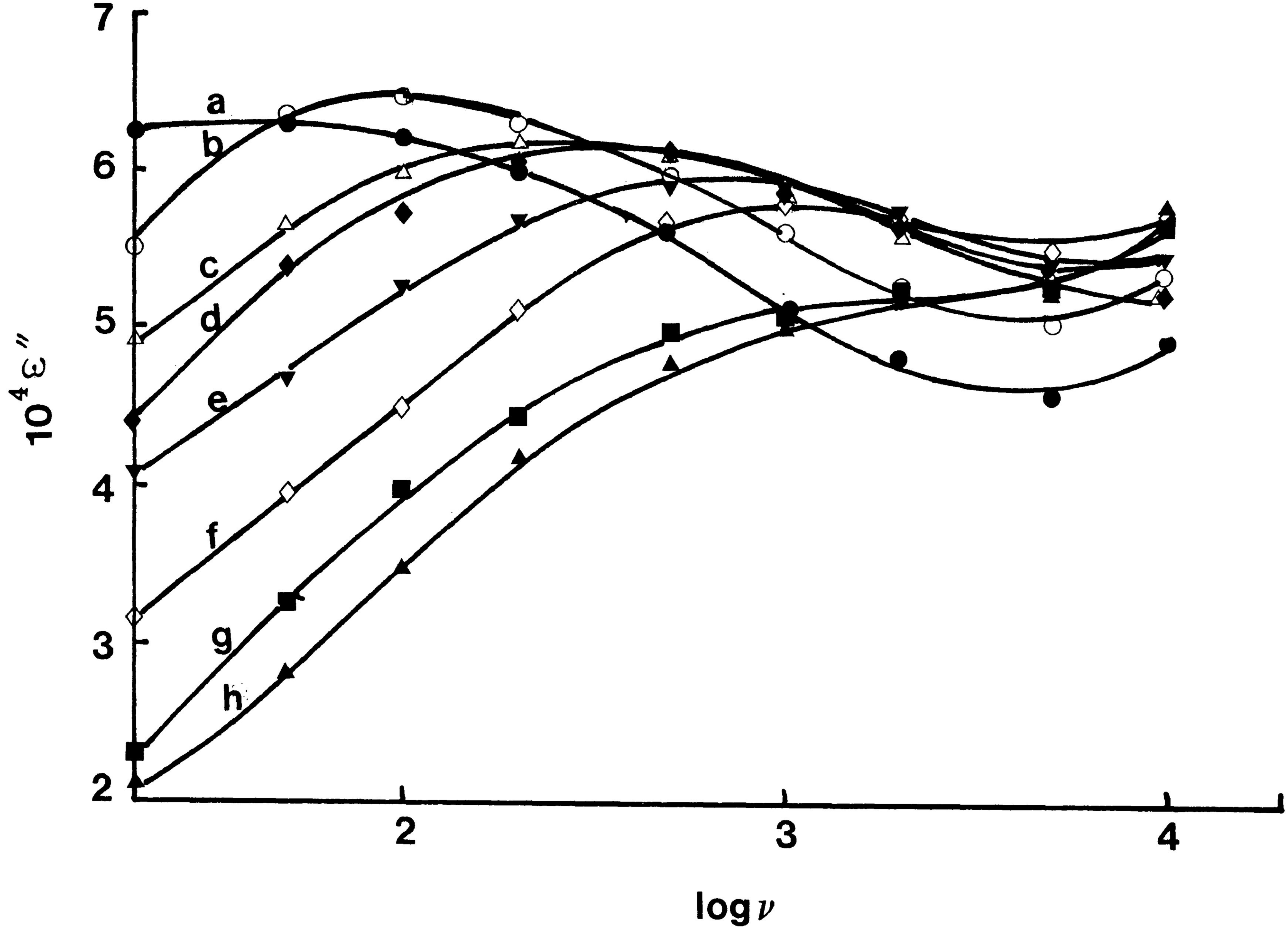


FIGURE V-5: Dielectric loss factor, ε'' versus $\log\nu$ for tert-butanol (0.58 M) in polystyrene at a = 241.3 K; b = 246.5 K; c = 249.3 K; d = 253.0 K; e = 257.1 K; f = 260.8 K; g = 265.8 K and h = 269.7 K.

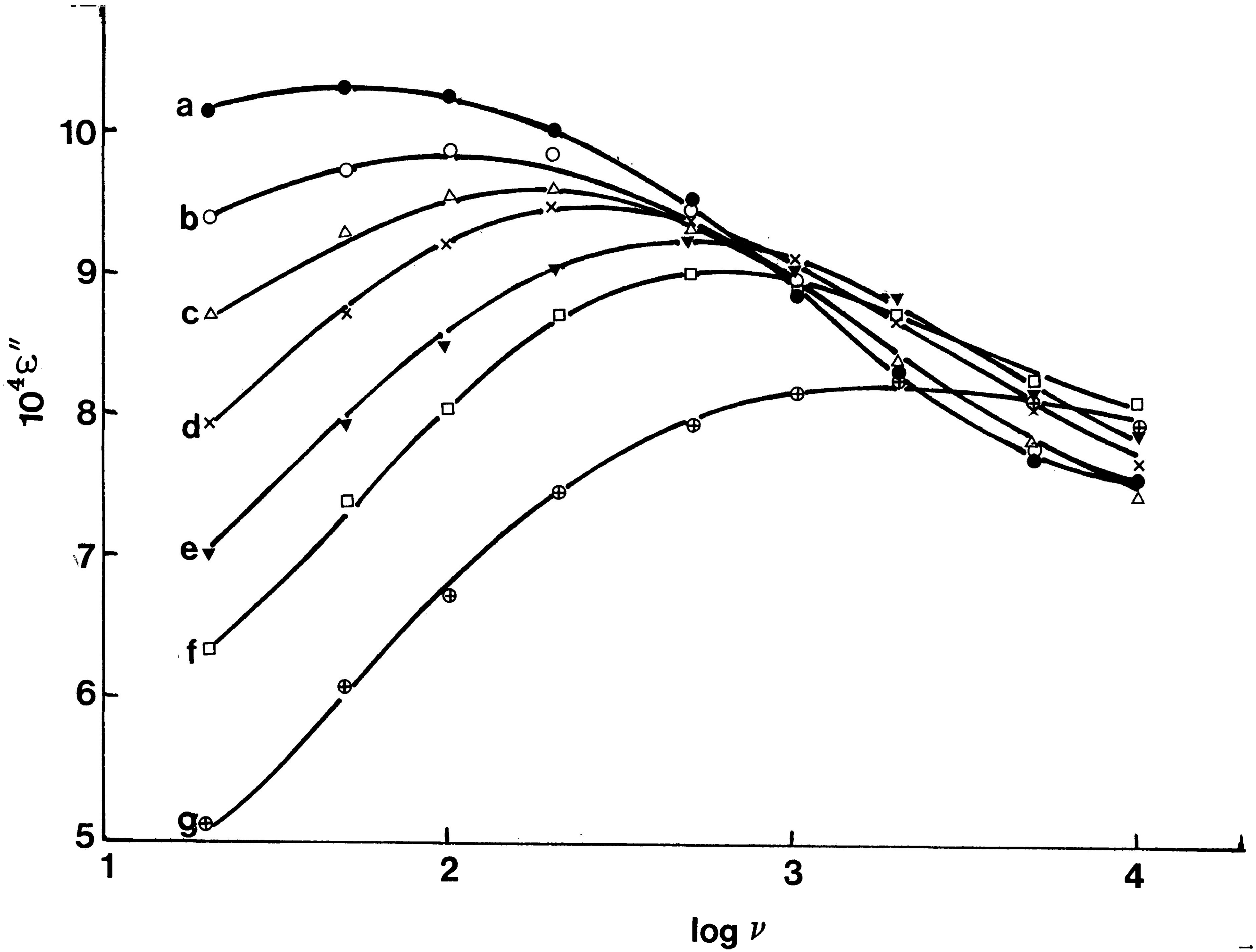


FIGURE V-6: Dielectric loss factor, ε'' versus logν for tert-butanol (2.64 M) in polystyrene at a = 242.3 K; be = 247.8 K; c = 250.7 K; d = 256.3 K; e = 260.5 K; f = 264.0 K and g = 272.1 K.

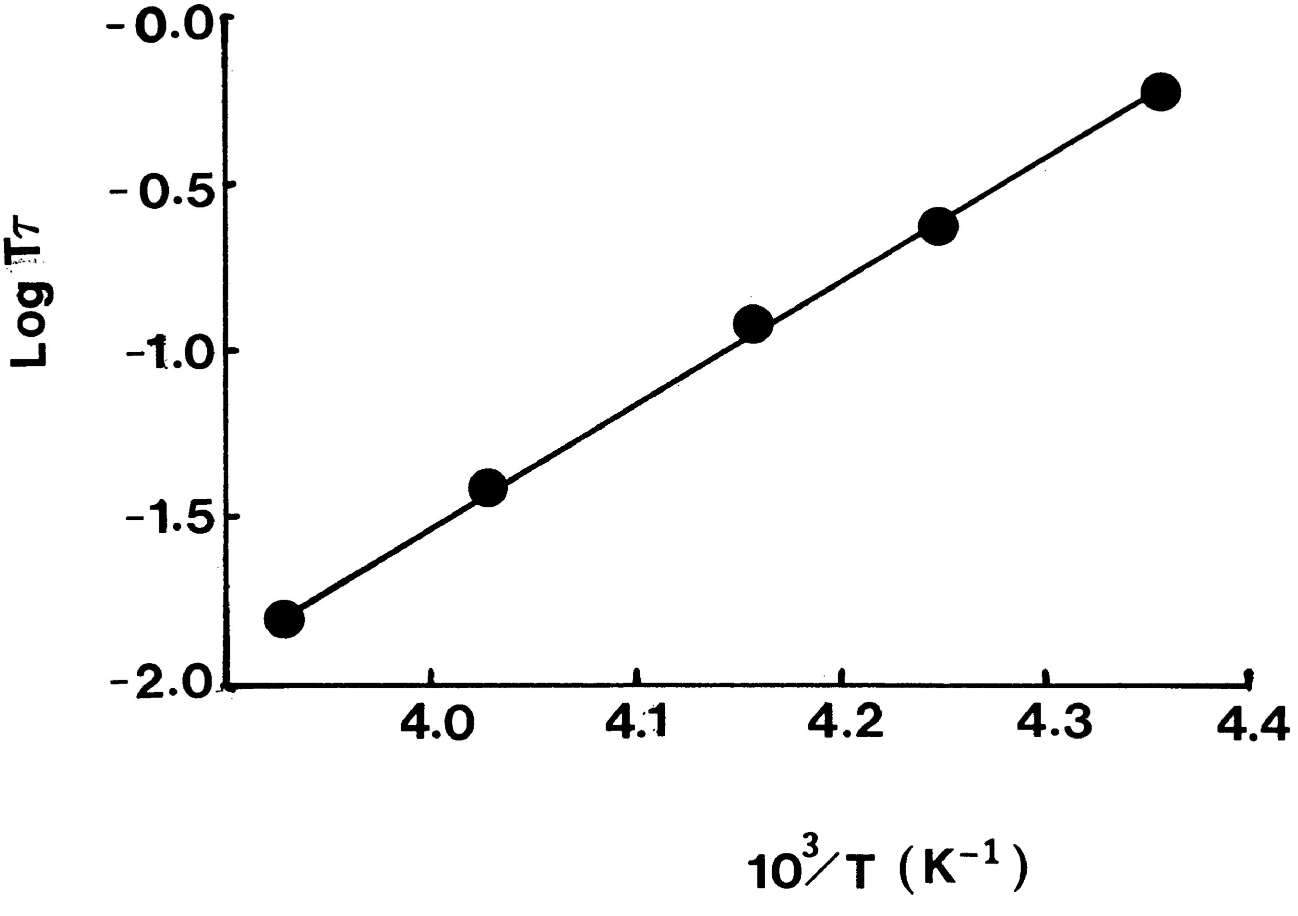
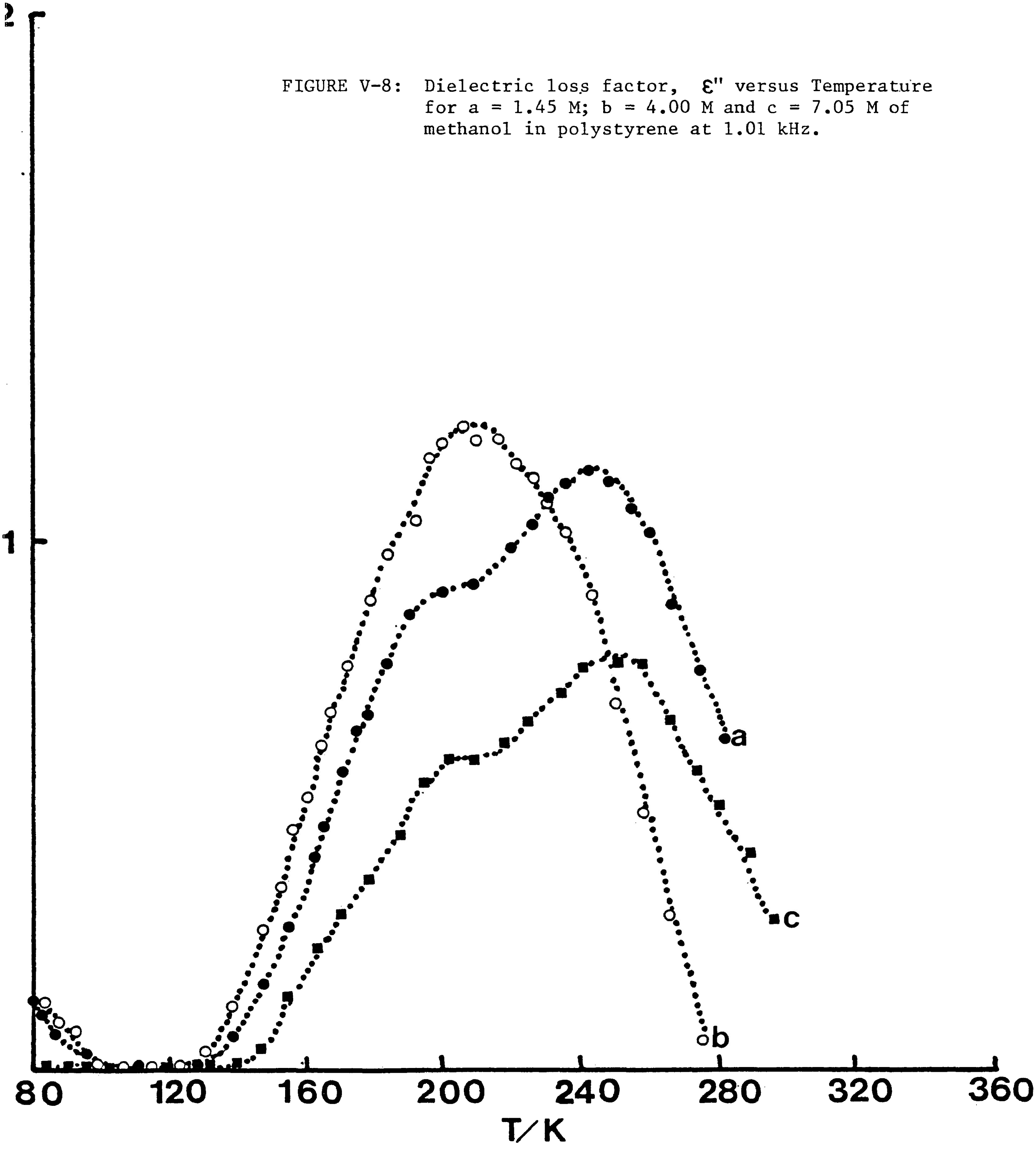


FIGURE V-7: Eyring rate plot of log Tτ versus 1/T for tert-butanol (2.11 M) in polystyrene.

FIGURE V-8: Dielectric loss factor, ε" versus Temperature for a = 1.45 M; b = 4.00 M and c = 7.05 M of methanol in polystyrene at 1.01 kHz.



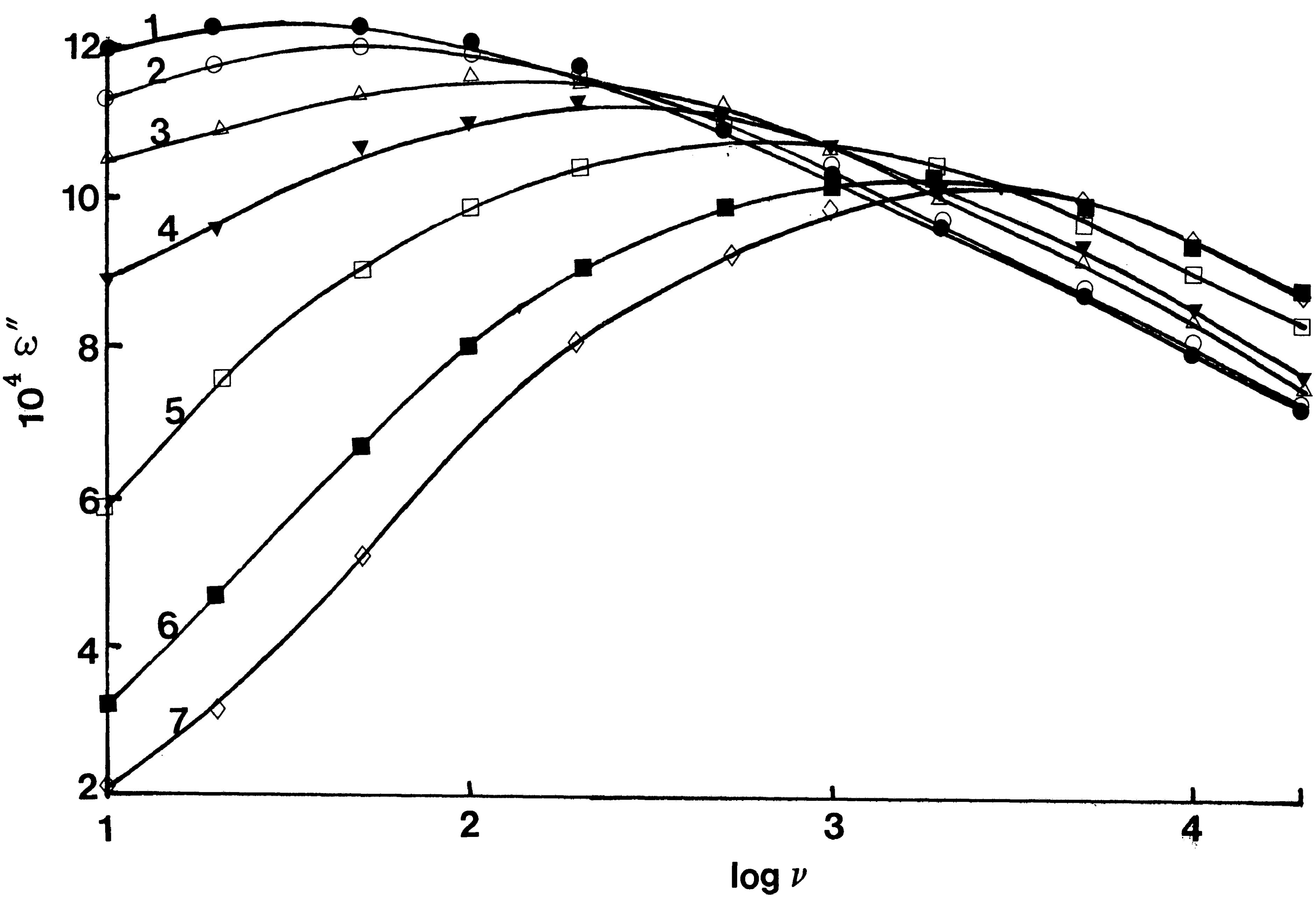
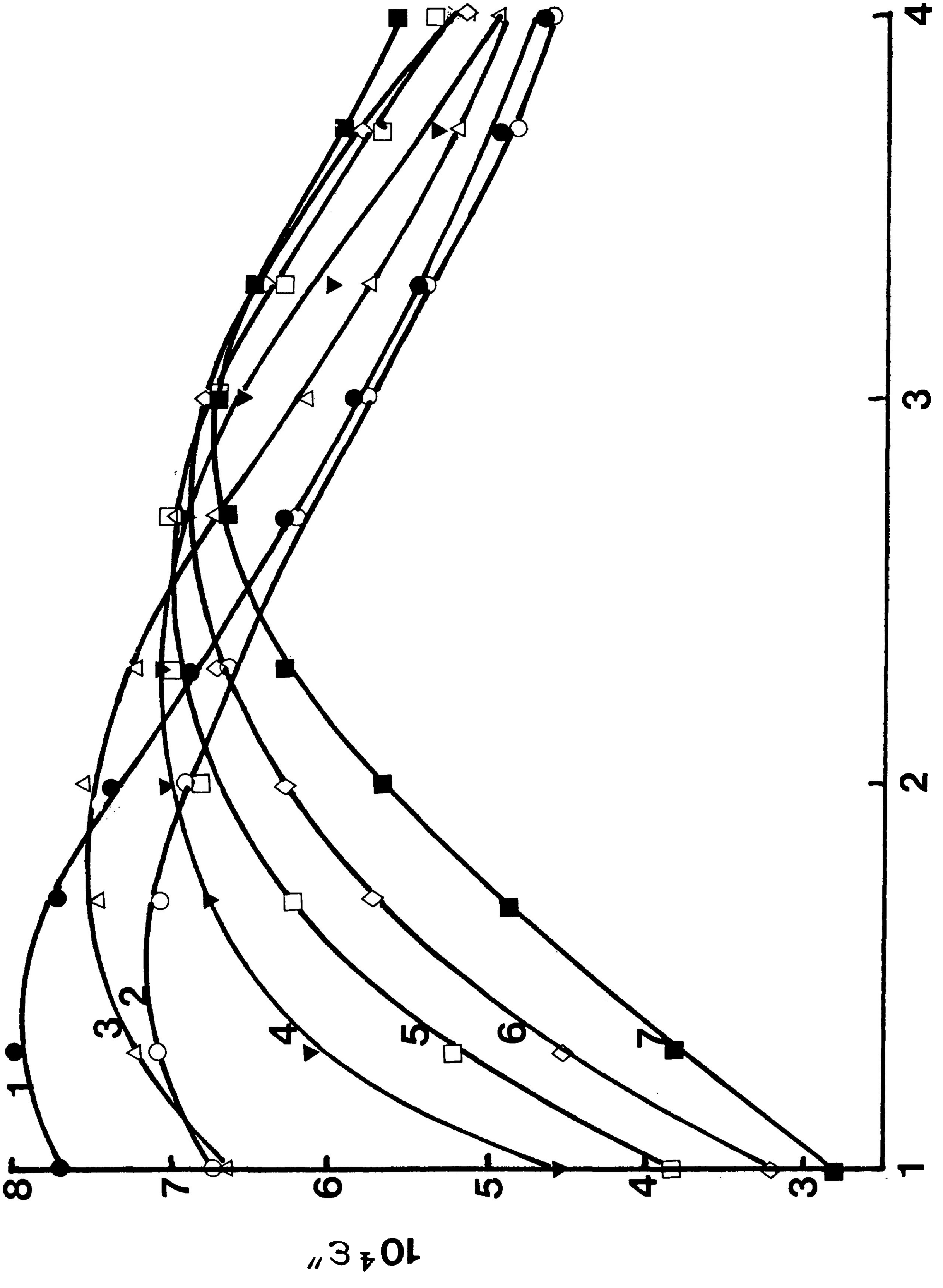


FIGURE V-9: Dielectric loss factor, ε'' versus logν for methanol (1.45 M) in polystyrene at 1 = 227.8 K; 2 = 230.8 K; 3 = 234.2 K; 4 = 240.3 K: 5 = 247.4 K; 6 = 255.6 K and 7 = 259.8 K.

FIGURE V-10: Dielectric loss factor, ε" versus logν for methanol (7.05 M) in polystyrene at 1 = 229.2 K; 2 = 232.7 K; 3 = 236.4 K; 4 = 243.9 K; 5 = 247.8 K; 6 = 251.3 K and 7 = 255.4 K.



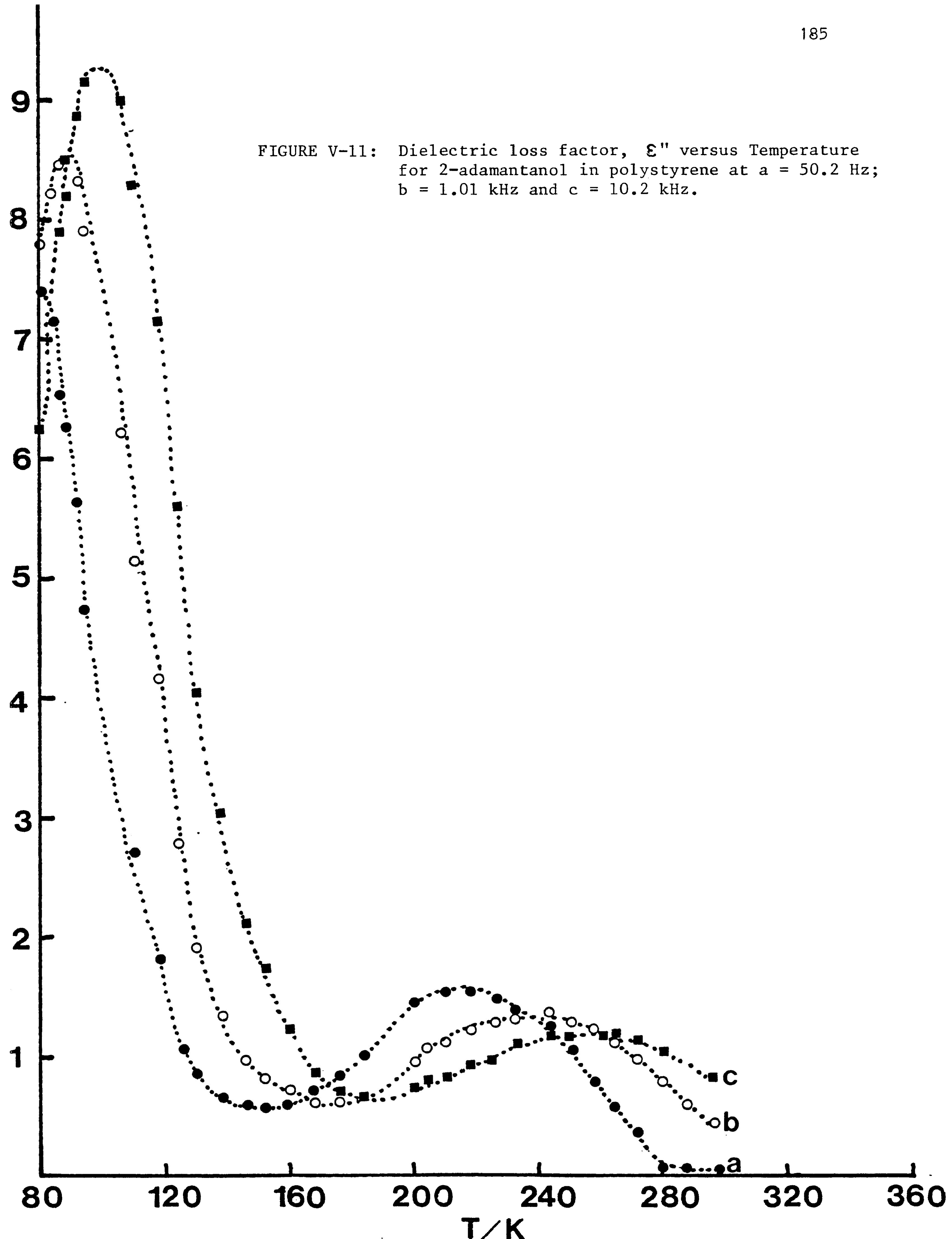


FIGURE V-11: Dielectric loss factor, ε" versus Temperature for 2-adamantanol in polystyrene at a = 50.2 Hz; b = 1.01 kHz and c = 10.2 kHz.

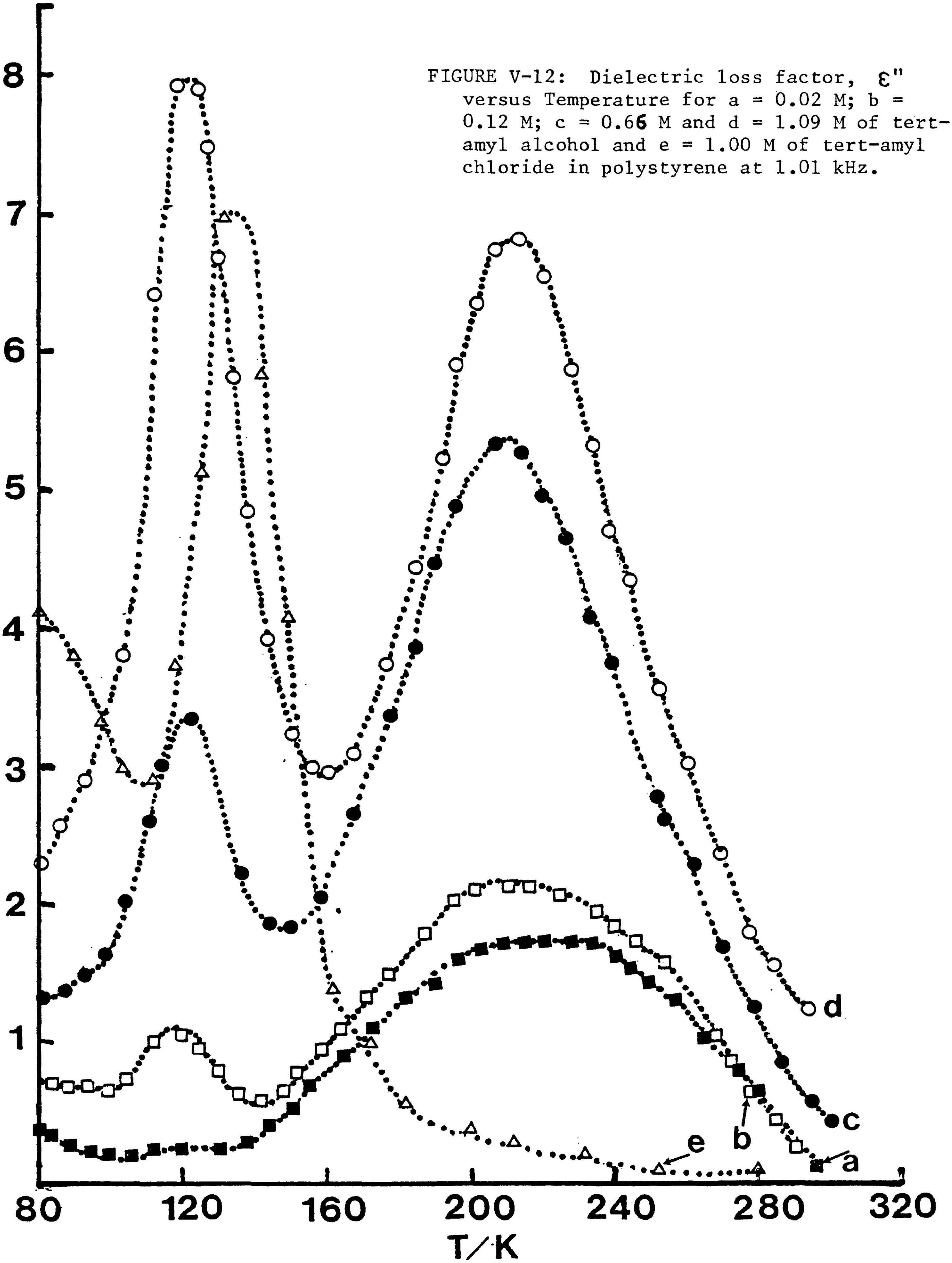


FIGURE V-12: Dielectric loss factor, ε" versus Temperature for a = 0.02 M; b = 0.12 M; c = 0.66 M and d = 1.09 M of tert-amyl alcohol and e = 1.00 M of tert-amyl chloride in polystyrene at 1.01 kHz.

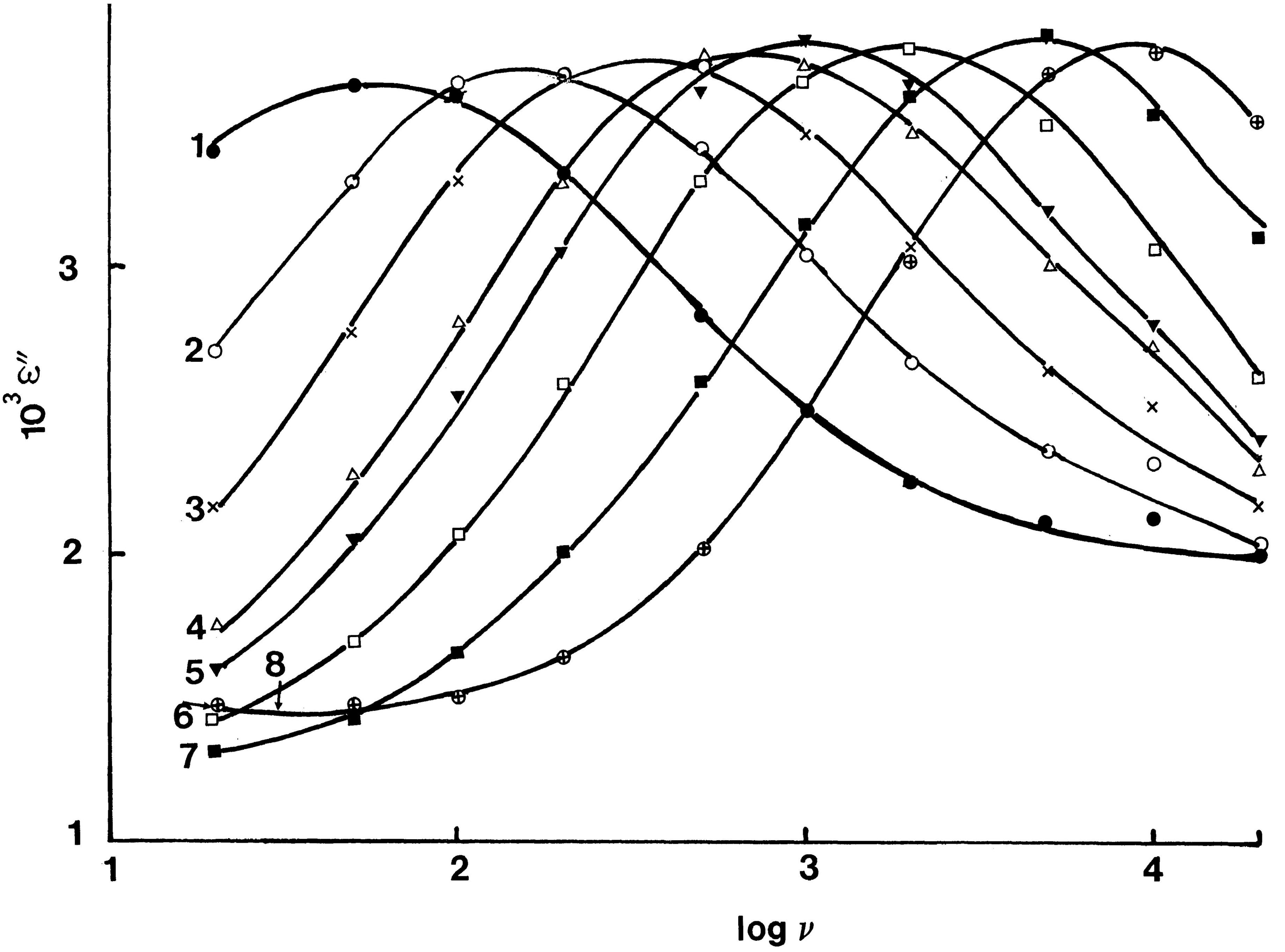


FIGURE V-13: Dielectric loss factor, ε″ versus log ν for low temperature process of tert-amyl alcohol (0.66 M) in polystyrene at 1 = 104.8 K; 2 = 109.6 K; 3 = 113.2 K; 4 = 116.8 K; 5 = 119.5 K; 6 = 122.5 K; 7 = 128.2 K and 8 = 134.0 K.

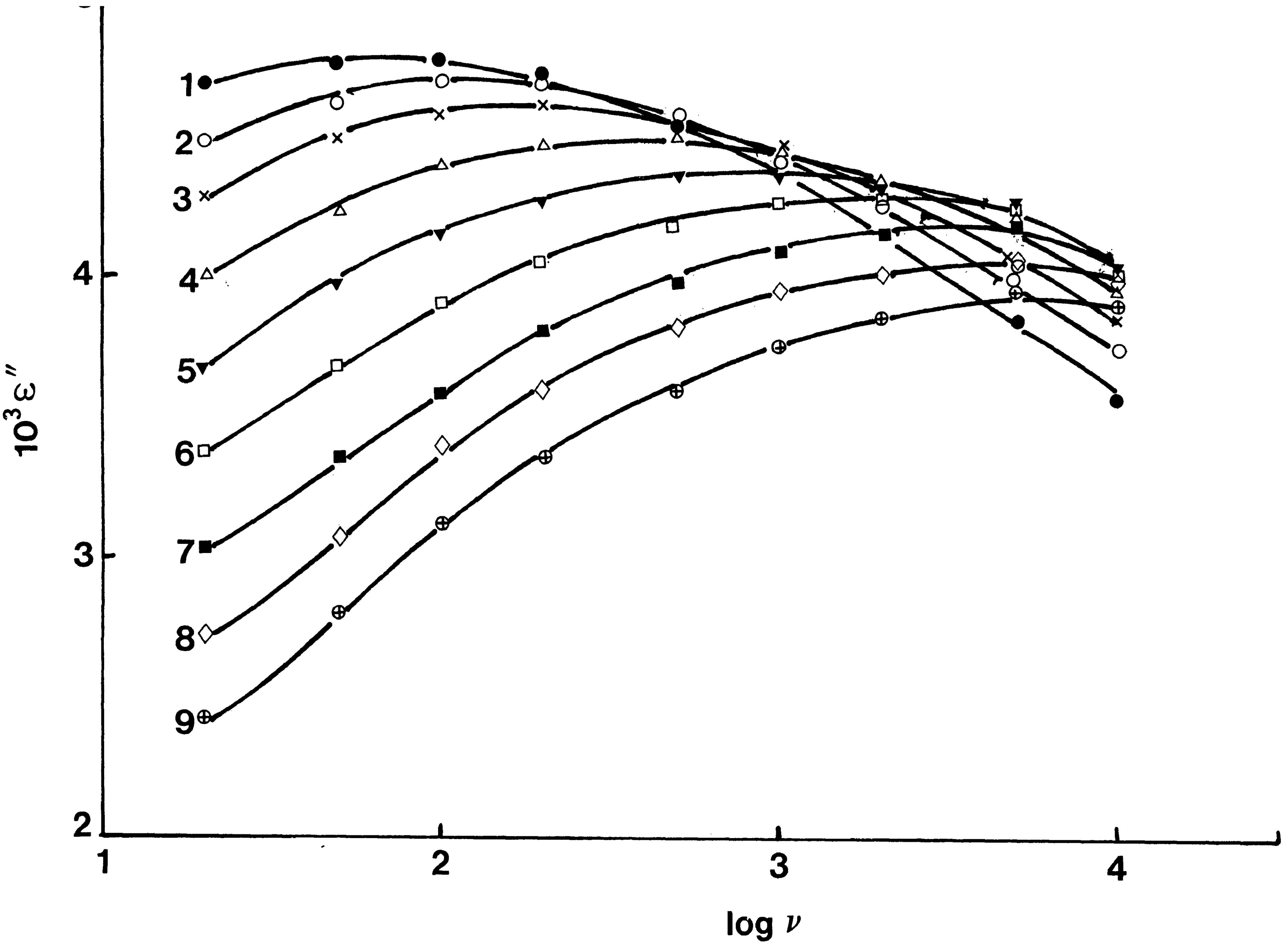


FIGURE V-14: Dielectric loss factor, ε″ versus log ν for high temperature process of tert-amyl alcohol (0.66 M) in polystyrene at 1 = 201.8 K; 2 = 205.4 K; 3 = 209.1 K; 4 = 212.8 K; 5 = 217.6 K; 6 = 221.4 K; 7 = 225.5 K; 8 = 229.6 K and 9 = 233.6 K.

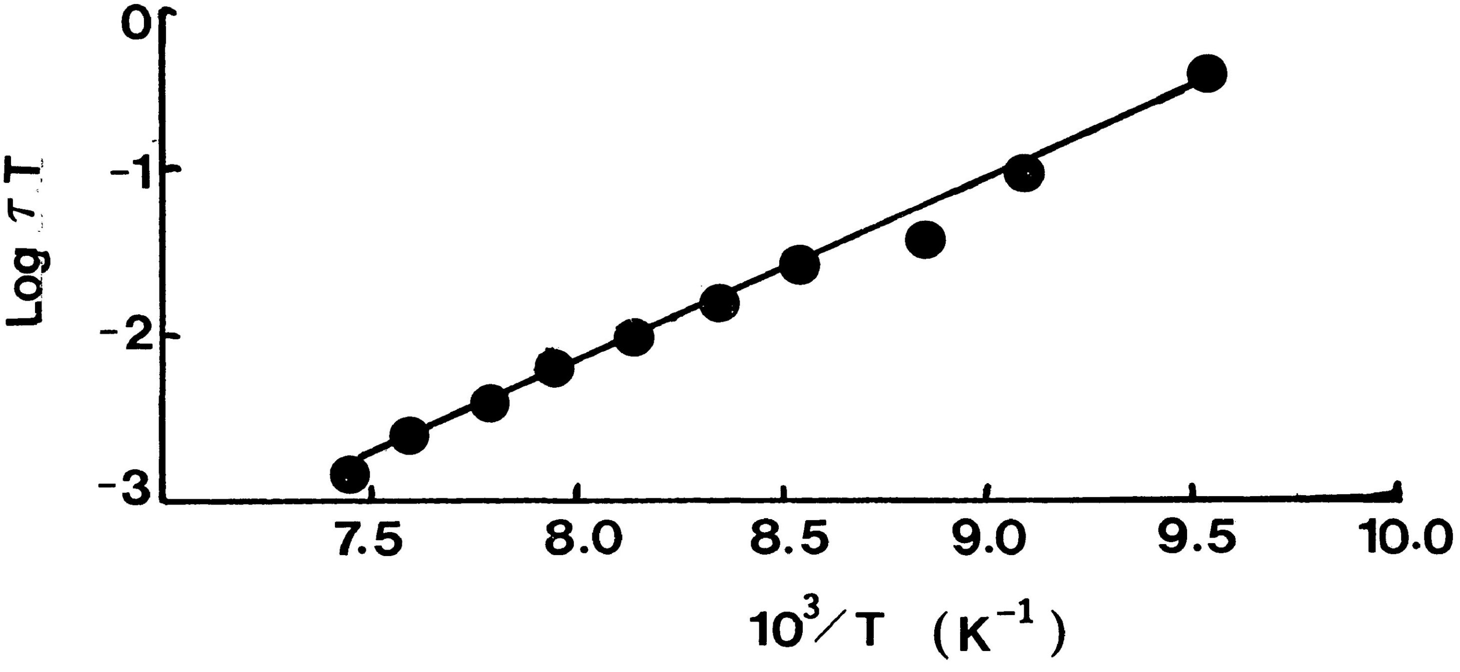


FIGURE V-15: Eyring rate plot of log Tτ versus 1/T for low temperature process of tert-amyl alcohol (0.66 M) in polystyrene.

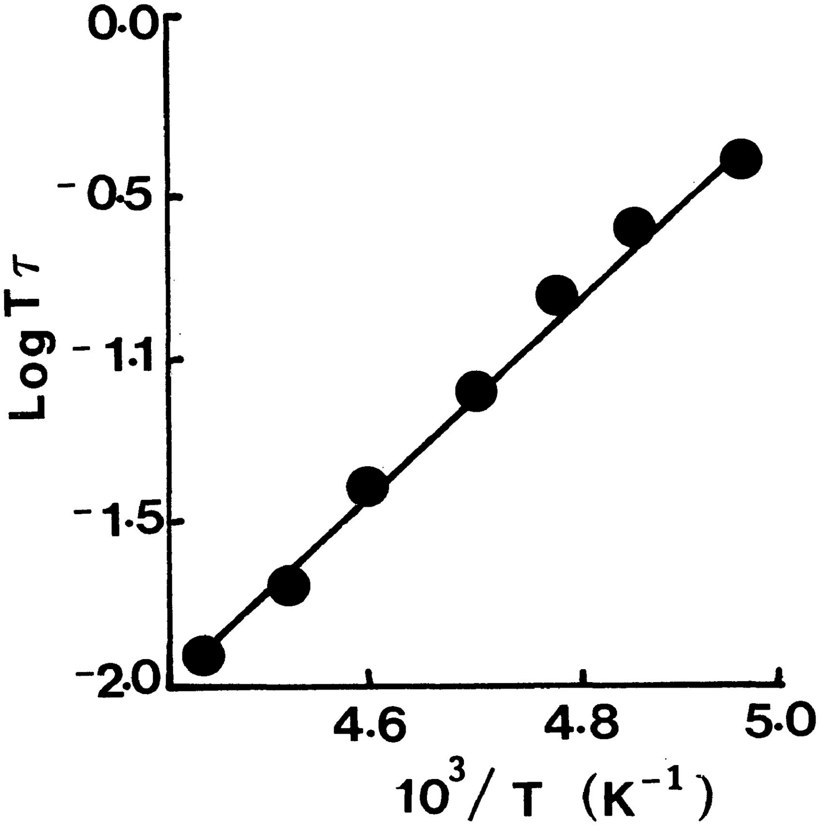


FIGURE V-16: Eyring rate plot of log Tτ versus 1/T for high temperature process of tert-amyl alcohol (0.66 M) in polystyrene.

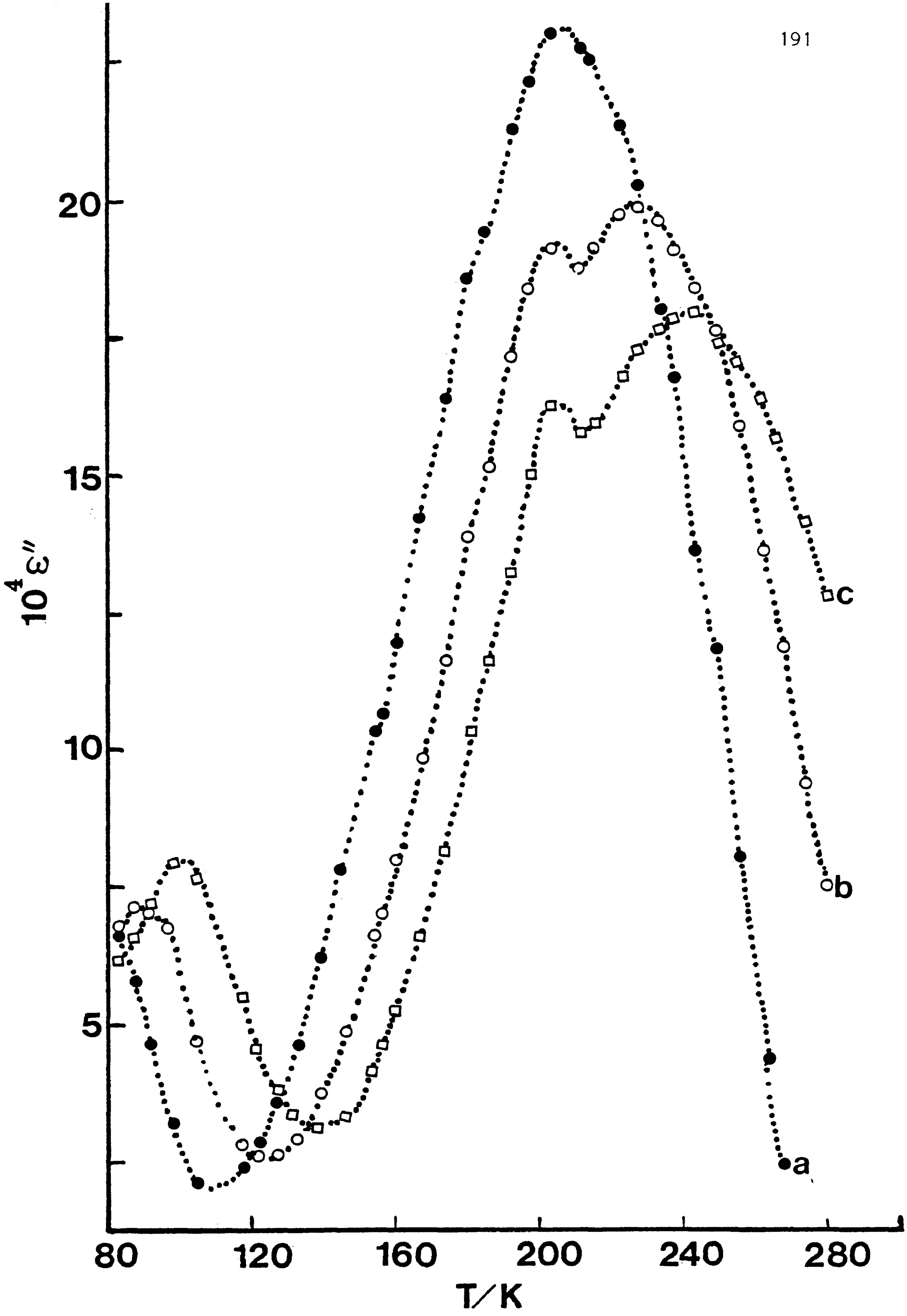


FIGURE V-17: Dielectric loss factor, ε" versus Temperature for 1-propanol in polystyrene at a = 50.2 Hz, b = 1.01 kHz and c = 10.2 kHz.

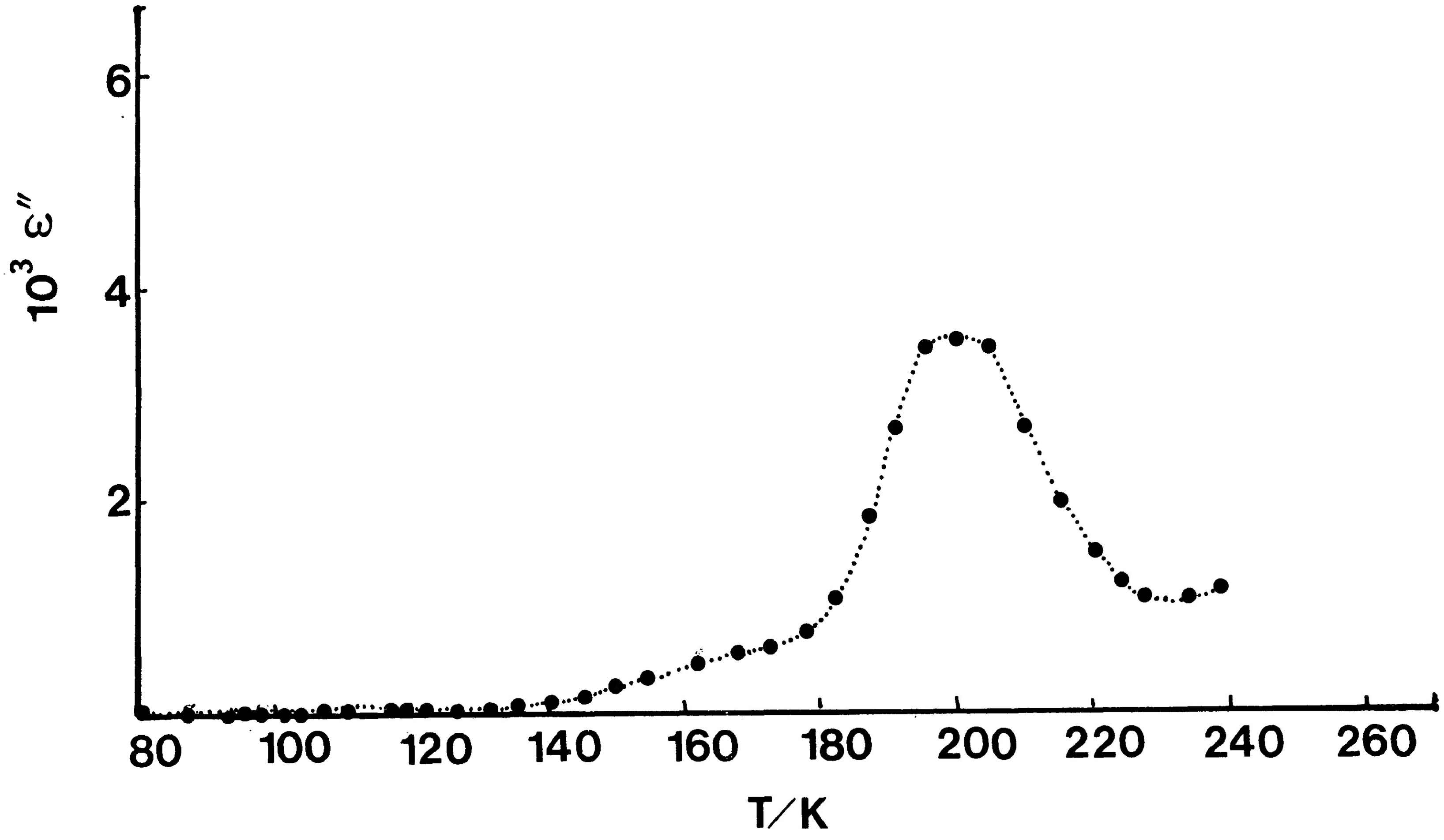


FIGURE V-18: Dielectric loss factor, ε'' versus Temperature for water in glassy o-terphenyl at 202 Hz.

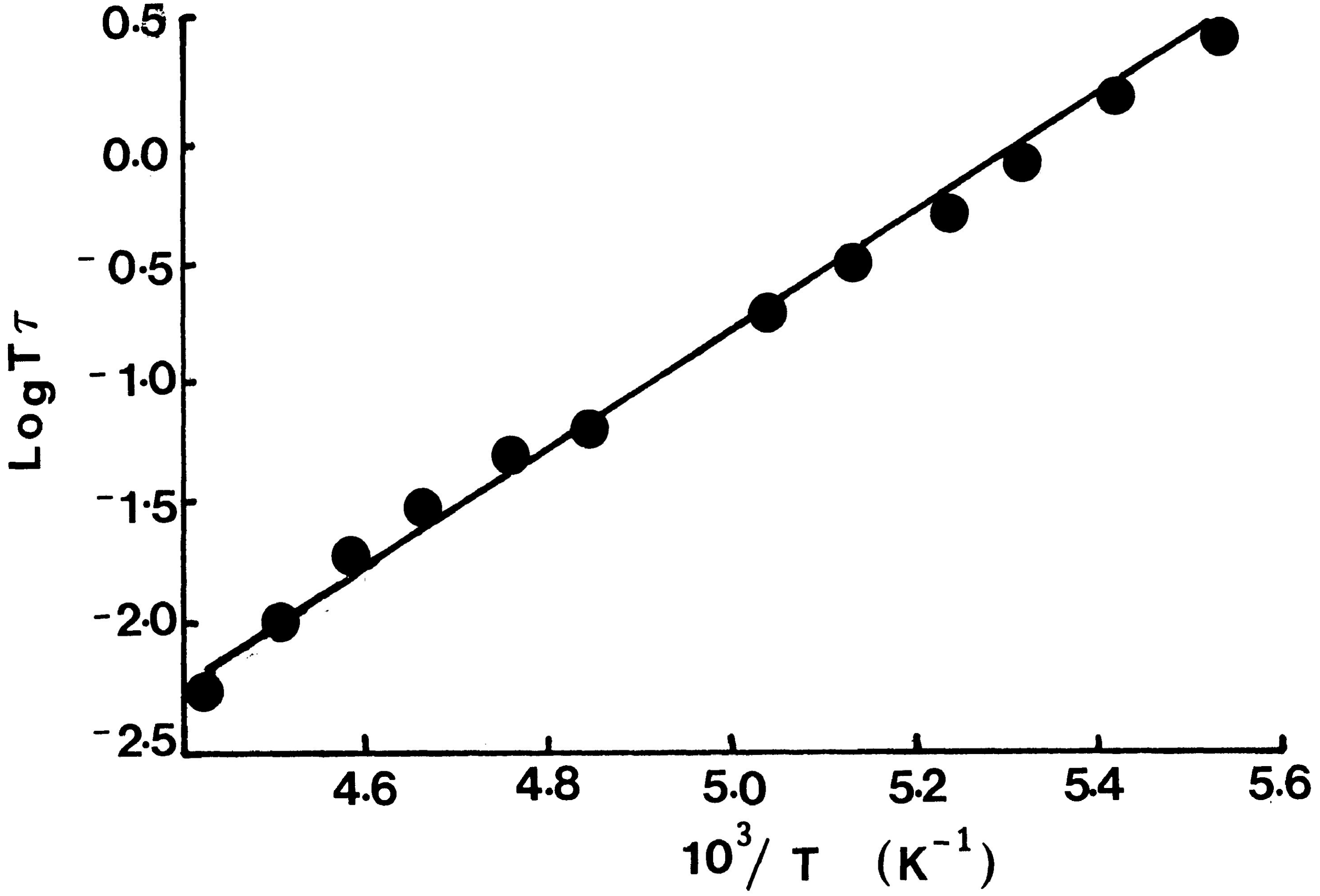


FIGURE V-19: Eyring rate plot of log Tτ versus 1/T for water in glassy o-terphenyl.

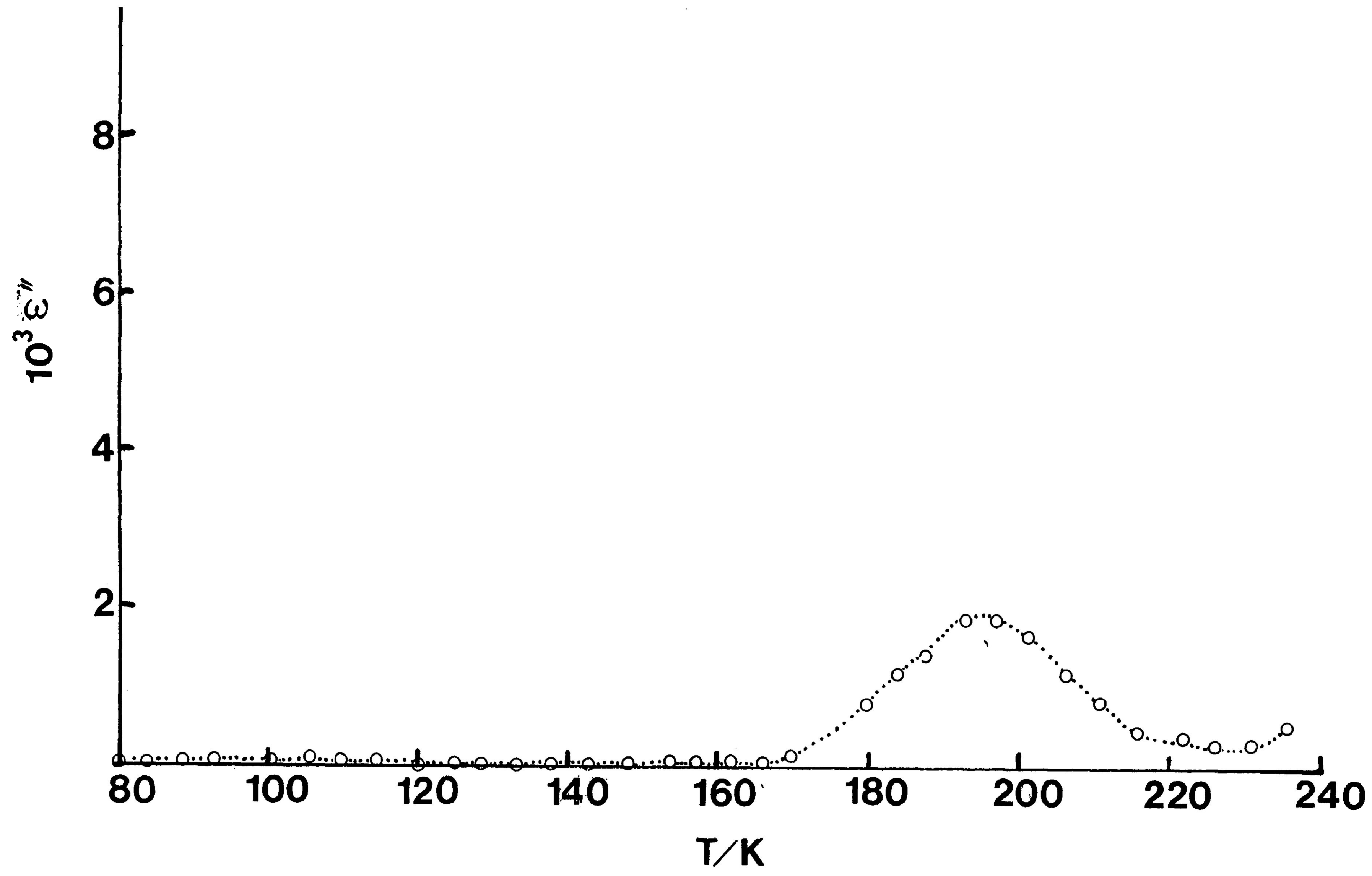


FIGURE V-20: Dielectric loss factor, ε'' versus Temperature for water in Santovac at 202 Hz.

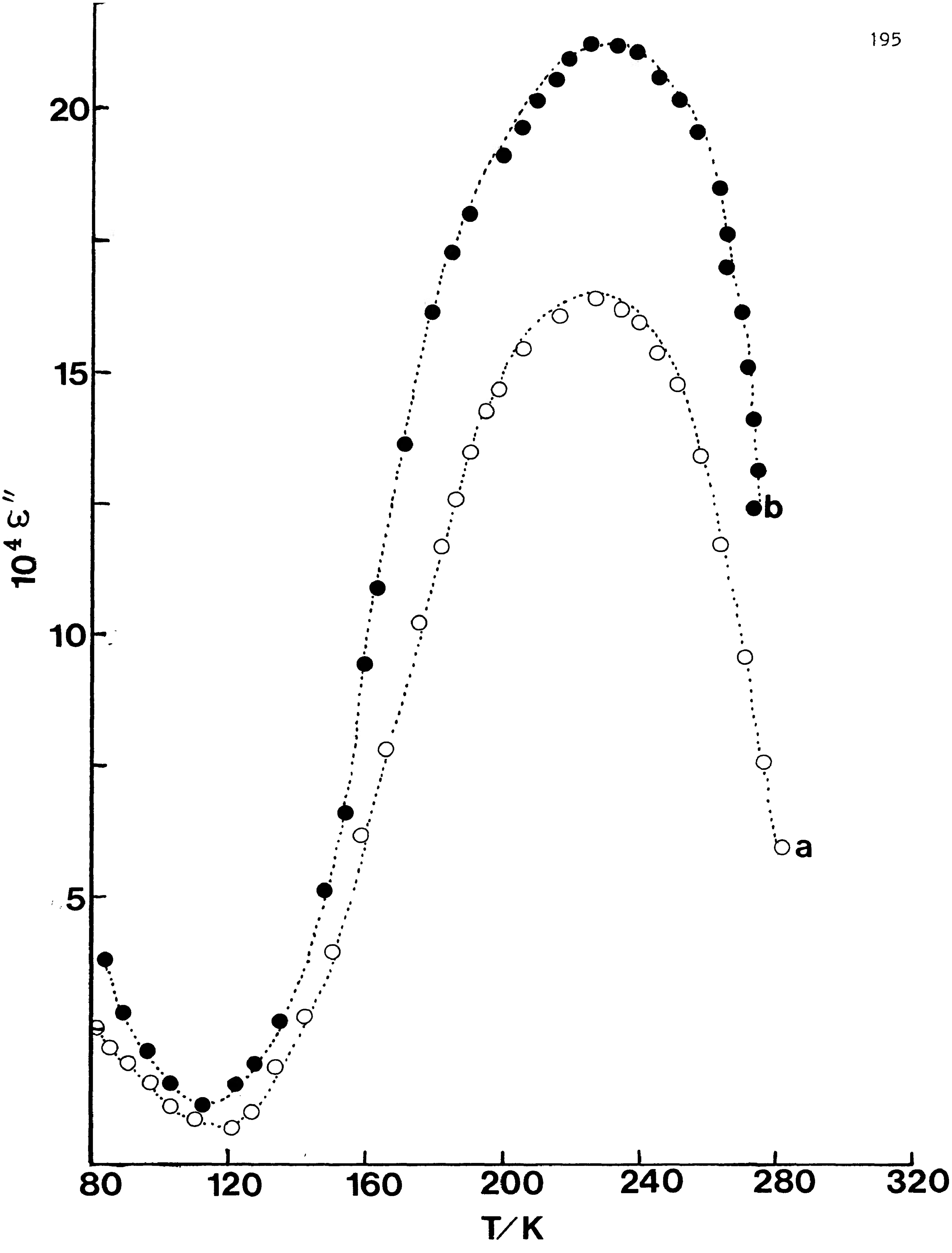


FIGURE V-21: Dielectric loss factor, ε" versus Temperature for a = water and b = heavy water in polystyrene at 1.01 kHz.

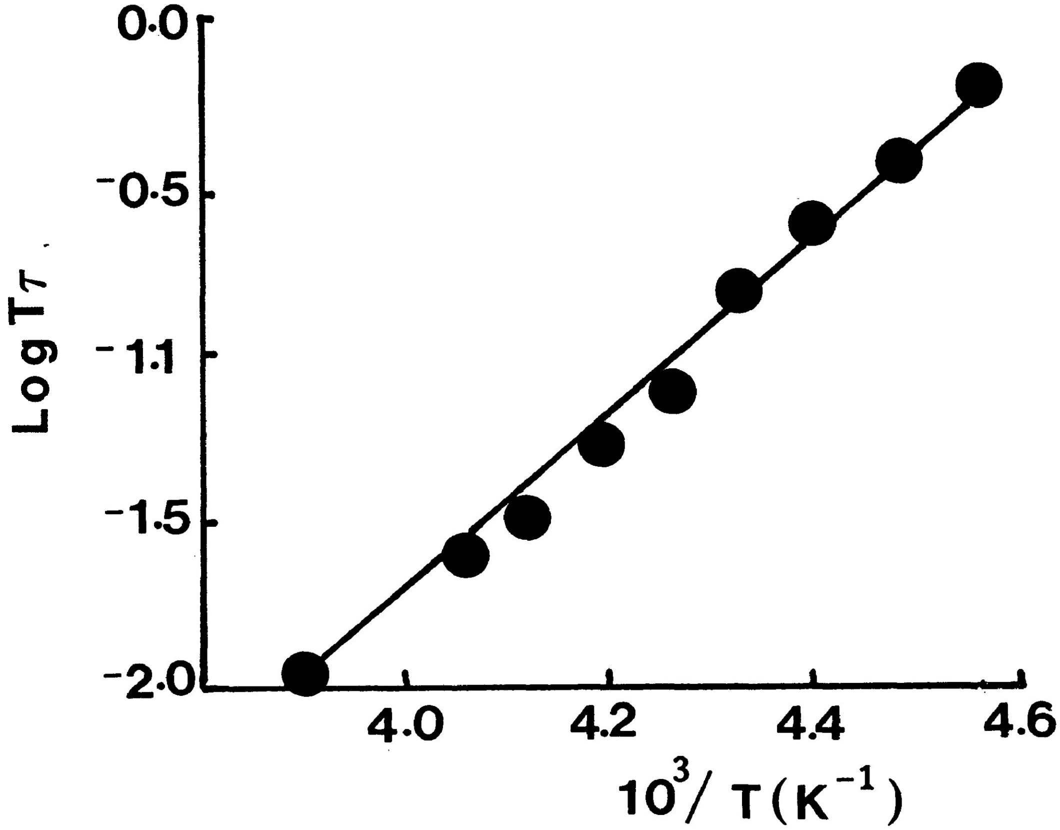


FIGURE V-22: Eyring rate plot of log Tτ versus 1/T for water in polystyrene

CHAPTER VI

DIELECTRIC STUDIES OF INTERACTIONS BETWEEN ALCOHOLS AND AMINES IN POLYSTYRENE

INTRODUCTION

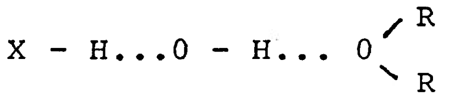
The formation of a molecular complex leads to modification in the charge distribution, reflected by the fact that the dipole moment differs from the vector sum of the interacting components. Formation of a molecular complex has been studied by numerous physical techniques including dielectric relaxation (1-6). Formation of molecular complex can be referred to as electron donor-acceptor interaction. Most commonly encountered electron donors are amines and ethers and electron acceptors (or proton donors) are amines, carboxylic acids, alcohols and polyhalogenated lower hydrocarbons, etc.

Davies and Sobczyk (7) have carried out dielectric relaxation studies of 1:1 complexes of pyridine with acetic, monochloroacetic and trichloroacetic acid in benzene solution. It was shown that very small conductance arises from minute concentrations of complexed ions. The relaxation times indicated the formation of rigid structures of complexes and ruled out the possibility of a proton-jumping process. Similar results were obtained by Gough and Price (8) for pyridine complexes with dichloro- and trichloroacetic acids.

Tucker and Walker (9) measured dielectric absorption of the heterocyclic amines, pyrrole and indole in cyclohexane and p-xylene solutions, and pyrrole in a 1:1 molar ratio with the non-polar 1,4-diazabicyclo [2.2.2] octane (DBO) in cyclohexane solution and indole with DBO in p-xylene solution. For pyrrole in cyclohexane at 298 K the mean relaxation time was 2.4×10^{-12} s and the dipole moment 1.7 D, whereas the pyrrole and DBO in cyclohexane solution gave a mean relaxation time of 3.4×10^{-11} s and a dipole moment of 2.0 D. Similarly, the addition of DBO to the indole in p-xylene solution lengthened the relaxation time from 1.9 to $\sim 6.0\times10^{-11}$ s and the dipole moment increased from 2.1 to 2.5 D. They were able to analyse their data for the mixture containing DBO in terms of two relaxation times due to rotation of uncomplexed pyrrole (or indole) and rotation of the H-bonded complex of pyrrole (or indole) and DBO.

Kraft et al (10) measured dielectric constants and losses of 2,4,6-trichlorophenol and 2,4,6-tribromophenol in a variety of solvents and 2,4,6-trichlorophenol in p-xylene containing different concentrations of strong electron-donor molecules, DBO. The mean relaxation time and the distribution coefficient values have shown the presence of more than one polar species in solutions of the trihalophenol, and hydrogen bonded complexes of the trihalophenol and DBO in a 1:1 and 2:1 ratio. Depending on the concentration of the component molecules, both nonionic and ionic forms of the complexes were indicated.

Shukla et al (11) have studied the various hydrogen bonded complexes of the type N—H.....N in a polystyrene matrix. By selection of suitable sized amines it was possible to separate completely the dielectric absorption of the complexes from the dielectric absorption of individual molecules. Unlike the complexes in liquid solutions, due to the overlap of absorptions from the other processes of individual molecules, in the case of polystyrene it was possible to determine activation parameters much more accurately for the rotation of the complexes.

Bellamy et al (12) have made an extensive infrared study of alcohols and phenols interaction with diethyl ether and dioxan in various solvents. It was shown that both monomer and self dimers of alcohols and phenols interact with electron-donors (ether and dioxan) and as well with the solvents. In alcohol/diethyl ether complexes the solvent interaction is limited to the  $\mathrm{X - H\ldots O - H\ldots O}\begin{smallmatrix}\diagup R\\ \diagdown R\end{smallmatrix}$ system.

Helm and Kratochwill (13) have carried out a nuclear magnetic relaxation study of the methanol-pyridine system. It was indicated that by interaction with pyridine the methanol self-association is reduced. Interaction of the pyridine with the OH of methanol monomer and methanol polymer was considered to explain the results.

There have been many studies on the interaction between alcohols and amines by means of spectroscopic techniques (14-17). However, not much work has been done on this type of interaction by the dielectric method. In liquid solutions of alcohols and amines the dielectric absorption obtained for the complex, usually, is not completely separated from other interfering absorptions (10). However, it has been shown that absorption due to complex can be separated by the parent molecules in a polystyrene matrix (11). The intent of this preliminary study is to explore the dielectric behaviour of some alcohols with tertiary amines in the polystyrene matrices so as to have some insight into the nature of molecular interactions.

EXPERIMENTAL RESULTS

The systems which are included in this work are divided into four groups depending upon the alcohols used and these are listed below.

	Alcohol	Amine
Group A		
	Di-ter-butyl carbinol	4-Phenyl pyridine
	Di-tert-butyl carbinol	Pyridine
	Di-tert-butyl carbinol	Pyrazine
Group B		
	Methanol	Pyridine
Group C		
	tert-Butanol	Pyridine
Group D		
	Dimethyl phenyl carbinol	Pyridine
	Dimethyl phenyl carbinol	Isoquinoline

All the alcohols and amines were obtained from commercial sources. Methanol, tert-butanol and pyridine were of spectroscopic grade and further purified by refluxing with suitable drying agents for several hours followed by distilling over

4 Å molecular sieves. Other alcohols and amines were of sufficient purity and were used without further pufification except di-tert-butyl carbinol which was recrystallized. While preparing and measuring the samples, all necessary care was taken to avoid atmospheric moisture.

DISCUSSION

Group A

As was discussed in Chapter IV, a 0.7 M of di-tert-butyl carbinol in polystyrene gives an absorption in the temperature range 90-115 K owing to the overlapping molecular and intramolecular motions. In addition, the infrared spectrum in the temperature range 213-293 K showed the presence of a dimer as the only H-bonded species which does not give any dielectric absorption in the 200-300 K range when the dispersion medium is polystyrene. 4-Phenyl pyridine (0.30 M) in a polystyrene matrix showed an absorption maximum at ∿220 K (at 50.2 Hz) with a dielectric loss factor of $\sim 15\times10^{-3}$ (at 50.2 Hz) (Figure VI-1). Mixing 0.70 M of di-tert-butyl carbinol with 0.30 M of 4-phenyl pyridine in polystyrene yielded a very strong absorption maximum at the temperature 253 K (at 50.2 Hz) with a dielectric loss of 21×10^{-3}s (at 50.2 Hz) and mean relaxation time of 1.0×10^{-1} s at 200 K. In the ε" versus T plot a shoulder at about 120 K has also been found (Figure VI-1). The infrared spectrum of 0.70M di-tert-butyl carbinol in polystyrene between 213 and 293 K has shown that there is only a monomer peak at ∿ 3610 and a dimer band at 3500 cm^{-1} (Figure III-2a). The infrared spectrum of 0.70 M di-tert-butyl carbinol and 0.30 M 4-phenyl pyridine in polystyrene at 233, 273 and 293 K, have shown indications of three types of OH-bands (Figure VI-2). A sharp peak at 3610 cm^{-1} may be attributed to the OH-stretching of monomeric di-tert-butyl carbinol. A shoulder at ∿3500 cm^{-1}, by analogy with the infrared spectrum of di-tert-butyl carbinol in polystyrene at corresponding concentration and temperatures, can be assigned to the presence of a dimer of di-tert-butyl carbinol. A broad band at ∿3330 cm^{-1} cannot be assigned to the presence of the polymer of di-tert-butyl carbinol because the infrared spectrum of di-tert-butyl carbinol in polystyrene at corresponding concerntration and temperatures does not show any band in the vicinity of 3330 cm^{-1}. Thus, the only candidate for 3330 cm^{-1} band seems to be the O —– H···N stretching of the di-tert-butyl carbinol and 4-phenyl pyridine complex. In short, infrared measurement on di-tert-butyl carbinol and 4-phenyl pyridine in a polystyrene matrix bears out that in the temperature range 233 - 293 K there is (a) a monomer of di-tert-butyl carbinol, (b) a dimer of di-tert-butyl carbinol, (c) a complex of monomeric di-tert-butyl carbinol with 4-phenyl pyridine and, (d) a complex of dimeric di-tert-butyl carbinol (if the dimer is open (18)) with 4-phenyl pyridine.

In the ε" versus T plot of 0.70 M di-tert-butyl carbinol and 0.30 M 4-phenyl pyridine in polystyrene, a shoulder at ∿120 K (at 50.2 Hz), in analogy with absorption maximum at 120 K (at 50.2 Hz) for di-tert-butyl carbinol at the same concentration, may be attributed to the uncomplexed di-tert-butyl carbinol. A strong absorption maximum at 253 K (at 50.2 Hz), in light of infrared measurements, seems to have some contribution from the di-tert-butyl carbinol (monomer and/or dimer) - 4-phenyl pyridine complex. Since 4-phenyl pyridine in polystyrene also absorbs in approximately the same temperature range as the di-tert-butyl carbinol and 4-phenyl pyridine in polystyrene, thus, it is not unlikely that the absorption maximum at 253 K (at 50.2 Hz) has some contribution from uncomplexed 4-phenyl pyridine. However, it is clear from Figure VI-1 that the dielectric loss of 4-phenyl pyridine in polystyrene at the same concentration as in the di-tert-butyl carbinol and 4-phenyl pyridine system, is lowered by a factor of 6. Since the dielectric loss depends upon (a) the dipole moment of the solute species, (b) the number of dipoles in a certain volume, and (c) the number of dipoles relaxing; the increased dielectric loss for di-tert-butyl carbinol and 4-phenyl pyridine system will come from the complex(es). To gain some indication of the form of the absorption curve with the absorption of the uncomplexed 4-phenyl pyridine removed, we have subtracted 25%, 50% and 75% of the total dielectric loss of 0.30 M 4-phenyl pyridine (curve E of Figure VI-1) from the total dielectric loss of 0.70 M di-tert-butyl carbinol and 0.30 M 4-phenyl pyridine (curve D of Figure VI-1). Thus, we obtained the curves A, B and C, respectively, representing 25%, 50% and 75% consumption of total 4-phenyl pyridine in complex formation. Roughly we can say that any of the three curves (A, B or C) with temperature of maximum loss at ∿260 K (at 50.2 Hz) give some indication of the magnitude of dielectric loss for the complex(es). Another maximum at ∿120 K in curves A, B and C is apparently due to an uncomplexed di-tert-butyl carbinol.

To further explore the interaction of di-tert-butyl carbinol with nitrogen heterocycles we have studied 0.30 M of di-tert-butyl carbinol and 1.10 M of pyridine in a polystyrene matrix. As discussed before, di-tert-butyl carbinol in polystyrene at 0.70 M yields only one absorption due to a merged molecular and intramolecular rotation and this occurs in the temperature range 90-115 K. Pyridine in a polystyrene matrix has been shown to give an absorption, due to the molecular relaxation, close to 80 K (11). We shall expect no dielectric absorption due to the uncomplexed di-tert-butyl carbinol and pyridine above 160 K in the range of our frequency (10-10^5 Hz). However, mixing 0.30 M di-tert-butyl carbinol with 1.10 M of pyridine in polystyrene yielded a dielectric absorption with a temperature of maximum absorption at 211 K (at 50.2 Hz) (Figure VI-3) a mean relaxation time of 2.8×10^{-2} s at 200 K. The infrared spectrum of 0.30 M di-tert-butyl carbinol and 1.10 M pyridine in polystyrene at room temperature yielded a sharp peak at

3620 cm^{-1} and a broad band at ∿3350 cm^{-1} with an asymmetry on the higher wave number side (Figure VI-4). A peak at 3620 cm^{-1}, and a band at ∿3350 cm^{-1} can be assigned to a monomeric di-tert-butyl carbinol and molecular complex of monomeric and/or dimeric di-tert-butyl carbinol with pyridine, respectively. Asymmetry in the ∿3350 cm^{-1} band most probably arises from the presence of a small amount of dimer of di-tert-butyl carbinol. Hence, in view of the infrared data, the dielectric absorption with a temperature of maximum absorption at 211 K (at 50.2 Hz) can be assigned to the presence of the complex of the monomeric and/or the dimeric di-tert-butyl carbinol with pyridine.

A mixture of 0.30 M of di-tert-butyl carbinol with 1.00 M of pyrazine has also been studied. Pyrazine is approximately the size of pyridine but instead of one nitrogen it has two nitrogens at 1,4 positions, thus making the planar molecule completely non polar. The mixture of di-tert-butyl carbinol with pyrazine in polystyrene yielded a dielectric absorption having a temperature of maximum absorption at 218 K (at 50.2 Hz) and with a mean relaxation time of 1.4 s at 200 K. Another very weak and broad absorption is also obtained between 80 and 160 K (Figure VI-5). The absorption obtained between 80 and 160 K cannot be assigned to non polar pyrazine. As is the case in the di-tert-butyl carbinol and 4-phenyl pyridine system di-tert-butyl carbinol is not totally complexed. It seems that the absorption between 80 and 160 K is due to the uncomplexed di-tert-butyl carbinol. The absorption maximum at 218 K (at 50.2 Hz), in analogy with di-tert-butyl carbinol and pyridine system in polystyrene, seems to arise from the presence of (a) 1:1 and/or 2:1 complex of monomeric di-tert-butyl carbinol and pyrazine and or (b) owing to the presence of 1:1 and/or 2:1 complex of dimeric di-tert-butyl carbinol and pyrazine. It is worth noting that the dielectric loss for di-tert-butyl carbinol and pyrazine system has a loss maximum at 118 K (at 50.2 Hz) is 2.8×10^{-3} (Figure VI-5) whereas for the di-tert-butyl carbinol and pyridine system, there is a loss maximum at 211 K (at 50.2 Hz) and at approximately the same concentration ratio is 30×10^{-3}, (Figure VI-3). This enormous difference in dielectric loss, which is proportional to the square of dipole moment, of an absorbing species, can be rationalized by considering that in di-tert-butyl carbinol and pyrazine systems there will be complex(es) of (a) two dimers (open) of di-tert-butyl carbinol with one pyrazine molecule, (b) two monomers of di-tert-butyl carbinol with one pyrazine molecule, (c) one dimer (open) of di-tert-butyl carbinol with one pyrazine molecule and/or (d) one monomer of di-tert-butyl carbinol with one pyrazine molecule. Possibilities (a) and (b), if they exist, owing to the low dipole moments compared to (c) and (d), will reduce the total absorption of 218 K maximum (at 50.2 Hz). Since in the case of di-tert-butyl carbinol and pyridine systems the possibility of the formation of low dipole moment complex (a) and (b) does not exist, therefore, the dielectric loss of 211 K maximum (at 50.2 Hz) is comparatively very high. Further, relaxation time at 200 K for di-tert-butyl carbinol and pyrazine is longer than the di-tert-butyl carbinol and pyridine system (c.f. 1.4 s and 2.8×10^{-2} s, respectively). This can be interpreted by considering that in the case of the former system the possibility (a) which does not exist in the latter is responsible for the longer relaxation time of the former system.

Group B

Methanol has been studied in a polystyrene matrix (see Chapter V). It has been discussed that the molecular and intramolecular motions of methanol (monomer) in polystyrene occur below 80 K in our frequency range. However, an absorption due to the presence of polymeric methanol is found in the temperature range ∿200-270 K with the magnitude of dielectric loss less than 2.0×10^{-3} s in the concentration range 1.45-7.05 M (Figure V-8). 0.30 M Methanol and 0.60 M pyridine and 0.30 M methanol and 1.10 M pyridine in polystyrene matrix showed a dielectric absorption maximum at 203 K (at 1.01 kHz) with the dielectric loss at this temperature 11×10^{-3} and 14×10^{-3}, respectively. A tail of an absorption near 80 K is also observed, apparently due to the excess pyridine. Figure VI-6 shows an ε" versus T plot of 1.45 M methanol in polystyrene. Comparing the dielectric loss of methanol and pyridine in polystyrene with that of methanol in polystyrene demonstrates that in the case of the former system we are dealing with higher dipole moment species than in the latter system. Dielectric absorption for the methanol-pyridine system with a temperature of maximum absorption at 203 K (at 1.01 kHz), thus, seems likely to arise from the methanol-pyridine complexes formed by the interaction of basic nitrogen of pyridine with OH-group of monomer and the terminal OH-groups of the polymers of methanol. The formation of these types of complexes of methanol with pyridine and other oxygen containing compounds has also been indicated by n.m.r. and infrared studies, respectively (13,12). Since a weak absorption owing to H-bonded species occurs for methanol in polystyrene in the temperature range ∿200-270 K, therefore, it is expected that absorption in methanol and pyridine systems with a T_{max} at 203 K (at 1.01 kHz) will also have some contribution from the self H-bonded species of polymers. A mean relaxation time for 0.30 M methanol and 0.60 M pyridine is found to be $2.3x10^{-3}$ s at 200 K whereas for 200-270 K the process of 1.45 M methanol in polystyrene is $3.0x10^{-1}$ s. Thus, the addition of pyridine to methanol shortens the relaxation time and this corresponds with the observation made by Koshii et al (19) that the addition of pyridine and dioxan to 1-propanol shortens the relaxation time of the alcohol for the first dispersion.

Group C

The system tert-butanol and pyridine (0.30:1.00 M) in polystyrene has also been studied. An asymmetric absorption in the ε'' versus T plot is observed with a temperature of maximum loss at 223 K (at 1.01 kHz) (Figure VI-7). 0.58 M tert-Butanol in polystyrene gave a dielectric absorption in the same temperature region with a difference that in the case of the 0.30 M tert-butanol and 1.00 M pyridine system, the dielectric loss maximum is 8.0×10^{-3} s (at 1.01 kHz) whereas in the case of 0.58 M tert-butanol the loss maximum is 0.6×10^{-3} s (at 1.01 kHz). Despite the fact that the concentration of tert-butanol in polystyrene is two times greater than the concentration of alcohol in tert-butanol and pyridine in polystyrene, the magnitude of dielectric loss (for T_{max} = 223 K at 1.01 kHz) in the case of the latter is ∿13 times higher than the former. This increase in dielectric loss for the tert-butanol and pyridine system in polystyrene matrix can be accounted for by the formation of the complex(es). The asymmetry in ε'' versus T plot of the tert-butanol and pyridine system is conspicuous which appears to indicate that the absorption in the higher temperature region (T_{max} = 223 K at 1.01 kHz) is due to the overlap of more than one process. The relaxation time at 200 K for tert-butanol and pyridine is 4.6×10^{-2} s whereas the ∿200-270 K process for tert-butanol in polystyrene gives 1.8 s which again shows that the addition of pyridine to alcohol shortens the relaxation time.

Group D

Dimethyl phenyl carbinol showed two absorptions in a polystyrene matrix (see Chapter IV). A low temperature absorption, which is observed with a temperature of maximum absorption at 101 K (at 1.01 kHz), is assigned to molecular relaxation whereas one which is observed with a temperature of maximum loss at 202 K (at 1.01 kHz), is attributed to the presence of the H-bonded species. 0.20 M Dimethyl phenyl carbinol and 1.00 M pyridine is studied in a polystyrene matrix. Besides a tail of an absorption near 80 K (probably owing to the molecular rotation of pyridine) an absorption maximum at 213 K (at 1.01 kHz) with a dielectric loss of 29×10^{-3} and relaxation time of 4.9×10^{-3} s at 200 K is observed (Figure VI-8). 0.50 M Dimethyl phenyl carbinol in polystyrene yielded an absorption (due to self H-bonded species) in the same temperature region with a dielectric loss maximum of 4.0×10^{-3} (at 1.01 kHz). The concentration of alcohol in 0.20 M dimethyl phenyl carbinol and 1.00 M pyridine in polystyrene is 2½ times lower than the alcohol concentration of dimethyl phenyl carbinol in polystyrene. However, the magnitude of dielectric loss is 7 times greater in the former than the latter. This bears out the formation of a molecular complex(es) of dimethyl phenyl carbinol and pyridine.

Dielectric measurements on 0.20 M dimethyl phenyl carbinol and 0.60 M isoquinoline in a polystyrene matrix showed an absorption maximum at 238 K (at 1.01 kHz) in ε" versus T plot and a shoulder at ∿160 K (Figure VI-8). It is shown by Shukla et al (11) that isoquinoline in polystyrene yields an absorption owing to the molecular rotation in the temperature range 129-153 K. Hence, the shoulder at ∿160 K in Figure VI-8 might be accounted for by the loss owing to the isoquinoline and probably some contribution from the molecular rotation of dimethyl phenyl carbinol also. An absorption maximum at 238 K (at 1.01 kHz) in the ε" versus T plot has a dielectric loss 30×10^{-3} which is a very strong loss compared to the one obtained for dimethyl phenyl carbinol in a polystyrene matrix (c.f. 4.0×10^{-3} at 1.01 kHz) in the same temperature region and at a concentration 2½ times higher. This bears out that the absorption maximum at 238 K is largely a contribution from complex(es) of dimethyl phenyl carbinol monomer and/or polymer with isoquinoline. However, a contribution from the self H-bonded species of dimethyl phenyl carbinol would also be expected to contribute. The relaxation time at 200 K of the process (T_{max} = 230 K at 1.01 kHz) in the dimethyl phenyl carbinol and isoquinoline system is found to be 4.8×10^{-1} s which, compared to the one obtained in the dimethyl phenyl carbinol and pyridine system (c.f. 4.9×10^{-3} s), is approximately 100 times longer. This can be accounted for by the formation of the larger complex by isoquinoline with alcohol rather than the pyridine with the same alcohol.

CONCLUSION

It has been demonstrated that alcohols interact with tertiary amines and result in an enhancement of the dielectric loss factor. The infrared spectra of alcohol and amine mixtures in polystyrene assisted in identifying the molecular interactions between the OH-group of an alcohol and the nitrogen of an amine. In most of the alcohol-amine systems, the dielectric absorption owing to the complex(es) seem to overlap the process(es) owing to the self H-bonded species of the alcohols, with an exception being di-tert-butyl carbinol and amines where only amine 4-phenyl pyridine interferes with the absorption owing to the complex(es). A survey of Table VI-1 reveals that as the size of an amine and/or alcohol increases the temperature of the maximum absorption also shifts to a higher temperature. This was further reflected in the relaxation times at 200 K of the alcohol and amine systems (Table VI-2). For example, the relaxation time of di-tert-butyl carbinol and 4-phenyl pyridine is $1.0\text{x}10^{1}$ s whereas for di-tert-butyl carbinol and pyridine systems it is $2.8\text{x}10^{-2}$ s. Inceasing the size of the alcohol molecule from methanol to tert-butanol leads to the lengthening of the relaxation time from $2.3\text{x}10^{-3}$ s to $4.6\text{x}10^{-2}$ s for methanol and pyridine and tert-butanol and pyridine systems, respectively. This suggests that the absorption contains a major contribution from the rotation of some of the complexed species. This is in harmony with a previous dielectric study of complexes of secondary amines with tertiary amines in polystyrene (11). However, the dielectric relaxation parameters in Table VI-2 do not enable us to identify precisely the types of species involved.

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TABLE VI-1: Dielectric Losses and Temperature of Loss Maxima of Some Alcohol-Amine Systems in Polystyrene

System	Concentration (mole/litre)	T_{max} (K)			$10^3 \times \varepsilon''$		
		50.2 Hz	1.01 kHz	10.2 kHz	50.2 Hz	1.01 kHz	10.2 kHz
Di-tert-butyl carbinol and 4-Phenyl pyridine	0.70:0.30	253	272	284	21.2	23.7	26.1
Di-tert-buty carbinol	0.70	120	134	138	8.1	8.9	9.7
4-Phenyl pyridine	0.30	220	251	272	15.2	17.4	19.4
Di-tert-butyl carbinol and Pyridine	0.30:1.10	211	228	240	29.9	29.2	28.1
Di-tert-butyl carbinol and pyrazine	0.30:1.00	218	227		2.8	2.6	
Methanol and Pyridine	0.30:0.60	186	203	215	11.9	11.1	10.1
Methanol and Pyridine	0.31:1.10	191	203	215	14.8	13.6	12.4
Methanol	1.45	220	242	267	1.3	1.1	1.0
tert-Butanol and Pyridine	0.30:1.00	197	223	232	9.1	8.1	7.3
tert-Butanol	0.58	239	247	262	0.6	0.6	0.6
Dimethyl phenyl carbinol and pyridine	0.20:1.00	202	213	229	30.1	29.4	28.5
Dimethyl phenyl carbinol and Isoquinoline	0.20:0.60	226	238	250	29.1	29.7	30.4
Dimethyl phenyl carbinol	0.50	89	101	113	4.4	5.2	5.8
		179	202	213	3.8	4.4	4.9

TABLE VI-2: Dielectric Relaxation Parameters of Some Alcohol-Amine Systems in Polystyrene

Systems (mole/litre)	ΔT(K)	Relaxation Time (200 K) (s)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
Di-tert-butyl carbinol and 4-Phenyl pyridine (0.70:0.30)	241-275	1.0×10^{1}	80±2	139±10
Di-tert-butyl carbinol and Pyridine (0.30:1.10)	212-240	2.8×10^{-2}	71±2	143±9
Di-tert-butyl carbinol and Pyrazine (0.30:1.00)	236-261	1.4	79±31	151±128
Methanol and Pyridine (0.30:0.60)	201-240	2.3×10^{-3}	45±3	36±3
Methanol (1.45)	240-265	3.0×10^{-1}	60±5	70±20
tert-Butanol and Pyridine (0.30:1.00)	214-278	4.6×10^{-2}	44±3	4±12
tert-Butanol (0.58)	253-270	1.8	67±15	88±58
Dimethyl phenyl carbinol and Pyridine (0.20:1.00)	204-231	4.9×10^{-3}	64±2	123±10
Dimethyl phenyl carbinol and Isoquinoline (0.20:0.60)	224-242	4.8×10^{-1}	79±7	158±30

TABLE VI-3: Fuoss-Kirkwood Analysis Parameters of Some Alcohol-Amine Systems in Polystyrene

T(K)	$10^6\tau$(s)	$\log\nu_{max}$	β	$10^3\varepsilon''_{max}$
Di-tert-butyl carbinol and 4-Phenyl pyridine (0.70 M and 0.30 M)				
241.8	1912.1	1.92	0.14	20.60
244.3	1323.7	2.08	0.14	21.00
247.0	1003.5	2.20	0.14	21.50
250.6	496.8	2.51	0.15	22.00
253.6	322.8	2.69	0.15	22.40
258.6	139.9	3.06	0.15	23.20
263.0	73.9	3.33	0.15	23.90
269.9	29.1	3.74	0.16	25.10
275.6	14.1	4.05	0.17	25.90
Di-tert-butyl carbinol and Pyridine (0.30 M and 1.10 M)				
212.1	2113.5	1.88	0.17	29.90
216.0	1142.9	2.14	0.17	29.80
219.9	578.1	2.44	0.17	29.80
223.6	280.1	2.75	0.17	29.50
288.0	129.1	3.09	0.17	29.10
232.2	62.0	3.41	0.17	28.60
235.2	40.0	3.60	0.18	28.40
238.0	27.0	3.77	0.18	28.20
240.1	17.9	3.95	0.18	28.10
Di-tert-butyl carbinol and Pyrazine (0.30 M and 1.00 M)				
236.4	649.1	2.38	0.10	2.60
240.1	489.9	2.51	0.13	2.60
243.9	210.2	2.88	0.14	2.50
257.0	48.4	3.52	0.19	2.40
261.4	9.7	4.21	0.19	2.50
Methanol and Pyridine (0.30 M and 0.60 M)				
201.2	1518.4	2.02	0.19	11.70
204.7	1398.9	2.06	0.15	11.00
208.4	678.3	2.37	0.15	10.70
212.3	421.3	2.58	0.13	10.50
218.0	241.5	2.82	0.15	10.20
223.0	123.0	3.11	0.14	9.80
228.1	64.3	3.39	0.15	9.60
232.9	41.7	3.58	0.16	9.30
239.7	23.1	3.84	0.17	8.90

TABLE VI-3: continued...

tert-Butanol and Pyridine (0.30 M and 1.00 M)

214.6	7057.4	1.35	0.13	9.00
223.0	3097.1	1.71	0.13	8.70
227.9	1773.9	1.95	0.13	8.60
231.5	1195.5	2.12	0.13	8.40
235.4	710.4	2.35	0.14	8.30
239.3	453.8	2.54	0.15	8.10
244.8	260.3	2.79	0.16	7.90
250.5	136.5	3.07	0.17	7.60
258.9	85.7	3.27	0.26	8.00
269.3	36.3	3.64	0.22	6.80
278.7	25.1	3.80	0.25	6.30

Dimethyl phenyl carbinol and Pyridine (0.20 M and 1.00 M)

204.6	2064.6	1.89	0.19	29.80
208.2	963.1	2.22	0.19	29.90
211.4	547.5	2.46	0.19	29.70
214.8	333.3	2.68	0.19	29.50
217.8	208.4	2.88	0.19	29.20
220.8	122.8	3.11	0.19	28.90
225.0	58.1	3.44	0.19	28.50
228.0	35.6	3.65	0.19	28.20
230.8	25.3	3.80	0.19	28.00

Dimethyl phenyl carbinol and Isoquinoline (0.20 M and 0.60 M)

224.3	2617.9	1.78	0.08	29.70
229.7	872.1	2.26	0.09	30.00
232.3	380.1	2.62	0.09	30.10
238.3	219.7	2.86	0.13	30.30
241.9	104.6	3.18	0.14	30.30

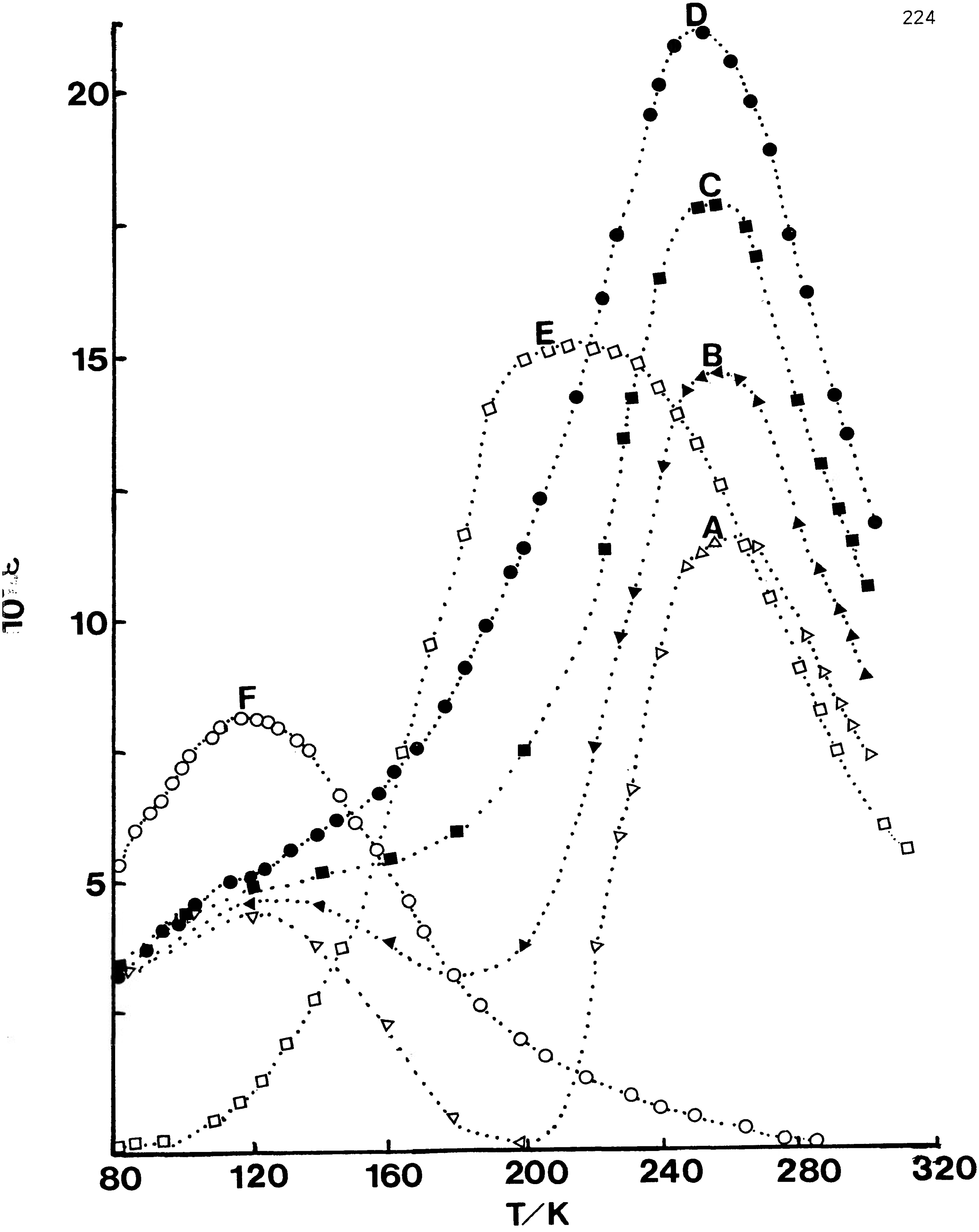


FIGURE VI-1: Dielectric loss factor, ε" versus Temperature for D = di-tert-butyl carbinol and 4-phenyl pyridine (0.70 M:0.30M), E = 4-phenyl pyridine (0.30 M) and F = di-tert-butyl carbinol (0.70 M) in polystyrene at 50.2 Hz. Curves A, B and C are subtracted curves.

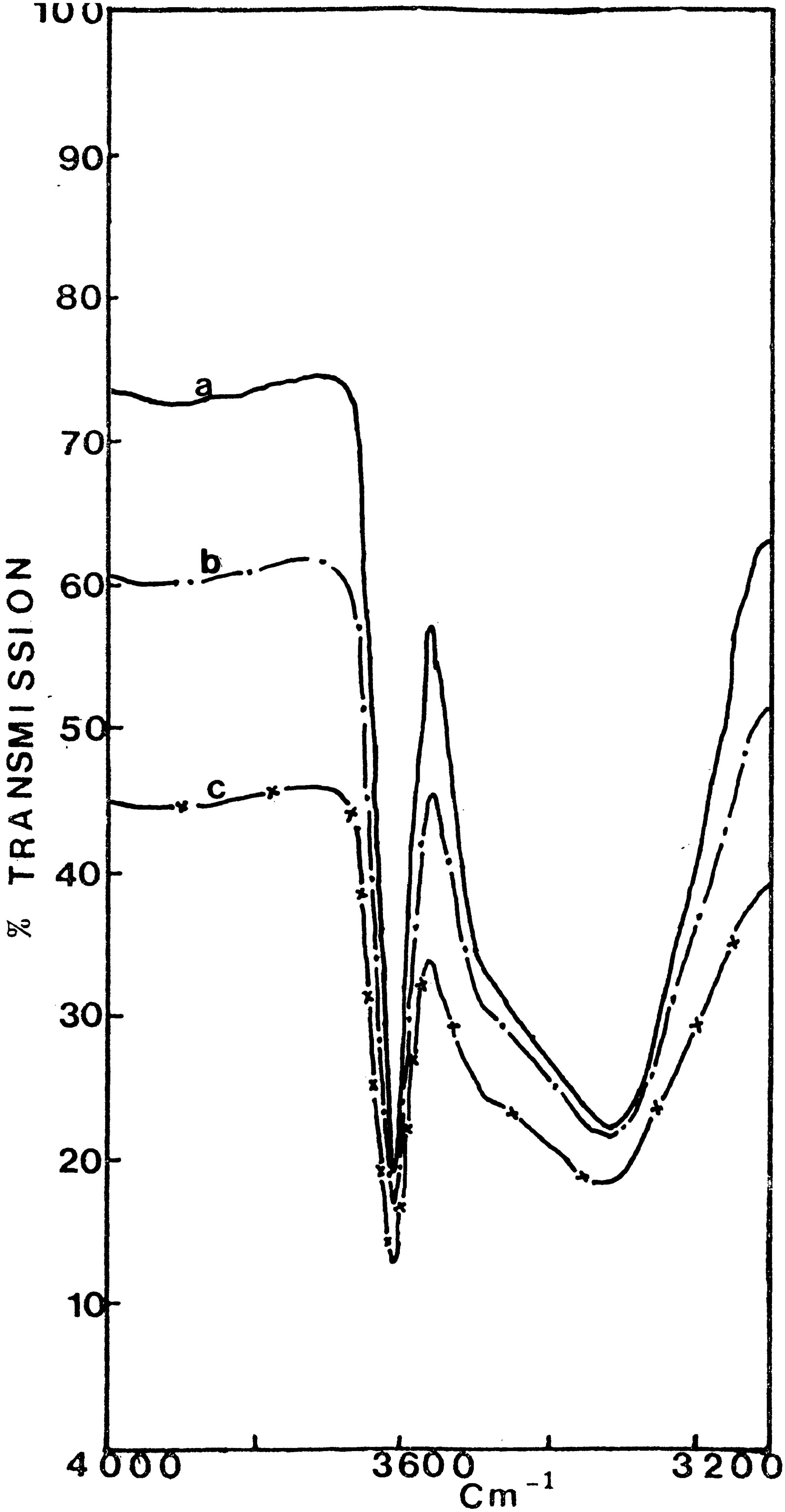
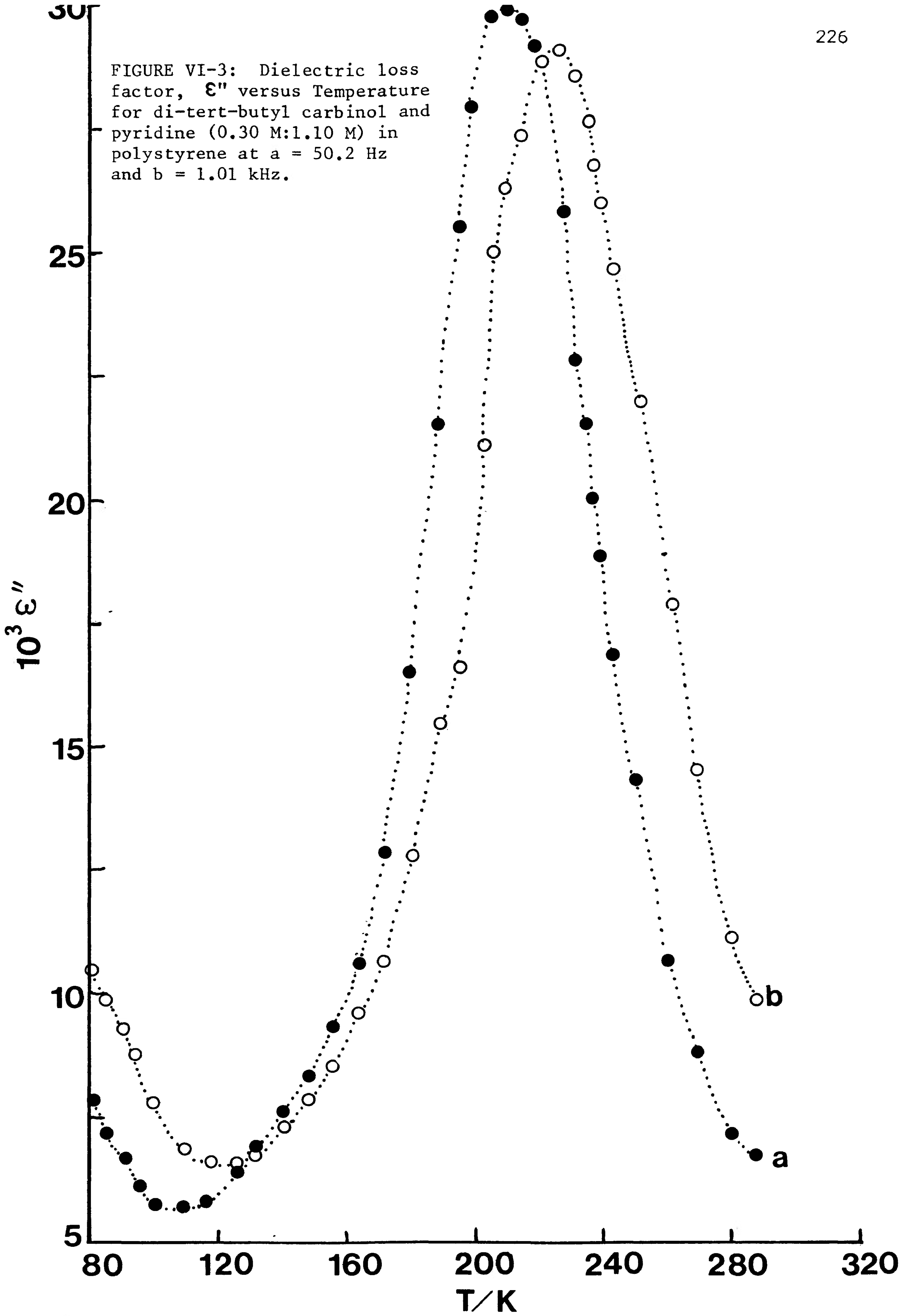


FIGURE VI-2: Infrared spectrum of di-tert-butyl carbinol and 4-phenyl pyridine (0.70 M:0.30 M) in polystyrene at a = 233 K; b= 273 K and c = 293 K.

FIGURE VI-3: Dielectric loss factor, ε" versus Temperature for di-tert-butyl carbinol and pyridine (0.30 M:1.10 M) in polystyrene at a = 50.2 Hz and b = 1.01 kHz.



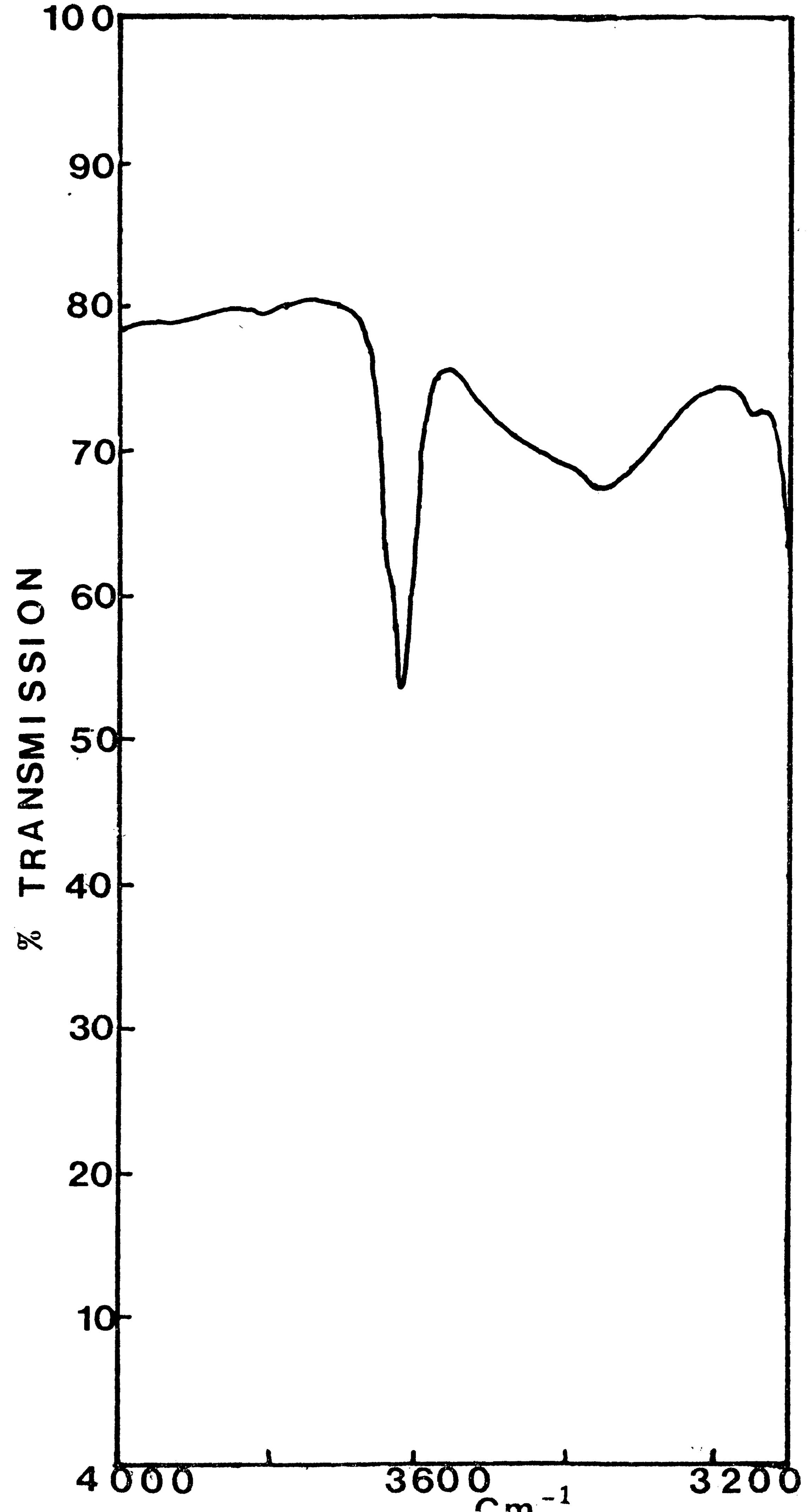


FIGURE VI-4: Infrared spectrum of di-tert-butyl carbinol and pyridine (0.30 M:1.10 M) in polystyrene at room temperature.

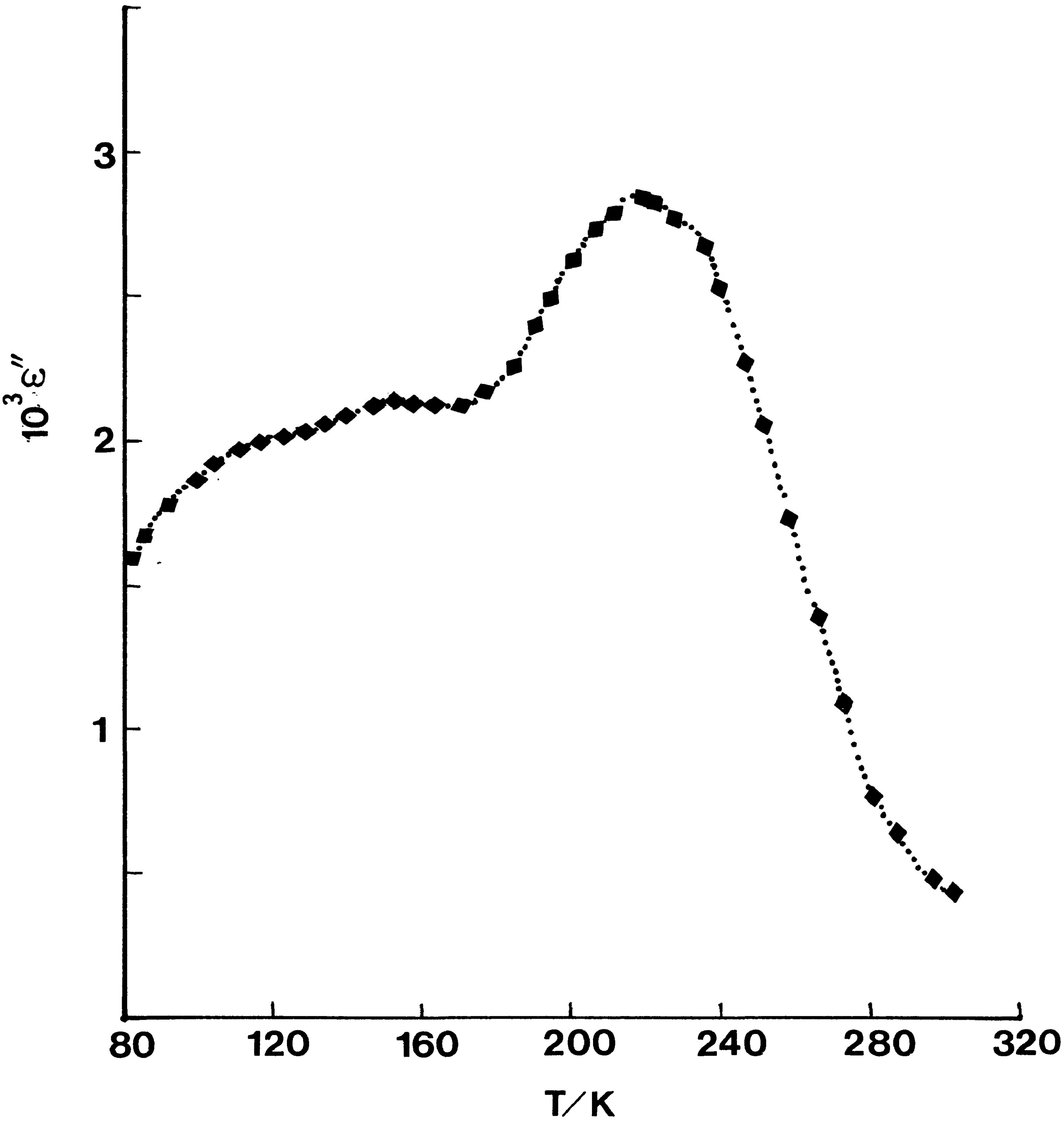


FIGURE VI-5: Dielectric loss factor, ε'' versus Temperature for di-tert-butyl carbinol and pyrazine (0.30 M:1.00 M) in polystyrene at 50.2 Hz.

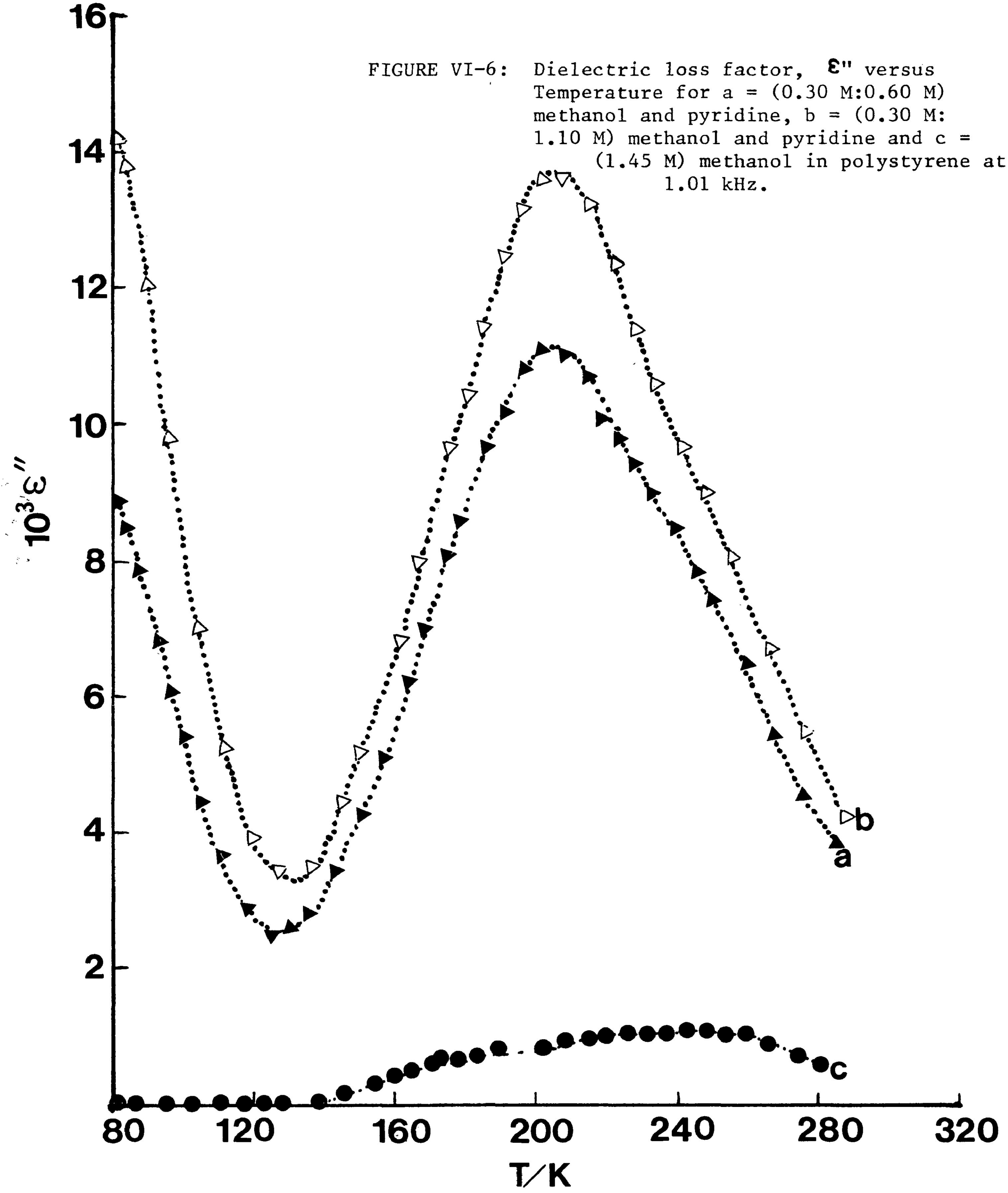


FIGURE VI-6: Dielectric loss factor, ε" versus Temperature for a = (0.30 M:0.60 M) methanol and pyridine, b = (0.30 M: 1.10 M) methanol and pyridine and c = (1.45 M) methanol in polystyrene at 1.01 kHz.

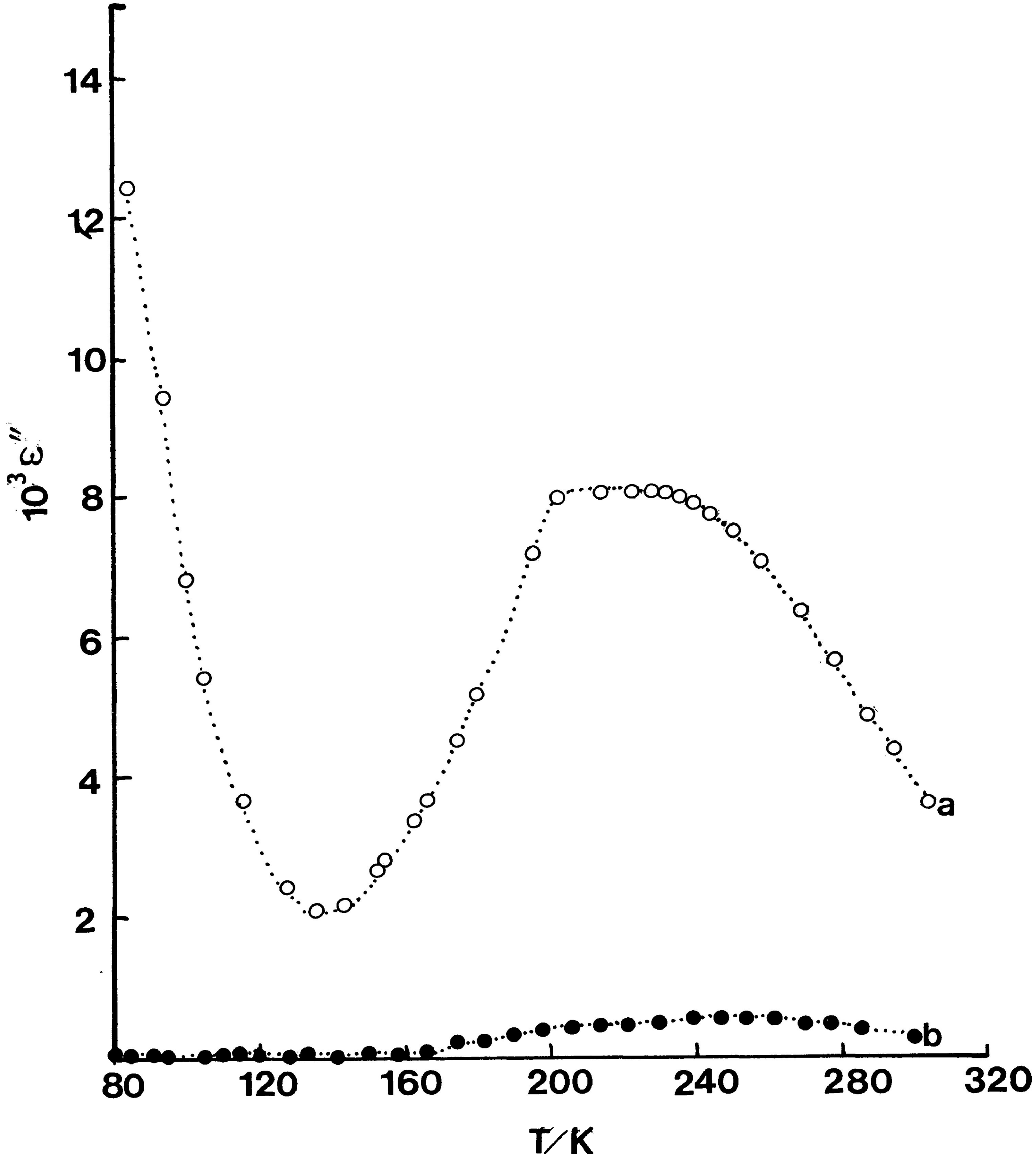


FIGURE VI-7: Dielectric loss factor, ε'' versus Temperature for a = (0.30 M: 1.00 M) tert-butanol and pyridine and b = (0.58 M) tert-butanol in polystyrene at 1.01 kHz.

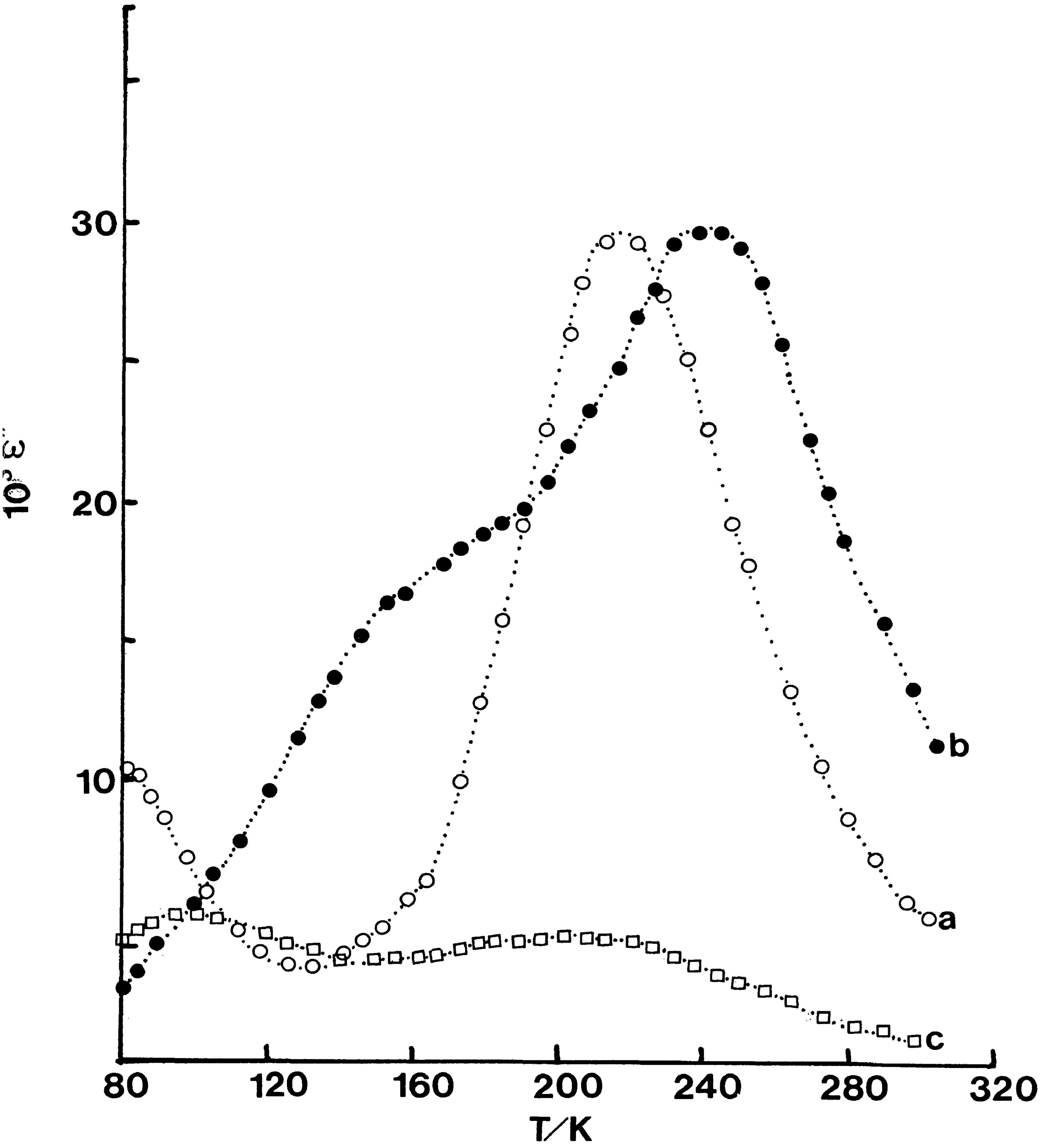


FIGURE VI-8: Dielectric loss factor, ε" versus Temperature for a = (0.20 M: 1:00 M) dimethyl phenyl carbinol and pyridine, b = (0.20 M:0.60 M) dimethyl phenyl carbinol and isoquinoline and c = (0.50 M) dimethyl phenyl carbinol in polystyrene at 1.01 kHz.

CHAPTER VII

SOME EXISTING MECHANISMS FOR THE FIRST DISPERSION OF ALCOHOLS

INTRODUCTION

The H-bond has been a topic of numerous books (1-5) and reviews (6-15) and studied extensively by several techniques including infrared, n.m.r. and dielectric. Alcohols which are typical of intermolecular H-bonding compounds have shown three dielectric dispersion regions characterized by corresponding relaxation times, τ_1, τ_2 and τ_3 (16). The relaxation times τ_3 and τ_2 have been attributed to intramolecular motion and molecular rotation respectively. However, as yet there is no agreed upon explanation for the relaxation time τ_1 (often referred to as the first dispersion or low frequency dispersion) which is characterized by having a Cole-Cole distribution parameter, $\alpha = 0$.

The present chapter will describe various proposed mechanisms and models for the first dispersion region and will assess them in the light of observations made for the various alcohols studied in the present work and by other workers.

DISCUSSION

One of the earliest mechanisms for the first dispersion in alcohols was given by Hassion and Cole (17,18). These workers demonstrated that alcohols such as ethanol and 2-propanol when studied at fairly low temperatures and in the range of audio and radio frequencies, give at least two dispersion regions. It was assumed that alcohols are H-bonded and the principal dispersion arises from the reorientation of a molecule's OH moment after the breaking of its intermolecular H-bond and subsequent forming of a bond to the oxygen of another molecule. The second dispersion interpreted as to arise from reorientation of the oxygen-alkyl group moment during the shift of the H-bond from one electron orbital to the bridged oxygen atom to the other of the two which is not used by the alkyl group and the proton of the alcohol molecule.

Brot et al (19-21) proposed a model to interpret the multiple dispersion regions in alcohols and proposed that the polymers of variable length exists in the liquid, together with free molecules, all in dynamic equilibrium. The lifetime τ of an H-bond is smaller than the time necessary for all but the very shortest polymers to reorient themselves as a whole in the applied field; it is the breaking of an H-bond that makes possible the orientation of liberated dipoles. $1/\tau$ consequently corresponds to the frequency of the main dispersion region. This region does not present any distribution of relaxation times because the lifetime of the H-bond is roughly independent of the size of the polymer. To interpret the second dispersion region two possibilities were considered (a) reorientation of very short polymers (e.g. polar dimers) and (b) reorientation of the small dipoles OC (along the hydrocarbon chain) inside a polymer, without breaking of the H-bond. The third dispersion was interpreted as resulting from the orientation of molecules which are, at a given instant, either free or at a terminal position of polymer.

Smyth and co-workers (16,22-24) made an extensive study of alcohols in the pure liquid state and in solutions. Some of the observations made by these workers are (a) all n-alcohols have three dispersion regions and the low frequency dispersion (first dispersion) characterized by a relaxation time τ_1 does not show any distribution of relaxation times, (b) the activation energy related with the first dispersion of pure n-alcohols increases with the increase in the chain length of the alcohols, (c) τ_1 is dependent upon the concentration of alcohols in an inert solvent and shortens rapidly as the concentration of alcohol decreases, (d) at approximately 0.25 mole fraction of alcohol in inert solvent (n-heptane) the τ_1 is independent of the chain length of n-alcohols, and (e) increasing the steric factors around the OH-group of an alcohol substituting bulkier alkyl groups leads to the disappearance of the τ_1 process.

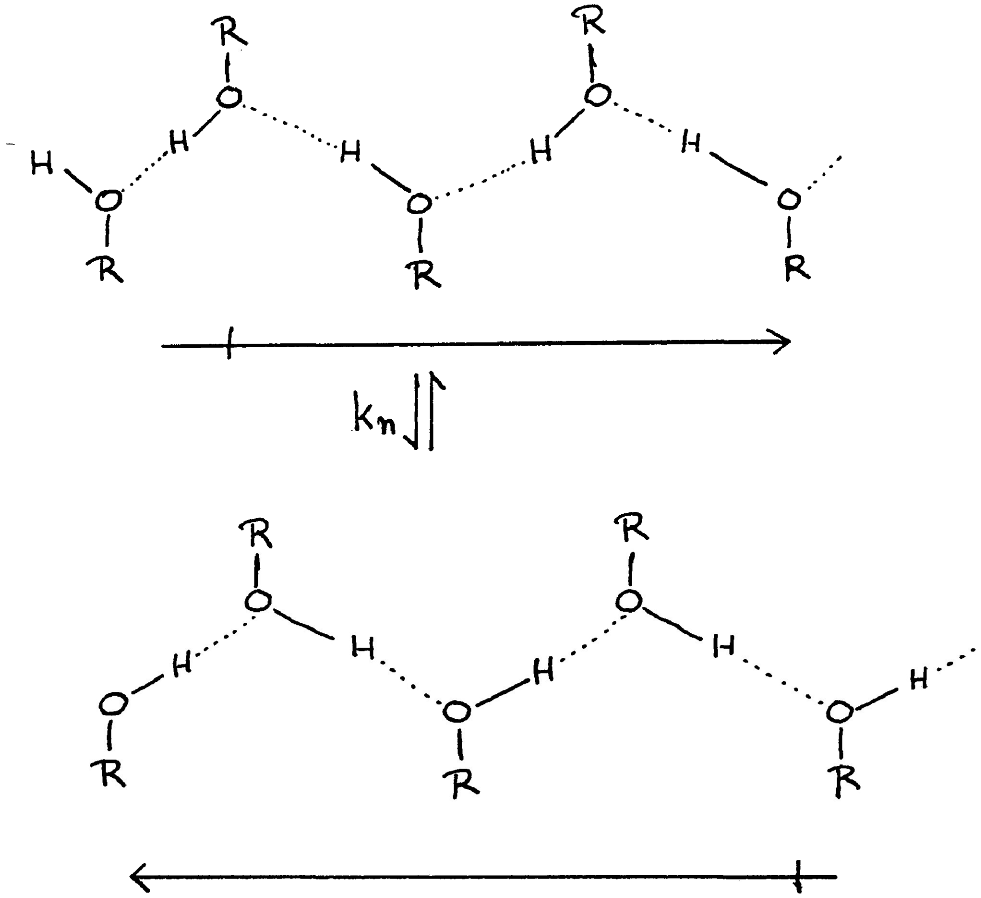
To account for the simple Debye behaviour of the first dispersion and increasing energy of activation with carbon chain length of the alcohols in the pure liquid state (16), it was considered that the alcohol molecules were associated by H-bonds in temporary microcrystalline structures. These structures are not stable, and at a given instant each of these has a finite length. At each instant some H-bonds are ruptured and others are formed. The dielectric relaxation process of the first dispersion involves the breaking and reforming of the H-bonds with consequent re-orientation of the dipole moment, and the rate of breaking off is the determining factor for the relaxation time. The increase in the activation energy, ΔH_1, of the first dispersion region with the increase in the carbon chain length of the alcohols was explained by considering that the H-bond breaking is an initial step in the relaxation process, but some molecular motion dependent upon the chain length is also required to give the observed increase in τ_1, hence, ΔH_1 increases with chain length. The third dispersion region, characterized by relaxation time τ_3, was suggested to be related with the OH group rotation. The second dispersion in pure liquid n-alcohols was assigned to the molecular rotation and terminal ROH rotation about the H-bond in a polymer chain (16). However, later studies (23, 24) of the alcohols in solution have suggested that small multimers contribute to the second dispersion, and a probable contributing relaxation proces is to be the orientation of the terminal -OR group about the -OH bond in an H-bonded species.

The dielectric studies of Dannhauser and associates (25-28) on some sterically hindered alcohols in the pure liquid state led them to propose a model where, contrary to Garg and Smyth's view (16), the H-bond breaking as the rate determining step for the first dispersion was refuted. This was based on the observation that the isomeric octanols in the pure state yield activation energies which differ greatly from one isomer to another. It was suggested that at relatively high temperatures those alcohols whose OH-group is most sterically hindered prefer to form rings (polymer) while those whose OH-group is relatively accessible tend to form open chains (polymer) (25,26). The enthalpy per mole, $\Delta \overset{o}{H}$, of H-bond formation in chains (polymer) is estimated to be about 28 kJ mol^{-1} and for polymer rings, about 19 kJ mol^{-1}. In their qualitative model (27) it was considered that the H-bond rupture is a prequisite for dipolar reorientation rather than the rate determining step. It was envisaged that a particular H-bond will break and reform many times without reorientation of either the donor or acceptor molecule. The dipolar reorientation is thought to be cooperative and occurs relatively seldom. When the dipolar reorientation occurs the rate of reorientation depends on the size and shape of the entire molecule insofar as this determines the interaction of a specific molecule with its "surroundings" and also because the structure of the molecule determines the nature of the surroundings.

Böttcher et al (29,30) advanced a model to explain the zero distribution of relaxation times for the first dispersion observed in the mixtures of 1-heptanol and 4-heptanol. They considered that the alcohols are H-bonded into the polar cyclic tetramers and less polar dimers. The first dispersion is related to the reorientation of polar tetramers because the rate of reorientation of the multimers is fast with respect to the rate of exchange. Zero distribution of relaxation times occurs because only one species (tetramer) is contributing to the first dispersion.

Sagal (31), on the basis of dielectric study of ethanol in cyclohexane (and some other alcohols in the pure liquid state) where the activation energy increases with dilution, have proposed a mechanism for dielectric relaxation. It is considered that the main mechanism of the dipolar relaxation related with first dispersion is the one where an H-bond of a polymerized chain breaks when another molecule of alcohol approaches the polymerized chain with its oxygen atom favourably oriented for a "switch". The presence of a third oxygen atom will lower the energy barrier for the breaking of an H-bond. The increase in activation energy on dilution of ethanol with cyclohexane has been explained as an increase in resistance to the motion of the ethyl group (during the "switch") owing to bulky cyclohexane molecules. The increase in activation energy of pure liquid alcohols with an increase in the length of carbon chain has been explained as the increase in resistance to the motion of the alkyl group.

Minami et al (32-34) have proposed a model for the first dispersion in alcohols. It was considered that (a) liquid alcohol molecules exist in association equilibria involving both H-bonded ring dimers and linear n-mer (multimer), (b) the rates of the reorientation and deformation of the multimer are slow enough to be neglected and, (c) when all the OH-groups rotate around the O-C axes, the dipole moment of the multimer reverses its direction as shown below.



It is assumed that the dipole inversion of the n-mer (multimer) always originates at the terminal molecule because in order to activate one of the terminal segments, only one H-bond needs to be broken.

To account for the increase in activation energies of alcohols with the increase in carbon chain length, it is suggested that a third alcohol molecule approaches with its oxygen atom oriented favorably to activate the OH-group of the terminal molecule of multimer. With the increase in the size of the alcohol molecules the proximate presence of the hydrogen-acceptor atom to the terminal OH-group becomes more and more scarce, causing the increase in the value of activation energy.

Hassion and Cole's mechanism (17,18) would predict that the energy barriers and relaxation times for the first dispersion of alcohols would be independent of the alcohol shape and size. However, it has been found that the energy barriers and relaxation times related to the first dispersion of alcohol in the pure liquid state increase with the increase in the size of the alcohols (16). Our results appear to indicate that the process for alcohols in polystyrene found in the temperature region ∿200-270 K (due to the H-bonded species) is not dependent on the size of alcohols (for example, methanol and dimethyl-tert-butyl carbinol are quite different in molecular size but they yield an absorption due to the H-bonded species in the temperature range ∿200-270 K). However, according to Hassion and Cole, only one H-bond needs to be broken to reorient the OH-dipole. Tay et al (35) have shown that 2,6-dinitrophenol in a polystyrene matrix gave a ΔH_E of ∿35 kJ mol^{-1} for the OH-group to reorient from one planar position to another after breaking a strong intramolecular H-bond. The strength of one intermolecular H-bond in alcohols has been suggested to be 18 ±2 kJ mol^{-1} (36-39). Almost all the alcohols and even water studied in polystyrene matrices yielded ΔH_E values of ∿60 ±20 kJ mol^{-1} which does not conform to Hassion and Cole's hypothesis.

Brot et al (19-21) independent suggestions for the first dispersion of alcohols are essentailly the same as Hassion and Cole's. Hence, the same arguments can be presented.

Garg and Smyth (16) observed that in the pure liquid state relaxation times and activation energies related to the first dispersion increase as the length of the alkyl group increases. They have interpreted their results on the basis of a proposed model where it was considered that the main mechanism for the first dispersion involves the breaking of an H-bond in the polymers, thus, partially liberating the molecule to reorient its dipole. The H-bond breaking was considered as a rate determining step and the increase in activation energies and relaxation times with increasing size of carbon skeleton of the alcohols was suggested to arise from the rotation of the partially liberated molecule. Garg and Smyth's mechanism would predict that the isomers of an alcohol in their pure liquid state would give similar values of energy barriers and relaxation times related to the first dispersion. However, some isomeric methylheptanols (27), isomeric phenyl propanols (28) and isomeric octanols (40) in their pure liquid state yield greatly different energy barriers for isomers. However, our results for ∿200-270 K process of alcohols in polystyrene matrices (due to H-bonded species) appear to indicate that the H-bond(s) breaking is a very important step because the value of ΔH_E for almost all the alcohols and water in polystyrene can be given by ∿60 ±20 kJ mol^{-1}. It is quite clear that the extent of H-bonding and types of species would be considerably different in the pure liquid alcohols than in the dilute solutions (2) and even the types of solvents (41-43) would determine the degree (and possibly types of) of polymerization. Hence, it is not necessary that the mechanisms developed for the pure liquid alcohols fit completely for the dilute solutions of alcohols as it has also been indicated by the observation that about 0.25 mole fraction of alcohol in n-heptane, the relaxation times, τ_1, for first dispersion of 1-butanol to 1-dodecanol are similar (24). This observation is contrary to the dependence of relaxation times (τ_1) for n-alcohols in the pure liquid state.

A model given by Dannhauser and associates (25-28) considers that the mechanism of relaxation of first dispersion of alcohols does not involve the H-bond breaking as a rate determining step rather it is a prerequisite. The relaxation time and activation energy for this process are determined by the strength of the interaction between the relaxing dipole and its surroundings, which is in turn influenced by the size and shape of the molecule. Our results for the ∿200-270 K process of alcohols in polystyrene matrices (owing to H-bonded species) do not appear to support the Dannhauser's view. Further, the dilution of an alcohol by an inert solvent leads to the initial lengthening of relaxation time, τ_1 (44), whereas Dannhauser's model would predict shortening of τ_1 which again indicates that the qualitative mechanism given by Dannhauser and co-workers does not fit the above observations.

A proposal given by Böttcher et al (29,30) that the highly polar, non-planar, cyclic tetramer is responsible for the first dispersion region in alcohols. This model was based on the study of pure 1- and 4-heptanol and their mixtures between 213 and 273 K. However, infrared measurements of strongly sterically hindered alcohols in dilute solution in polystyrene at low temperatures show the presence of a variety of H-bonded species. Thus, it is obvious that unhindered alcohols such as 1-heptanol and 4-heptanol in their pure state and at low temperatures are expected to have a higher degree of polymerization than the tetramer. Böttcher et al's hypothesis does not seem to explain the observation that at 0.25 mole fraction of alcohol in n-heptane, the relaxation time τ_1 of 1-butanol to 1-dodecanol are similar (24), and our observation that the ∿200-270 K process for the alcohols in polystyrene is virtually independent of the size of the molecules.

Sagal's (31) mechanism explains the initial lengthening of relaxation time, τ_1, on dilution of an alcohol, however it does not explain the shortening of relaxation time on further dilution. However, an extended version of Sagal's concept as given by Campbell et al (44) where it is assumed that as the alcohol is diluted initially the solvent molecule hinders the approach of a favourably oriented third oxygen atom for a switch with the polymer chain, thus causing an initial lengthening of the relaxation time, τ_1. However, the degree of self-association is also important which decreases on dilution which will increase the proportion of favourably oriented third oxygens (as a monomer and terminal OH groups of polymer). Thus, if the degree of association, due to further dilution, becomes dominant over the screening effect of the solvent, then the dilution leads to the shortening of relaxation time, τ_1, of the alcohol. This mechanism cannot explain adequately why some long-chain n-alcohols on dilution do not yield a maximum in τ_1 versus the concentration plot. Further, our results for ∿200-270 K process of alcohols in polystyrene do not appear to conform to the Sagal's mechanism completely since activation energies do not seem to be dependent on the molecular size.

A model given by Minami et al (32-34) for the first dispersion in alcohols considers a dipolar relaxation as a co-operative process where to reorient the OH-dipole of a polymer chain one H-bond must be broken and the energy barrier for the first dispersion of an alcohol is a contribution from the energy to reorient an OH-group in multimer and energy to break one H-bond. Minami et al have used Sagal's concept of "switch" to explain the increase in the energy barrier for first dispersion of alcohols with the increase in carbon chain length. It has been suggested that the third alcohol molecule approaches with its oxygen atom oreiented favourably to activate an OH-group of the terminal molecule H-bonded to a neighbouring one, and with an increase in the size of the alcohol molecule, the approach of a third alcohol oxygen oriented favourably will reduce causing an increase in the value of activation energy. This concept was also invoked to explain the decrease in τ_1 of 1-propanol on addition of donor H-bonding solvents such as pyridine and dioxan since these solvents provide a new possibility to activate terminal OH of the polymer chain (45). However, the idea of the approach of a third alcohol molecule with its oxygen favourably oriented to activate terminal

OH group of the polymer, has to be treated cautiously since a most recent infrared study (46) has shown that the degree of polymerization in n-alcohols in dilute solution is independent of the length of the alkyl chain where for $C_nH_{2n+1}OH$ n was varied from 1 to 18.

This seems to indicate that, at least in dilute solutions of alcohols, the approach of a third alcohol molecule with its oxygen oriented favourably to activate the terminal OH-group of polymer chain would not be reduced with an increase in the length of the hydrocarbon portion of the alcohol molecule.

CONCLUSION

It is evident from the discussion on the models proposed to explain the first dispersion (low frequency dispersion) that in fact, none of them adequately explain all the experimental observations. Thus, some of the mechanisms explain the results of pure liquid alcohols in a better way whereas others are better applied to a solution of alcohols.
Most of the mechanisms discussed in this chapter for dipolar relaxation related to first dispersion, consider the H-bond breaking as the most important step with the exception of Böttcher et al's (29,30) view where they propose reorientation of cyclic, nonplanar, polar, tetramer as the main mechanism for the first dispersion.

Dielectric studies of all the alcohols except di-tert-butyl carbinol, diphenyl methyl carbinol and tricyclohexyl carbinol in polystyrene matrices show an absorption in the temperature range $\sim$200-270 K in our frequency range ($10-10^5$ Hz) owing to H-bonded species. The activation energies for this process are of a similar order of magnitude for all the alcohols which are not dependent on the size of the molecule. This can be seen from the fact that the ΔH_E for water in a polystyrene matrix is 55 kJ mol^{-1} whereas molecules which are much larger than water e.g. tert-amyl alcohol and tert-butyl ethyl methyl carbinol, also yield similar ΔH_E values (c.f. ∿55 and 56 kJ mol^{-1}, respectively). Thus, it appears that a mechanism which invokes H-bond breaking as an important factor involved in the mechanism(s) to account for our observations. Since the strength of one H-bond in alcohols is found to be 18 ±2 kJ mol^{-1}, therefore, it seems likely that the ∿200-270 K process found in alcohols in polystyrene (owing to H-bonded species) involves breaking of more than one H-bond.

Di-tert-butyl carbinol (0.70 M) in polystyrene has been shown to form only the dimer as a H-bonded species in the temperature range, 213-293 K, but it does not yield any dielectric absorption in the temperature range ∿200-270 K. Since the dimer (if open) will have only one H-bond, thus, it supports that dielectric absorption observed for other alcohols and water in polystyrene in the temperature range ∿200-270 K region would involve the breaking of more than one H-bond.

Small alcohols such as methanol, 1-propanol, tert-butanol, tert-amyl alcohol and water in polystyrene, yield an activation enthalpy of 61 ±11 kJ mol^{-1} for the ∿200-270 K process. Various forms of ice also yield an activation energy of similar order of magnitude which has been explained on the basis of the Bjerrum mechanism where the propagation of defects require the breaking of the H-bond (47-51).

From the ΔH_E values alone, obtained for the ∿200-270 K process of alcohols in polystyrene, it might be considered that for our alcohols in a polystyrene matrix involves, on average, the breaking of two, three, or occasionally, four H-bonds. There are many indications that for a given alcohol in a polystyrene matrix more than one H-bond breaking process occurs (in the ∿200-270 K region). Further, appreciable steric factors appear to influence the types of species present. Often, with the complexity of species present, it seems difficult to envisage a model which fits all cases.

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CHAPTER VIII

SUGGESTIONS FOR FURTHER WORK

This thesis contains the dielectric relaxation studies in conjunction with infrared studies of various H-bonding systems in matrices. Various aspects of H-bonding, especially in alcohols dispersed in polystyrene matrices, are discussed.

It has been shown that some alcohols (e.g. tert-butanol) when dissolved in other glassy media than polystyrene give a process due to H-bonded species at lower temperatures (in a fixed frequency range i.e. $10-10^5$ Hz). Thus, it would be interesting to study the effect of a medium at a fixed concentration of alcohols by employing various non H-bonding solvents such as polypropylene, polyethylene, cyclohexane, cis-decalin and carbon tetrachloride, etc.

In the present work we have concluded that a process(es) owing to H-bonded species found for alcohols in polystyrene, involves, besides some other factors, H-bonds breaking as a very important step. In fact, one of our alcohols (di-tert-butyl carbinol) in a polystyrene matrix has shown that the breaking of one H-bond will not lead to a dielectric absorption in the 200-270 K region, whereas the absorption in the 200-270 K region is usually found for the alcohols possesing H-bonded species with more than one H-bond. It would be interesting to synthesize alcohols with suitable steric factors which at certain temperatures and concentrations in polystyrene form the H-bonded species with two, three and four H-bonds. Similar studies can also be carried out in other polymer matrices (e.g. polypropylene and polyethlyene).

Our dielectric studies on alcohol and amine systems in polystyrene have shown that alcohols interact with amines to form complexes. However, in many cases absorption owing to the complex and H-bonded species of alcohol and/or the molecular process of amine were overlapped. To extend this work further we can study some small size alcohols, which at certain temperatures and concentrations do not form H-bonded species larger than dimer (e.g. di-tert-butyl carbinol, tri-tert-butyl carbinol, di-tert-butyl phenyl carbinol and diisopropyl ethyl carbinol, etc.), with small size tert-amines (e.g. pyridine, quinuclidine, 4-methyl pyridine, 2.4.6-collidine, pyrazine, 1,4-diazabicyclo[2.2.2]octane, N-methyl piperidine and piperazine, etc.) in polystyrene. Instead of using amines some oxygen containing small molecules (e.g. dioxan, tetrahydrofuran, furan, acetone, dimethyl ether and tetrahydropyran, etc.) can also be studied with the above mentioned alcohols in a polystyrene matrix. We hope that this type of study might lead to more definite information about molecular complexes and their mechanism of dielectric relaxation.

PUBLICATIONS

One paper has been published from the work related to this thesis and two papers are being prepared for publication.

Published Work

Dielectric Studies of the β_1 and β_2 Process of Poly(Alkyl Methacrylate) Polymers, M.A. Desando, M.A. Kashem, M.A. Siddiqui, and S. Walker, J. Chem. Soc., Faraday Trans. 2, 1984, 80, 747.