DIELECTRIC AND INFRARED STUDIES OF RADIO FREQUENCY PROCESSES IN SOME ALCOHOLS

By

HUMAYUN MANDAL ©

A Thesis submitted to
Lakehead University
Thunder Bay, Ontario
Canada

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

1988

ISBN 0-315-48202-8

To my Parents

Abstract

In this thesis, the results of dielectric studies on a number of aliphatic alcohol molecules with variable chain lengths are presented. This investigation was complemented by infrared and viscosity measurements. Dielectric studies were confined to the radio frequency range using an H.P. 4191A RF Inpedance Analyzer. The experimental data, as a function of frequency and temperature, were subjected to analysis by a series of computer programs written in APL language. The activation energy barriers for the dielectric relaxation were obtained by application of the Eyring rate equation.

Initially, a number of pure liquid alcohol molecules were studied with increasing chain length in a wide temperature and frequency range. The effect of size on the relaxation parameters could then be revealed. In all cases a Debye type process was observed which is in accordance with the literature report.

A few of these alcohols were also studied in a variety of solvents ranging from inert to stongly interacting. The experimental relaxation times were compared with the theoretical ones obtained using Higasi's theory of the dielectric relaxation mechanism. Furthermore, the relaxation parameters were analysed in terms of solute-solute and solute-solvent interactions.

The importance of chain length on the associative equilibria was examined. Methanol, which has no chain length and no intramolecular motion within the experimental temperature and frequency ranges, was selected for this purpose. A detailed dielectric study for this alcohol was carried out in different media.

An attempt was made to gain insight into the impact of steric hindrance on the relaxation times and energy parameters. Small alcohols were substituted by

larger alcohol molecules in three component systems. The position of the dipole was varied for different alcohols in two component systems. These studies constitute the latter part of this thesis.

Acknowledgements:

This research was conducted at Lakehead University, Canada during 1985-87 under the supervision of Dr. S. Walker and Dr. D.G. Frood. I express my sincere gratitude to them for their unfailing interest, continuous encouragement and invaluable guidance.

I am greatly indebted to Mr. M.A. Siddiqui, Miss L. Humenik, Dr. M. Hawton, Dr. M.A. Saleh and Dr. M. Habibullah for their help and co-operation throughout this work. I am very thankful to Mr. B.K. Morgan for his unforgettable technical assistance through every stage of this research.

I would like to thank Mrs. J. Parnell for initial typing and Mrs. J. Boucher for her help in typing some of the important parts of my thesis. I must thank Miss Karen Knudsen for her excellent work in typing the entire text of this thesis. I would also like to thank Ms Alanna Barich for her constant help and support during my stay in Thunder Bay.

Finally, I would like to thank the financial assistance provided by the Graduate School and Physics Department of Lakehead University throughout my years of graduate study.

Table of Contents

CHAPTER I

INTRODUCTION AND THEORY

Introduction

Hydrogen bonding occurs between a proton donor group A-H and a proton acceptor group B, where A is an electronegative atom, and B is the lone pair of an electronegative atom or a π-electron orbital of an unsaturated system. There are two types of hydrogen bonds: 1) intramolecular, involving donor and acceptor sites within the same molecule (ie. ethylene glycol, salicylaldehyde) and 2) intermolecular, involving two or more separate molecules (ie. water, alcohols, phenols). Intermolecular H-bonds can yield two different types of multimers: (a) open/linear, where the monomer units are joined together linearly and (b) cyclic/closed, where the multimer formed by association is cyclic.

Infrared and nuclear magnetic resonance spectroscopy have provided sensitive means of detecting H-bond formation and have been extensively used for both qualitative and quantitative studies of H-bonded systems. Dielectric relaxation, however, is becoming an increasingly useful tool for studying the hydrogen bonding phenomenon. The dielectric study of H-bonding has been described in detail in several books and reviews [10-12].

In this work, the basic aim was to study H-bonding in some liquid alcohols in their pure form as well as in solution by dielectric relaxation. A wide temperature and frequency range was employed.

The study began with the selection of a set of normal aliphatic alcohols of the general formula $C_nH_{2n+1}OH$ where n = 1, 2, 3...12. The chain length was increased steadily in order to investigate its effect on the dielectric relaxation parameters. The macroscopic viscosity of these alcohols were also measured to explore if viscosity is somehow related to the relaxation mechanism. An interesting trend of the relaxation parameters, particularly for the long chain alcohols, was observed.

This work continued with the selection of five alcohols of increasing chain length from the previous set. These were studied at various concentrations in three different solvents ranging from inert to highly interacting. The purpose was to study the behaviour of these alcohols in different media. The behaviour of the alcohols in completely inert and weakly interacting solvents were almost the same. They were, however, very different from those in highly interacting solvents. This helped us predict, to some extent, the type of association present in these systems.

Methanol (CH_3OH) was also the subject of extensive study. We chose this alcohol basically to examine the effect of chain length on the type of mechanism involved in these alcohols. Interestingly, methanol showed contradictory behaviour to the rest of the alcohols when studied in the same solvents.

Three sets of isomeric alcohols were also selected for this study. They were studied in the weakly interacting solvent, toluene. The dipoles were gradually blocked to hinder easy association. The impact of steric hindrance on the dielectric relaxation parameters was thus examined. Infrared spectra for these systems were taken at room temperature to visualize the type of species present in the solution.

The appendix of this thesis is divided into two parts, AI and AII. All the tabulated data are presented in Appendix AI whereas all the figures are included in Appendix AII.

Theory

To date, there are two basic types of dielectric materials known; non-polar and polar. All the electrons are bound in non-polar dielectrics and the only motion possible in the presence of an electric field is a very limited displacement of positive and negative charge in opposite directions. Under this condition the material is said to be polarized, and its molecules possess induced dipole moments. A polar dielectric material is one which has a permanent electric dipole moment. Clausius-Mossotti-Debye theories [1] describe the total molar polarizability (p_T) of a dielectric material in an applied electric field as follows:

$$
\begin{aligned}
p_T &= p_D + p_O \\
&= \frac{4\pi N}{3}\left[\alpha_D + \frac{\mu_v^2}{3kT}\right] \qquad \text{(I-1)} \\
&= \frac{\varepsilon_O - 1}{\varepsilon_O + 2} \cdot \frac{M}{d}
\end{aligned}
$$

where α_D = displacement polarizability
M = gram molecular weight
d = density (g/m^3)
N = Avogadro's number
k = Boltzmann Constant
μ_v = electric dipole moment of the molecule in a vacuum.
T = absolute temperature
ε_O = static dielectric constant

The subscripts, D and O in p indicate the displacement and orientation polarization components, respectively, of the total molar polarizability, p_T.

The quantity (ε_o - 1)M/(ε_o + 2)d is called the molar polarizability. From Equation (I-1) it is quite obvious that 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 polarizability 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 leads to the dipole moment of the molecule.

The Clausius-Mossotti-Debye theories are applicable to gases, but are inadequate when applied to polar liquids, due to the inability of the Lorentz field used in these theories to represent adequately the local field in a dipolar dielectric material. When an insulating material is placed in an electric field it becomes polarized, due to the relative displacement of positive and negative electric charges in the material. The ratio of the field strength without any dielectric to that in the presence of the dielectric is called the static dielectric constant, ε_o, of the material. If a dielectric material is placed in an electric field; which alternates at low frequency, the polarization will follow it. As the frequency of the applied field is increased above 10^8 Hz, the dipoles begin to lag behind the field and the polarization (p_o) falls so that its contribution to the total permittivity decreases. 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 orientation causes a dissipation of energy, or Joule heating which is measured by the dielectric loss (ε'') defined below as:

$$\varepsilon'' = \varepsilon' \tan\delta \qquad \text{(I-2)}$$

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 dielectric constant in the dispersion region can be represented by the following equation and diagram:

$$\varepsilon^* = \varepsilon' - i\varepsilon'', \text{ where } i = \sqrt{-1} \qquad \text{(I-3)}$$

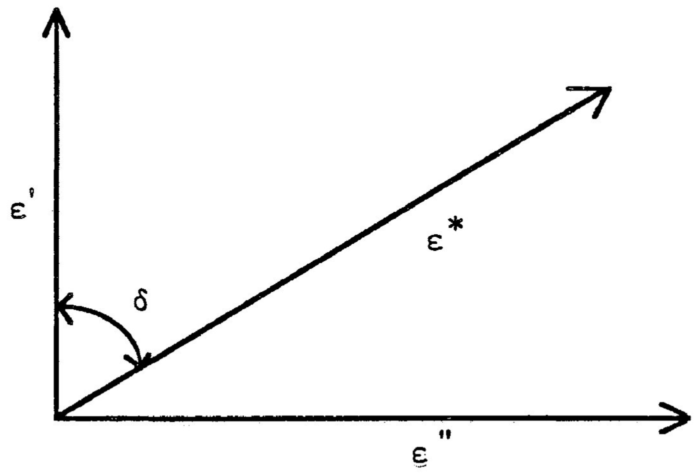


Figure I-1: The Complex Dielectric Constant. Showing $\delta = \tan^{-1}(\varepsilon''/\varepsilon')$.

The absorption regions associated with different mechanisms of polarization occurs in different parts of the electromagnetic spectrum, as shown in Figure I-2:

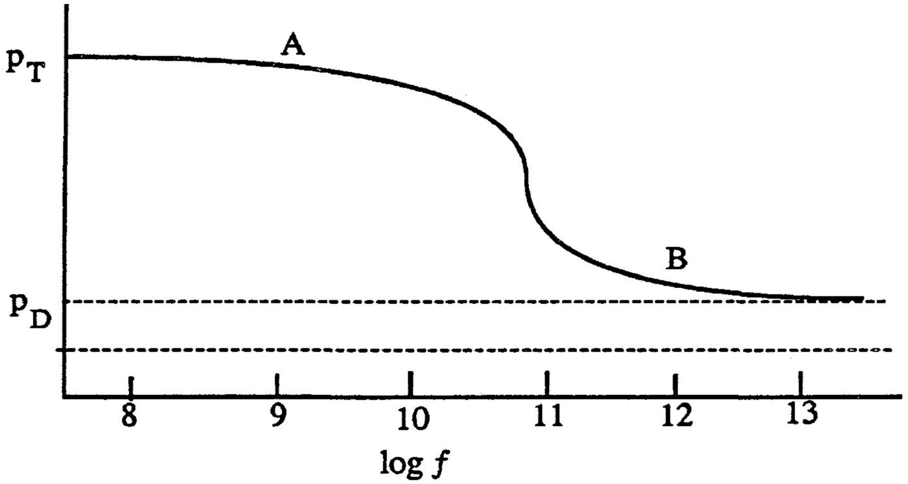


Figure I-2: Total polarization versus log frequency curve

Between points A and B on Figure I-2, the total molar polarizability (p_T) decreases expectedly as the frequency increases and the dielectric constant becomes complex.

It is over the region A to B that the dipole moment begins to lag behind the applied field. When the applied frequency is beyond that of molecular reorientation, displacement polarization arises with resonances at frequencies of 10^{12} to 10^{14} Hz, corresponding to the infrared region of the electromagnetic spectrum, further resonances occur with a frequency of about 10^{15} Hz which corresponds to a frequency in the ultraviolet region.

Dielectric relaxation is the decay with time of the polarization in a dielectric when an external field is removed. For exponential decay, the relaxation time, τ, is defined as the time (t) in which the molar polarizability is reduced to 1/e times it original value (p_O), therefore:

$$p(t) = p_O \exp(-t/\tau) \tag{I-4}$$

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:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_O - \varepsilon_\infty}{1 + i\omega\tau} \tag{I-5}$$

where ω is the angular frequency. On separation into real and imaginary parts, equation (I-5) becomes:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_O - \varepsilon_\infty}{1 + \omega^2\tau^2} \tag{I-6}$$

and

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2\tau^2} \tag{I-7}$$

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

$$\left(\varepsilon' - \frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2 \tag{I-8}$$

This is the equation of a circle with the centre lying on the ε'-axis. This function leads to a Cole-Cole plot of semi-circle of radius $\frac{\varepsilon_0 - \varepsilon_\infty}{2}$ when ε'' is plotted against ε' [2].

For many molecules, the dielectric absorption is not characterized by a single discrete relaxation time. Cole and Cole [2] considered the case of a symmetrical distribution about the mean relaxation time, τ_0, and obtained:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\,\omega\tau_0)^{1-\alpha}} \tag{I-9}$$

where α is the distribution parameter which may have values between 0 and 1. When $\alpha = 0$, the Debye equation is obtained.

A number of functions have been considered for a non-Debye type of absorption. Cole and Davidson have formulated a function which describes right-skewed arcs [3]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\,\omega\tau)^\beta} \tag{I-10}$$

where ß is the asymmetric distribution co-efficient whose value lies in the range $0<\beta<1$.

Fuoss and Kirkwood [4] also developed a theory regarding the distribution of relaxation times. The equation is:

$$\cosh^{-1}\left(\frac{\varepsilon''_{max}}{\varepsilon''}\right) = 2.303\ ß \log\left(\frac{f_{max}}{f}\right) \tag{I-11}$$

where ß is a significant empirical parameter whose inverse measures the width of the absorption relative to the Debye process which follows from (I-11) for ß=1. f_{max} is the frequency at which the dielectric loss value (ε'') is maximized.

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 [5] considered that for multiple discrete relaxation processes the complex dielectric constant could be represented by the superimposition of overlapping Debye curves. Crossley, Tay and Walker [6] described the use of the Budó equation to evaluate relaxation parameters.

A number of models have been suggested to account for the mechanism of the various molecular relaxation processes.

The Eyring rate theory [7] 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:

$$\frac{1}{\text{rate constant}} = \tau = \frac{h}{k_B T}\exp(\Delta G_E/RT) \tag{I-12}$$

where T is the absolute temperature, h is the Planck's constant, R is the universal gas constant, and k_B is the Boltzmann's constant.

Since:

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

it follows that:

$$\tau = (h/k_BT) \exp(\Delta H_E/RT) \exp(-\Delta S_E/R) \qquad \text{(I-13)}$$

which, on taking logarithms and rearrangement, gives:

$$\ln\tau T = (\Delta H_E/RT) + \ln(h/k_B) - (\Delta S_E/R) \qquad \text{(I-14)}$$

When $\ln(\tau T)$ is plotted against $1/T$, a straight line is obtained, the slope of which gives $\Delta H_E/R$. The entropy change, ΔS_E, is obtained from the intercept.

Infrared

The formation of H-bonds (X-H···Y) yields the following effects in the infrared spectra of the systems:

(*i*) The stretching mode ($\nu_{X\text{-}H}$) and its harmonics are shifted to lower wavenumbers.

(*ii*) The stretching mode ($\nu_{X\text{-}H}$) and its harmonics are broadened.

(*iii*) Both the wavenumber and intensity of stretching mode ($\nu_{X\text{-}H}$) may be altered radically by a temperature change of several degrees.

(*iv*) Similarly, the wavenumber and intensity of stretching mode ($\nu_{X\text{-}H}$) change with the change in concentration.

(*v*) The absorption of stretching mode ($\nu_{X\text{-}H}$) may be altered either by an acidic or basic solvent.

For a diatomic molecule X-H, which is treated as a harmonic oscillator, the quantum mechanical solution yields the following equation for the vibrational frequency ($\omega \mathrm{cm}^{-1}$ units):

$$\frac{\Delta E}{h} = c\omega = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad \text{(I-15)}$$

where h = Planck's constant

c = velocity of light

μ = reduced mass of the two atoms

k = force constant

The force constant k may be regarded as a measure of the stiffness of the springlike X-H bond.

The lowering of the $\nu_{X\text{-}H}$ frequency was first ascribed to the weakening of the X-H bond on the formation of the H-bond. Semi empirical calculations [8], 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. Change in anharmonicity of the stretching vibration when an H-bonded complex is formed [9] is another significant factor that modifies the frequency.

References

1. P. Debye, "Polar Molecules", Chemical Catalog Co., New York (1929).
2. K.S. Cole and R.H. Cole, J Chem. Phys., 9, 341(1941).
3. D.W. Davidson and R.H. Cole, J. Chem. Phys., 19, 1484 (1951).
4. R.M. Fuoss and J.G. Kirkwood, J. Am. Chem. Soc., 63, 385 (1941).
5. A. Budó, Z. Phys., 39, 706 (1938).
6. J. Crossley, S.P. Tay and S. Walker, Adv. Mol. Relax. Processes, 6, 79 (1974).
7. S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes (McGraw-Hill, New York, 1941).
8. L.A. Curtiss and J.A. Pople, J. Mol. Spectroscopy, 48, 413 (1973).
9. M. Asselin and C. Sandorfy, J. Mol. Structure, 8, 145 (1971).
10. M. Remko, Adv. Mol. Relax. Processes, 11, 291 (1977).
11. N.E. Hill, W.E. Vaughan, A.H. Price and M. Davies, "Dielectric Properties and Molecular Behaviour", Van Nostrand, Reinhold, London, 320 (1969).
12. V.V. Daniel, "Dielectric Relaxation," Academic Press, New York, 1967.

CHAPTER II

EXPERIMENTAL PROCEDURE

Dielectric properties of a polar material can be considered by assuming it to be situated between the parallel plates of a condenser such that the dielectric constant (ε) of the material may be defined by the equation:

$$\varepsilon = \frac{C}{C_O} \tag{II-1}$$

where C and C_O are the capacitance values for the condenser with the dielectric material and with vacuum respectively. When a sinusoidal potential of amplitude V and frequency ω ($\mathrm{rad\cdot s^{-1}}$) is applied to the capacitor, the current, I, flowing through the circuit is given by:

$$I = V\omega C = V C_O(\varepsilon' - i\,\varepsilon'') \tag{II-2}$$

In this equation the real component $V\omega C_O\,\varepsilon'$, known as charging current is 90° out of phase with the applied potential and therefore, does not involve any electrical work. The imaginary component $V\omega C_O\,\varepsilon''$, 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:

$$VI = V^2\omega C_O\varepsilon''$$

If δ is 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:

$$\tan \delta = \frac{\text{Loss Current}}{\text{Charging Current}} = \frac{\varepsilon''}{\varepsilon'}$$

where ε' is the observed dielectric constant according to Equation (II-1) and ε'' is known as the loss factor.

Chemicals

The names of the chemicals and their sources are listed below:

CHEMICALS	SOURCE
Methanol	Aldrich Chemical Co.
Ethanol	Aldrich Chemical Co.
1-Propanol	Aldrich Chemical Co.
1-Butanol	Matheson Coleman & Bell
1-Pentanol	Aldrich Chemical Co.
1-Hexanol	Aldrich Chemical Co.
1-Heptanol	ICN, K&K Inc.
2-Heptanol	ICN, K&K Inc.
3-Heptanol	ICN, K&K Inc.
4-Heptanol	ICN, K&K Inc.
1-Octanol	Aldrich Chemical Co.
2-Octanol	ICN, K&K Inc.
3-Octanol	ICN, K&K Inc.
4-Octanol	ICN, K&K Inc.
1-Nonanol	ICN, K&K Inc.
1-Decanol	ICN, K&K Inc.

2-Decanol	ICN, K&K Inc.
3-Decanol	ICN, K&K Inc.
4-Decanol	ICN, K&K Inc.
1-Undecanol	ICN, K&K Inc.
1-Dodecanol	ICN, K&K Inc.
1-Heptane	Aldrich Chemical Co.
p-Cymene	Matheson Coleman & Bell
Toluene	BDH Chemicals
Dichloromethane	Caledon Laboratories Ltd.
Ethyl ether	Caledon Laboratories Ltd.
Butyl ether	Eastman Kodak Co.
Pyridine	Aldrich Chemical Co.
Carbon tetrachloride	Fisher Scientific Co

Most of the chemicals used in the present work were sufficiently pure for our purpose. However, some of them were purified by refluxing with drying agents like CaH_2 , $CaSO_4$, etc. and then distilled over 4 Å molecular sieves.

A. Dielectric Measurements

Dielectric measurements were carried out on the samples placed in a co-axial cell and by measuring the capacitance, C, and conductance, G, of the samples,using an HP 4191A impedance analyzer in the frequency range 10^6 to 10^9 Hz.

Sample Preparation for Dielectric Measurements

The solution of desired concentration was prepared by adding a given quantity of solute to the solvent. For a chemical system, the sample was cooled to near liquid nitrogen temperature (~80K) and slowly heated to the glass transition temperature while capacitance and conductance at selected temperatures 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 $\log f_{\max}$ range as possible. Temperatures were controlled to within ±0.1K and were recorded with an omega 450 AET thermocouple thermometer.

The Co-axial Cell

The co-axial cell used for the dielectric measurements of liquid samples was designed by Mr. B.K. Morgan of this laboratory. The cell assembly is diagrammatically represented in Figure II-1. The non-magnetic, stainless steel, co-axial cell was mounted in an airtight aluminum casing. A teflon seal was put on the sample to get rid of the excess liquid and to attain a flat surface of the liquid inside the cell. The 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.

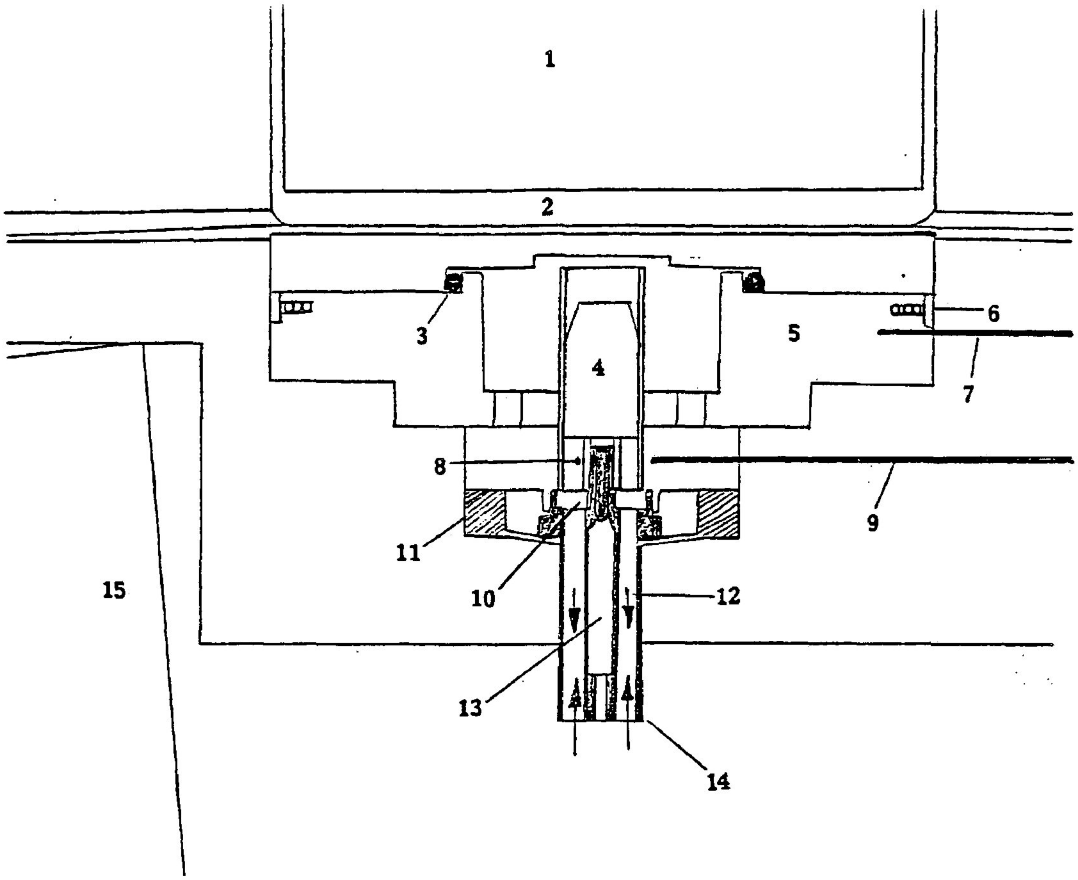


FIG. II-1: The Co-axial Cell Assembly

1 → Liquid Nitrogen
2 → 3L Aluminum Container
3 → O-Ring
4 → Teflon
5 → Aluminum Body
6 → Heater
7 → Control Thermocouple
8 → Sample
9 → Temperature Thermocouple
10 → Kel-F Window
11 → Brass Compression Flange
12 → Thin Tubular Outer Conductor
13 → Hollow Central Conductor
14 → 304 Stainless Steel
15 → H.P. Impedance Meter

The Impedance Analyzer

The 4191A Radio Frequency Impedance Analyzer is manufactured by the Hewlett Packard Company, Tokyo, Japan. The Impedance Analyzer is linked with the HP85 Computer by HPIB Cable. The measuring system is calibrated with short-circuited, open-circuited and 50Ω terminations at the position of the cell at 51 frequencies with equal logarithmic frequency interval between 1 and 1,000 MHz.

The analyzer measures the reflection coefficient (Γ) on a co-axial line and converts it to impedance (Z) or the admittance (Y) of a load at 51 frequencies over the above selected frequency range. The impedance (Z) and the admittance (Y) can be related to the reflection co-efficient (Γ) by the following equation:

$$\frac{Z_x}{Z_o} = \frac{1+\Gamma}{1-\Gamma} \longrightarrow \frac{Y_x}{Y_o} = \left(\frac{Z_x}{Z_o}\right)^{-1}$$

or (II-3)

$$\frac{Z_x}{Z_o} = \frac{G + i\omega C}{Z_o} \longrightarrow \varepsilon' + \varepsilon''$$

Where G and C denote the conductance and capacitance, respectively. The sample is treated as though it is electrically equivalent to a capacitance (C_x) in parallel with resistance (R_x).

Admittance of the sample is given as :

$$Y_x = \frac{1}{R_x} + i\omega C_x \qquad \text{(II-4)}$$

$$\varepsilon' = \frac{C_x}{C_o} \qquad \text{(II-5)}$$

and

$$\varepsilon'' = \frac{1}{R_x C_o \omega} \qquad \text{(II-6)}$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{R_x C_x \omega} \qquad \text{(II-7)}$$

The computer printout gives us, C_x and $G_x = 1/R_x$ at the angular frequency $\omega = 2\pi x$, ε' and ε'' were obtained by the use of the above equations.

Analysis of Experimental Data

The experimental data, obtained by dielectric measurements, were analyzed by a series of computer programs, written in APL language. For each measurement of temperature, the data of dielectric loss factor as a function of frequency were analyzed by the computer according to the Fuoss-Kirkwood equation [1] the linear form of which is:

$$\operatorname{Cosh}^{-1}\left(\frac{\varepsilon''_{max}}{\varepsilon''}\right) = 2.303\beta(\log f_{max} - \log f) \qquad \text{(II-8)}$$

by a procedure employed by Davies and Swain [2]. 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 $\log f$; the slope of this straight line gives the ß-value and the f_{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 [2,3] which can be rearranged to the linear form:

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

The plot of log(τT) against l/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. This program also calculates the relaxation times, τ , and free energies of activation, ΔG_E , at different temperatures by employing the Equations (II-10) and (II-11), respectively:

$$\tau = \frac{h}{kT} e^{\frac{-\Delta G_E}{RT}} \tag{II-10}$$

$$\Delta G_E = \Delta H_E - T\Delta S_E \tag{II-11}$$

Standard statistical techniques [4] provide a means of estimating errors in fitting a straight line to a set of graph points. The FUOSSK computer program calculates errors in logf_{max} and 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 logf_{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 infrared spectra were obtained in the range 3100-4000 cm^{-1} using a Beckman spectrophotometer, IR4250. Sodium chloride windows were used to hold the samples. During the sample preparation and measurement, extreme care was taken to avoid the moisture.

The scan speed of most of the samples was 600 cm^{-1}/minute.

References

1. N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, Dielectric Properties and Molecular Behaviour, (Van Nostrand, London, 1969).
2. M. Davies and J. Swain, Trans. Faraday Soc., 67, 1637 (1971).
3. M. Davies and A. Edwards, Trans. Faraday Soc., 63, 2163 (1967).
4. B. Ostle, Statistics in Research (Iowa State University Press, Ames, Iowa, 1963).

CHAPTER III

DIELECTRIC INVESTIGATION OF THE LOW FREQUENCY DISPERSION REGION OF PRIMARY LIQUID ALCOHOLS

It is now reasonably well established that there are at least three distinct dispersion regions [3-12] in primary and secondary alcohols. Mizushima [1] was first to initiate these dielectric studies which were then discussed by Debye[2].

The lowest, intermediate and highest frequency dispersions may be characterized by three relaxation times, τ_1, τ_2 and τ_3 respectively. The highest frequency process (τ_3) is sometimes designated by -OH group reorientation around the C-O bond. This is not susceptible to the concentration of the medium or the chain length of the molecule [10,13-15]. The τ_2 process has been ascribed to rotation of monomer or small multimers or end group rotation on the polymerized chain [8,10,11,16]. The lowest frequency dispersion is said to have Debye behaviour (distribution parameter α is zero) [3,5-10].

Many models have been developed to account for this dispersion which is still a very controversial subject. The main features of some of the important models will be described briefly.

(a) Brot and Magat [8] proposed that alcohol multimers of variable length exist in the liquid together with free molecules, all in dynamic equilibrium. The lifetime τ_1 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 the liberated dipoles. This region does not present any distribution of relaxation times because the lifetime of the H-bonds is roughly independent of the size of the polymer.

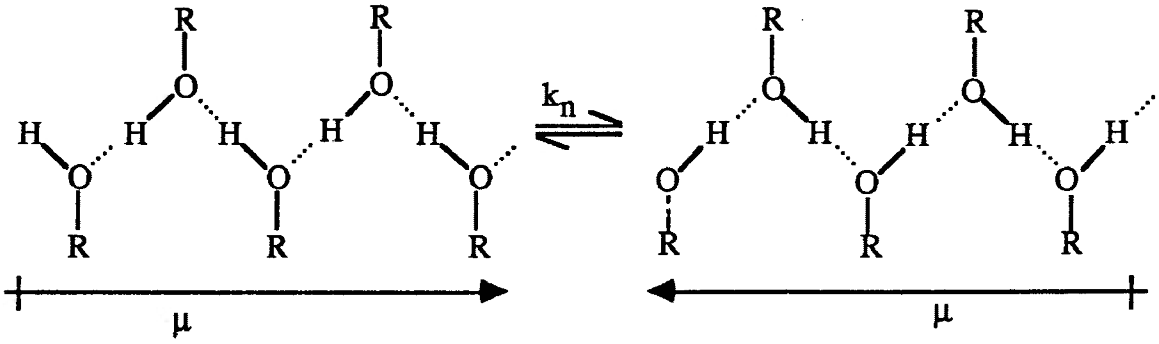
(b) Garg and Smyth [10], from their study on liquid normal alcohols, proposed a similar type of mechanism. They describe the τ_1 process as the breaking of an H-bond followed by rotation of a new partially liberated ROH.

(c) On the basis of dielectric study of some isomeric octanols, Dannhauser *et al* [11,12,17] modified the previous mechanism. They proposed that H-bond rupture is a prerequisite rather than a rate-determining step for the τ_1 process.

(d) Böttcher and co-workers [18,19] investigated the mixture of 1- and 4-heptanol at different concentrations, and deduced that the τ_1 process is related to the formation of a highly polar, non-planer, cyclic tetramer. This was said to account for the zero distribution of relaxation times.

(e) According to Malecki [20], however, only the trimers are cyclic while the tetramers and pentamers are open-bonded units.

(f) Higasi *et al* [21,22] described the dipole relaxation of the τ_1 process as the activation of the terminal -OH of the multimer chain and then successive inversions of the monomer units by the breaking of only one H-bond each time leading to the dipolar inversion of the whole polymer chain. This can be diagrammatically represented as:



The following study is thus primarily focussed on a detailed investigation of the lowest frequency dispersion for the liquid alcohols in a wide temperature and frequency range.

Experimental Results

The dielectric measurements of the following normal aliphatic alcohols were done by using a Hewlett Packard 4191A RF Impedance Analyzer in the frequency range of 10^6 Hz to 10^9 Hz. The operational temperature limit of the cell were from 74 K to 363 K and were controlled to within ±0.1 K. The procedure is being described in Chapter II in more detail.

NAME	STRUCTURAL FORMULA
Methanol	CH_3OH
Ethanol	$CH_3(CH_2)OH$
1-Propanol	$CH_3(CH_2)_2OH$
1-Butanol	$CH_3(CH_2)_3OH$
1-Pentanol	$CH_3(CH_2)_4OH$
1-Hexanol	$CH_3(CH_2)_5OH$
1-Heptanol	$CH_3(CH_2)_6OH$
1-Octanol	$CH_3(CH_2)_7OH$
1-Nonanol	$CH_3(CH_2)_8OH$
1-Decanol	$CH_3(CH_2)_9OH$
1-Undecanol	$CH_3(CH_2)_{10}OH$
1-Dodecanol	$CH_3(CH_2)_{11}OH$

All the alcohols were obtained commercially and were purified by refluxing with a suitable drying agent and distilling over 4Å molecular sieves.

The ε'' values as a function of frequency were then analyzed by computer for the best linear fit to the Fuoss-Kirkwood equation:

$$\cosh^{-1}(\varepsilon''_{max}/\varepsilon'') = \beta(\ln f_{max} - \ln f)$$

The parameters obtained as a result of the analysis are ε''_{max}, the maximum loss factor of the absorption at a fixed temperature, the mean relaxation time, τ_1 at the frequency f_{max} at which dielectric loss value is a maximum and β, the Fuoss-Kirkwood distribution parameter.

Once the relaxation time had been evaluated at a given temperature, the free energy of activation (ΔG_E) was determined from the Eyring rate equation.

Enthalpy and entropy of activation were determined from the slope and intercept respectively of the plot $\log\tau T$ against $1/T$. In order to obtain more precise ΔH_E and ΔS_E values than previous workers a greater number of temperatures were employed. Figures III-1 to III-7 demonstrate the dielectric loss factor versus temperature plots, absorption curves, Cole-Cole plots, relaxation time and enthalpy of activation versus the number of methylene groups, ΔS_E versus ΔH_E and Eyring rate plots of some of the normal alcohols.

Discussion

The dielectric absorption of all the alcohols of the general formula CH_3-$(CH_2)_n$-OH, where n is the number of methylene groups, range between temperatures 170K and 320K for the available frequency range (10^6 to 10^9 Hz). The dielectric relaxation and the Fuoss-Kirkwood analyses parameters are given in Table III-1 and Table III-2, respectively.

For comparison, the aliphatic bromides of the same chain length were also examined in the above temperature range but no dielectric dispersion was observed. It would seem likely that the τ_1 process for the primary alcohols is related to the presence of the -OH group and its capacity for intermolecular hydrogen bond formation. A survey of the Fuoss-Kirkwood distribution parameters indicates high values which approach one for absorption at the highest temperatures employed. This is in harmony with the conclusions of Garg and Smyth that the process is of Debye type for the temperatures which they employed at 293, 313 and 323 K.

At this stage of development in the alcohol saga there would seem little doubt that the low frequency absorption of alcohols is caused by fluctuations within the network of H-bonds rather than by rotational motion of single molecules [23-25]. Further, some studies on octyl alcohol isomers suggest that this process does not occur in solutions where the -OH group is effectively shielded as in 3-methyl -3 heptanol [11]. However, Crossley *et al* [26] found that this alcohol presents two relaxation processes at concentrations 0.2 and 0.35 mole fractions in n-heptane. The relaxation times for the low frequency dispersion are much longer than the ones for molecular rotations which leads to the conclusion that τ_1 cannot be attributed solely to molecular rotation. Some workers [8,11,29] related this relaxation time (τ_1) with the breakup of linear complexes. This view is supported by the results in Figure-III-6a where τ_1 at 300 K changes by a factor of 4 from methanol to ethanol whereas it changes by only 10 from ethanol to 1-dodecanol.

The values for the enthalpy of activation (ΔH_E) from this experiment agree quite well with those quoted by Böttcher [28] and of Garg and Smyth [10] with a few exceptions as can be seen from Figure III-10.

From Figure III-10, the following observations are made:

(*i*) The ΔH_E values exhibit only a small increment from 1-octanol to 1-decanol.

(*ii*) ΔH_E values obtained by Garg and Smyth decrease after 1-nonanol.

(*iii*) Böttcher's ΔH_E values almost level off at n=9.

In addition, the entropy values (ΔS_E) obtained here increase rapidly from methanol to 1-nonanol after which the increment is small, whereas in Garg and Smyth's data, a steady increment is observed from 1-propanol to 1-nonanol. No specific trend is obvious after that as shown in Figure III-11.

From Figure III-12

(*i*) Relaxation times (τ_1) at T=293K increases linearly from methanol to 1-decanol and then either level out or decrease.

(*ii*) τ_1 values at T=293K obtained by Garg and Smyth increase almost linearly from 1-propanol to 1-nonanol and then decrease.

From Figure III-13

The free energy of activation values (ΔG_E) obtained in this experiment by Garg and Smyth at T=293K agree quite well. They almost coincide with each other from 1-propanol to 1-decanol.

From Figure III-14

It is quite obvious that τ_1 is not directly proportional to the chain length of the alcohols as might be expected from Debye behaviour for a molecular relaxation process of the monomer since the curve tends to level off at approximately n=9. However, since each alcohol has a different viscosity at 293K,a more accurate comparison may be achieved by utilizing the τ_1/η values. The plot of τ_1/η versus the number of carbons (n) clearly demonstrates that this does not increase with size above 1-hexanol. Thus, a molecular process alone cannot account for this behaviour.

The ΔH_E value (13.0 kJ mol^{-1}) determined in this experiment for methanol is similar to the theoretical value of the enthalpy of activation for methanol dimer formation (15.5 kJ mol^{-1}), predicted by Curtiss [30]. This is also in good agreement with the ΔH_E value of 13.44 kJ mol^{-1} found by other measurements [31, 32]. Moreover, it has been stated by several workers [33-38] that the strength of one H-bond is about 18±2 kJ mol^{-1}. Therefore, on the basis of this information it can be said that the enthalpy of activation of the τ_1 process for methanol is of the order required to break one mole of H-bonds.

The dielectric loss (ε'') values at 293 K are slightly lower than those obtained by Garg and Smyth for different alcohols. These losses are demonstrated in the Cole-Cole plots [Figure III-8(a) - 8(e)] and in the plots of ε'' versus log*f* [Figure III-9(a) - 9(e)]. However, their data have been shown to be slightly in error [26-27] and a satisfactory comparison for ε'' values cannot be made. Nevertheless, on the whole, the parameters deduced from the ε'' such as τ_1, ΔH_E (Figure III-10) and ΔG_E (Figure III-13) are in reasonable agreement with the literature values. The errors found in our measurements for ε' and ε'' values of 1-nonanol are 0.35% and 1.3% respectively when compared with the literature values [27(a)].

Conclusion

From the dielectric measurements of pure normal alcohols obtained in this study and also the ones obtained by previous researchers, it can now be concluded that the lowest frequency dispersion is related to the presence of intermolecular H-bonding. In addition, the size of the monomer appears to increase τ_1, ΔH_E, ΔG_E and ΔS_E values as the number of carbon atom increases up to approximately 1-nonanol. After this their values tend to level off.

The closeness of the H-bond dissociation energy for methanol with the enthalpy of activation value, suggests that this is the simplest case and that a H-bond breaking process is involved. The intramolecular relaxation of $\mathrm{C}\overset{\circlearrowleft}{-}\mathrm{OH}$ in monomeric methyl alcohol occurs below liquid nitrogen temperature [39]. Thus, methanol is potentially the simplest case as all the other primary alcohols have possible contributions from rotation about the C-C bond involving movement of the end dipole (COH).

However, the behaviour of τ_1/η versus n could suggest that the first dispersion cannot be accounted for in terms of a molecular relaxation process contribution from the increasing size of the monomer. This is borne out by their values becoming constant for 1-decanol, 1-undecanol and 1-dodecanol.

References

1. S. Mizushima, Bull. Chem. Soc. Jpn., 1, 47, 83, 115, 143, 163, (1926), Physik, Z., 28, 418 (1927).
2. P. Debye, "Polar Molecules" Chemical Catalog Co., New York, p. 95 (1929).
3. D.W. Davidson and R.H. Cole, J. Chem. Phys., 19,1484 (1951).
4. C. Brot, M. Magat and L. Reizisch, Kolloid Z., 134,101 (1953).
5. F.X. Hassion and R.H. Cole, J. Chem. Phys., 23, 1756 (1955).
6. W. Dannhauser and R.H. Cole, J. Chem. Phys., 23, 1762 (1955).
7. D.J. Denney and R.H. Cole, J. Chem. Phys., 13, 1767 (1955).
8. C. Brot and M. Magat, J. Chem. Phys., 39, 841 (1963).
9. M. Magat, "H-bonding", D. Hadzi and H.W. Thompson eds., (Pergamon N.Y., 1959) p. 309
10. S.K. Garg and C.P. Smyth, J. Phys. Chem., 69, 1294 (1965).
11. W. Dannhauser, J. Chem. Phys., 48, 1911 (1968), 1918 (1968).
12. W. Dannhauser and A. F. Flueckinger, Phys. Chem. Liquids, 2, 37 (1970).
13. J. Crossley, Advances in Mol. Relax. Processes, 2. 69-99 (1970).
14. J. Crossley, L. Glasser, C.P. Smyth, J. Chem. Phys., 52, 6203 (1970).
15. J. Crossley, J. Phys. Chem., 75, 1790 (1971)
16. L. Glasser, J. Crossley and C.P. Smyth, J. Chem. Phys., 57, 3977 (1972).
17. G.P. Johari and W. Dannhauser, Phys. Chem. Liquids, 3, 1 (1972).
18. P. Bordewijk, F. Gransch and C.J.F. Böttcher, J. Phys. Chem. 73, 3255 (1969).
19. C.J.F. Böttcher and P. Bordewijk, Theory of Electric Polarization, Vol. 11, (Elsevier, Amsterdam, 1978).
20. J. Malecki, J. Chem. Phys., 43, 1351 (1965).
21. R. Minami, K. Itoh, H. Takahashi and K. Higasi, J. Chem. Phys., 73(7), 3396

(1981).

22. R. Minami, K. Itoh, H. Takahashi and K. Higasi, Bull. Chem. Soc. Jpn., 54, 3684 (1981).
23. E. Bauer and M. Magat, Bull. Soc. Chim. Fr., 341 (1949).
24. C. Brot, M. Magat and L. Reinisch, Koll. Z., 134, 101 (1953).
25. C. Brot, Ann. Phys. Paris (13)2, 714 (1957).
26. J. Crossley, L. Glasser and C.P. Smyth, J. Chem Phys., 55, 2197 (1971).
27. J. Middlehock and C.J.F. Böttcher, Mol. Relax. Processes, Chem. Soc. Spec. Publ., 20, 69 (1966).
27a. Floyd Buckley and Arthur A. Maryott, "Tables of dielectric dispersion data for pure liquids and dilute solutions", p. 46, (1958).
28. C.J.F. Bottcher, P. Bordewijk, "Theory of electric polarization", vol. II, Elsevier Scientific Publishing Company, p. 254, (1978) and the references cited therein.
29. W. Dannhauser, L.W. Bahe, F.Y. Lin and A.F. Flueckinger, J. Chem. Phys., 43, 257 (1965).
30. L.A. Curtiss, J. Chem. Phys. 67, 3 (1977).
31. W. Weltner and K.S. Pitzer, J. Am. Chem. Soc., 73, 2606 (1951).
32. G.S. Kell and G.E. McLaurin, J. Chem. Phys., 51, 4345 (1969).
33. M.A. Siddiqui, M. Sc. Thesis (Lakehead University, 1985).
34. G.P. Johari and W. Dannhauser, J. Phys. Chem., 12, 3273 (1968).
35. H. Landeck, H. Wolff and R. Gotz, J. Phys. Chem., 81, 718 (1977).
36. G.M. Mavridis, M. Servanton and J. Biais, J. Chim. Phys., 3, 436 (1972).
37. J.C. Davis, Jr., K.S. Pitzer and C.N.R. Rao, J. Phys. Chem., 64, 1744 (1960).
38. W. Liddel and E.D. Becker, Spectrochimica Acta, 10, 70 (1957).

39. R. Isnard and J. Gilchrist, Chem. Phys., 52, 405 (1980).

CHAPTER IV

DIELECTRIC STUDIES OF ALCOHOLS WITH CHAINS
IN DIFFERENT SOLVENTS
AND
THE TEST OF HIGASI'S MECHANISM

A number of dielectric studies has been performed on pure liquid alcohols and on alcohol solutions [1-9], and three different relaxation times, namely, τ_1, τ_2, and τ_3 have been evaluated as is discussed in Chapter III. We are mainly concerned with the first dispersion region of the alcohols on which no definite model is existent till now, albeit a few important ones had been described in the previous Chapter. However, it would now seem that the presence of intermolecular hydrogen bonding is responsible for this dispersion.

The steric environment of the hydroxyl group and the change in temperature are two of the vital factors that control the self-association in liquid alcohols, as was stated by Dannhauser [10]. Crossley [11] found out from his dielectric study on alcohol solutions that the basicity of the solvent plays an important role in determining the extent of self-association. It has also been found out for pure n-alkanols that τ_1 increases with the increase in the number of carbon atoms in the alkyl group [6]. Sagal [12] related the chain length dependence of the dielectric relaxation time of the normal aliphatic alcohol to a hydrogen bonded switching mechanism from the dielectric study of ethanol and isomeric butanols in cyclohexane solutions. This switching mechanism can be explained as follows:

> "The H-bond will break when another molecule approaches with its oxygen oriented favorably for a switch. It is reasonable to assume that the presence of this third oxygen atom will lower the energy barrier to break the H-bond."

Higasi *et al* [13-15] studied 1- and 2-propanol and 1-butanol in a variety of

H-bonding and non H-bonding solvents and found out the change in principal relaxation time (τ_1) for these alcohols with concentration of alcohol is dependent on the H-bonding ability of the solvents. In another work on 1-propanol in a number of H-bonding solvents, they [16] found that the molecular weight of the H-bonding solvents is one of the important factors in solute-solvent interactions.

In 1980, they [17-18] came up with a mechanism for 1-alkanols in inert as well as interacting solvents. Some of the pictorial features about the Higasi model are:

(*i*) An associative equilibrium between H-bonded chain multimers and ring dimers is assumed.

(*ii*) Dipole inversion arises from the co-operative rotation of the -OH goup of the multimers.

In a dielectric study of isomeric butanols in cyclohexane, Higasi and co-workers [19] found that the dielectric behaviour of 2-methyl-2-propanol is very different from that in other butanols. The steric effects in this alcohol are probably more effective in promoting dissociation of the H-bonded complex.

The decrease in principal relaxation time with the dilution of alcohol in a variety of solvents has been interpreted as arising from deformation or destruction of H-bonded clusters of alcohols [20-22]. Higasi *et al* [23] also studied 1-propanol in 1,4-dioxane and in cyclohexane obtaining a single relaxation process for 1-propanol in 1,4-dioxane whereas two separate relaxation processes were observed in inert cyclohexane. They assigned these two relaxation times as primary and secondary. The primary relaxation process is believed to be a co-operative process in large multimers of alcohols arranged in straight chains [17,23]. The secondary relaxation was thought to be due to the relaxation of small alcohol multimers.

In order to examine the influence of various solvents on the τ_1 process, a dielectric study of five 1-alkanols of increasing chain length in three different solvents ranging from inert to strongly interacting was carried out:

(A) to compare the experimental relaxation times with the theoretical ones obtained by applying Higasi's theory [17-18] in a wide temperature range in order to check how well Higasi's mechanism applies to different systems in a widely different temperature range.

(B) to examine other relaxation parameters and verify how they correlate to the mechanism posed by Higasi [17-18].

Experimental Results

The same Hewlett Packard 4191A Impedance Analyzer in the frequency range of 10^6 Hz to 10^9 Hz was used for the dielectric measurements of different 1-alkanols. The names and fomulae of these alcohols have already been mentioned in Chapter III.

All the alcohols and solvents were obtained commercially and purified by suitable methods. Tables IV-1 to IV-3 describe the relaxation parameters for all the systems studied.

Figures IV-1 to IV-15 demonstrate the absorption curves and Cole-Cole plots for the 1-alkanols at 0.5MF alcohol concentration in n-heptane, toluene and diethyl ether.

Figures IV-16 to IV19 describe the variations of experimental and theoretical relaxation times with the alcohol concentrations in three different solvents at different temperatures.

Plots of enthalpies of activation (ΔH_E), entropies of activaiton (ΔS_E) and ln τ against the alcohol concentrations are given in Figures IV-20 to IV-23.

Discussion

This section is divided into two parts as follows:

(*i*) Comparison of the experimental relaxation times (τ_1) with those of the theoretical ones calculated by employing Higasi's equations [17,18].

(*ii*) A detailed study of the important relaxation parameters such as enthalpies of activation (ΔH_E) and entropies of activation (ΔS_E), etc.

The important equations used to calculate the theoretical relaxation times are derived as follows: According to Higasi's theory, the equations involving the equilibrium among open chain n-mers A_n and ring dimer A_2 can be represented as:

$$\left.\begin{array}{l} A_1 + A_1 \xrightleftharpoons{K_{2'}} A_{2'} \\ A_1 + A_{(n-1)} \xrightleftharpoons{K} A_{(n=2,3\ldots)} \end{array}\right\} \qquad \text{(IV-1)}$$

where A_1 stands for the monomer and $K_{2'}$ and K are the equilibrium constants of the ring dimer and chain multimer formations, respectively. The dipole inversion rate of the n-mer, i.e. K_n, is determined basically by two factors. The first is the rate K_H in which the terminal molecule of the n-mer is activated rotationally. Once the terminal molecule is activated rotationally, this activated state starts propagating from the left to the right end, according to their scheme. Hence, the second factor that determines the rate of the dipole inversion is the possibility of this transfer. The stochastic process, in which the transition state of one end segment of the n-mer propagates to the other end, takes place with the probability of 1/(n+1). Therefore, K_n can be represented as:

$$K_n = K_H/(n+1) \tag{IV-2}$$

and the relaxation time τ_n is given by

$$\tau_n = \tau_H(n+1) \tag{IV-3}$$

where τ_n is the reciprocal of the dipole inversion rate of the n-mer, K_n, and τ_H is the reciprocal of the rate constant, K_H, in which the terminal -OH groups of the n-mer are activated rotationally.

By the use of Equation IV-3 together with the stoichiometric relationships for the association equilibrium [10,24-25], the analytical equations for the dielectric dispersions of pure alcohols and alcohol solutions were obtained. The principal relaxation time, τ_1, has been defined by these workers as a function of K, K_b, and x_A, where K is the equilibrium constant of the formation of chain multimers, K_b is the constant of the association between the chain multimers and a solvent with hydrogen-bonding capacity, and x_A is the mole fraction of alcohols.

For alcohol/inert solvent systems $K_b = 0$, which gives the following equation:

$$\tau_1 = \frac{\tau_{1'}}{(1 + Kx_A)^2} + 2\left\{1 + Kx_A - \frac{1}{(1 + Kx_A)^2}\right\}\tau_H \tag{IV-4}$$

where $\tau_{1'}$ is the dipole relaxation time of alcohol monomers. When $x_A >> 1$, Equation IV-4 can be approximated as:

$$\tau_1 = 2(1 + Kx_A)\tau_H \tag{IV-5}$$

The final equation, applying Eyring's absolute rate theory and some approximation, is given by:

$$\tau_1 = \frac{(1 - x_B)A(0)}{T} \exp\left\{ \frac{Ea(0)}{RT} - \left(\beta/R - \frac{\alpha}{RT} \right) x_B \right\} \tag{IV-6}$$

where x_B is the mole fraction of an inert solvent and α and β are constants characteristic of the solution in question. R is the gas constant, T is the termperature in Kelvin.

Also,

$$E_a(x_B) = -\Delta H^o + \Delta H^\dagger (x_B) \tag{IV-7}$$

and

$$A(x_B) = \frac{2h}{k_B} \exp\left\{ \frac{\Delta S^o - \Delta S^\dagger (x_B)}{R} \right\} \tag{IV-8}$$

$\Delta H^\dagger(x_B)$ and $\Delta S^\dagger(x_B)$ are the enthalpy and entropy of acivation, respectively for the rotation of relaxing unit - $C\circlearrowleft OH$.

When $x_B = 0$,

$$E_a(0) = -\Delta H^o + \Delta H^\dagger (0) \tag{IV-9}$$

and

$$A(O) = \frac{2h}{k_B} \exp\left\{\frac{\Delta S^o - \Delta S^{\dagger}(O)}{R}\right\} \quad \text{(IV-10)}$$

where ΔH^o and ΔS^o are the enthalpy and entropy changes, respectively, due to the H-bond formation between multimers and a monomer. h and k_B are the Planck and Boltzmann constants, respectively.

Again,

$$E_a(x_B) = E_a(0) + \alpha x_B \quad \text{(IV-11)}$$

and:

$$\ln\left\{\frac{A(x_B)}{1 - x_B}\right\} = \ln\{A(0)\} - \frac{\beta x_B}{R} \quad \text{(IV-12)}$$

$E_a(x_B)$ and ln $\{A(x_B)\}$ are obtained by the slope and intercept of a straight line when $\ln(T \cdot \tau_1)$ is plotted against 1/T.

Also, $E_a(0)$ and α are obtained from the intercept and slope of the straight line when $E_a(x_B)$ is plotted against x_B. Similarly, $\ln\{A(0)\}$and β/R are computed from the intercept and slope of straight line when $\ln\{A(x_B)/(1-x_B)\}$ is plotted against x_B.

Equation (IV-6) gives theoretical τ_1 as a function of x_B and T. By the use of the least-squares method, $E_a(0)$, α ,A(0) and β are determined.

Comparison of the experimental τ_1 values with the theoretical ones obtained for our systems.

Both the experimental and theoretical τ_1 values for methanol in all three solvents at all temperatures are substantially smaller than those of other 1-alkanols. That is why the experimental τ_1 values for methanol are plotted separately and compared with the theoretical ones at different temperatures.

The variations of τ_1(experimental) and τ_1(theoretical) with the concentrations of methanol are given in Figures IV-16(a)-(b).

Figures IV-17 to IV-19 describe the variations of τ_1(expt) and τ_1(theor) with the concentrations of the alcohol for the rest of the 1-alkanols at different temperatures. The following may be noted:

1) The closest agreement between the τ_1(expt) and τ_1(theor) against concentration for methanol is observed at T = 293 K.

2) For the short chain alcohols such as 1-butanol and 1-hexanol in n-heptane, good agreement between the τ_1(expt) and τ_1(theor) is observed only at low temperatures i.e. at T = 200 K and T = 225 K.

3) For the long chain alcohols, i.e. 1-octanol and 1-decanol in n-heptane, the best fit between the τ_1(expt) and τ_1(theor) is observed only at the highest temperature, i.e. at T = 293 K.

4) Consistently the same pattern is observed for these 1-alkanols in the other two solvents, toluene and diethyl ether, and thus changing the solvent from inert to interacting does not change the trend in the variation of relaxation times with the concentrations of alcohols. In addition, this shows that Higasi's theory fits for the 1-alkanols studied only at certain temperatures.

A study of the enthalpies of activation (ΔH_E) of the first dispersion region.

(*i*) 1-alkanols in n-heptane:

When the alcohol concentration is increased from 0.3 to 1.0 MF for 1-butanol in n-heptane the enthalpy of activation (ΔH_E) changes only very slightly. Similar behaviour is noticed for 1-hexanol and 1-octanol, except for 1-decanol whose energy barrier goes up from 34 to 41 kJ mol^{-1} with the increase in alcohol concentration.

(*ii*) 1-alkanols in toluene:

For methanol in toluene, the enthalpy of activation (ΔH_E) increases from 13 kJ mol^{-1} to 22 kJ mol^{-1}. When the alcohol concentration is decreased. The same type of behaviour is also prevalent for 1-butanol in toluene where a difference in energy barrier of ~6 kJ mol^{-1} is noted between the pure and diluted states of alcohol. This difference, however, is only 1 to 3 kJ mol^{-1} when the behaviour of long chain alcohols in toluene is studied.

(*iii*) 1-alkanols in diethyl ether:

A different kind of behaviour is observed for these systems. There is hardly any change in enthalpy of activation (ΔH_E) for methanol (which has no chain at all) when its concentration in diethyl ether is increased from 0.3 MF to 1.0 MF. For the other 1-alkanols with chains, the ΔH_E values increase steadily with the increase in alcohol concentration in diethyl ether.

It is interesting to note that as the chain length is increased, the energy barriers (ΔH_E) increase, especially at high alcohol concentration. However, at low alcohol concentrations, i.e. at 0.3 MF, an energy barrier (ΔH_E) of ~13 kJ mol^{-1} is observed for all the alcohols, which is in fact, equivalent to the energy barrier of pure methanol. A similar kind of trend, i.e. the linear increase in ΔH_E with the increase in alcohol concentration, was found for 1-propanol in 1,4-dioxane and pyridine by Higasi *et al* [15].

Entropies of activation (ΔS_E)

The entropies of activation (ΔS_E) decrease with the increase in alcohol concentrations for all the 1-alkanols in n-heptane although the decrease is not linear.

In toluene the 1-alkanols show almost a linear decrease in entropy with the increase in alcohol concentrations. In diethyl ether, however, the alcohols show an increase in entropies of activation (ΔS_E) with the increase in alcohol concentrations.

The trends in the variations of entropies of activation (ΔS_E) are similar to those of the enthalpies of activation (ΔH_E) for the 1-alkanols in different solvents.

Variations of ln τ_1 with the concentrations of alcohols at T = 300 K.

When ln τ_1 values at T = 300 K are plotted against the concentrations of alcohols, straight lines were obtained for all the 1-alkanols in three different solvents. The points for methanol are clearly separated from the remainder of the alcohols. The values for the rest of the alcohols overlap each other but they all lie on a straight line.

This shows that the τ_1 values change exponentially with the change in alcohol concentrations. The same type of behaviour is again observed for 1-propanol in 1,4-dioxane and pyridine by Higasi and co-workers [15].

Conclusion

1) All the 1-alkanols exhibit a straight line plot for $E_a(x_B)$ vs x_B, according to Equation (IV-11) in all three solvents; n-heptane, toluene and diethyl ether.

2) In general the relationship has been tested for $x_B = 0$ to 0.6 except for methanol

in toluene where it was possible to extend x_B to 0.9 MF. In all cases the linearity is observed.

3) Despite the lack of success in correlating τ_1 with x_B by a precise equation, Equation (IV-11) seems satisfactory.

4) Equation (IV-6) is the key equation since this gives the theoretical τ_1 values as a function of T and x_B and which is then compared with the experimental values against the concentration of alcohols. If the theoretical points do not match well with the experimental points, then some inadequacies in Equation (IV-6) as well as in Higasi's theory are expected.

5) Matching between the theoretical and experimental points is poor at low temperatures for long-chain alcohols and at high temperature for short-chain alcohols. This result is true for the 1-alkanols except methanol in all the solvents used for this study.

6) Therefore, the Higasi model does not stand up to wide temperature variations. The basic concept may be roughly true although our system may be too complex for analysis by such a relatively simple model.

7) It is interesting that Higasi in his very recent work [23], analysed the principal relaxation time in terms of $\tau_{1'}(\tau_1) + \tau_{2'}(\tau_2)$ in cyclohexane but in his earlier work, his theory involved an equation such as:

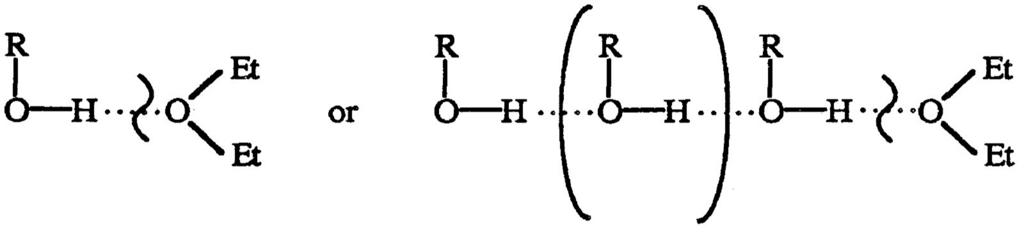
$$\tau_1 = 2\,(1 + kx_A)\tau_H$$

and no account was given to $\tau_{2'}$. He did not give any correlation between the two approaches. It seem reasonable to assume τ_1 to be a function not only of τ_H but of $\tau_{2'}(\tau_2)$ as well.

8) The chain length of the alcohol is not taken into account in Higasi's mechanism, although chain length has been found to be one of the most important factors from our study of the enthalpies of activation (ΔH_E) of the straight chain alcohols in

diethyl ether at various concentrations.

9) From Figure IV-22(a), it is quite obvious that at high alcohol concentration, in the solvent diethyl ether, ΔH_E increases with the increase in chain length, whereas at low alcohol concentration (i.e. at 0.3 MF), all the alcohols yield almost the same ΔH_E, which is, in fact, equal to the ΔH_E of methanol in its pure state, and of the magnitude for the breaking of one mole of H-bond in each case. Therefore, the chain length is probably not the important factor at very low alcohol concentrations. For the solvent diethyl ether or any other strongly interacting solvent at such low concentrations, probably the following type of association leads to the low values of ΔH_E.



10) The above postulate can be supported by the fact that the enthalpies of activation (ΔH_E) for the same alcohols do not decrease drastically when diluted in an inert solvent such as n-heptane.

References

1. D.W. Davidson and R.H. Cole, J. Chem. Phys., 19, 1484 (1951).
2. R.H. Cole and D.W. Davidson, J. Chem. Phys., 20, 1398 (1952).
3. C. Brot, M. Magat and L. Reinisch, Kolloid Z., 134, 101 (1953).
4. W. Dannhauser and R.H. Cole, J. Chem. Phys., 23, 1762 (1955).
5. C. Brot and M. Magat, J. Chem. Phys.,39, 841 (1963).
6. S.K. Garg and C.P. Smyth, J. Phys. Chem., 69, 1294 (1965).
7. J. Crossley, L. Glasser and C.P. Smyth, J. Chem. Phys., 55, 2197 (1971).
8. L. Glasser, J. Crossley and C.P. Smyth, J. Chem. Phys., 57, 3977 (1972).
9. C. Campbell, J. Crossley and L. Glasser, Adv. Mol. Relax. Processes, 9, 63 (1976).
10. W. Dannhauser, J. Chem. Phys., 48, 1911 (1968).
11. J. Crossley, J. Phys. Chem. 75, 1790 (1971).
12. Mathew W. Sagal, J. Chem. Phys., 36, 9 (1962).
13. E Arie, M. Nakamura, H. Takahashi and K. Higasi, Chem, Letters, Chem. Soc. Jpn., pp. 533-34 (1973).
14. T. Koshii, E. Arie, M. Nakamura, H. Takahashi and K. Higasi, Bull. Chem. Soc. Jpn., 47(3), 618 (1974).
15. T. Koshii, H. Takahashi and K Higasi, Bull. Chem. Soc. Jpn., 48(3), 993 (1975).
16. H. Sato, H. Takahashi and K. Higasi, Chem. Letters, p.623-24 (1976).
17. R. Minami, K. Itoh, H. Takahashi and K. Higasi, J. Chem. Phys., 73(7), 3396 (1980).
18. R. Minami, K. Itoh, H. Takahashi and K. Higasi, Bull. Chem. Soc. Jpn., 54, 3684 (1981).

19. H. Sato, H. Nakamura, K. Itoh and K. Higasi, Chem. Letters. Chem. Soc. Jpn., 1167-68 (1985).

20. H. Sato, T. Koshii, H. Takahashi, and K. Higasi, Chem. Letters, Chem. Soc. Jpn., 579 (1974).

21. H. Sato, T. Koshii, H. Takahashi and K. Higasi, Chem. Letters, 491 (1975).

22. R. Minami, K. Itoh, H. Takahashi, and K. Higasi, Bull. Chem. Soc. Jpn., 54, 3684 (1981).

23. S. Yagihara, R. Nozaki, S. Mashimo and K. Higasi, Chem. Letters, Chem. Soc. Jpn., 137-40 (1985).

24. I. Prigogine and R. Defan, "Chemical Thermodynamics", Longmans Green, London (1954) Chapter 26.

25. W. Dannhauser and L. W. Bahe, J. Chem. Phys., 40, 3058 (1964).

CHAPTER V

DIELECTRIC STUDIES OF ALCOHOLS (ROH) WHERE R IS A RIGID UNIT

Dielectric properties of pure liquid alcohols have been studied quite extensively [2-7] since the first study initiated by Mizushima [1]. From the study of the pure liquid alcohols and their solutions [8-12], three dispersion regions have been found to exist which are distinguished by three different relaxation times; τ_1, τ_2, and τ_3.

The relaxation time, τ_3, of the highest frequency dispersion can sometimes be attributed to -OH group rotation [5,9]. The intermediate relaxation time, τ_2, is assigned to the orientational motions of the -OR group or of small hydrogen bonded species [5,6,13].

The dominant, lowest frequency relaxation time, τ_1, is attributed basically to the H-bonded structures although the establishment of a definite model is still a matter of great controversy [5,6,7,14-17].

From their dielectric study on six isomeric octyl alcohols in n-heptane solution, Crossley *et al* [8], found that for the alcohols with a less shielded -OH group, a low frequency relaxation process exists at a higher concentration of alcohol, in addition to two other relaxation processes; τ_2 and τ_3. They assigned this result to the presence of one or more higher polymers at higher concentrations.

Glasser *et al* [13] found the occurrence of the same type of phenomenon for normal alcohols in n-heptane solutions also again above a certain minimal concentration which in this case is a lower one.

In another work on the solution of normal alcohols, Campbell *et al* [11] suggested that for longer alkanols, the relaxation time, τ_1, increases progressively with concentration in cyclohexane, but the shorter alkanols (from 1-butanol) show a maximum in their relaxation times. Higasi *et al* [18,19] studied 1- and 2-propanols in a variety of solvents and concluded that the principal relaxation times of 1- and 2-propanols change with concentration in two different ways, depending upon the H-bonding ability of the solvent and the steric factors in the solute. In addition, they found that the activation energy, ΔH_E, and entropy, ΔS_E, are also concentration dependent but again in two distinct ways, i.e. whether the solvent is H-bonding or non H-bonding.

Recently, Yagihara and Higasi [28] studied 1-propanol in 1,4-dioxane and cyclohexane and observed that a single relaxation process appears when an H-bonding solvent is employed but two separate relaxation processes are obtained when an inert solvent is used.

Dielectric behaviour of 2-methyl-2-propanol in benzene and pyridine solutions together with that of other butanol isomers in cyclohexane were also studied by Higasi *et al* [20-22]. The behaviour of 2-methyl-2-propanol is found to be insensitive to the H-bonding ability of the solvent and very different from those of the other isomeric butanols.

Normal hexanol was studied by Hakim [23] who observed only the principal absorption region and attributed it to the rotation of the H-bonding associates.

Stockhausen and Dachwitz [24] described the relaxation of the methanol-acetonitrile mixture in terms of two Debye components, one being due to the multimers of methanol. This component is explained by them by means of two simple models as due to the rotational tumbling of associates or the fluctuation of H-bonds. They found the latter model more suitable.

It has been observed earlier that the activation energy (ΔH_E) is dependent strongly on the number of carbon atoms, the structure of the carbon skeleton [7], and the location of the hydroxyl group in the carbon chain [25-26]. Dilution of the alcohol by a non-polar solvent is also one of the major factors which influences the activation energy of the alcohols as is found in the literature.

In short, to observe the effects of H-bonding and non H-bonding solvents on the principal relaxation, which is based primarily on H-bonding association, we made a detailed study of methanol, which is free from any intramolecular motions in our temperature range which starts from above 80K, in six different solvents.

Experimental Results

The dielectric study of methanol was carried out in the following solvents categorized into two different types. A Hewlett Packard 4191A RF Impedance Analyzer in the frequency range 10^6 Hz - 10^9 Hz was used to do the dielectric measurements. The operational temperature limit of the cell was from 74K to 363K and controlled to within ±0.1K. Chapter II details the experimental procedures.

SOLVENT TYPE:

(*i*) Weakly Interacting: This is being divided into two different types namely,

(a) π-electron-donating

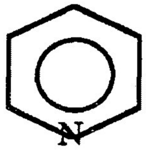
NAME	FORMULA
1. Toluene	$C_6H_5CH_3$
2. p-Cymene	$CH_3C_6H_4CH(CH_3)_2$

(b) non-π-electron-donating

NAME	FORMULA
1. Dichloromethane	CH_2Cl_2

(*ii*) Strongly Interacting

NAME	FORMULA

1. Diethyl ether	C_2H_5-O-C_2H_5
2. Di-n-Butyl ether	C_4H_9-O-C_4H_9
3. Pyridine	

The methanol and the solvents were obtained commercially and were purified by refluxing with a suitable drying agent and distilled over 4Å molecular sieves. Tables V-1 to V-6 present the relaxation and Eyring parameters for all the systems. Figures V-1 to V-8 show the absorption curves, the dielectric loss factor, ε'' vs temperature plots, Cole-Cole plots, plots of relaxation time ($\tau_{1(200)}$) and the free energy of activation ($\Delta G_{E(200)}$), the enthalpy of activation (ΔH_E) and entropy of activation (ΔS_E) vs mole fraction of alcohol for some of the systems studied.

The symbols being employed here are:

$\Delta T(K)$	Temperature range in absolute scale
ΔG_E	Eyring free energy of activation
ΔH_E	Eyring enthalpy of activation
ΔS_E	Eyring entropy of activation

Discussion

The solvents used have been classified into two different types, namely, Weakly Interacting and Strongly Interacting and most of the figures and tables have been made according to this classification. Now let us examine the different relaxation and Eyring parameters from these figures and tables. The dependence of the principal relaxation time (τ_1) at 200K is presented in figures V-5a and V-5b.

In figure V-5a, the behaviour of the principal relaxation times at T=200K with the change in concentration of methanol in different weakly interacting solvents is displayed.

The range of $\tau_{1(200)}$ values are from 0.3 x 10^{-9} to 7.0 x 10^{-9}s which (i.e. the range of values) is a little higher than that of pure methanol. The $\tau_{1(200)}$ values seem to decrease with the increase in methanol concentration in each solvent of this group except that the values are higher in p-Cymene and toluene than in the rest. The behaviour of methanol in different weakly interacting solvents is quite contradictory to that of other 1-alkanols with chain as described in Chapter IV. This striking difference in dielectric behaviour of methanol may well be related to the fact that methanol has no chain at all.

The alteration of the principal relaxation time (τ_1) at 200K with the change in concentration of methanol in strongly interacting solvents is demonstrated in figure V-5b.

The $\tau_{1(200)}$ values for methanol in pyridine and in diethyl ether are very similar; also similar is the way they change with concentration. In both cases, $\tau_{1(200)}$ rises steadily with the increase in concentration and also the trend in methanol/pyridine system are in harmony with that of 1-propanol/pyridine at higher temperatures (from 273K to 313K) observed by Higasi *et al* [19].

In the methanol/Di-n-butyl ether system, however, $\tau_{1(200)}$ increases with the increase in concentration of methanol, reaches the maximum at 0.6 mol fraction of methanol and then decreases.

We shall now examine the Eyring parameters of methanol in different media. The free energies of activation at 200K, $\Delta G_{E(200)}$, the activation enthalpies, ΔH_E, and the entropies, ΔS_E, are plotted against the concentration of methanol in Figures V-6, V-7 and V-8 respectively.

The trends in free energies of activation values at 200K, $\Delta G_{E(200)}$, are about the same as those of the principal relaxation time, τ_1 at 200K in two different classes of solvents as evident from figures V-6a and V-6b.

The change in activation enthalpies, ΔH_E, with the change in concentration of methanol in different weakly interacting solvents is shown in figure V-7a. There is no specific pattern for the change of ΔH_E with the concentration of methanol. However, the ΔH_E values for methanol in p-Cymene and toluene are higher than those of methanol in dichloromethane.

Figure V-7b demonstrates the behaviours of ΔH_E values of methanol in different strongly interacting solvents. Again, in the case of methanol in strongly interacting solvents, there is no specific trend of the ΔH_E values with the change in methanol concentrations. However, the ΔH_E values for methanol in pyridine are higher than those of methanol in butyl and ethyl ethers. In this case the enthalpy of activation values (ΔH_E) for methanol in pyridine show completely opposite trend to that of 1-propanol in pyridine given by Higasi *et al* [19]. The entropies of activation values ΔS_E for methanol in different solvents behave in the same way as the enthalpies of activation , but the trend is more haphazard in the former. Perhaps the high enthalpies and entropies of activation for methanol in interacting solvents are due to a higher order of interactions in those systems.

Let us now examine the different tables (i.e. from Table V-1 to V-6) which detail the relaxation and Eyring parameters in different methanol concentrations.

In almost all the concentrations from a 0.3 mole fraction to a 0.7 mole fraction of methanol in p-Cymene, toluene and dichloromethane, the trend in the change of ΔH_E, $\Delta G_{E(200)}$ and $\tau_{1(200)}$ is p-Cymene>toluene>CH_2Cl_2 which is, interestingly, their sequence of ability to undergo molecular interaction.

In Tables V-4 to V-6 these parameters are being compared in terms of three arbitrary classes for methanol in different solvents in different concentrations. The relaxation time (τ_1) at 200K is considered first.

The range of $\tau_{1(200)}$ values is given for various concentrations of methanol in different solvents classified as A, B and C.

[A] The solvents include butyl ether, ethyl ether and pyridine.

[B] The solvent is dichloromethane.

[C] This group contains π-electron donating solvents such as p-Cymene and toluene.

<u>In Group [A]</u>

For 0.3 mole fraction of methanol, $\tau_{1(200)}$ lies between 0.1 and 4 x 10^{-10}s.

For 0.4 mole fraction of methanol, $\tau_{1(200)}$ lies between 3 and 14 x 10^{-10}s.

For 0.5 mole fraction of methanol, $\tau_{1(200)}$ lies between 3 and 16 x 10^{-10}s.

<u>In Group [B]</u>

For 0.3 mole fraction of methanol, $\tau_{1(200)}$ is 16 x 10^{-10}s.

For 0.4 mole fraction of methanol, $\tau_{1(200)}$ is 18 x 10^{-10}s.

For 0.5 mole fraction of methanol, $\tau_{1(200)}$ is 17 x 10^{-10}s.

<u>In Group [C]</u>

For 0.3 mole fraction of methanol, $\tau_{1(200)}$ lies between 50 and 70 x 10^{-10}s.

For 0.4 mole fraction of methanol, $\tau_{1(200)}$ lies between 52 and 59 x 10^{-10}s.

For 0.5 mole fraction of methanol, $\tau_{1(200)}$ lies between 49 and 54 x 10^{-10}s.

It seems from the above, taken in three groups that for different concentrations of methanol, $\tau_{1(200)}$ values do not show any correlation with the electron donor capacity of the solvent.

The ranges of values for the Eyring parameters of methanol in different solvents at three different concentrations are given below:

The ranges of ΔH_E values are from 13 to 22 kJ mol^{-1}.

The ranges of ΔS_E values are from -4 to 48 J deg^{-1} mol^{-1}.

The ranges of $\Delta G_{E(200)}$ values are from 11 to 17 kJ mol^{-1}.

It seems from these comparisons that the relaxation times, free energies and enthalpies of activation values do not reflect the capacity of methanol to hydrogen bond with these solvents at all concentrations.

Table V-3 presents the relaxation and Eyring parameters for methanol and other alcohol mixtures in toluene. Several points can be noted from this table as follows:

(1) Replacement of methanol by norborneol or fenchyl alcohol substantially increases all the parameters.

(2) Increasing the concentration of methanol and 1-octanol at the cost of decreasing the concentration of toluene in a three component system also increases these parameters, but the increment is not very substantial.

(3) Replacement of 1-octanol by fenchyl alcohol also increases the parameters significantly.

The dielectric loss (ε ") against logf plots are not perfectly symmetrical, and Cole-Cole plots do not fit a complete semi-circle, particularly in the case of methanol in interacting solvents as is obvious from figures V-1 to V-4. This probably shows the presence of more than one relaxation process.

Conclusions

The primary relaxation process is assumed to be a co-operative process in large multimers of alcohol molecules as is favoured by several workers [5,16].

The decrease in the principal relaxation time observed for butanol in non-interacting and interacting solvents has been interpreted as resulting from the deformation or destruction of hydrogen bonded clusters of the alcohols [17,20,21].

Both the enthalpies and entropies of activation values of 1-propanol were found to decrease upon the addition of hydrogen bonding solvents by Higasi *et al* [21].

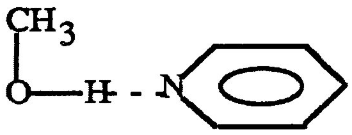
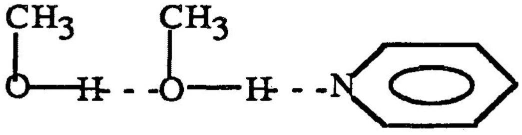
This result showed that the H-bonding capacity of the solvents could be a very important factor in determining the principal relaxation of the alcohol.

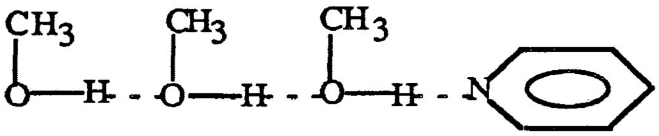
On this basis they argued that the principal relaxation is associated with multimers as molecules in the hydrogen-bonded clusters. Using this argument they predicted that the large enthalpies and entropies of activation in a non-interacting solvent like benzene would point to large clusters and the small values in pyridine to small clusters. The addition of pyridine to primary alcohols, therefore, tends to modify the alcohol clusters, while the weak hydrogen bonding benzene would not be expected to produce such an appreciable effect.

This postulation is also supported by the sharp increase of τ_1 values with the increase in alcohol concentration for 1-butanol in pyridine as observed by Higasi *et al* [20]. Our work supports this to some extent by showing the increment of $\tau_{1(200)}$ values with the increase in alcohol concentration for methanol in pyridine and diethyl ether systems. At the same time, it is also true that the principal relaxation cannot be explained solely by over-all rotation of the clusters.

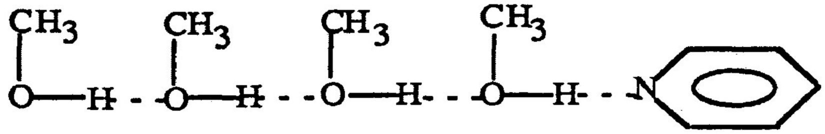
As far as our work is concerned, in groups A, B and C, we probably have in solution , the monomers, dimers, trimers and multimers of methanol.

However, when, say the most interacting solvent, pyridine, is added to the solution, we get additional species of the type


,



,

and also multimers,



and for a switching mechanism for the multimers this could conceivably alter the relaxation parameters. The formation of the same type of species in solution was also evidenced by Bellamy *et al* [27] from their IR study of the effects of solvents on H-bonded systems. According to Bellamy and coworkers, the point of solvent attachment can be at either end of the dimer system:

X-H···O-H···O-H, or O-H···O-H···Y,

where XH is a proton donor solvent and Y is a proton acceptor. The donor hydroxyl group oxygen becomes more basic, while any hydrogen attached to the acceptor oxygen becomes more acidic. They also concluded that the frequency shift is largely dependent on this phenomenon.

It is striking that the results for pure methanol and methanol at various concentrations in ethyl and butyl ether are very similar. Bellamy *et al* [27] restricted the solvent interaction in alcohol/ether complexes to the X-H···O-H···OR system so that they mainly interact with the proton donors. However, in our case, similar results would not be expected if the hydrogen bonding were solely MeOH···O(Et)$_2$ and the rate process was MeOH··|··O(Et)$_2$.

The extent of multimerization of methanol must vary in different solvents particularly from saturated hydrocarbons to pyridine. This is apparent from the considerable amount of material in a book by Pimentel and McClellan [29]. This can also be understood from the dielectric loss maxima (ε''_{max}) values. The greater the number of linear complexes in the solution, the higher will be the dipole moments which in turn will increase the ε''_{max} values.

It has been found out that ε''_{max} of methanol in the interacting solvents >>non-interacting solvents. However, the $\tau_{1(200)}$ and Eyring parameters do not reflect the extent of multimerization in the solution. Even pure methanol gives similar parameters to methanol (0.5MF) in dichloromethane although the degree of multimerization varies considerably.

It can be concluded from these observations that the principal relaxation time (τ_1) of methylalcohol is not highly dependent on the extent of multimerizations.

References

1. S. Mizushima, Bulletin of the Chemical Society of Japan, 1, 163 (1926).
2. R.H. Cole and D.W. Davidson, J. Chem. Phys., 20, 1389 (1952).
3. F.X. Hassion and R.H. Cole, J. Chem. Phys., 23, 1756 (1955).
4. W. Dannhauser and R.H. Cole, *ibid.*, 23, 1762 (1955).
5. S.K. Garg and C.P. Smyth, J. Phys. Chem., 69, 1294 (1965).
6. W. Dannhauser, J.Chem. Phys., 48, 1911, 1918, (1968).
7. W. Dannhauser and A.F. Flueckinger, Phys. Chem. Liquids, 2, 37(1970).
8. J. Crossley, L. Glasser and C.P. Smyth, J. Chem. Phys., 55, 2197(1971).
9. J. Crossley, J. Phys. Chem., 75, 1790 (1971).
10. J. Crossley, Can. J. Chem., 49, 712 (1971).
11. C. Campbell, J. Crossley and L. Glasser, Adv. Mol. Relax. Processes, 9, 79 (1976).
12. J.G. Krishna and J. Sobhandri, J. Chem. Soc., Faraday Trans., 2, 9, 79 (1983).
13. L. Glasser, J. Crossley and C.P. Smyth, J. Chem. Phys., 57, 3977(1972).
14. G.P. Johari and W. Dannhauser, Phys. Chem. Liquids, 3, 1 (1972).
15. P. Bordewijk, F. Gransch and C.J.F. Böttcher, J. Phys. Chem., 73, 3255 (1969).
16. R. Minami, K. Itoh, H. Takahashi and K. Higasi, J. Chem. Phys., 73, 3396 (1980).
17. R. Minami, K. Itoh, H. Takahashi and K. Higasi, Bull. Chem. Soc. Jpn., 54, 3684 (1981).
18. E. Arie, M. Nakamura, H. Takahashi and K. Higasi, Chem. Letters, Chem. Soc. of Japan, 33, 5 (1973).
19. Taro Kashii, H. Takahashi and K. Higasi, Bulletin of the Chemical Society

of Japan, Vol. 48(3), 993 (1975).

20. Hiroshi Sato, Taro Koshi, Hiroaki Takahashi, and K. Higasi, Chemistry Letters, Chem. Soc. Jpn., 579 (1974).
21. H. Sato, T. Koshi, H. Takahashi, K. Higasi, *ibid.*, 491 (1975).
22. H. Sato, H. Nakamura, K. Itoh and K. Higasi, *ibid.*, 1167 (1985).
23. Itedal K. Hakim, Egypt J. Phys., 14, 2, 275 (1983).
24. M. Stockhausen and E. Dachwitz, Z. Naturforsch, 39a, 646 (1984).
25. J. Middlehock and C.J.F. Böttcher, Mol. Relax. Processes, Chem. Soc., Spec. Publ., 20, 69 (1966).
26. J. Middlehock, Thesis, Leiden, 1967.
27. L.J. Bellamy, K.J. Morgan and R.J. Pace, Spectrochimica Acta, 22, 535-45 (1966).
28. S. Yagihara, R. Nozaki, S. Mashimo and K. Higasi, Chem. Letters, Chem. Soc. Jpn., 137-40 (1985).
29. G.C. Pimentel and A.L. McClellan, The Hydrogen Bond, (Freeman, San Francisco, 1960).

CHAPTER VI

DIELECTRIC AND IR-STUDIES OF SOME ISOMERIC HEPTANOLS, OCTANOLS AND DECANOLS IN SOLUTION

Numerous experimental and theoretical studies have been carried out on the intermolecular association of liquid alcohols and the effects of steric factors on these associations [1]. The dielectric dispersion of primary aliphatic alcohols is designated by three relaxation times, dominated by a low frequency Debye type process [2-7].

It is also evident that the low frequency process is related to the existence of hydrogen bonds between the various monomeric alcohol units. Recently, Jorgensen [8,9] found out that in the liquid phase a molecule of n-alcohols can have a maximum of two H-bonds with its next neighbors to form open or cyclic multimer chains of various lengths but the exact nature of these species and the type of associative equilibria involved are still very controversial. The dielectric study [10-12] of aliphatic alcohols shows that the contribution from the low frequency process is high at higher alcohol concentrations in non-polar solvents.

Dannhauser [13] showed that the isomeric octanols present two different types of dispersions, dependent on the amount of steric hindrance around the hydroxyl group. The relaxation times found for more sterically hindered alcohols were relatively shorter than those of the normal straight chain alcohols which showed Debye kind of behaviour. The activation energy for the Debye-type dispersion was found to be very much dependent on the steric hindrance exhibited by the groups adjacent to the -OH group. It was stated earlier by Dannhauser [14] that the enthalpy of activation (ΔH^o) for H-bond formation was virtually constant at -28.14 kJ mol^{-1} for all the isomeric octanols. Therefore, the activation energy should remain almost the same when the position of the -OH group is varied from terminal to the middle of the carbon backbone for these isomeric alcohols. But the energy of activation increased significantly when this was done. On this basis Dannhauser stated that the increase in the activation energies for different isomeric octanols is not just because of the change in the position of the -OH group but also because of the steric factors associated with it. And also the rupture of the H-bond is not the rate determining step.

Also, Bordewijk and Böttcher [15] suggested that the breaking of the H-bond cannot be the rate-determining step by a dielectric study of the mixture of 1- and 4-heptanols. According to Crossley *et al* [16], most of the hydroxyl are H-bonded at 0.3 MF of alcohol.

Higasi *et al* [17] proposed a mechanism for the first dispersion region of liquid alcohols, which is stated below:

(i) The existence of an associative equilibrium between H-bonded chain multimers is assumed.

(ii) The inversion of the dipole arises from co-operative rotation of the -OH group of the multimers.

This is diagrammatically represented in Chapter IV. This is a well established fact now that the variation of the concentration of a H-bonding substance in an inert solvent causes drastic spectral change in the IR-spectrum. This was demonstrated by the IR spectra of benzyl alcohol in CCl_4 at various concentrations by Coggeshall [18] in 1950. In the IR- spectrum, it has generally been found that the free hydroxyl groups absorb at about 3650 cm^{-1}, whereas the bonded hydroxyl groups exhibit absorption between 3500 and 3300 cm^{-1} [19].

Liddel *et al* [20] made a quantitative study of the intensity of absorption of CH_3OH as a function of concentration in CCl_4 or CS_2. They found out that the bands in the 3400-3640 cm^{-1} region show intensity variations with concentration with a monomer- multimer equilibrium.

We chose twelve different isomers namely 1-, 2-, 3- and 4-isomers of heptanol, octanol and decanol for our present study. The dielectric studies of these alcohols at different concentrations in toluene and also the infra-red study of the isomers of octanol and decanol in carbon tetrachloride were accomplished. The IR-study was carried out only at room temperature. Our main purpose is to investigate the effects of the geometry of alcohol molecules on the H-bond association process. The dielectric study was supplemented by infrared study with a view to having more insight into the type of species present at very low concentrations of these alcohols. The solvent carbon tetrachloride was preferred owing to its highly non-interacting characteristics.

Experimental Results

A Hewlett Packard 4191A RF Impedance Analyzer described in the previous chapters, was used for the dielectric measurements of isomeric heptanols, octanols and decanols in toluene. A Beckman spectrophotometer IR 4250 was used to obtain the infrared spectra in the range 3100-4000 cm^{-1}. More experimental details were given in Chapter II. The names and formulae of the alcohols are presented below:

NAME	FORMULA
1-Heptanol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$
2-Heptanol	$CH_3CH_2CH_2CH_2CH_2CHOHCH_3$
3-Heptanol	$CH_3CH_2CH_2CH_2CHOHCH_2CH_3$
4-Heptanol	$CH_3CH_2CH_2CHOHCH_2CH_2CH_3$

1-Octanol	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$
2-Octanol	$CH_3CH_2CH_2CH_2CH_2CH_2CHOHCH_3$
3-Octanol	$CH_3CH_2CH_2CH_2CH_2CHOHCH_2CH_3$
4-Octanol	$CH_3CH_2CH_2CH_2CHOHCH_2CH_2CH_3$
1-Decanol	$CH_3(CH_2)_8CH_2OH$
2-Decanol	$CH_3(CH_2)_7CHOHCH_3$
3-Decanol	$CH_3(CH_2)_6CHOHCH_2CH_3$
4-Decanol	$CH_3(CH_2)_5CHOHCH_2CH_2CH_3$

All the alcohols and the solvent toluene were obtained commercially and most of them were distilled and dried by the appropriate procedures. The relaxation and Eyring parameters for all the systems studied are summarized in Tables VI-2 to VI-4. Figures VI-1 to VI-5 show absorption curves and Cole-Cole plots for isomeric heptanols and decanols at 0.6 MF alcohol concentration in toluene plots of relaxation time at 300K ($\tau_{1(300)}$), the free energy of activation at 300K ($\Delta G_{E(300)}$), the enthalpy of activation (ΔH_E) and the entropy of activation (ΔS_E) versus alcohol concentrations for all the isomeric alcohols are described in Figures VI-6 to VI-9.

Discussion

Section I: Dielectric Study

For each set of isomeric alcohols, the dielectric properties of 1-, 2-, 3- and 4-alkanols have been investigated and compared with the literature values, where feasible, to check the reliability of our results. The enthalpies of activation (ΔH_E) values obtained from our study are compared with the literature values in Table VI-1. The ΔH_E values for the 1- and 2-isomers of heptanol and octanol are in good agreement with those of the literature [21-25].

The Fuoss-Kirkwood distribution parameters, ß, for these alcohols, is close to 1, which shows approximately Debye type of behaviour that has earlier been confirmed for isomeric octyl alcohols by Dannhauser [13].

Now, we will discuss separately the important dielectric relaxation parameters for these alcohols in toluene.

A. The enthalpies of activation (ΔH_E) of the principal relaxation process

For 1-heptanol in toluene, the extrapolated ΔH_E value remains almost the same as the original ΔH_E of the pure alcohol. This shows that chain interlocking is not the major factor in 1-heptanol. Amongst the isomeric alcohols (i.e. 2-, 3-, and 4-heptanols), the enthalpies of activa tion (ΔH_E) keep decreasing as we lower the concentrations of alcohol. For 2-heptanol no appreciable decrease in ΔH_E value is observed. But for 3- and 4-heptanols, the ΔH_E values decrease by larger factors from the pure state of alcohol to the lowest concentration measurable. The range of the decrease is (9-26) kJ mol^{-1} as shown in Tables VI-2(a)-(c).

The ΔH_E values for isomeric octanols and decanols behave in a similar fashion as those of heptanols as is evident from Tables VI-3 and VI-4. The variation of ΔH_E with concentrations of alcohols are represented in Figures VI-8(a)-(c).

For 1- and 2-isomers, the extrapolated ΔH_E at infinite dilution is (42±6) kJ mol^{-1}. But the extrapolated ΔH_E for 3- and 4-isomers at infinite dilution is (17±4) kJ mol^{-1}.

B. The entropies of activation (ΔS_E)

The entropies of activation (ΔS_E) for the isomeric heptanols, octanols and decanols are plotted against the concentrations of alcohol in Figures VI-9(a)-(c). As far as the isomeric heptanols are concerned, it is quite obvious from Tables VI-2(a)-(c) and Figures VI-9(a) that the entropies of activation (ΔS_E) change in a similar way as do the enthalpies of activation (ΔH_E). The changes are very drastic again for 3- and 4-isomers. From Tables VI-3-VI-4 and Figures VI-9(b)-(c), it is also clear that the isomeric octanols and decanols present the same kind of behaviour.

C. The free energies of activation (ΔG_E)at 300K.

Figures VI-7(a)-(c) and Tables VI-2 to VI-4 describe the change in $\Delta G_{E(300)}$ with the change in alcohol concentration for all the someric alcohols included in this chapter.

The range of $\Delta G_{E(300)}$ values for isomeric heptanols is from 16 to 22 kJ mol^{-1}. For isomeric octanols the range is from 13 to 22 kJ mol^{-1} and for isomeric decanols it is from 15 to 23 kJ mol^{-1}.

Therefore, the range of $\Delta G_{E(300)}$ value is almost the same for each set of isomeric alcohols.

D. The principal relaxation times (τ_1) at 300K.

The variation of $\tau_{1(300)}$ values with the concentrations of different isomeric alcohols in toluene is presented in Figures VI-6(a)-(c). They all increase exponentially with the increase in alcohol concentration in toluene. The range of $\tau_{1(300)}$ values for isomeric heptanols is from 0.83×10^{-10}s to 9.9×10^{-10}s. The range for isomeric octanols is from 0.26×10^{-10}s to 11.3×10^{-10}s and for isomeric decanols is from 0.74×10^{-10}s to 14.1×10^{-10}s. This tells us that the relaxation time (τ_1) at 300K is dependent on the size of the alcohol but not directly proportional to the concentration of alcohol in toluene. Some other factor/factors are associated with the exponential increase in $\tau_{1(300)}$ values with alcohol concentration. Also, the values change the same way as do the $\Delta G_{E(300)}$ values for all the isomeric alcohols.

Comparison of the relaxation parameters at three different concentrations:

(i) at 0.6MF alcohol concentration:

The ΔH_E for heptanols is (42±3) kJ mol^{-1}.

The ΔH_E for octanols is (42±5) kJ mol^{-1}.

The ΔH_E for decanols is (44±6) kJ mol^{-1}.

The ΔG_E for heptanols is (18±2) kJ mol^{-1}.

The ΔG_E for octanols is (18±2) kJ mol^{-1}.

The ΔG_E for decanols is (18±2) kJ mol^{-1}.

The range of ΔS_E for heptanols is (63-93) J K^{-1} mol^{-1}.

The range of ΔS_E for octanols is (57-99) J K^{-1} mol^{-1}.

The range of ΔS_E for decanols is (71-112) J K^{-1} mol^{-1}.

The range of $\tau_{1(300)}$ for heptanols is $(1\text{-}4)\times10^{-10}$s.

The range of $\tau_{1(300)}$ for octanols $(1\text{-}4)\times10^{-10}$s.

The range of $\tau_{1(300)}$ for decanols is $(1\text{-}5)\times10^{-10}$s.

(ii) At 0.7MF alcohol concentration:

The ΔH_E for heptanols is (42±4)kJ mol^{-1}.

The ΔH_E for octanols is (45±5)kJ mol^{-1}.

The ΔH_E for decanols is (45±4)kJ mol^{-1}.

The $\Delta G_{E(300)}$ for heptanols is (19±1) kJ mol^{-1}.

The $\Delta G_{E(300)}$ for octanols is (18±2) kJ mol^{-1}.

The $\Delta G_{E(300)}$ for decanols is (18±2) kJ mol^{-1}.

The range of ΔS_E for heptanols is (57-91) J $K^{-1}mol^{-1}$.

The range of ΔS_E for octanols is (68-107) J $K^{-1}mol^{-1}$.

The range of ΔS_E for decanols is (69-105) J K^{-1} mol^{-1}.

The range of $\tau_{1(300)}$ for heptanols is $(2\text{-}6)x10^{-10}s$

The range of $\tau_{1(300)}$ for octanols is $(2\text{-}6)x10^{-10}s$

The range of $\tau_{1(300)}$ for decanols os $(2\text{-}10)x10^{-10}s$.

(iii) At 0.8MF alcohol concentration:

The range of ΔH_E for heptanols is (37-52) kJ mol^{-1}

The range of ΔH_E for octanols is (40-51) kJ mol^{-1}

The range of ΔH_E for decanols is (41-50) kJ mol^{-1}

The range of $\Delta G_{E(300)}$ for heptanols is (20±1) kJ mol^{-1}

The range of $\Delta G_{E(300)}$ for octanols is (19±2) kJ mol^{-1}

The range of $\Delta G_{E(300)}$ for decanols is (20±2) kJ mol^{-1}

The range of ΔS_E for heptanols is (55-110) J K^{-1} mol^{-1}

The range of ΔS_E for octanols is (61-108) J K^{-1} mol^{-1}

The range of ΔS_E for decanols is (64-105) J K^{-1} mol^{-1}

The range of $\tau_{1(300)}$ for heptanols is $(3\text{-}7)\times10^{-10}$s

The range of $\tau_{1(300)}$ for octanols is $(3\text{-}8)\times10^{-10}$s

The range of $\tau_{1(300)}$ for decanols is $(2\text{-}10)\times10^{-10}$s

It is evident from Tables VI-5 to VI-7 that the 2-isomers of heptanols, octanols and decanols have always comparatively high values of enthalpies and entropies of activation at the aforementioned concentrations of alcohol in toluene. As far as the free energies of activation and relaxation time at 300 K are concerned, it is always the 1-alkanols that have slightly higher values than the rest.

When we increase the alcohol concentration from 0.6 MF to 0.8 MF, for 1- and 2-isomers of alcohols there is virtually no change in the enthalpies and entropies of activation but, for 3- and 4-isomers, these two parameters keep increasing with the increase in alcohol concentrations. On the contrary, when at any particular concentration e.g. at 0.7 MF, the size of the alcohols is increased, we find that ΔH_E increases for 1- and 2-isomers but remains almost the same for 3- and 4-isomers of alcohols.

This demonstrates first of all that the 3- and 4-isomers behave differently from their 1- and 2- counterparts in toluene. Secondly, these data reveal that the species formed in the solution for 1- and 2-alkanols are dependent on the size of the alcohol but independent of the alcohol concentration whereas for 3- and 4-alkanols they are susceptible to alcohol concentration without having any dependence on the size of the alcohol.

Since $\Delta G_{E(300)}$ and $\tau_{1(300)}$ do no change appreciably when the concentration of the alcohol or the alcohol size is varied, no conclusion can be made on the basis of these parameters. The dielectric loss (ε'') against $\log f_{max}$ plots are not perfectly symmetrical and Cole-Cole plots do not fit a complete semicircle for all the someric alcohols in toluene as is evident from Figures VI-1 to VI-5.

This is similar to the behaviour of methanol in interacting solvents as described in Chapter V.

Section II: IR-study of different isomeric alcohols:

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 CCl_4 to toluene as was observed by Bellamy *et al* [26]. The -OH stretching frequency of monomeric methanol in carbon tetrachloride is found at 3642 cm^{-1} whereas for triethyl carbinol in the same solvent this is found at 3620 cm^{-1} [27].

This shows the dependence of the -OH stretching frequency of the monomeric form on the alkyl part of the alcohol. The infrared spectrum of a 0.2 M solution of n-hexanol in carbon tetrachloride shows monomer, dimer and multimer bands at 3640,3480 and 3345 cm^{-1} respectively.

All the other n-alcohols from C_3 to C_{18} in $C_nH_{2n+1}OH$ at 0.2 M concentration show almost identical behaviour [28]. The H-bonded OH-stretching frequency for the open dimer of triethyl carbinol in CCl_4 is at 3500 cm^{-1} [27].

Our main objective to include IR-study in this context is to get a more revealing picture of the type of species present in solutions at very dilute concentrations of alcohols.

We studied the isomeric octanols and decanols at two different concentrations, 0.4M and 0.04M in carbon tetrachloride.

For 1-octanol and 1-decanol at 0.4M in CCl_4, the monomer band appears in the range of 3630-40 cm^{-1} and the multimer band at 3330 cm^{-1}.

But when the concentration of alcohol is reduced to 0.04M, the monomer band in both cases still appears on the aforementioned range of frequency but the multimer band shifts to a higher wave number (around 3400 cm^{-1}).

For 1-octanol at 0.04M in CCl_4, in addition to the multimer band at 3340 cm^{-1}, there is a hump due to the dimer at around 3500 cm^{-1} whereas for 1-decanol the broad multimeric band centres at around 3400 cm^{-1}. There is virtually no distinction between the dimeric and multimeric band in this case.

If we compare our IR-spectrum for 0.04M 1-octanol in CCl_4 with that of 0.2M 1-hexanol and methanol in CCl_4 with that of 0.2M 1-hexanol and methanol in CCl_4 observed by Sandorfy *et al* [28], one thing is quite clear that as we decrease the concentration from 0.2M to 0.04M, the dimer band predominates. For 2-, 3- and 4-octanols at 0.4M in CCl_4, the monomer band appears in the frequency range 3630-40 cm^{-1}, the multimer band in the range 3330–80 cm^{-1} and the dimer band in the range of 3430-85 cm^{-1}. The shift in the band position toward high frequencies is observed as we move from 2- to 4-octanol. For 2-, 3- and 4-decanol at the same concentration in CCl_4, the monomer peak is observed in the range 3625-30 cm^{-1}, the dimer peak at 3480 cm^{-1} and the multimer peak in the range 3350-70 cm^{-1}.

At 0.04M concentration in CCl_4, for 2-, 3- and 4-octanols, the monomer peak appears in the range 3625-40 cm^{-1}, the dimer peak at 3480 cm^{-1} and the multimer peak in the range 3360-80 cm^{-1}.

At 0.04M concentration in CCl_4, for 2-, 3- and 4-decanols, the monomer band appears in the range 3630-50 cm^{-1}, the dimer band in the range 3480-3500 cm^{-1} and the multimer band at 3360-3400 cm^{-1}.

Conclusion

The infrared and N.M.R. of pure 4-heptanol at different temperatures indicate that 4-heptanol is still appreciably associated at temperatures far above 60°C [29]. This implies that all the isomers of heptanols, octanols and decanols are extensively hydrogen bonded at all temperatures of our range.

At relatively high temperatures those species whose -OH group is most sterically blocked, prefer to form cyclic structures, while those whose -OH group is relatively accessible tend to form open chains. In all cases, chains become the preferred species at low temperatures [30].

From the dielectric study it has been found out that the 1- and 2-isomers behave differently from the 3- and 4-isomers of alcohols, specially when we consider the variation of the enthalpies of activation in these systems. When the ΔH_E values are extrapolated to infinite dilutions, however, 1- and 2-isomeric alcohols yield about the same values of ΔH_E and these are not substantially different from those of the corresponding pure alcohol.

When the 3- and 4- isomers are subjected to infinite dilutions, the extrapolated ΔH_E values (i.e. 17 ± 4 kJ mol^{-1}) amount to the breaking of one mole of H-bonds.

According to infrared study, for all the isomeric alcohols at high concentration, the amount of monomeric and multimeric species are present in high quantity. At higher concentration, although for 1-alkanols, the multimeric band predominates, in the case of 2-, 3- and 4-isomers of alcohols, fair amount of dimers are also evident in the solution.

The following tentative postulates can be proposed on the basis of this dicussion:

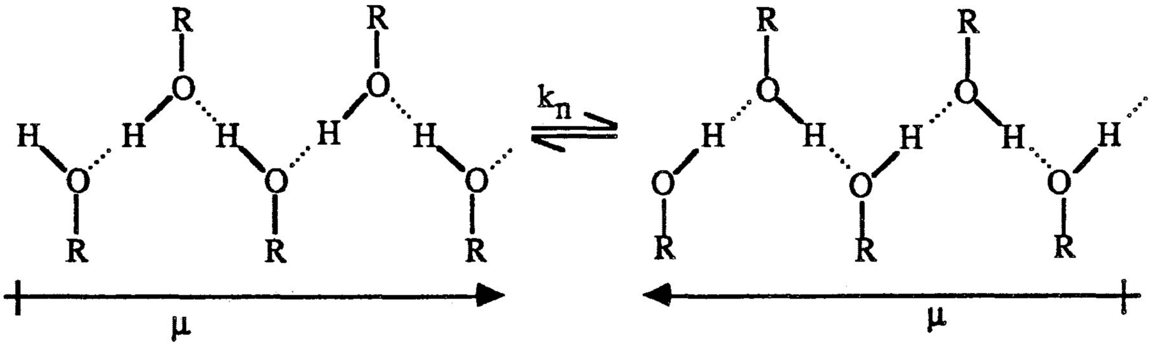
1. The isomeric alcohols probably form cyclic species at higher concentration of alcohols and when diluted they form linear type structures like 1-alkanols with both monomer and multimer present in solution.

2. At intermediate concentrations, both cyclic and linear structures probably exist.

3. ΔH_E values for the pure 3- and 4-isomers are ~10-20 kJ mol^{-1} higher than those of pure 1-isomer. The principal relaxation region cannot be completely attributed to the formation of a particular multimer e.g. dimer. If we are just concerned with dimers, then, in 1-alkanols, the H-bond would be much stronger than 3- and 4-alkanols since OH—O distance would be shorter in primary alcohols than in secondary or tertiary alcohols.

4. The higher energy barriers of the highly sterically hindered isomeric alcohols in the pure liquid form are probably due to the presence of more steric factors, in addition to the breaking of 1-mole of H-bonds in each case.

5. IR-study reveals that even at very low alcohol concentration, both monomeric and multimeric species exist. An enthalpy of activation value of (17±4) kJ mol^{-1} at infinite dilution for 3- and 4-isomers is, therefore, possibly due to the breaking of one mole of H-bonds in a molecular aggregate by the following type of mechanism proposed by Higasi *et al* [17]:


R
O
H
k_n
μ

References

1. G.C. Pimentel and A.L. McLellan, The Hydrogen Bond (W. Freeman & Co., San Francisco, Calif. 1960).
2. D.W. Davidson and R.H. Cole, J. Chem. Phys., 19, 1484 (1951).
3. R.H. Cole and D.W. Davidson, J. Chem. Phys., 20, 1389 (1952).
4. F.X. Hassion and R.H. Cole, J. Chem. Phys., 23, 1756 (1955).
5. D.J. Denny and R.H. Cole, J. Chem. Phys., 23, 1767 (1955).
6. M. Magat, in Hydrogen Bonding (Lj-Ub ljana, 1957), edited by D. Madzi and H.W. Thompson (Pergamon, New York, 1959), p. 309.
7. S. K. Garg and C. P Smyth, J. Phys. Chem., 69, 1294 (1965).
8. W. L. Jorgensen, J. Am. Chem. Soc., 102, 543 (1980).
9. W. L. Jorgensen, J. Am. Chem. Soc., 103, 345 (1981).
10. D. J. Denney and J. W. Ring, J. Chem. Phys. 39, 1268 (1963).
11. M. Moriamez and A. Lebrun, Arch-Sci. Geneva 13, 40 (1960).
12. J. Crossley, L Glasser and C. P. Smyth, J. Chem. Phys., 55, 5 (1971).
13. W. Dannhauser, J. Chem. Phys., 48, 1918 (1968).
14. W. Dannhauser, J. Chem. Phys., 48 (5), 1911 (1968).
15. P. Bordewijk, F. Gransch and C.J.F. Böttcher, J. Phys.Chem., 73(10), 3255 (1969).
16. J. Crossley, L. Glasser and C.P. Smyth, J. Chem. Phys., 55(5), 2197 (1971).
17. R. Minami, K. Itoh, H. Takahashi and K. Higasi, J. Chem. Phys., 73(7), 3396 (1981).
18. N.D. Coggeshall, J. Chem. Phys., 18, 980 (1950).
19. G. C. Pimentel and A. L. McClellan, The Hydrogen Bond (Freeman and Co., San Francisco, 1960).

20. Urner Liddel and Edwin D. Becker, J. Chem. Phys., 25, 173 (1956).

21. C. Oppenheim, J. Chem. Phys., 48, 377 (1954).

22. J. Middlehock, Thesis Leiden, 1967.

23. P. Bordewijk, Thesis Leiden, 1968.

24. R. Dalbert, J. Chim. Phys., 50, 329 (1950).

25. G. Klages and D. Roth, Z. Naturforsch, 14a, 628 (1959).

26. L. J. Bellamy, K. J. Morgan and R. J. Pace, Spectrochimica Acta, 22, 535 (1966).

27. M. Kunst, D. Van Duijn and P. Bordewijk, Ber. Bunsenges, Phys. Chem., 80, 839 (1976).

28. L. Wilson, R. Bicca de Alencastro and C. Sandorfy, Can. J. Chem., 63, 40 (1985).

29. P. Bordewijk, F. Gransch and C.I.F. Böttcher, Trans. Farad. Soc., Part-II, 66, 566 (1970).

30. W. Dannhauser, J. Chem. Phys., 48(5), 1911 (1968).

CHAPTER VII

DISCUSSION AND SUMMARY

Discussion

In the previous chapters, we have discussed the behaviour of intermolecularly H-bonded compounds, specifically pure liquid alcohols and alcohols in different solvents for the first, or radio frequency, dispersion region of alcohols. Unfortunately, there is no unique mechanism for understanding the relaxation time, τ_1, which is attributed to this dispersion.

In the present chapter, some important mechanisms and models for the first dispersion region will be described and evaluated in the light of the experimental results obtained for the alcohols in the present work and works done by other researchers. One of the earliest models was proposed by Brot and co-workers [1] which has already been described in Chapter III.

Some of the important observations made by Smyth and co-workers [2-5] are (a) the activation energy for the first dispersion of pure n-alcohols increases with the increase in the chain length of the alcohols, (b) the relaxation time, τ_1, decreases rapidly with the decrease in alcohol concentration in an inert solvent, (c) at approximately 0.25 mole fraction of alcohol in inert solvent, the τ_1 is independent of the chain length of n-alkanols and (d) increasing the steric factors around the OH-group of an alcohol makes the τ_1 process disappear.

According to them, the dielectric relaxation for the first dispersion involves the breaking and reforming of the H-bonds with consequent reorientation of the dipole moment, and the rate of hydrogen bond breaking is the determining factor for the relaxation time. The increment of the enthalpies of activation, ΔH_E, with the increase in chain length, was explained by assuming that the H-bond breaking is an initial step, but some molecular motion dependent upon the chain length is also needed to give the observed increase.

Dannhauser *et al* [6-7] suggested that at relatively high temperatures, the alcohols with most sterically hindered OH-group prefer to form polymer rings whereas those with OH-groups relatively accessible tend to form open chain polymer. They [8] considered that the H-bond rupture is a prerequisite rather than the rate determining step for dipolar reorientation. According to them a particular H-bond will break and reform many times without reorientation of either the donor or acceptor molecule and the reorientation is assumed to be co-operative in nature.

Sagal [9] introduced the so-called switch over mechanism, from the dielectric study of ethanol in cyclohexane and some other alcohols in the pure liquid state. According to this mechanism, for the first dispersion region, the H-bond will break when another molecule approaches with its oxygen atom oriented favorably for a "switch". The energy barrier for the breaking of the H-bond will be lowered in the presence of the third oxygen atom. Therefore, the dilution of ethanol with bulky cyclohexane molecules would decrease the possibility of approach of a third oxygen atom for a switch over and consequently increase the energy barrier of ethanol.

The models proposed by Böttcher et al [10-11] and Higasi and co-workers [12-13] has also been described in the previous chapters. Higasi *et al* assumed that the dipole inversion of the 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. The increase in activation energies of alcohols with the increase in carbon chain length was explained by a proposal that a third alcohol molecule approaches with its oxygen atom oriented favorably to activate the terminal, OH-group of the multimer. The approach of this third alcohol molecule toward the multimer becomes more difficult with the increase in the size of the alcohol molecules, resulting in an increase in the value of activation energy.

According to Brot and Magat [1], the energy barriers and relaxation times for the first dispersion of alcohols would be independent of the size of the alcohol. However, it has been found from the results obtained by our study and by other researchers [2] for pure liquid 1-alkanols that the above two parameters were dependent on the size and shape of the alcohol molecules. According to Garg and Smyth [2], the main mechanism for the first dispersion is a two step process i.e., the breaking of the H-bond and then the reorientation of the partially liberated dipole. The H-bond breaking was considered as the rate determining step. Rotation of the partially liberated dipole which increases in size with increasing size of the carbon skeleton, was suggested to give rise to the gradual increase in enthalpies of activation and the relaxation times. However, the experimental results obtained in our work for pure liquid 1-alkanols show that the enthalpies of activation and the relaxation times increase linearly with the increase in chain length only up to 1-nonanol and then they tend to level off.

It has been reported in the literature [14-17] that the strength of one intermolecular H-bond is 18±2 kJ mol^{-1}. The enthalpy of activation (ΔH_E) for pure methanol is 13 kJ mol^{-1}. This predicts that a H-bond breaking process is involved since no contribution from the intramolecular relaxation $C\circlearrowright OH$ is expected for monomeric methanol in the temperature range studied. The linear increase in the enthalpies of activation (ΔH_E) and relaxation times (τ_1) with the increase in the size of the alcohol suggests that these parameters are somehow dependent on the size and shape of the alcohols. However, there is a tendency to level off for the higher alcohols as was observed in our work, and reveals that the first dispersion region cannot be explained solely in terms of a molecular relaxation process.

Böttcher and co-workers [10-11] proposed that a highly polar, non-planer, cyclic tetramer was responsible for the first dispersion region in alcohols on the basis of their study of pure 1- and 4-heptanol and their mixtures between 213 and

273 K. However, the infrared measurements of 1- and 4-isomers of octanol and decanol in dilute solutions, obtained by us, showed the presence of multimers rather than just a tetramer. Thus, Böttcher's hypothesis seems inadequate to explain this phenomenon.

The increase in energy barriers of pure liquid alcohols with the increase in carbon chain length could be accounted for by increasing steric effects. This seems to match Sagal's mechanism that the energy barrier would increase when there is less possibility of approach of the third alcohol molecule for a switch over.

Higasi *et al* [18] considered that the dilution of l-propanol with benzene and chlorobenzene obstructs the approach of an alcohol molecule to the multimer and therefore decreases the possibility of OH-switch over. This accounted for the slightly increasing energy barriers of l-propanol when diluted in the above two solvents. On the contrary, the addition of a strongly H-bonding solvent (e.g. dioxane or pyridine) would provide a new possibility of switch over to the electronegative atom of the solvent, thus, lowering the energy barrier of alcohol. The experimental results obtained by Higasi *et al* [18] for 1-propanol in 1,4-dioxane and pyridine and the ones obtained by us for 1-alkanols of different chain lengths in ethyl ether, are in good agreement with this proposal. Moreover, the Sagal mechanism does seem to measure up to the small variation in energy barriers obtained from our study when 1-alkanol is diluted with inert solvents such as n-heptane and toluene.

Higasi *et al* [12-13] described the primary relaxation as a co-operative process in large multimers of alcohol arranged in a straight chain. They assumed the dielectric absorption for liquid alcohols which consist of H-bonded open chains and cyclic dimers as the sum of the contributions from the dipole relaxation of each n-mer where the cyclic dimer with zero dipole moment does not contribute to the absorption. They used Sagal's mechanism to illustrate the increase in the enthalpies of activation for the first dispersion of alcohols with the increase in carbon chain length. Also the same concept was used to explain the dielectric behaviour of 1-propanol in strongly H-bonding and non H-bonding solvents, as described in the previous paragraph.

It has been found by infrared studies that the degree of polymerization in n-alcohols from C_3 to C_{18} in $C_nH_{2n+1}OH$ in dilute solution is independent of the length of the alkyl chain in contradiction to the explanation given by Higasi and co-workers [12-13] for the increase in energy barriers with the increase in carbon chain length. Therefore, it can be said that, at least in dilute solutions of alcohols, the approach of a third alcohol molecule to activate the terminal OH-group of multimer chain would not be decreased with the increase in the chain length of alcohols. It has also been found out from our dielectric study on 1-alkanols of varying chain lengths in three different solvents, ranging from non-interacting to highly interacting, that Higasi's mechanism does not stand up to wide temperature variations. However, the enthalpies of activation value of 17 ± 4 kJ mol^{-1} at infinite dilution for 3- and 4-isomers of octanols and decanols, obtained in our study, seem to support Higasi's mechanism.

References

1. C. Brot and M. Magat, J. Chem. Phys., 39, 841 (1963).
2. S.K. Garg and C.P. Smyth, J. Phys. Chem., 69, 1294 (1965).
3. J. Crossley, L. Glasser and C.P. Smyth, J. Chem. Phys., 52, 6203 (1970).
4. J. Crossley, L. Glasser and C.P. Smyth, J. Chem. Phys., 55, 2197 (1971).
5. L. Glasser, J. Crossley and C.P. Smyth, J. Chem. Phys., 57, 3977 (1972).
6. W. Dannhauser, J. Chem. Phys., 48, 1911, 1918 (1968).
7. G.P. Johari and W. Dannhauser, J. Phys. Chem., 72, 3273 (1968).
8. W. Dannhauser and A.F. Flueckinger, Phys. Chem. Liquids, 2, 37 (1970).
9. M.W. Sagal, J. Chem. Phys., 36, 2437(1962).
10. P. Bordewiik, F. Gransch and C.J.F. Böttcher, J. Phys. Chem., 73, 3255 (1969).
11. C.J.F. Böttcher and P. Bordewiik, Theory of Electric Polarization (Elsevier, Vol. II, Amsterdam, 1978).
12. R. Minami, K. Itoh, H. Takahashi and K. Higasi, J. Chem. Phys., 73(7), 3396 (1980).
13. R. Minami, K. Itoh, H. Takahashi and K. Higasi, Bull. Chem. Soc. Jpn., 54, 3684 (1981).
14. J.C. Davies, Jr., K.S. Pitzer and C.N.R. Rao, J. Phys. Chem., 64, 1744 (1960).
15. U. Liddel and E.D. Becker, Spectro-Chimica Acta, 10, 70 (1957).
16. G. Mavridis, M. Servanton and J. Blais, J. Chim. Phys., 3, 436 (1972).
17. H. Landeck, H. Wolff and R. Gotz, J. Phys. Chem., 81, 718 (1977).
18. T. Koshii, H. Takahashi and K. Higasi, Bull. Chem. Soc. Jpn., 48(3), 993-96 (1975).

19. L. Wilson, R. Bicca de Alencastro and C. Sandorfy, Can. J. Chem., 63, 40 (1985).

CHAPTER VIII

CONCLUSIONS

For the pure liquid alcohols, the increase in chain length increased the dielectric relaxation parameters. This, however, was only observed up to 1-nonanol. The relaxation parameters tended to level off for the higher alcohols. This shows that the chain length of the alcohol is not the only parameter that influences the radio frequency dispersion of the pure liquid alcohols.

When the straight chain alcohols were studied in a strongly interacting solvent, diethyl ether, the chain length was found to have greater effect on the enthalpies of activation (ΔH_E). At higher alcohol concentration, the ΔH_E value increased significantly with the increase in chain length. At low alcohol concentration (ie. 0.3MF), however, the enthalpies of activation (ΔH_E) gave almost similar values. This was of the order of breaking 1 mole of H-bonds. A different mechanism independent of chain length is, therefore, more probable in dilute solutions of alcohols.

The extent of multimerization for these alcohols must vary from one solvent to another. It has been observed that the dielectric loss maxima for methanol in interacting solvents are greater than those in non-interacting solvents. The extent of multimerization in solutions, nevertheless, is not reflected in the study of the Eyring activation parameters. Pure methanol yields an energy barrier (13 kJ mol^{-1}) which is equivalent to the breaking of 1 mole of H-bonds.

It has also been found out, from the study of 1-, 2-, 3- and 4-isomers of three primary alcohols of different chain length, that 1- and 2- isomers behave differently from 3- and 4-isomers. This difference was prominent in the study of the enthalpies of activation (ΔH_H) of these systems. For 3- and 4- isomers, at infinite dilutions, the extrapolated ΔH_E values (ie. 17±4 kJ mol^{-1}) amount to the breaking of one mole of H-bonds.

It now seems quite obvious that none of the models described in Chapter VII can interpret all the experimental observations adequately. Because of the diversity in the type of H-bonded equilibria present for different systems, it is almost impossible at this stage to find a unique model that would account for all the experimental observations of alcohols in their pure states as well as in solutions. From our own study, however, it is evident that H-bond breaking is the most important step in each case and is in good agreement with most of the other mechanisms proposed earlier.

APPENDICES AI, AII AND AIII

FOR THESIS:

DIELECTRIC AND INFRARED STUDIES OF RADIO FREQUENCY PROCESSES IN SOME ALCOHOLS

BY

HUMAYUN MANDAL

DEPARTMENT OF PHYSICS
LAKEHEAD UNIVERSITY
THUNDER BAY, ONTARIO
CANADA

1988

TABLE III - 1: Dielectric Relaxation Parameters of some liquid 1-alkanols

Alcohol mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Methanol	176-234	0.99-1.0	1.8×10^{-8}	10.2×10^{-10}	5.0×10^{-11}	13.7	13.9	14.3	13±0.6	-4±3
Ethanol	178-227	0.82-0.98	3.3×10^{-7}	75.3×10^{-10}	15.2×10^{-11}	17.3	17.2	17.1	17±0.9	1±5
1-Propanol	214-257	0.89-0.98	6.5×10^{-6}	4.9×10^{-8}	32.2×10^{-11}	20.9	20.3	18.9	23±0.3	13±1
1-Butanol	224-281	0.70-0.97	3.2×10^{-5}	13.2×10^{-8}	48.1×10^{-11}	22.9	21.9	19.9	26±0.4	20±2
1-Pentanol	252-286	0.93-0.96	1.5×10^{-4}	33.1×10^{-8}	64.3×10^{-11}	24.9	23.5	20.7	29±0.6	28±2
1-Hexanol	245-293	0.83-0.96	1.0×10^{-3}	96.8×10^{-8}	80.7×10^{-11}	27.3	25.3	21.3	33±0.7	40±3
1-Heptanol	257-309	0.85-0.97	3.8×10^{-3}	2.1×10^{-6}	101.7×10^{-11}	28.9	26.6	21.8	36±1	47±4
1-Octanol	262-309	0.86-0.97	7.7×10^{-3}	3.3×10^{-6}	123.7×10^{-11}	29.8	27.3	22.3	37±0.7	50±3
1-Nonanol	269-307	0.85-0.96	2.1×10^{-2}	5.6×10^{-6}	132.9×10^{-11}	31.0	28.2	22.5	40±0.5	57±2
1-Decanol	273-308	0.84-0.96	3.2×10^{-2}	7.1×10^{-6}	141.1×10^{-11}	31.6	28.6	22.7	41±3	59±12
1-Undecanol	289-306	0.87-0.93	4.3×10^{-2}	7.8×10^{-6}	128×10^{-11}	31.9	28.8	22.4	42±0.7	64±3
1-Dodecanol	300-317	0.90-0.93	1.1×10^{-1}	13.4×10^{-6}	143×10^{-11}	33.1	29.7	22.7	44±0.7	70±2

TABLE: III-2: Fuoss - Kirkwood Analyses Parameters for the Pure Primary Alcohols

T (K)	τ_1(s)	$\log f_{max}$	β	ε''_{max}
Methanol				
176	3.56×10^{-9}	7.65	0.99	25.5
179.9	2.79×10^{-9}	7.76	0.99	25.0
184.6	2.11×10^{-9}	7.88	1.00	24.3
189.3	1.63×10^{-9}	7.99	1.00	23.8
195.3	1.21×10^{-9}	8.12	1.00	23.0
200.3	0.95×10^{-9}	8.22	1.00	22.6
206.5	0.74×10^{-9}	8.33	1.00	21.9
213.3	0.57×10^{-9}	8.45	1.00	21.3
224.0	0.40×10^{-9}	8.59	1.00	19.8
233.7	0.30×10^{-9}	8.73	1.00	19.3
Ethanol				
177.6	3.49×10^{-8}	6.66	0.83	20.7
181.6	2.49×10^{-8}	6.81	0.84	19.6
187.3	1.57×10^{-8}	7.01	0.90	19.5
192.0	1.13×10^{-8}	7.15	0.93	18.9
196.5	0.90×10^{-8}	7.25	0.93	18.3
200.4	0.68×10^{-8}	7.37	0.95	17.7
205.9	0.54×10^{-8}	7.47	0.96	17.4
212.2	0.39×10^{-8}	7.61	0.97	16.7
219.3	0.28×10^{-8}	7.75	0.98	16.0
226.5	0.20×10^{-8}	7.89	0.98	15.3

TABLE: continued.....

T (K)	τ_1(s)	$\log f_{max}$	β	ε''_{max}
<u>1 - Propanol</u>				
213.8	1.91×10^{-8}	6.92	0.89	14.3
218.9	1.33×10^{-8}	7.08	0.91	13.7
223.6	1.00×10^{-8}	7.20	0.93	13.6
228.5	0.75×10^{-8}	7.32	0.93	12.7
233.3	0.58×10^{-8}	7.44	0.96	12.8
238.3	0.44×10^{-8}	7.56	0.97	12.4
242.8	0.35×10^{-8}	7.66	0.96	11.8
247.9	0.27×10^{-8}	7.77	0.98	11.6
252.2	0.22×10^{-8}	7.86	0.97	11.2
257.0	0.18×10^{-8}	7.95	0.98	11.0
<u>1 - Butanol</u>				
224.3	2.11×10^{-8}	6.88	0.87	11.3
230.2	1.51×10^{-8}	7.02	0.89	11.2
235.8	1.05×10^{-8}	7.18	0.92	10.9
241.6	0.73×10^{-8}	7.34	0.93	10.2
248.0	0.52×10^{-8}	7.48	0.95	10.0
253.6	0.38×10^{-8}	7.63	0.96	9.60
260.3	0.28×10^{-8}	7.76	0.97	9.29
267.4	0.19×10^{-8}	7.91	0.97	8.86
274.1	0.14×10^{-8}	8.06	0.97	8.49
280.9	0.10×10^{-8}	8.19	0.70	8.12

TABLE: continued.....

T (K)	τ_1(s)	$\log f_{max}$	β	ϵ''_{max}
<u>1 - Pentanol</u>				
251.9	6.98×10^{-9}	7.36	0.93	8.52
255.8	5.70×10^{-9}	7.45	0.94	8.42
259.1	4.68×10^{-9}	7.53	0.95	8.17
263.2	3.80×10^{-9}	7.62	0.95	7.83
267.4	3.00×10^{-9}	7.72	0.96	7.64
271.3	2.50×10^{-9}	7.80	0.95	7.33
274.9	2.02×10^{-9}	7.90	0.96	7.16
277.6	1.80×10^{-9}	7.95	0.96	7.00
281.8	1.45×10^{-9}	8.04	0.96	6.75
285.7	1.19×10^{-9}	8.12	0.94	6.51
<u>1 - Hexanol</u>				
244.7	1.95×10^{-8}	6.91	0.83	7.66
249.2	1.54×10^{-8}	7.01	0.85	7.51
253.6	1.09×10^{-8}	7.16	0.88	7.26
258.3	0.84×10^{-8}	7.28	0.88	6.84
264.4	0.55×10^{-8}	7.46	0.92	6.61
270.3	0.39×10^{-8}	7.62	0.94	6.20
276.0	0.28×10^{-8}	7.76	0.95	5.90
281.5	0.21×10^{-8}	7.89	0.96	5.59
287.2	0.15×10^{-8}	8.01	0.96	5.31
292.9	0.11×10^{-8}	8.14	0.97	5.02

TABLE: continued.....

T (K)	τ_1(s)	logf_{max}	β	ε''_{max}
<u>1 - Heptanol</u>				
257.2	$1.40\text{x}10^{-8}$	7.06	0.86	6.28
262.9	$0.89\text{x}10^{-8}$	7.25	0.89	5.93
268.6	$0.59\text{x}10^{-8}$	7.43	0.92	5.68
274.3	$0.41\text{x}10^{-8}$	7.58	0.95	5.34
280.0	$0.30\text{x}10^{-8}$	7.72	0.96	5.05
284.7	$0.23\text{x}10^{-8}$	7.85	0.95	4.71
290.2	$0.18\text{x}10^{-8}$	7.96	0.97	4.55
297.0	$0.12\text{x}10^{-8}$	8.12	0.97	4.19
302.8	$0.09\text{x}10^{-8}$	8.26	0.98	3.91
308.8	$0.67\text{x}10^{-8}$	8.38	0.96	3.67
<u>1 - Octanol</u>				
261.9	$1.20\text{x}10^{-8}$	7.12	0.86	5.17
266.8	$0.93\text{x}10^{-8}$	7.23	0.87	5.00
273.4	$0.58\text{x}10^{-8}$	7.44	0.91	4.68
278.6	$0.43\text{x}10^{-8}$	7.57	0.93	4.44
284.6	$0.29\text{x}10^{-8}$	7.73	0.94	4.13
290.2	$0.21\text{x}10^{-8}$	7.88	0.95	3.84
294.8	$0.16\text{x}10^{-8}$	8.00	0.96	3.63
299.6	$0.12\text{x}10^{-8}$	8.10	0.97	3.42
303.5	$0.10\text{x}10^{-8}$	8.20	0.97	3.28
308.8	$0.08\text{x}10^{-8}$	8.30	0.97	3.08

TABLE: continued.....

T (K)	τ_1(s)	$\log f_{max}$	β	ε''_{max}
1 - Nonanol				
268.5	9.56×10^{-9}	7.22	0.85	4.11
273.3	6.78×10^{-9}	7.37	0.88	3.86
276.8	5.53×10^{-9}	7.46	0.89	3.78
280.7	4.24×10^{-9}	7.57	0.91	3.60
284.5	3.30×10^{-9}	7.68	0.92	3.37
289.2	2.53×10^{-9}	7.80	0.93	3.22
293.8	1.90×10^{-9}	7.92	0.95	3.04
299.3	1.37×10^{-9}	8.07	0.96	2.81
302.6	1.14×10^{-9}	8.15	0.97	2.68
307.1	0.09×10^{-9}	8.25	0.96	2.51
1 - Decanol				
280	5.26×10^{-9}	7.48	0.84	1.43
286.7	3.56×10^{-9}	7.65	0.90	2.76
289.7	2.88×10^{-9}	7.74	0.92	2.67
292.3	2.49×10^{-9}	7.81	0.92	2.57
295.4	2.02×10^{-9}	7.90	0.94	2.45
298.1	1.74×10^{-9}	7.96	0.95	2.37
301.0	1.47×10^{-9}	8.03	0.95	2.28
303.7	1.23×10^{-9}	8.11	0.96	2.16
306.3	1.08×10^{-9}	8.17	0.96	2.10

TABLE: continued.....

T (K)	τ_1(s)	$\log f_{max}$	β	ε''_{max}
1 - Undecanol				
288.5	$2.59\text{x}10^{-9}$	7.79	0.88	2.11
290.8	$2.27\text{x}10^{-9}$	7.85	0.87	2.01
293.5	$1.87\text{x}10^{-9}$	7.93	0.90	1.96
296.3	$1.59\text{x}10^{-9}$	8.00	0.90	1.87
298.1	$1.43\text{x}10^{-9}$	8.05	0.91	1.84
300.0	$1.29\text{x}10^{-9}$	8.09	0.92	1.79
301.5	$1.16\text{x}10^{-9}$	8.14	0.91	1.74
302.9	$1.08\text{x}10^{-9}$	8.17	0.93	1.72
304.6	$1.00\text{x}10^{-9}$	8.21	0.93	1.67
306.1	$0.90\text{x}10^{-9}$	8.25	0.92	1.63
1 - Dodecanol				
300.1	$1.41\text{x}10^{-9}$	8.05	0.91	1.53
302.0	$1.26\text{x}10^{-9}$	8.10	0.91	1.48
303.4	$1.15\text{x}10^{-9}$	8.14	0.91	1.44
304.9	$1.06\text{x}10^{-9}$	8.18	0.92	1.42
306.5	$1.00\text{x}10^{-9}$	8.21	0.92	1.38
308.4	$0.90\text{x}10^{-9}$	8.26	0.93	1.34
310.4	$0.80\text{x}10^{-9}$	8.32	0.92	1.30
312.3	$0.70\text{x}10^{-9}$	8.37	0.92	1.26
314.2	$0.62\text{x}10^{-9}$	8.41	0.93	1.23
316.5	$0.54\text{x}10^{-9}$	8.47	0.91	1.18

BLE: 1V-1b; Dielectric Relaxation Parameters of 1-Butanol in n-Heptane Solution.

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Butanol (0.3)	224-257	0.73-0.95	6.2×10^{-5}	1.2×10^{-7}	2.1×10^{-10}	23.8	21.8	17.9	30±0.8	40±3
1-Butanol (0.4)	229-270	0.81-0.97	7.0×10^{-5}	1.7×10^{-7}	3.6×10^{-10}	23.9	22.4	19.2	29±0.8	31±3
1-Butanol (0.5)	233-273	0.78-0.93	12.6×10^{-5}	2.2×10^{-7}	3.5×10^{-10}	24.7	22.8	19.1	30±1.0	37±5
1-Butanol (0.6)	234-271	0.84-0.96	5.6×10^{-5}	1.8×10^{-7}	5.1×10^{-10}	23.7	22.5	20.1	27±0.5	24±2
1-Butanol (0.7)	238-275	0.89-0.96	5.2×10^{-5}	1.7×10^{-7}	5.1×10^{-10}	23.6	22.4	20.1	27±0.7	23±3
1-Butanol (0.8)	237-275	0.90-0.97	3.6×10^{-5}	1.5×10^{-7}	5.4×10^{-10}	23.1	22.2	20.2	26±0.6	19±2
1-Butanol (0.9)	234-267	0.90-0.96	3.0×10^{-5}	1.4×10^{-7}	5.4×10^{-10}	22.9	22.0	20.3	26±0.6	18±2
1-Butanol (1.0)	224-281	0.70-0.97	3.2×10^{-5}	1.3×10^{-7}	4.8×10^{-10}	22.9	21.9	19.9	26±0.4	20±2

ABLE:1V-1c: Dielectric Relaxation Parameters of 1-Hexanol in n-Heptane Solution.

Alcohol nole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Hexanol (0.3)	243-273	0.66-0.88	1.3x10^{-4}	1.7x10^{-7}	2.0x10^{-10}	24.8	22.4	17.8	32±0.9	46±3
1-Hexanol (0.4)	243-278	0.73-0.91	6.1x10^{-4}	4.6x10^{-7}	3.0x10^{-10}	26.6	24.0	18.8	34±0.9	52±4
1-Hexanol (0.5)	244-282	0.77-0.92	11x10^{-4}	7.2x10^{-7}	4.3x10^{-10}	27.4	24.8	19.7	35±0.9	52±4
1-Hexanol (0.6)	248-287	0.84-0.96	7.8x10^{-4}	7.0x10^{-7}	5.6x10^{-10}	27.0	24.8	20.4	34±0.5	44±2
1-Hexanol (0.7)	252-286	0.87-0.96	11.5x10^{-4}	8.9x10^{-7}	6.1x10^{-10}	27.4	25.2	20.6	34±0.4	46±2
1-Hexanol (0.8)	255-288	0.87-0.96	11.2x10^{-4}	9.4x10^{-7}	7.1x10^{-10}	27.4	25.3	20.9	34±0.5	43±2
1-Hexanol (0.9)	258-299	0.87-0.96	11.6x10^{-4}	10.3x10^{-7}	8.0x10^{-10}	27.5	25.4	21.3	34±0.9	41±3
1-Hexanol (1.0)	245-293	0.83-0.96	10.3x10^{-4}	9.7x10^{-7}	8.1x10^{-10}	27.3	25.3	21.3	33±0.7	40±3

BLE: 1V-1d: Dielectric Relaxation Parameters of 1-Octanol in n-Heptane Solution.

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Octanol (0.4)	257-288	0.70-0.82	4.2×10^{-3}	1.2×10^{-6}	3.1×10^{-10}	29.1	25.7	18.9	39±2	68±6
1-Octanol (0.5)	258-293	0.76-0.87	7.1×10^{-3}	2.2×10^{-6}	6.2×10^{-10}	29.7	26.7	20.6	39±1	61±5
1-Octanol (0.6)	258-293	0.80-0.91	8.6×10^{-3}	2.6×10^{-6}	7.2×10^{-10}	30.0	27.0	21.0	39±2	60±6
1-Octanol (0.7)	257-289	0.80-0.92	13.6×10^{-3}	3.5×10^{-6}	8.1×10^{-10}	30.5	27.4	21.3	40±1	62±4
1-Octanol (0.8)	257-287	0.81-0.93	14.9×10^{-3}	4.1×10^{-6}	10.0×10^{-10}	30.6	27.7	21.8	39±1	59±4
1-Octanol (0.9)	256-292	0.84-0.96	10.2×10^{-3}	3.6×10^{-6}	11.3×10^{-10}	30.2	27.5	22.1	38±2	54±8
1-Octanol (1.0)	262-309	0.86-0.97	7.6×10^{-3}	3.3×10^{-6}	12.4×10^{-10}	29.8	27.3	22.3	37±0.7	50±3

LE: IV-1e: Dielectric Relaxation Parameters of 1-Decanol in n-Heptane Solution

Alcohol le fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Decanol (0.3)	278-293	0.69-0.93	0.6×10^{-3}	5.3×10^{-7}	3.7×10^{-10}	26.8	24.3	19.3	34±3	50±10
Decanol (0.4)	273-297	0.75-0.92	1.0×10^{-3}	6.6×10^{-7}	3.8×10^{-10}	27.3	24.7	19.4	35±1.0	53±3
Decanol (0.5)	273-298	0.78-0.92	5.5×10^{-3}	18.2×10^{-7}	5.3×10^{-10}	29.4	26.3	20.2	39±2	61±7
Decanol (0.6)	272-302	0.81-0.91	9.8×10^{-3}	28.6×10^{-7}	7.5×10^{-10}	30.1	27.1	21.1	39±1	60±5
Decanol (0.7)	275-304	0.84-0.95	26.1×10^{-3}	53.9×10^{-7}	9.9×10^{-10}	31.3	28.1	21.8	41±1	64±3
Decanol (0.8)	275-308	0.86-0.95	30.7×10^{-3}	63.1×10^{-7}	11.6×10^{-10}	31.5	28.4	22.2	41±0.7	62±2
Decanol (0.9)	277-308	0.87-0.96	30.3×10^{-3}	67.2×10^{-7}	13.3×10^{-10}	31.5	28.5	22.5	41±2	60±7
Decanol (1.0)	273-308	0.72-0.90	3.2×10^{-2}	7.1×10^{-6}	1.4×10^{-9}	31.6	28.6	22.7	41±3	59±12

BLE: IV-2a: Dielectric Relaxation Parameters of Methanol in toluene solution

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
ethanol (0.1)	213-223	0.63-0.75	1.2×10^{-7}	1.9×10^{-9}	2.7×10^{-11}	16	15	13	19±2	22±10
ethanol (0.2)	203-236	0.76-0.81	4.1×10^{-7}	4.4×10^{-9}	4.2×10^{-11}	18	16	14	21±1	24±5
ethanol (0.3)	192-221	0.69-0.82	5.5×10^{-7}	5.0×10^{-9}	4.1×10^{-11}	18	16.5	13.8	22±1	27±5
ethanol (0.4)	188-225	0.75-0.85	4.3×10^{-7}	5.2×10^{-9}	5.6×10^{-11}	17.6	16.6	14.6	21±0.5	20±3
ethanol (o.5)	182-214	0.66-0.79	2.1×10^{-7}	4.9×10^{-9}	10.0×10^{-11}	17	16	16	17±1	4±3
ethanol (0.6)	182-235	0.75-0.90	1.6×10^{-7}	2.9×10^{-9}	4.8×10^{-11}	16	16	14	18±1	14±5
ethanol (0.7)	189-221	0.8-0.91	1.2×10^{-7}	2.9×10^{-9}	6.2×10^{-11}	16	15.6	14.8	17±0.8	8±4
ethanol (0.8)	179-210	0.86-0.93	0.80×10^{-7}	2.0×10^{-9}	4.7×10^{-11}	15.4	15.0	14.1	17±0.5	8±2
ethanol (0.9)	178-211	0.93-0.97	3.9×10^{-8}	1.5×10^{-9}	5.2×10^{-11}	14.6	14.6	14.4	15±0.3	1±2
ethanol (1.0)	176-234	0.98-1.0	1.8×10^{-8}	1.0×10^{-9}	5.0×10^{-11}	13.7	13.9	14.3	13±0.6	-4±0.6

BLE: IV-2b: Dielectric Relaxation Parameters of 1-Butanol in Toluene Solution.

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
-Butanol (0.3)	222-269	0.70-0.92	8.0×10^{-5}	10×10^{-8}	1.1×10^{-10}	24.1	21.5	16.3	32±0.9	52±4
-Butanol (0.4)	224-258	0.75-0.96	11.8×10^{-5}	14.0×10^{-8}	1.5×10^{-10}	24.6	22.1	17.0	32±1.0	50±5
-Butanol (0.5)	222-265	0.78-0.98	9.1×10^{-5}	14.6×10^{-8}	2.1×10^{-10}	24.3	22.1	17.9	31±1	42±5
-Butanol (0.6)	223-271	0.84-0.97	5.7×10^{-5}	13.5×10^{-8}	2.8×10^{-10}	23.7	22.0	18.6	29±0.3	34±1
-Butanol (0.7)	223-263	0.83-0.95	5.8×10^{-5}	14.5×10^{-8}	3.3×10^{-10}	23.7	22.1	19.0	28±0.6	31±3
-Butanol (0.8)	223-268	0.84-0.97	4.5×10^{-5}	14.0×10^{-8}	3.9×10^{-10}	23.4	22.1	19.4	27±0.4	27±2
-Butanol (0.9)	229-262	0.88-0.96	3.6×10^{-5}	13.7×10^{-8}	4.8×10^{-10}	23.1	22.0	19.9	26±0.8	22±3
-Butanol (1.0)	224-281	0.70-0.97	3.2×10^{-5}	13.0×10^{-8}	4.8×10^{-10}	22.9	21.9	19.9	26±0.4	20±2

BLE: IV-2C : Dielectric Relaxation Parameters of 1-Hexanol in Toluene Solution

Alcohol ole fraction)	$\Delta T(K)$	β-Range	Relaxation time $\tau_1(s)$			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Hexanol (0.3)	238-268	0.67-0.84	$2.7\text{x}10^{-4}$	$1.9\text{x}10^{-7}$	$1.1\text{x}10^{-10}$	25.6	22.5	16.3	35±2	62±9
1-Hexanol (0.4)	239-271	0.69-0.89	$4.9\text{x}10^{-4}$	$3.2\text{x}10^{-7}$	$1.8\text{x}10^{-10}$	26.4	23.4	17.6	35±1	59±5
1-Hexanol (0.5)	233-268	0.69-0.91	$2.4\text{x}10^{-3}$	$7.5\text{x}10^{-7}$	$2.0\text{x}10^{-10}$	28.4	24.9	17.8	39±3	70±10
1-Hexanol (0.6)	238-283	0.78-0.99	$8.6\text{x}10^{-4}$	$5.8\text{x}10^{-7}$	$3.5\text{x}10^{-10}$	27.1	24.4	19.2	35±0.8	53±3
1-Hexanol (0.7)	237-281	0.78-0.96	$11.9\text{x}10^{-4}$	$7.6\text{x}10^{-7}$	$4.3\text{x}10^{-10}$	27.5	24.9	19.7	35±0.9	52±3
1-Hexanol (0.8)	241-283	0.78-0.95	$12.8\text{x}10^{-4}$	$8.8\text{x}10^{-7}$	$5.4\text{x}10^{-10}$	27.6	25.1	20.3	35±1	49±6
1-Hexanol (0.9)	247-287	0.83-0.96	$11.6\text{x}10^{-4}$	$9.2\text{x}10^{-7}$	$6.5\text{x}10^{-10}$	27.5	25.2	20.7	34±0.6	45±2
1-Hexanol (1.0)	245-293	0.83-0.96	$10.3\text{x}10^{-4}$	$9.7\text{x}10^{-7}$	$8.1\text{x}10^{-10}$	27.3	25.3	21.3	33±0.7	40±3

BLE:IV-2d: Dielectric Relaxation Parameters of 1-Octanol in toluene solution

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
-Octanol (0.4)	258-287	0.74-0.77	$4.7x10^{-3}$	$1.1x10^{-6}$	$2.1x10^{-10}$	29.2	25.4	17.9	40±1	75±4
-Octanol (0.5)	258-297	0.77-0.83	$1.2x10^{-2}$	$2.0x10^{-6}$	$3.1x10^{-10}$	30.3	26.5	18.8	42±1	77±5
-Octanol (0.6)	258-302	0.76-0.86	$2.6x10^{-2}$	$3.4x10^{-6}$	$4.0x10^{-10}$	31.3	27.4	19.5	43±3	79±12
-Octanol (0.7)	258-302	0.78-0.88	$1.5x10^{-2}$	$3.1x10^{-6}$	$5.8x10^{-10}$	30.6	27.2	20.4	41±1	68±4
-Octanol (0.8)	262-302	0.82-0.91	$1.2x10^{-2}$	$3.2x10^{-6}$	$7.9x10^{-10}$	30.3	27.3	21.2	40±0.6	61±2
-Octanol (0.9)	262-297	0.81-0.90	$1.4x10^{-2}$	$3.8x10^{-6}$	$9.4x10^{-10}$	30.5	27.5	21.6	39±0.8	59±3
-Octanol (1.0)	262-309	0.86-0.97	$7.6x10^{-3}$	$3.3x10^{-6}$	$12.4x10^{-10}$	29.8	27.3	22.3	37±0.7	50±3

ABLE IV-2e: Dielectric Relaxation Parameters of 1-Decanol in toluene solution

Alcohol nole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
1 - Decanol (0.4)	268-288	0.62-0.75	$1.6\text{x}10^{-2}$	$2.0\text{x}10^{-6}$	$0.2\text{x}10^{-9}$	30.7	26.5	17.9	44±5	85±18
1 - Decanol (0.5)	268-296	0.67-0.80	$1.6\text{x}10^{-2}$	$2.5\text{x}10^{-6}$	$0.4\text{x}10^{-9}$	30.7	26.9	19.1	42±1	77±5
1 - Decanol (0.6)	273-298	0.75-0.85	$2.9\text{x}10^{-2}$	$4.1\text{x}10^{-6}$	$0.5\text{x}10^{-9}$	31.5	27.7	20.1	43±1	76±5
1 - Decanol (0.7)	273-298	0.81-0.86	$2.8\text{x}10^{-2}$	$4.9\text{x}10^{-6}$	$0.8\text{x}10^{-9}$	31.4	27.9	21.0	42±2	69±6
1 - Decanol (0.8)	273-298	0.81-0.88	$2.4\text{x}10^{-2}$	$5.1\text{x}10^{-6}$	$1.0\text{x}10^{-9}$	31.2	28.0	21.7	41±0.6	64±2
1 - Decanol (0.9)	276-298	0.78-0.90	$3.5\text{x}10^{-2}$	$6.8\text{x}10^{-6}$	$1.2\text{x}10^{-9}$	31.7	28.5	22.2	41±1	63±4
1 - Decanol (1.0)	273-308	0.72-0.90	$3.2\text{x}10^{-2}$	$7.1\text{x}10^{-6}$	$1.4\text{x}10^{-9}$	31.6	28.6	22.7	41±3	59±12

LE IV - 3a: Dielectric Relaxation Parameters of Methanol in Diethylether solution

Alcohol le fraction)	$\Delta T(K)$	β-Range	Relaxation time $\tau_1(s)$			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Methanol (0.4)	156-169	0.61-0.76	$3.6X10^{-9}$	$2.6X10^{-10}$	$1.6X10^{-11}$	11.6	11.6	11.5	12±0.5	0.7±3
Methanol (0.5)	151-177	0.70-0.84	$5X10^{-9}$	$2.9X10^{-10}$	$1.5X10^{-11}$	12.0	11.8	11.4	13±0.5	4±3
Methanol (0.6)	153-179	0.76-0.86	$6X10^{-9}$	$3.6X10^{-10}$	$1.8X10^{-11}$	12.3	12.2	11.8	13±0.2	3±1
Methanol (0.7)	163-183	0.78-0.87	$8X10^{-9}$	$4.4X10^{-10}$	$2.2X10^{-11}$	12.6	12.5	12.2	13±0.3	2±2
Methanol (0.8)	163-186	0.78-0.93	$10.5X10^{-9}$	$5.9X10^{-10}$	$2.9X10^{-11}$	12.9	12.9	12.9	13±0.5	0.06±3
Methanol (0.9)	173-191	0.77-0.90	$15X10^{-9}$	$6.8X10^{-10}$	$2.7X10^{-11}$	13.4	13.2	12.8	14±0.4	4±2
Methanol (1.0)	176-234	0.98-1.0	$18X10^{-9}$	$10.1X10^{-10}$	$5.0X10^{-11}$	13.7	13.9	14.3	13±0.6	-4±0.6

ABLE IV-3b Dielectric Relaxation Parameters of 1-Butanol in Diethyl ether solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Butanol (0.3)	188-223	0.61-0.83	$2.8\text{x}10^{-8}$	$1.4\text{x}10^{-9}$	$6.3\text{x}10^{-11}$	14.2	14.4	14.9	13±0.7	-5±3
1-Butanol (0.4)	188-223	0.64-0.84	$6.7\text{x}10^{-8}$	$2.5\text{x}10^{-9}$	$8.6\text{x}10^{-11}$	15.3	15.4	15.7	15±0.5	-3±3
1-Butanol (0.5)	202-238	0.69-0.88	$1.4\text{x}10^{-7}$	$4.7\text{x}10^{-9}$	$13.5\text{x}10^{-11}$	16.2	16.4	16.8	16±0.6	-4±2
1-Butanol (0.6)	194-239	0.71-0.90	$3.3\text{x}10^{-7}$	$7.6\text{x}10^{-9}$	$15.9\text{x}10^{-11}$	17.3	17.2	17.2	17±0.7	0.4±3
1-Butanol (0.7)	208-253	0.78-0.92	$6.8\text{x}10^{-7}$	$13.3\text{x}10^{-9}$	$22.9\text{x}10^{-11}$	18.2	18.2	18.1	18±0.7	0.3±3
1-Butanol (0.8)	219-263	0.83-0.93	$1.7\text{x}10^{-6}$	$23.8\text{x}10^{-9}$	$30.1\text{x}10^{-11}$	19.3	19.1	18.8	20±0.5	3±2
1-Butanol (0.9)	217-266	0.84-0.95	$3.9\text{x}10^{-6}$	$42.9\text{x}10^{-9}$	$41.9\text{x}10^{-11}$	20.4	20.1	19.6	21±0.6	5±2
1-Butanol (1.0)	224-281	0.70-0.97	$3.2\text{x}10^{-5}$	$1.3\text{x}10^{-7}$	$48.0\text{x}10^{-11}$	22.9	21.9	19.9	26±0.4	20±2.0

BLE IV-3c Dielectric Relaxation Parameters of 1-Hexanol in Diethyl ether solution

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
-Hexanol (0.3)	206-233	0.58-0.79	5.1x10^{-8}	2.3x10^{-9}	9.5x10^{-11}	14.9	15.3	15.9	14±0.4	-7±2
-Hexanol (0.4)	207-240	0.58-0.81	1.8x10^{-7}	5.4x10^{-9}	1.4x10^{-10}	16.5	16.7	16.9	16±1	-3±6
-Hexanol (0.5)	212-254	0.66-0.87	[illegible]8x10^{-7}	1.2x10^{-8}	1.7x10^{-10}	18.4	18.0	17.4	19±0.5	7±2
-Hexanol (0.6)	236-270	0.77-0.92	1.8x10^{-6}	2.4x10^{-8}	2.7x10^{-10}	19.4	19.1	18.6	20±0.6	6±2
-Hexanol (0.7)	238-278	0.80-0.93	6.3x10^{-6}	4.8x10^{-8}	3.2x10^{-10}	20.9	20.3	19.0	23±0.8	13±3
-Hexanol (0.8)	240-281	0.83-0.94	2.1x10^{-5}	10.1x10^{-8}	4.3x10^{-10}	22.5	21.5	19.7	25±0.7	18±3
-Hexanol (0.9)	250-293	0.84-0.95	1.3x10^{-4}	29.6x10^{-8}	5.8x10^{-10}	24.8	23.3	20.4	29±1.0	29±4
-Hexanol (1.0)	245-293	0.83-0.96	10.3x10^{-4}	9.7x10^{-7}	8.1x10^{-10}	27.3	25.3	21.3	33±0.7	40±3

TABLE IV- 3d: Dielectric Relaxation Parameters of 1- Octanol in Diethyl ether solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
-Octanol (0.3)	240-258	0.74-0.80	6.3×10^{-8}	3.3×10^{-9}	1.5×10^{-10}	15.2	15.9	17.1	13±3	-13±11
-Octanol (0.4)	248-275	0.79-0.87	1.1×10^{-6}	1.4×10^{-8}	1.5×10^{-10}	18.8	18.2	17.1	20±0.6	11±2
-Octanol (0.5)	247-277	0.80-0.91	2.2×10^{-6}	2.4×10^{-8}	2.3×10^{-10}	19.6	19.1	18.2	21±1	10±5
-Octanol (0.6)	252-293	0.82-0.93	1.2×10^{-5}	6.5×10^{-8}	3.1×10^{-10}	21.8	20.8	18.9	25±0.7	19±3
-Octanol (0.7)	258-293	0.85-0.94	3.7×10^{-5}	1.3×10^{-7}	4.2×10^{-10}	23.1	22.0	19.7	27±0.4	23±1
-Octanol (0.8)	263-298	0.87-0.95	1.7×10^{-4}	3.3×10^{-7}	5.9×10^{-10}	25	23.5	20.5	30±0.2	30±0.8
-Octanol (0.9)	268-308	0.89-0.96	1.1×10^{-3}	1.0×10^{-6}	8.3×10^{-10}	27.4	25.4	21.3	33±0.5	40±2
-Octanol (1.0)	262-309	0.86-0.97	7.6×10^{-3}	3.3×10^{-6}	12.4×10^{-10}	29.8	27.3	22.3	37±0.7	50±3

ABLE IV-3e: Dielectric Relaxation Parameters of 1- Decanol in Diethyl Ether Solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Decanol (0.5)	271-293	0.85-0.91	2.8×10^{-5}	8.8×10^{-8}	2.5×10^{-10}	22.8	21.3	18.3	27±0.8	30±3
1-Decanol (0.6)	272-291	0.85-0.91	4.6×10^{-5}	1.5×10^{-7}	4.2×10^{-10}	23.4	22.2	19.7	27±0.8	25±3
1-Decanol (0.7)	277-305	0.87-0.92	2×10^{-4}	3.3×10^{-7}	5×10^{-10}	25.3	23.5	20.0	30±0.6	35±2
1-Decanol (0.8)	281-318	0.89-0.94	1.1×10^{-3}	9.3×10^{-7}	7×10^{-10}	27.4	25.2	20.9	34±1	43±4
1- Decanol (0.9)	288-323	0.89-0.95	7.7×10^{-3}	2.9×10^{-6}	9.7×10^{-10}	29.8	27.1	21.7	38±1.2	54±4
1-Decanol (1.0)	273-308	0.72-0.90	3.2×10^{-2}	7.1×10^{-6}	1.4×10^{-9}	31.6	28.6	22.7	41±3	59±12

TABLE: V-1a: Dielectric Relaxation Parameters of Methanol in toluene solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Methanol (0.1)	213-223	0.63-0.75	1.2×10^{-7}	1.9×10^{-9}	2.7×10^{-11}	16	15	13	19±2	22±10
Methanol (0.2)	203-236	0.76-0.81	4.1×10^{-7}	4.4×10^{-9}	4.2×10^{-11}	18	16	14	21±1	24±5
Methanol (0.3)	192-221	0.69-0.82	5.5×10^{-7}	5.0×10^{-9}	4.1×10^{-11}	18	16.5	13.8	22±1	27±5
Methanol (0.4)	188-225	0.75-0.85	4.3×10^{-7}	5.2×10^{-9}	5.6×10^{-11}	17.6	16.6	14.6	21±0.5	20±3
Methanol (o.5)	182-214	0.66-0.79	2.1×10^{-7}	4.9×10^{-9}	10.0×10^{-11}	17	16	16	17±1	4±3
Methanol (0.6)	182-235	0.75-0.90	1.6×10^{-7}	2.9×10^{-9}	4.8×10^{-11}	16	16	14	18±1	14±5
Methanol (0.7)	189-221	0.8-0.91	1.2×10^{-7}	2.9×10^{-9}	6.2×10^{-11}	16	15.6	14.8	17±0.8	8±4
Methanol (0.8)	179-210	0.86-0.93	0.80×10^{-7}	2.0×10^{-9}	4.7×10^{-11}	15.4	15.0	14.1	17±0.5	8±2
Methanol (0.9)	178-211	0.93-0.97	3.9×10^{-8}	1.5×10^{-9}	5.2×10^{-11}	14.6	14.6	14.4	15±0.3	1±2
Methanol (1.0)	176-234	0.98-1.0	1.8×10^{-8}	1.0×10^{-9}	5.0×10^{-11}	13.7	13.9	14.3	13±0.6	-4±0.6

TABLE: V-1b: Dielectric Relaxation Parameters of Methanol in P-Cymene Solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Methanol (0.3)	205-239	0.63-0.88	7.3×10^{-7}	7.0×10^{-9}	6.0×10^{-11}	18.2	17.1	14.8	22±1	23±6
Methanol (0.4)	230-247	0.82-0.89	3.4×10^{-7}	5.9×10^{-9}	9.3×10^{-11}	17.3	16.8	15.8	19±0.7	10±3
Methanol (0.5)	205-223	0.74-0.83	2.8×10^{-7}	5.4×10^{-9}	9.5×10^{-11}	17.0	16.7	15.9	18±1	7±4
Methanol (0.6)	205-238	0.79-0.84	2.4×10^{-7}	4.8×10^{-9}	8.6×10^{-11}	16.8	16.5	15.7	18±0.3	8±1
Methanol (0.7)	202-235	0.79-0.88	1.5×10^{-7}	3.6×10^{-9}	7.8×10^{-11}	16.3	16.0	15.4	17±0.3	6±1
Methanol (0.8)	177-191	0.84-0.89	2.6×10^{-8}	1.2×10^{-9}	5.3×10^{-11}	14.1	14.2	14.4	14±1	-2±8
Methanol (0.9)	177-196	0.74-0.95	1.9×10^{-8}	1.3×10^{-9}	7.9×10^{-11}	13.7	14.3	15.5	12±1	-12±8
Methanol (1.0)	176-234	0.98-1.0	1.8×10^{-8}	10.1×10^{-10}	5.0×10^{-11}	13.7	13.9	14.3	13±0.6	-4±0.6

ABLE V - 1c: Dielectric Relaxation Parameters of Methanol in Dichloromethane solution

Alcohol (mole fraction)	$\Delta T(K)$	β-Range	Relaxation time $\tau_1(s)$			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Methanol (0.3)	179-211	0.66-0.80	6.6×10^{-8}	1.6×10^{-9}	3.5×10^{-11}	15.2	14.6	13.4	17±0.6	12±3
Methanol (0.4)	182-206	0.79-0.86	5.5×10^{-8}	1.8×10^{-9}	5×10^{-11}	15.0	14.7	14.3	16±0.3	5±2
Methanol (0.5)	178-206	0.82-0.87	4.5×10^{-8}	1.7×10^{-9}	5.7×10^{-11}	14.8	14.7	14.7	15±0.3	0.9±2
Methanol (0.6)	173-206	0.83-0.90	3.8×10^{-8}	1.5×10^{-9}	5.3×10^{-11}	14.6	14.5	14.4	15±0.2	0.7±2
Methanol (0.7)	174-206	0.83-0.92	3.1×10^{-8}	1.3×10^{-9}	4.6×10^{-11}	14.3	14.2	14.1	14±0.2	1±1
Methanol (0.8)	173-204	0.88-0.94	2.3×10^{-8}	1.0×10^{-9}	4.2×10^{-11}	13.9	13.9	13.9	14±0.2	0.3±0.9
Methanol (0.9)	174-209	0.87-0.93	2.2×10^{-8}	0.8×10^{-9}	2.8×10^{-11}	13.9	13.6	12.9	15±0.4	7±2
Methanol (1.0)	176-234	0.98-1.0	1.8×10^{-8}	10.1×10^{-10}	5.0×10^{-11}	13.7	13.9	14.3	13.0±0.6	-4±0.6

TABLE V - 2a: Dielectric Relaxation Parameters of Methanol in Diethyl ether solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Methanol (0.4)	156-169	0.61-0.76	3.6×10^{-9}	2.6×10^{-10}	1.6×10^{-11}	11.6	11.6	11.5	12±0.5	0.7±3
Methanol (0.5)	151-177	0.70-0.84	5×10^{-9}	2.9×10^{-10}	1.5×10^{-11}	12.0	11.8	11.4	13±0.5	4±3
Methanol (0.6)	153-179	0.76-0.86	6×10^{-9}	3.6×10^{-10}	1.8×10^{-11}	12.3	12.2	11.8	13±0.2	3±1
Methanol (0.7)	163-183	0.78-0.87	8×10^{-9}	4.4×10^{-10}	2.2×10^{-11}	12.6	12.5	12.2	13±0.3	2±2
Methanol (0.8)	163-186	0.78-0.93	10.5×10^{-9}	5.9×10^{-10}	2.9×10^{-11}	12.9	12.9	12.9	13±0.5	0.06±3
Methanol (0.9)	173-191	0.77-0.90	15×10^{-9}	6.8×10^{-10}	2.7×10^{-11}	13.4	13.2	12.8	14±0.4	4±2
Methanol (1.0)	176-234	0.98-1.0	18×10^{-9}	10.1×10^{-10}	5.0×10^{-11}	13.7	13.9	14.3	13±0.6	-4±0.6

LE V - 2b: Dielectric Relaxation Parameters of Methanol in Di-n-butyl ether solution

Alcohol le fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
Methanol (0.4)	188-215	0.46-0.82	0.55×10^{-7}	14.4×10^{-10}	33.2×10^{-12}	15.0	14.5	13.3	17±2	12±8
Methanol (0.5)	195-229	0.76-0.84	0.5×10^{-7}	16.1×10^{-10}	46.9×10^{-12}	14.9	14.6	14.2	16±0.5	5±2
Methanol (0.6)	184-225	0.72-0.86	0.63×10^{-7}	17.6×10^{-10}	43.2×10^{-12}	15.2	14.8	13.9	16±0.6	8±3
Methanol (0.7)	177-211	0.69-0.87	0.65×10^{-7}	17.2×10^{-10}	40.5×10^{-12}	15.2	14.7	13.8	17±0.8	10±4
Methanol (0.8)	177-213	0.82-0.90	0.49×10^{-7}	15.5×10^{-10}	43.8×10^{-12}	14.9	14.6	14.0	16±0.3	6±1
Methanol (0.9)	179-201	0.91-0.94	0.37×10^{-7}	13.6×10^{-10}	44.1×10^{-12}	14.5	14.4	14.0	15±0.5	3±3
Methanol (1.0)	176-234	0.98-1.0	1.8×10^{-8}	10.1×10^{-10}	50×10^{-12}	13.7	13.9	14.3	13.0±0.6	-4±0.6

ABLE V-2c: Dielectric Relaxation Parameters of Methanol in Pyridine solution

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
Methanol (0.3)	173-199	0.79-0.87	$2.6\text{X}10^{-8}$	$3.7\text{X}10^{-10}$	$4.6\text{X}10^{-12}$	14.1	12.2	8.4	20±1	38±5
Methanol (0.4)	166-199	0.75-0.90	$3.1\text{X}10^{-8}$	$3.9\text{X}10^{-10}$	$4.3\text{X}10^{-12}$	14.3	12.3	8.2	20±0.6	41±4
Methanol (0.5)	163-197	0.74-0.90	$3.8\text{X}10^{-8}$	$3.6\text{X}10^{-10}$	$3.1\text{X}10^{-12}$	14.6	12.2	7.4	22±1.0	48±6
Methanol (0.6)	171-200	0.84-0.93	$2.6\text{X}10^{-8}$	$4.4\text{X}10^{-10}$	$6.7\text{X}10^{-12}$	14.1	12.5	9.3	19±0.6	32±3
Methanol (0.7)	172-197	0.87-0.95	$2.5\text{X}10^{-8}$	$4.8\text{X}10^{-10}$	$8.5\text{X}10^{-12}$	14.0	12.6	9.9	18±1	28±6
Methanol (0.8)	164-194	0.84-0.95	$2.5\text{X}10^{-8}$	$5.2\text{X}10^{-10}$	$9.3\text{X}10^{-12}$	14.1	12.8	10.1	18±1	26±7
Methanol (0.9)	168-201	0.90-0.95	$2.0\text{X}10^{-8}$	$6.9\text{X}10^{-10}$	$21\text{X}10^{-12}$	13.7	13.2	12.2	15±0.4	10±2
Methanol (1.0)	176-234	0.98-1.0	$1.8\text{X}10^{-8}$	$10.1\text{X}10^{-10}$	$50\text{X}10^{-12}$	13.7	13.9	14.3	13.0±0.6	-4±0.6

TABLE: V-3: Relaxation Parameters for Methanol and Other Alcohol Mixtures in Toluene

Alcohol mixture with concentration in mole fraction	ΔT (°K)	τ (200) (sec)	ΔG_E (kJ mol^{-1})	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
Methanol (0.4) + Toluene (0.6)	188.2-225.0	5.2×10^{-9}	16.6	20.6±0.5	20.0±2.5
Methanol (0.8) + Toluene (.2)	178.5-209.5	2.0×10^{-9}	15.0	16.7±0.5	8.5±2.1
Methanol (0.4) + Norborneol (0.4)+ Toluene (0.2)	216.5-257.2	106×10^{-9}	21.6	29.9±1.2	41.6±5.1
Methanol (0.4) + 1-Octanol (0.4) + Toluene (0.2)	238.5-265.2	68×10^{-9}	20.9	26.4±0.4	27.8±1.6
Methanol (0.5) + 1-Octanol (0.5)	265.0-293.8	227×10^{-9}	22.9	32.6±2.8	48.4±10.1
Methanol (0.3) + Toluene (0.7)	192.1-220.9	5.0×10^{-9}	16.5	22.0±1.0	27.3±5.0
Methanol (0.6) + Toluene (0.4)	182.0-235.0	2.9×10^{-9}	16.0	18.4±1.0	14.0±5.0
Methanol (0.3) + Norborneol (0.3) + Toluene (0.4)	216.7-256.0	88×10^{-9}	21.3	29.5±0.6	41.0±2.5
Methanol (0.3) + 1- Octanol (0.3)+ Toluene (0.4)	239.7-253.6	63.3×10^{-9}	20.7	26.7±1.9	29.8±7.9
Methanol (0.4) + 1-Octanol (0.4) + Toluene (0.2)	238.5-265.2	68×10^{-9}	20.9	26.4±0.4	27.8±1.6

TABLE: V-3: Relaxation Parameters for Methanol and other Alcohol Mixtures in Toluene continued

Alcohol mixture with concentration in mole fraction	ΔT (°K)	τ (200) (sec)	ΔG_E (kJ mol^{-1})	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
Methanol (0.15) + Fenchyl Alcohol (0.15) + Toluene (0.7)	211.9-238.2	$67.6\text{x}10^{-9}$	20.8	46.1±2.5	126.3±10.9
Methanol (0.3) + Toluene (0.7)	192.1-220.9	$5.0\text{x}10^{-9}$	16.5	22.0±1.0	27.3±5.0
Methanol (0.15) + 1-Octanol (0.15) Toluene (0.7)	224.8-260.7	$45.4\text{x}10^{-9}$	20.2	29.9±0.5	48.6±2.3
Fenchyl Alcohol (0.3) + 1-Octanol (0.7)	267.9-301.7	$10500\text{x}10^{-9}$	29.2	43.9±1.5	73.3±5.3
Methanol (0.5) + 1-Octanol (0.5)	265.0-293.8	$227\text{x}10^{-9}$	22.9	32.6±2.8	48.4±10.1

Table V-4: Key Relaxation Parameters for Methanol (0.3mf) in different solvents

Relaxation Parameters	Di-n-butyl ether	Pyridine	Dichloromethane	Toluene	p-Cymene
[A]					
ΔH_E (kJ mol^{-1})	13±1.2	20±1			
ΔS_E (J K^{-1} mol^{-1})	-4.3±6	38±5.3			
ΔG_E (kJ mol^{-1})	13.9	12.2			
$\tau_{1(200)}$ (s)	$0.1X10^{-10}$	$3.7X10^{-10}$			
[B]					
ΔH_E (kJ mol^{-1})			17±0.6		
ΔS_E (J K^{-1} mol^{-1})			12.2±3.4		
ΔG_E (kJ mol^{-1})			14.6		
$\tau_{1(200)}$ (s)			$16X10^{-10}$		
[C]					
ΔH_E (kJ mol^{-1})				22±1	21.7±1.3
ΔS_E (J K^{-1} mol^{-1})				27±5	23±6.0
ΔG_E (kJ mol^{-1})				16.5	17.1
$\tau_{1(200)}$ (s)				$50X10^{-10}$	$70X10^{-10}$

Table V-5: Key Relaxation Parameters for Methanol (0.4mf) in different solvents

Relaxation Parameters	Di-n-butyl ether	Diethyl ether	Pyridine	Dichloro-methane	Toluene	P-Cymene
[A]						
ΔH_E (kJ mol^{-1})	16.8±1.6	11.7±0.5	20.4±0.6			
ΔS_E (J K^{-1} mol^{-1})	11.6±8.2	0.7±2.9	40.8±3.6			
$\Delta G_{E(200)}$ (kJ mol^{-1})	14.5	11.6	12.3			
$\tau_{1(200)}$ (s)	$14.4\text{X}10^{-10}$	$2.6\text{X}10^{-10}$	$3.9\text{X}10^{-10}$			
[B]						
ΔH_E (kJ mol^{-1})				15.7±0.3		
ΔS_E (J K^{-1} mol^{-1})				4.7±1.8		
$\Delta G_{E(200)}$ (kJ mol^{-1})				14.7		
$\tau_{1(200)}$ (s)				$1.8\text{X}10^{-9}$		
[C]						
ΔH_E (kJ mol^{-1})					20.6±0.5	18.7±0.7
ΔS_E (J K^{-1} mol^{-1})					20.0±2.5	9.5±2.8
$\Delta G_{E(200)}$ (kJ mol^{-1})					16.6	16.8
$\tau_{1(200)}$ (s)					$5.2\text{X}10^{-9}$	$5.9\text{X}10^{-9}$

Table V-6: Key Relaxation Parameters for Methanol (0.5mf) in different solvents

Relaxation Parameters	Di-n-butyl ether	Diethyl ether	Pyridine	Dichloro-methane	Toluene	P-Cymene
[A]						
ΔH_E (kJ mol^{-1})	15.6±0.5	12.7±0.5	21.8±1.0			
ΔS_E (J K^{-1} mol^{-1})	4.8±2.2	4.4±2.9	47.9±6			
$\Delta G_{E(200)}$ (kJ mol^{-1})	14.6	11.8	12.2			
$\tau_{1(200)}$ (s)	16.1×10^{-10}	2.9×10^{-10}	3.6×10^{-10}			
[B]						
ΔH_E (kJ mol^{-1})				14.9±0.3		
ΔS_E (J K^{-1} mol^{-1})				0.9±1.7		
$\Delta G_{E(200)}$ (kJ mol^{-1})				14.7		
$\tau_{1(200)}$ (s)				1.7×10^{-9}		
[C]						
ΔH_E (kJ mol^{-1})					17.4±1	18.1±1.0
ΔS_E (J K^{-1} mol^{-1})					4.4±3	7.4±4.5
$\Delta G_{E(200)}$ (kJ mol^{-1})					16.0	16.7
$\tau_{1(200)}$ (s)					4.9×10^{-9}	5.4×10^{-9}

TABLE VI - 1: Comparison of the Enthalpies of Activation (ΔH_E) Obtained by our study with those of the literature for some isomeric alcohols.

Enthalpy of Activation (ΔH_E) kJ mol^{-1}	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
our work	36	51	55	54.8								
literature	32	49	65	65								
our work					39	52	51	50				
literature					35	52	68	68				
our work									40.5	48	57	53
literature									43	48	--	--

ABLE: V1-2a Dielectric Relaxation Parameters of 1 - Heptanol in Toluene Solution

Alcohol mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Heptanol (0.3)	239-273	0.63-0.95	4.4×10^{-4}	2.5×10^{-7}	1.3×10^{-10}	26.2	23.1	16.8	36±0.6	63±8
1-Heptanol (0.4)	250-279	0.64-0.90	9.4×10^{-4}	5.0×10^{-7}	2.4×10^{-10}	27.2	24.2	18.2	36±2	60±6
1-Heptanol (0.5)	239-279	0.73-0.93	28×10^{-4}	9.7×10^{-7}	3.0×10^{-10}	28.5	25.3	18.8	38±2	65±6
1-Heptanol (0.6)	242-280	0.71-0.94	42×10^{-4}	14×10^{-7}	4.2×10^{-10}	29.0	25.9	19.6	39±1	63±5
1-Heptanol (0.7)	247-285	0.75-0.95	39×10^{-4}	15.8×10^{-7}	5.7×10^{-10}	28.9	26.1	20.4	38±1	57±4
1-Heptanol (0.8)	248-291	0.80-0.98	45×10^{-4}	18.7×10^{-7}	6.9×10^{-10}	29.1	26.4	20.9	37±0.4	55±2
1-Heptanol (0.9)	247-291	0.77-0.96	67×10^{-4}	25×10^{-7}	8.3×10^{-10}	29.6	26.9	21.3	38±1	55±4
1-Heptanol (1.0)	253-295	0.77-0.97	36×10^{-4}	20.1×10^{-7}	9.9×10^{-10}	28.9	26.5	21.8	36±0.6	47±2

BLE: V1-2b Dielectric Relaxation Parameters of 2-Heptanol in Toluene Solution

Alcohol ole fraction)	$\Delta T(K)$	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
2-Heptanol (0.4)	245-273	0,66-0.73	$3.9x10^{-3}$	$6.0x10^{-7}$	$0.84x10^{-10}$	28.9	24.5	15.6	42±0.8	89±3
2-Heptanol (0.5)	253-281	0.74-0.79	$1.0x10^{-2}$	$1.2x10^{-6}$	$1.3x10^{-10}$	30.1	25.6	16.6	44±0.6	90±2
2-Heptanol (0.6)	253-286	0.76-0.82	$2.7x10^{-2}$	$2.3x10^{-6}$	$1.8x10^{-10}$	31.4	26.7	17.5	45±3	93±10
2-Heptanol (0.7)	253-290	0.79-0.86	$5.2x10^{-2}$	$4.1x10^{-6}$	$2.9x10^{-10}$	32.2	27.7	18.7	46±0.7	90±3
2-Heptanol (0.8)	253-299	0.78-0.89	$1.4x10^{-1}$	$7.8x10^{-6}$	$3.9x10^{-10}$	33.4	28.7	19.4	47±1	93±4
2-Heptanol (0.9)	253-299	0.76-0.90	$3.5x10^{-1}$	$1.5x10^{-5}$	$5.5x10^{10}$	34.6	29.8	20.3	49±0.6	95±2
2-Heptanol (1.0)	253-299	0.76-0.90	1.3	$3.2x10^{-5}$	$7.3x10^{-10}$	36.1	31.1	21.0	51±1	101±5

TABLE: V1-2c: Dielectric Relaxation Parameters of 3-Heptanol in toluene solution

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
3-Heptanol (0.4)	245-267	0.59-0.78	1.2×10^{-4}	1.1×10^{-7}	0.84×10^{-10}	24.6	21.6	15.6	34±0.5	60±6
3-Heptanol (0.5)	246-274	0.62-0.85	1.2×10^{-3}	3.8×10^{-7}	1.1×10^{-10}	27.5	23.7	16.2	39±2	76±8
3-Heptanol (0.6)	250-278	0.70-0.90	4.7×10^{-3}	9.4×10^{-7}	1.7×10^{-10}	29.2	25.2	17.4	41±4	79±14
3-Heptanol (0.7)	261-290	0.79-0.93	3.6×10^{-2}	3.1×10^{-6}	2.3×10^{-10}	31.7	27.2	18.1	45±3	91±12
3-Heptanol (0.8)	265-296	0.82-0.95	3.8×10^{-1}	1.2×10^{-5}	3.3×10^{-10}	34.7	29.4	19.0	50±4	104±15
3-Heptanol (0.9)	268-296	0.82-0.96	5.1	5.1×10^{-5}	4.5×10^{-10}	37.9	31.9	19.8	56±3	121±12
3-Heptanol (1.0)	276-303	0.90-0.98	5.7	6.8×10^{-5}	7.1×10^{-10}	38.1	32.3	20.9	55±3	114±10

TABLE: V1-2d: Dielectric Relaxation Parameters of 4-Heptanol in Toluene Solution.

Alcohol (mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
4-Heptanol (0.4)	245-266	0.59-0.86	2.1×10^{-5}	5.0×10^{-8}	1.0×10^{-10}	22.5	20.4	16.2	29±1	42±6
4-Heptanol (0.5)	247-271	0.59-0.81	3.3×10^{-4}	1.2×10^{-7}	1.1×10^{-10}	25.9	22.7	16.2	36±1	64±5
4-Heptanol (0.6)	254-277	0.64-0.86	5.6×10^{-3}	9.3×10^{-7}	1.4×10^{-10}	29.4	25.2	16.8	42±2	84±8
4-Heptanol (0.7)	261-284	0.75-0.91	2.7×10^{-2}	2.5×10^{-6}	2.0×10^{-10}	31.4	26.8	17.7	45±3	91±9
4-Heptanol (0.8)	262-296	0.77-0.94	5.0×10^{-1}	1.3×10^{-5}	2.8×10^{-10}	35.0	29.5	18.6	52±3	110±9
4-Heptanol (0.9)	270-298	0.83-0.95	2.8	3.6×10^{-5}	4.2×10^{-10}	37.1	31.3	19.6	55±2	117±8
4-Heptanol (1.0)	278-304	0.83-0.96	4.8	6.0×10^{-5}	6.7×10^{-10}	37.8	32.1	20.8	55±3	114±9

BLE: VI-3a: Dielectric Relaxation Parameters of 1-Octanol in Toluene Solution.

Alcohol mole fraction)	$\Delta T(K)$	β-Range	Relaxation time $\tau_1(s)$			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
1-Octanol (0.4)	258-287	0.74-0.77	4.7×10^{-3}	1.1×10^{-6}	2.1×10^{-10}	29.2	25.4	17.9	40±1	75±4
1-Octanol (0.5)	258-297	0.77-0.83	1.2×10^{-2}	2.0×10^{-6}	3.1×10^{-10}	30.3	26.5	18.8	42±1	77±5
1-Octanol (0.6)	258-302	0.76-0.86	2.6×10^{-2}	3.4×10^{-6}	4.0×10^{-10}	31.3	27.4	19.5	43±3	79±12
1-Octanol (0.7)	258-302	0.78-0.88	1.5×10^{-2}	3.1×10^{-6}	5.8×10^{-10}	30.6	27.2	20.4	41±1	68±4
1-Octanol (0.8)	262-302	0.82-0.91	1.2×10^{-2}	3.2×10^{-6}	7.9×10^{-10}	30.3	27.3	21.2	40±0.6	61±2
1-Octanol (0.9)	262-297	0.81-0.90	1.4×10^{-2}	3.8×10^{-6}	9.4×10^{-10}	30.5	27.5	21.6	39±0.8	59±3
1-Octanol (1.0)	262-309	0.86-0.97	7.6×10^{-3}	3.3×10^{-6}	12.4×10^{-10}	29.8	27.3	22.3	37±0.7	50±3

ABLE: V1-3b: Dielectric Relaxation Parameters of 2-Octanol in Toluene Solution.

Alcohol nole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
2-Octanol (0.4)	245-268	0.59-0.64	1.1×10^{-1}	2.2×10^{-6}	3.7×10^{-11}	33.1	26.6	13.6	53±3	130±12
2-Octanol (0.5)	253-273	0.66-0.70	5.6×10^{-2}	2.4×10^{-6}	8.8×10^{-11}	32.3	26.7	15.7	49±4	110±16
2-Octanol (0.6)	253-283	0.63-0.78	4.5×10^{-2}	2.8×10^{-6}	1.5×10^{-10}	32	27	17.1	47±0.8	99±3
2-Octanol (0.7)	253-290	0.62-0.78	2.2×10^{-1}	7.2×10^{-6}	2.1×10^{-10}	34	29	18	50±2	107±8
2-Octanol (0.8)	253-295	0.60-0.82	4.9×10^{-1}	1.3×10^{-5}	3.0×10^{-10}	35	30	19	51±2	108±9
2-Octanol (0.9)	253-299	0.59-0.83	3.5	4.4×10^{-5}	5.0×10^{-10}	37.4	31.6	20.0	55±4	116±15
2-Octanol (1.0)	258-299	0.66-0.87	1.2	2.8×10^{-5}	5.7×10^{-10}	36.1	30.9	20.4	52±3	105±9

ABLE: V1-3c: Dielectric Relaxation Parameters of 3-Octanol in Toluene Solution.

Alcohol nole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
3-Octanol (0.5)	253-272	1.0-1.0	$1.5\text{x}10^{-5}$	$1.3\text{x}10^{-7}$	$0.9\text{x}10^{-10}$	22.1	21.9	21.5	23±6	3±23
3-Octanol (0.6)	247-267	1.0-1.0	$1.8\text{x}10^{-3}$	$9.0\text{x}10^{-7}$	$4.0\text{x}10^{-10}$	28.0	25.2	19.5	37±2	57±8
3-Octanol (0.7)	260-277	1.0-1.0	$1.9\text{x}10^{-2}$	$3.0\text{x}10^{-6}$	$4.4\text{x}10^{-10}$	30.9	27.2	19.7	42±4	75±15
3-Octanol (0.8)	259-289	1.0-1.0	$5.6\text{x}10^{-2}$	$6.0\text{x}10^{-6}$	$5.8\text{x}10^{-10}$	32.3	28.3	20.4	44±2	79±6
3-Octanol (1.0)	283-307	0.84-0.97	1.0	$2.9\text{x}10^{-5}$	$7.0\text{x}10^{-10}$	35.9	30.9	20.9	51±2	100±8

BLE V1-3d: Dielectric Relaxation Parameters of 4-Octanol in Toluene Solution.

Alcohol ole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
			150 K	200 K	300 K	150 K	200 K	300 K		
4-Octanol (0.5)	238-252	0.39-0.58	5×10^{-3}	3.8×10^{-7}	0.3×10^{-10}	29.3	23.8	12.7	46±5	110±22
4-Octanol (0.6)	250-270	0.53-0.76	7.1×10^{-4}	3.1×10^{-7}	1.2×10^{-10}	26.8	23.4	16.5	37±5	69±18
4-Octanol (0.7)	256-279	0.60-0.84	7.4×10^{-3}	1.2×10^{-6}	1.6×10^{-10}	29.8	25.6	17.3	42±4	83±14
4-Octanol (0.8)	265-287	0.68-0.88	4.0×10^{-2}	3.3×10^{-6}	2.5×10^{-10}	31.8	27.3	18.3	45±3	90±11
4-Octanol (0.9)	262-293	0.82-0.89	3.1×10^{-1}	1.1×10^{-5}	3.1×10^{-10}	34.4	29.2	18.9	50±2	104±7
4-Octanol (1.0)	273-303	0.70-0.96	5.6×10^{-1}	1.8×10^{-5}	5.4×10^{-10}	35.1	30.2	20.2	50±4	99±15

ABLE V1-4a: Dielectric Relaxation Parameters of 1-Decanol in Toluene Solution.

Alcohol mole fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
1-Decanol (0.4)	268-288	0.62-0.75	1.6×10^{-2}	2.0×10^{-6}	0.2×10^{-9}	30.7	26.5	17.9	44±5	85±18
1-Decanol (0.5)	268-296	0.67-0.80	1.6×10^{-2}	2.5×10^{-6}	0.4×10^{-9}	30.7	26.9	19.1	42±1	77±5
1-Decanol (0.6)	273-298	0.75-0.85	2.9×10^{-2}	4.1×10^{-6}	0.5×10^{-9}	31.5	27.7	20.1	43±1	76±5
1-Decanol (0.7)	273-298	0.81-0.86	2.8×10^{-2}	4.9×10^{-6}	0.8×10^{-9}	31.4	27.9	21.0	42±2	69±6
1-Decanol (0.8)	273-298	0.81-0.88	2.4×10^{-2}	5.1×10^{-6}	1.0×10^{-9}	31.2	28.0	21.7	41±0.6	64±2
1-Decanol (0.9)	276-298	0.78-0.90	3.5×10^{-2}	6.8×10^{-6}	1.2×10^{-9}	31.7	28.5	22.2	41±1	63±4
1-Decanol (1.0)	273-308	0.72-0.90	3.2×10^{-2}	7.1×10^{-6}	1.4×10^{-9}	31.6	28.6	22.7	41±3	59±12

LE VI-4b: Dielectric Relaxation Parameters of 2-Decanol in Toluene Solution.

Alcohol le fraction)	ΔT(K)	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
-Decanol (0.5)	243-274	0.39-0.72	3.9×10^{-2}	1.8×10^{-6}	0.74×10^{-10}	31.8	26.3	15.3	48±5	110±19
-Decanol (0.6)	257-278	0.52-0.65	8.1×10^{-2}	2.9×10^{-6}	0.95×10^{-10}	32.7	27.1	15.9	50±2	112±9
-Decanol (0.7)	257-275	0.54-0.81	1.2×10^{-1}	4.9×10^{-6}	1.8×10^{-10}	33.2	28.0	17.5	49±2	105±7
-Decanol (0.8)	260-287	0.57-0.73	2.3×10^{-1}	7.9×10^{-6}	2.4×10^{-10}	34	28.8	18.3	50±0.8	105±3
-Decanol (0.9)	266-290	0.60-0.70	4.9×10^{-1}	12.4×10^{-6}	2.8×10^{-10}	35	29.5	18.6	51±2	109±2
-Decanol (1.0)	273-298	0.65-0.77	2.1×10^{-1}	10.3×10^{-6}	4.4×10^{-10}	33.9	29.2	19.7	48±0.9	95±3

BLE VI-4c: Dielectric Relaxation Parameters of 3-Decanol in toluene solution

Alcohol ole fraction)	$\Delta T(K)$	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
-decanol (0.5)	253-280	0.47-0.76	1.9×10^{-3}	5.0×10^{-7}	1.2×10^{-10}	28.0	24.2	16.5	40±4	77±14
-decanol (0.6)	257-287	0.54-0.78	1.1×10^{-2}	1.5×10^{-6}	1.9×10^{-10}	30.2	26.0	17.6	43±2	84±7
-decanol (0.7)	275-296	0.59-0.82	3.2×10^{-2}	3.3×10^{-6}	3.1×10^{-10}	31.6	27.3	18.9	44±0.8	85±3
-decanol (0.8)	275-301	0.59-0.89	3.1×10^{-1}	1.2×10^{-5}	4.1×10^{-10}	34.4	29.5	19.6	49±3	99±9
-decanol (0.9)	280-304	0.59-0.84	3.5	4.7×10^{-5}	5.6×10^{-10}	37.4	31.7	20.3	55±2	114±8
-decanol (1.0)	283-304	0.65-0.92	13.7	11.2×10^{-4}	8.2×10^{-10}	39.1	33.2	21.3	57±5	119±18

ABLE VI-4d: Dielectric Relaxation Parameters of 4-Decanol in toluene solution

Alcohol (mole fraction)	$\Delta T(K)$	β-Range	Relaxation time τ_1(s)			ΔG_E (kJ mol^{-1})			ΔH_E	ΔS_E
			150 K	200 K	300 K	150 K	200 K	300 K	(kJ mol^{-1})	(J K^{-1} mol^{-1})
4-Decanol (0.6)	256-282	0.41-0.70	1.4×10^{-3}	4.9×10^{-7}	1.5×10^{-10}	27.7	24.1	17.0	38±2	71±9
4-Decanol (0.7)	261-291	0.46-0.75	9.1×10^{-3}	1.5×10^{-6}	2.1×10^{-10}	30.0	25.9	17.9	42±3	81±10
4-Decanol (0.8)	277-291	0.63-0.78	2.3×10^{-2}	2.8×10^{-6}	3.0×10^{-10}	31.2	27.0	18.8	44±1	83±4
4-Decanol (0.9)	276-292	0.59-0.82	1.1×10^{-1}	7.1×10^{-6}	4.1×10^{-10}	33.1	28.6	19.6	47±4	90±12
4-Decanol (1.0)	274-292	0.55-0.86	1.6	3.2×10^{-5}	5.6×10^{-10}	36.5	31.0	20.3	53±6	107±22

TABLE VI-5: The Dielectric relaxation parameters for the isomeric alcohols at 0.6 MF of Alcohol Concentration.

	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
ΔH_E (kJ mol^{-1})	39	45	39	42								
ΔS_E (J K^{-1} mol^{-1})	63	93	76	84								
$\Delta G_{E(300)}$ (kJ mol^{-1})	20	18	16	17								
$\tau_{1(300)}$(s)	4x10^{-10}	2x10^{-10}	1x10^{-10}	1x10^{-10}								
ΔH_E (kJ mol^{-1})					43	47	37	37				
ΔS_E (J K^{-1} mol^{-1})					79	99	57	69				
$\Delta G_{E(300)}$ (kJ mol^{-1})					20	17	20	17				
$\tau_{1(300)}$ (s)					4x10^{-10}	2x10^{-10}	4x10^{-10}	1x10^{-10}				

TABLE VI-5:

CONTINUED

	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
ΔH_E (kJ mol^{-1})									43	50	43	38
ΔS_E (J K^{-1} mol^{-1})									76	112	84	71
$\Delta G_{E(300)}$ (kJ mol^{-1})									20	16	18	17
$\tau_{1(300)}$ (s)									$5x10^{-10}$	$1x10^{-10}$	$2x10^{-10}$	$2x10^{-10}$

TABLE VI-6: The Dielectric Relaxation Parameters for the Isomeric Alcohols at 0.7 MF of Alcohol Concentration.

Relaxation Parameters	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
ΔH_E (kJ mol^{-1})	38	46	45	45								
ΔS_E (J K^{-1} mol^{-1})	57	90	91	91								
$\Delta G_{E(300)}$ (kJ mol^{-1})	20	19	18	18								
$\tau_{1(300)}$ (s)	6x10^{-10}	3x10^{-10}	2x10^{-10}	2x10^{-10}								
ΔH_E (kJ mol^{-1})					41	50	42	42				
ΔS_E (J K^{-1} mol^{-1})					68	107	75	83				
$\Delta G_{E(300)}$ (kJ mol^{-1})					20	18	20	17				
$\tau_{1(300)}$(s)					6x10^{-10}	2x10^{-10}	4x10^{-10}	2x10^{-10}				

TABLE VI-6: The Dielectric Relaxation Parameters for the Isomeric Alcohols at 0.7MF of Alcohol Concentration.

CONTINUED

Relaxation Parameters	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
ΔH_E (kJ mol^{-1})									42	49	44	42
ΔS_E (J K^{-1} mol^{-1})									69	105	85	81
$\Delta G_{E(300)}$ (kJ mol^{-1})									21	18	19	18
$\tau_{1(300)}$ (s)									$8x10^{-10}$	$2x10^{-10}$	$3x10^{-10}$	$2x10^{-10}$

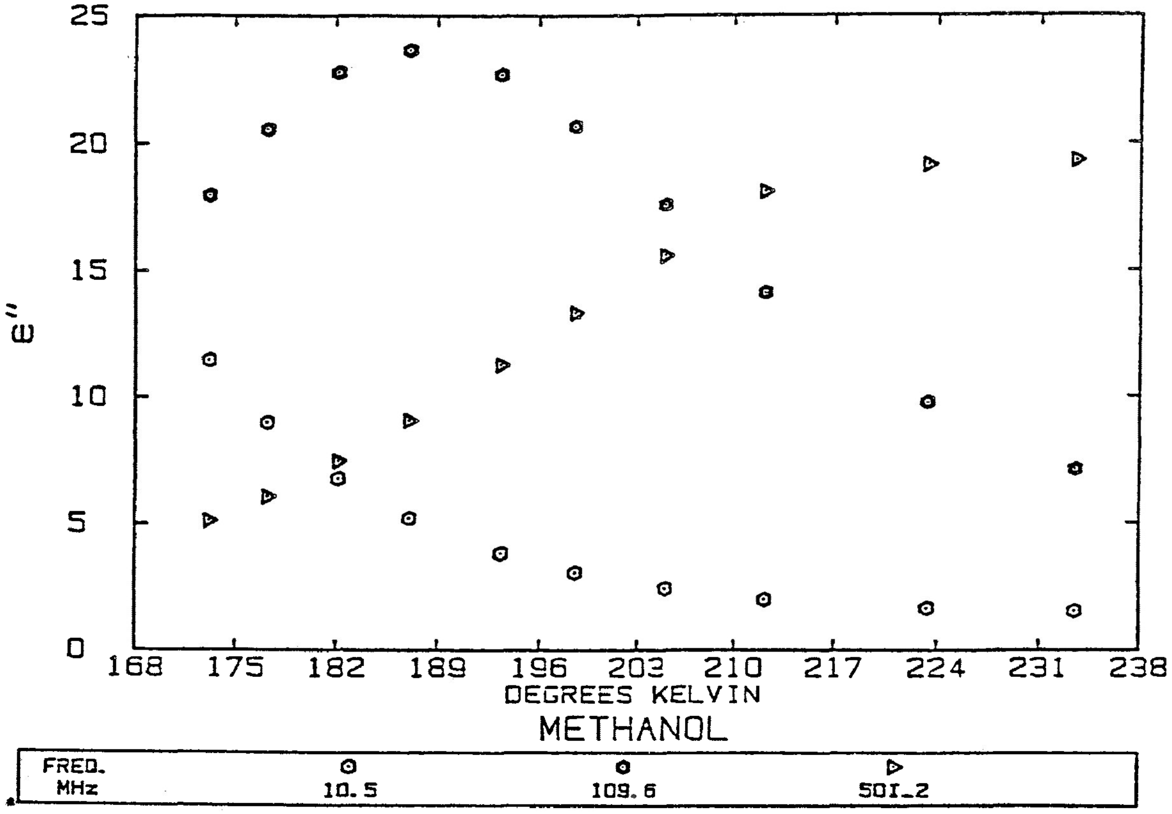
TABLE VI-7: The dielectric relaxation parameters for the isomeric Alcohols at 0.8 MF of Alcohol Concentration.

Relaxation Parameter	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
ΔH_E (kJ mol^{-1})	37	47	50	52								
ΔS_E (J K^{-1} mol^{-1})	55	93	104	110								
$\Delta G_{E(300)}$ (kJ mol^{-1})	21	19	19	19								
$\tau_{1(300)}$ (s)	7×10^{-10}	4×10^{-10}	3×10^{-10}	3×10^{-10}								
ΔH_E (kJ mol^{-1})					40	51	44	45				
ΔS_E (J K^{-1} mol^{-1})					61	108	79	90				
$\Delta G_{E(300)}$ (kJ mol^{-1})					21	19	20	18				
$\tau_{1(300)}$ (s)					8×10^{-10}	3×10^{-10}	6×10^{-10}	3×10^{-10}				

TABLE VI-7: The dielectric relaxation parameters for the isomeric Alcohols at 0.8 MF of Alcohol Concentration.

CONTINUED

Relaxation Parameter	1-heptanol	2-heptanol	3-heptanol	4-heptanol	1-octanol	2-octanol	3-octanol	4-octanol	1-decanol	2-decanol	3-decanol	4-decanol
ΔH_E (kJ mol^{-1})									41	50	49	44
ΔS_E (J K^{-1} mol^{-1})									64	105	99	83
$\Delta G_{E(300)}$ (kJ mol^{-1})									22	18	20	19
$\tau_{1(300)}$ (s)									$10x10^{-10}$	$2x10^{-10}$	$4x10^{-10}$	$3x10^{-10}$



<u>FIGURE III-1a</u>: Dielectric loss factor, ε" versus temperature for methanol.

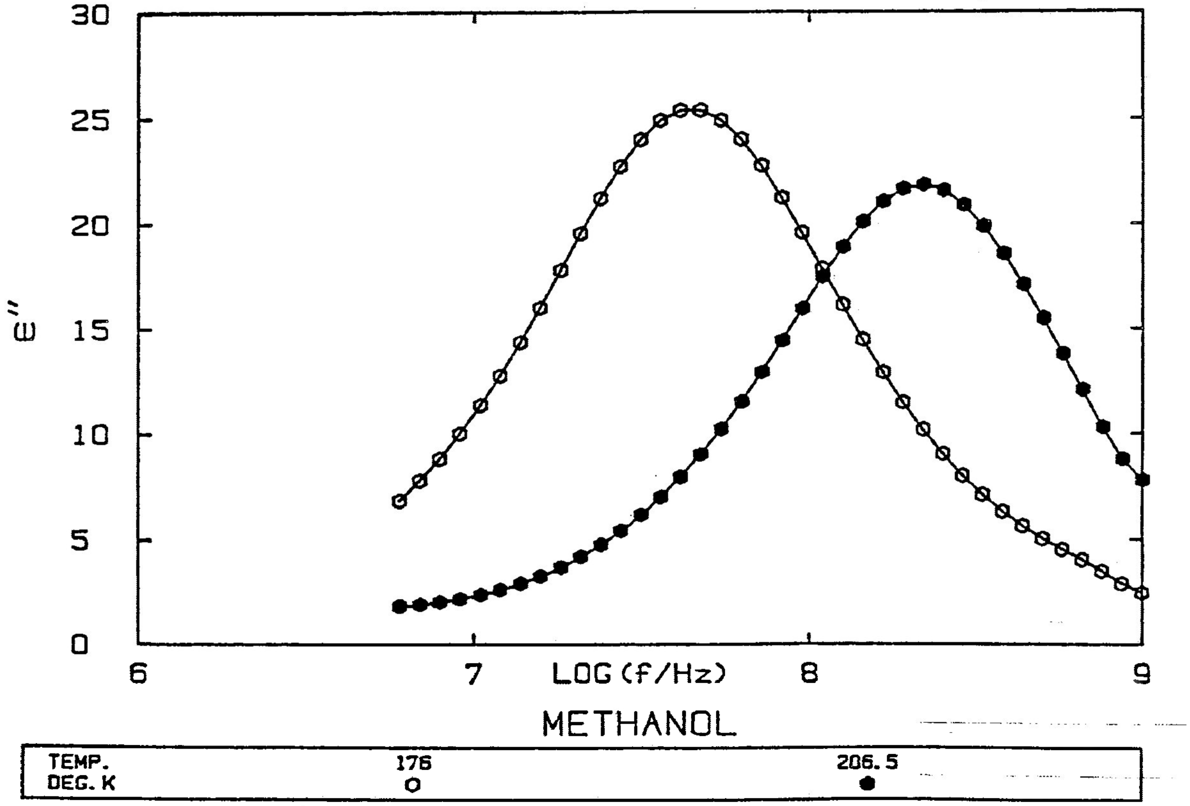


FIGURE III-1b: Dielectric loss factor, ε" versus log frequency for methanol.

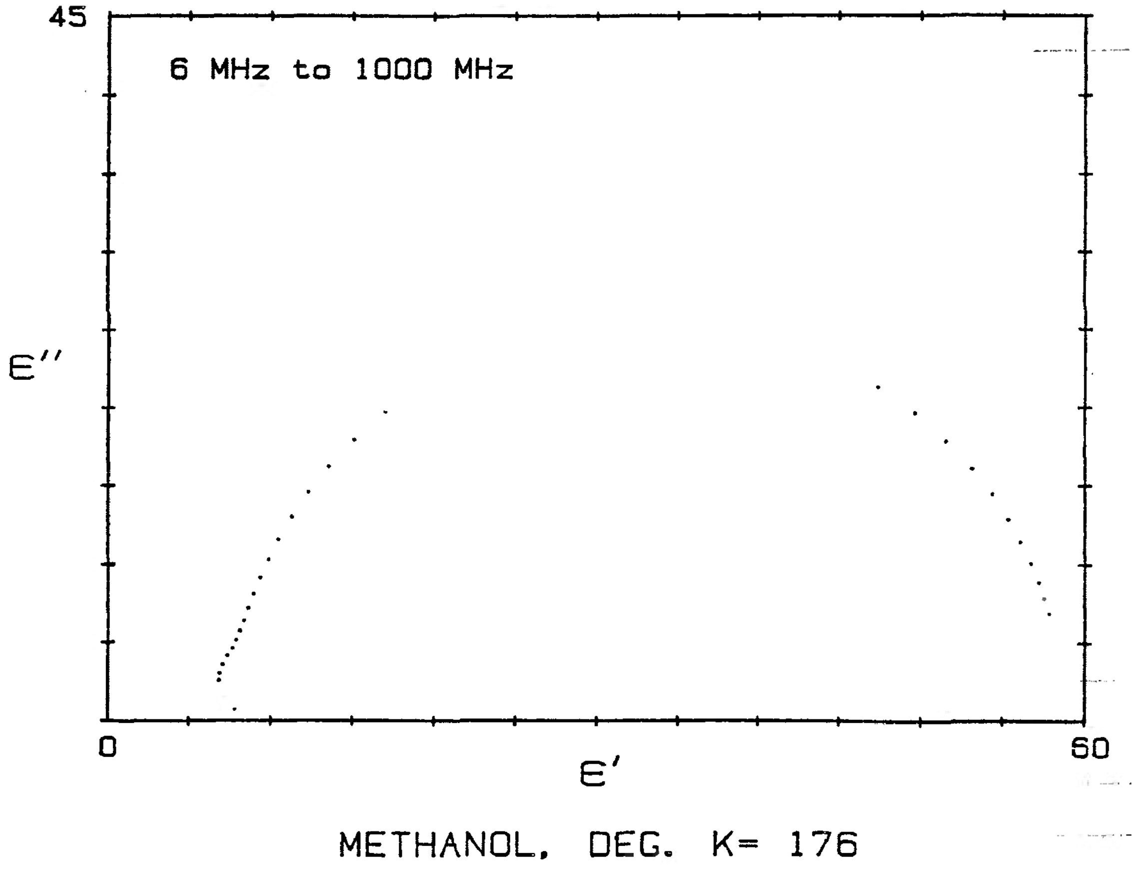
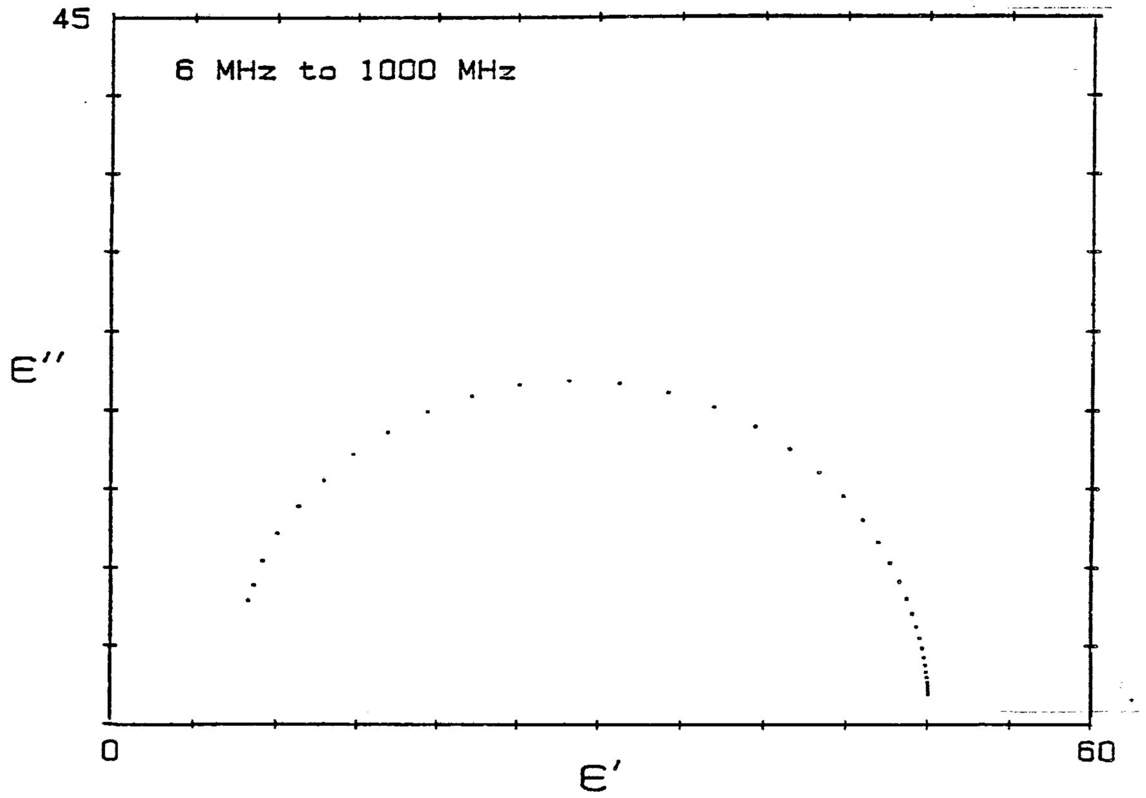


FIGURE III-1c: Cole-Cole plot for methanol at 176 K.



METHANOL. DEG. K= 206.5

FIGURE III-1d: Cole-Cole plot for methanol at 206.5 K.

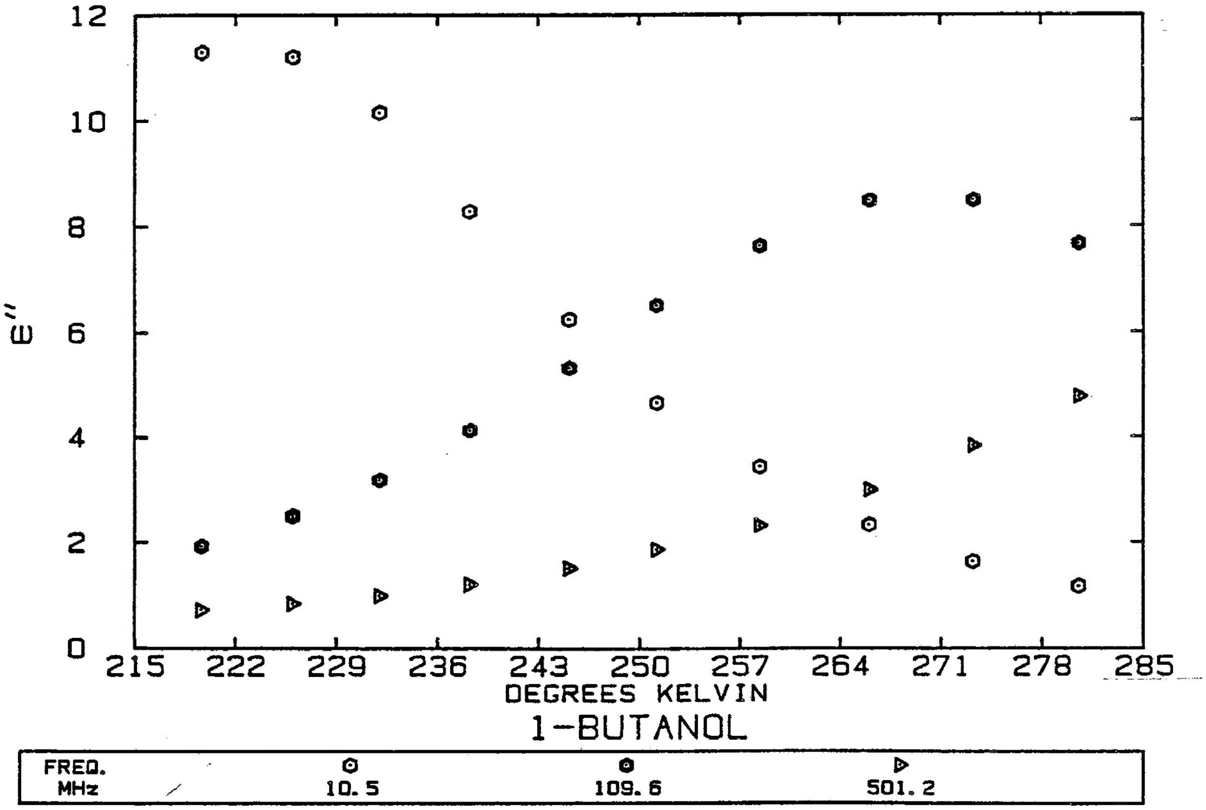


FIGURE III-2a: Dielectric loss factor ε" versus temperature for 1-butanol.

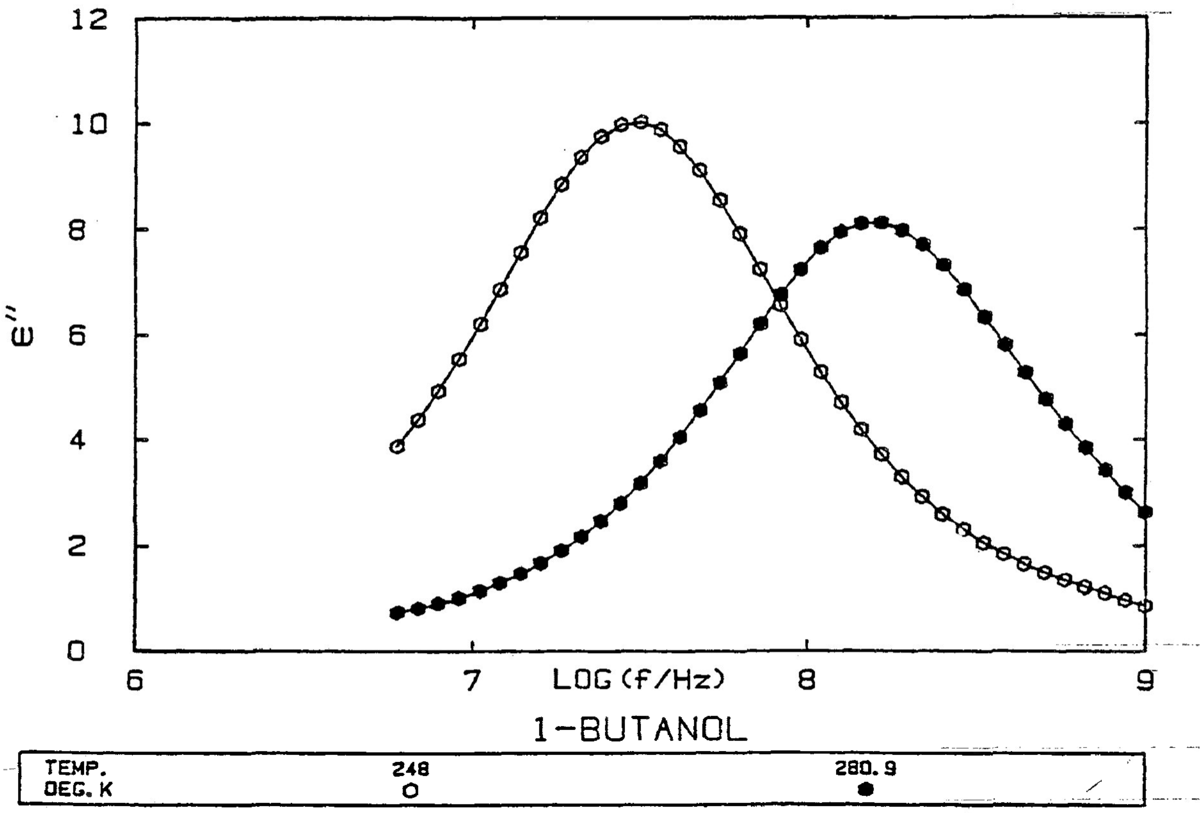


FIGURE III-2b: Dielectric loss factor, ε" versus log frequency for 1-butanol.

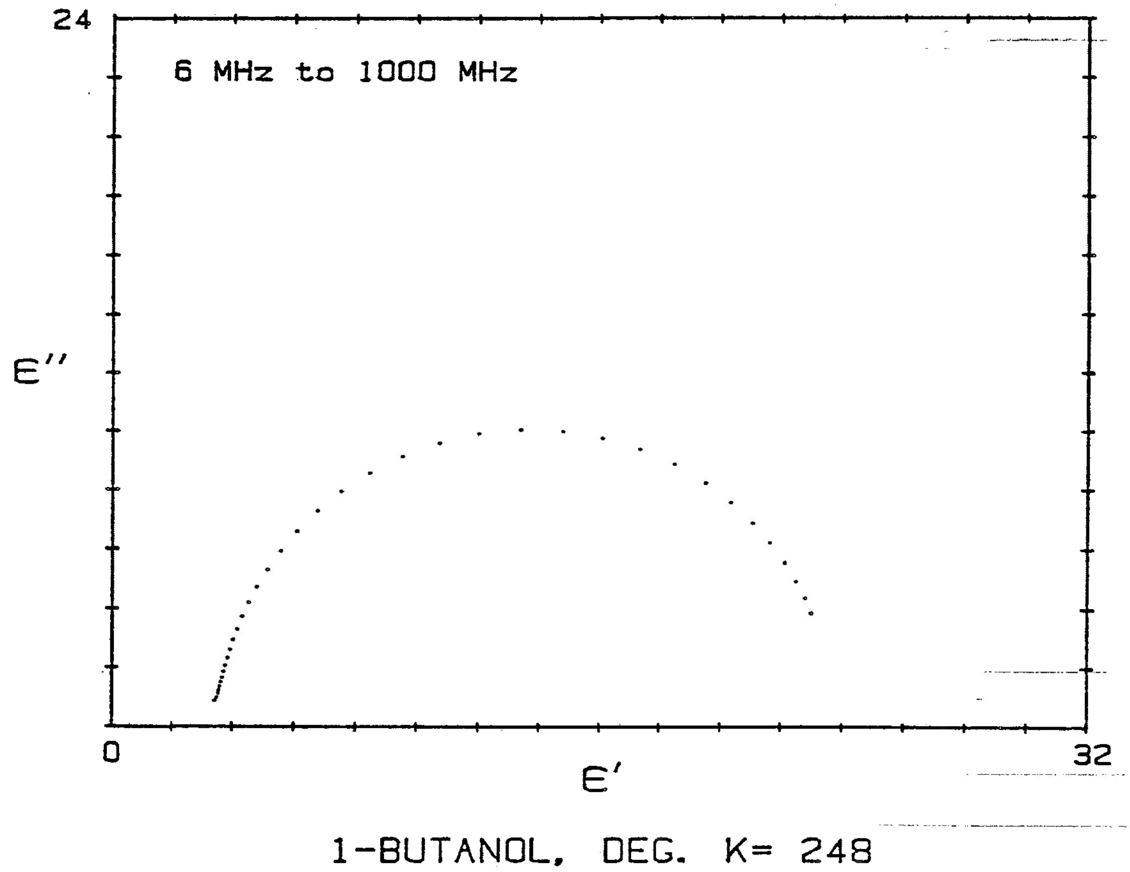
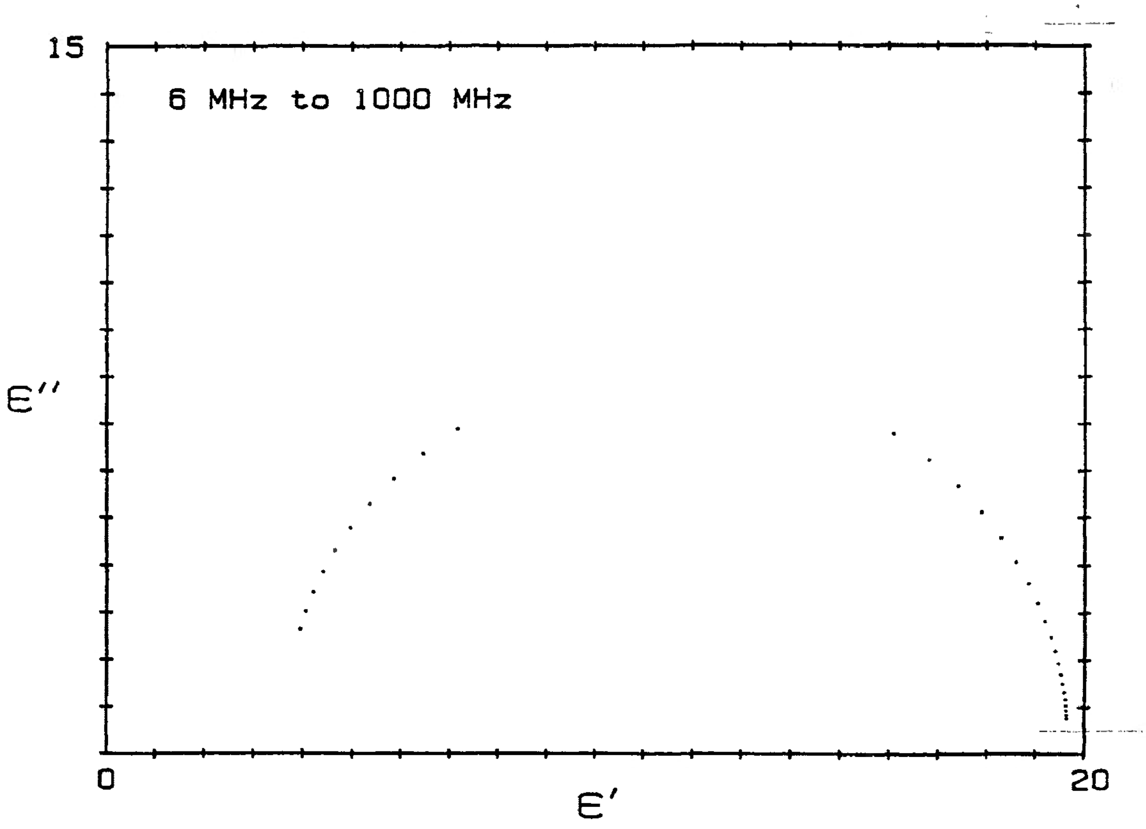


FIGURE III-2c: Cole-Cole plot for 1-butanol at 248 K.



1-BUTANOL, DEG. K= 280.9

FIGURE III-2d: Cole-Cole plot for 1-butanol at 280.9 K.

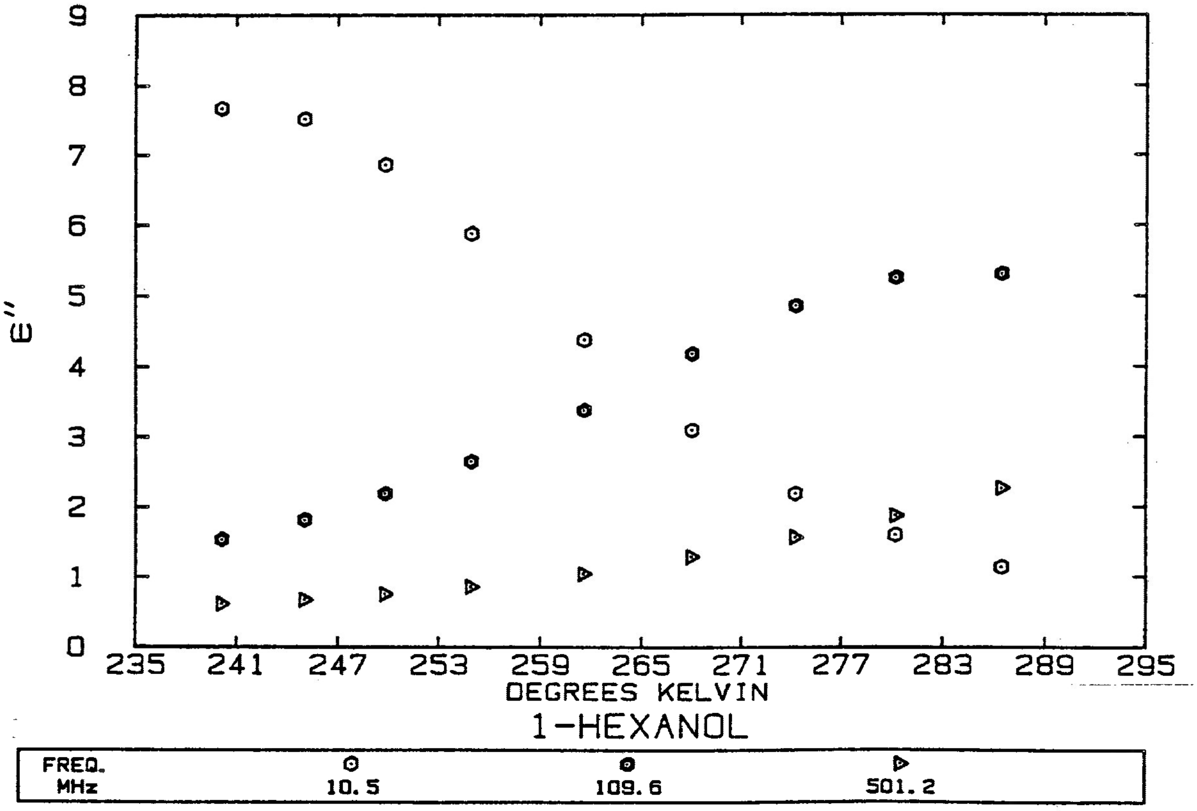


FIGURE III-3a: Dielectric loss factor, ε" versus temperature for 1-hexanol.

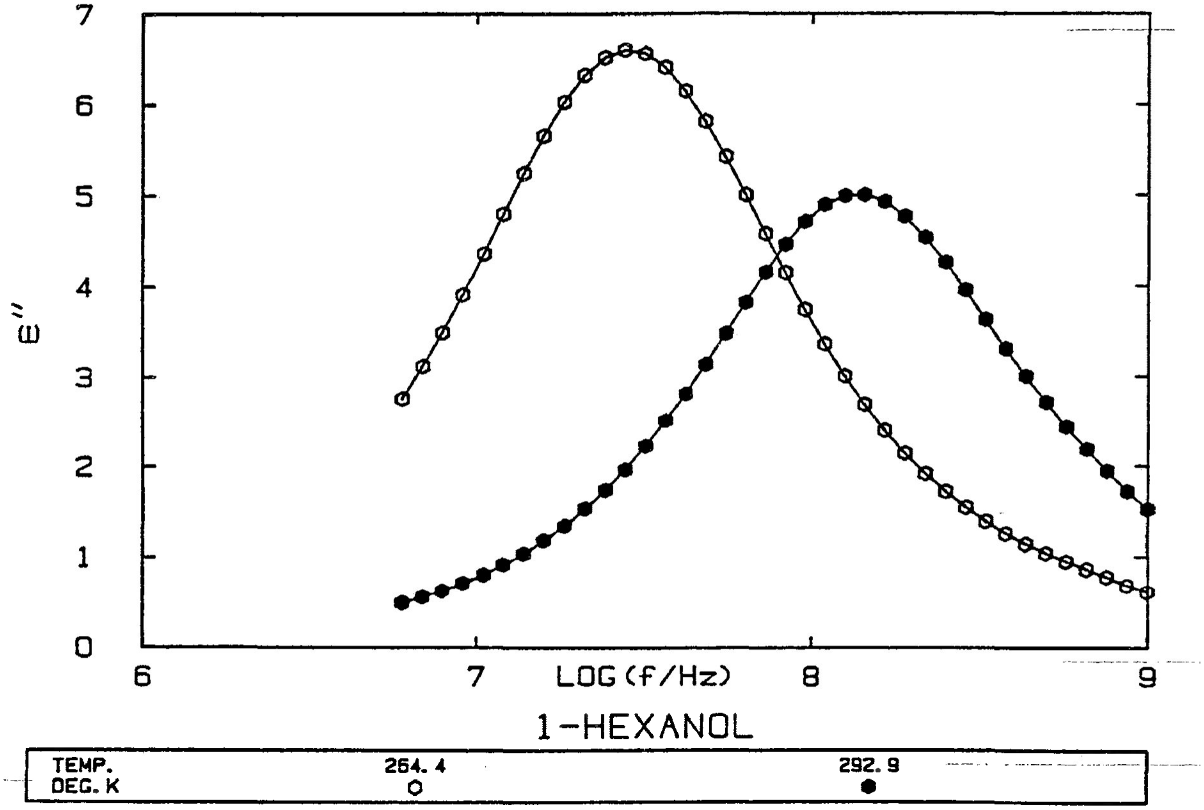


FIGURE III-3b: Dielectric loss factor, ε" versus log frequency for 1-hexanol.

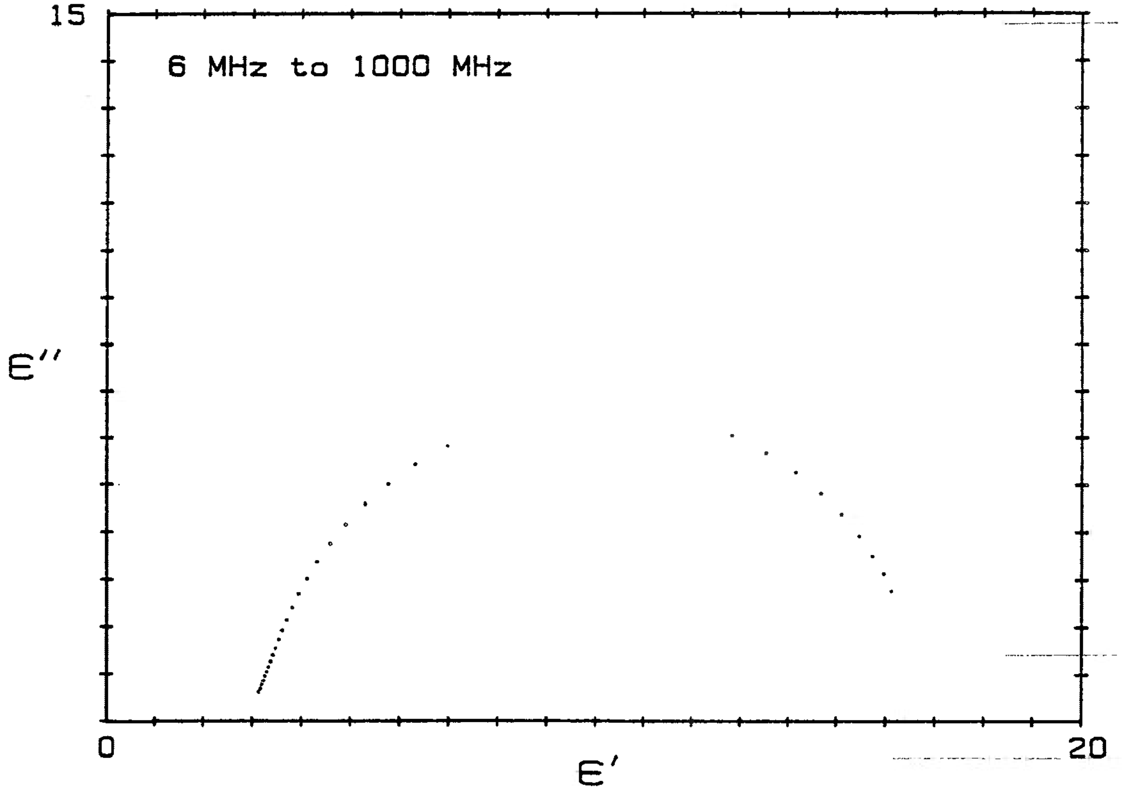
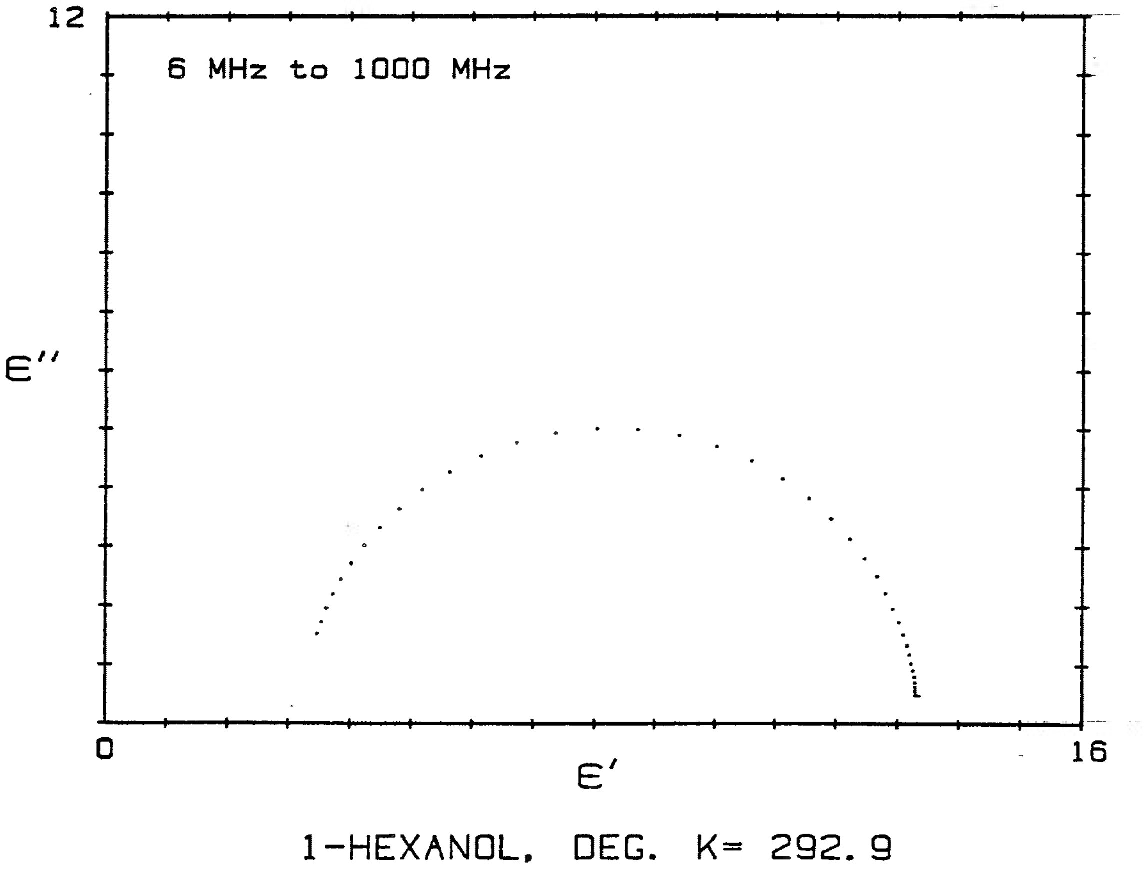


FIGURE III-3c: Cole-Cole plot for 1-hexanol at 264.4 K.



<u>FIGURE III-3d</u>: Cole-Cole plot for 1-hexanol at 292.9 K.

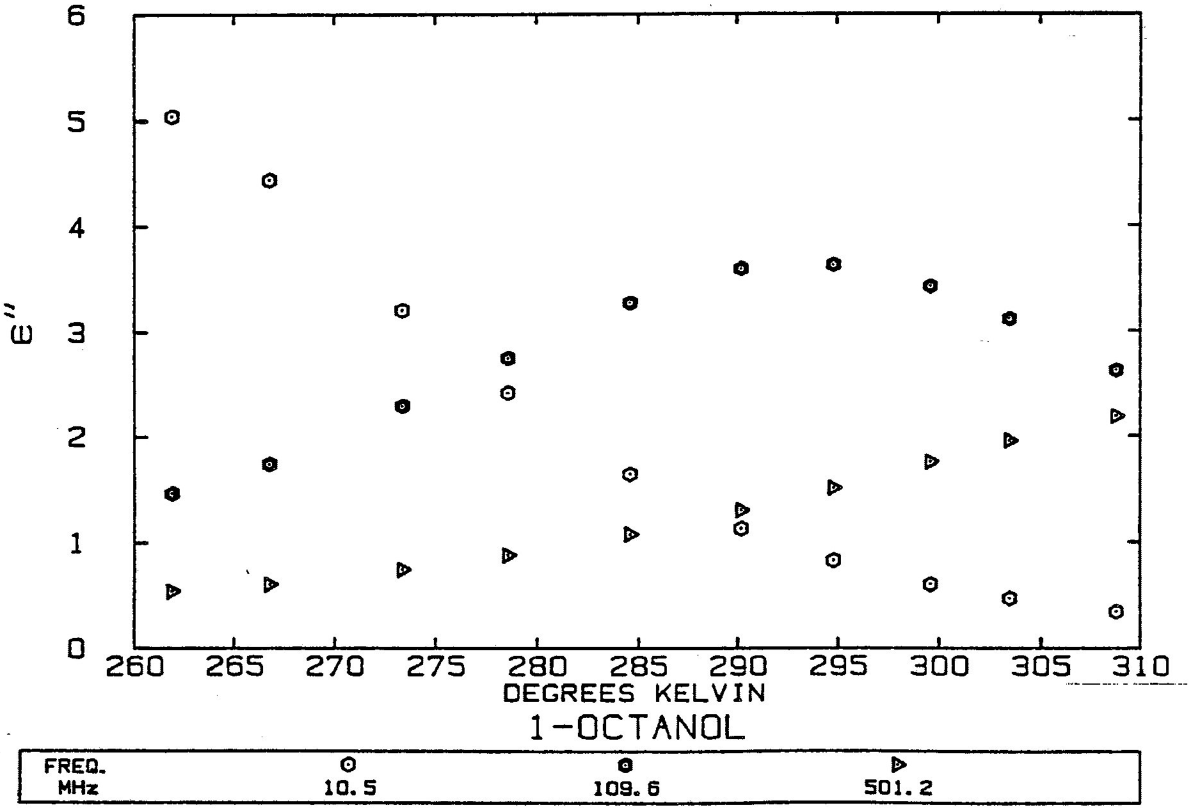


FIGURE III-4a: Dielectric loss factor, ε" versus temperature for 1-octanol.

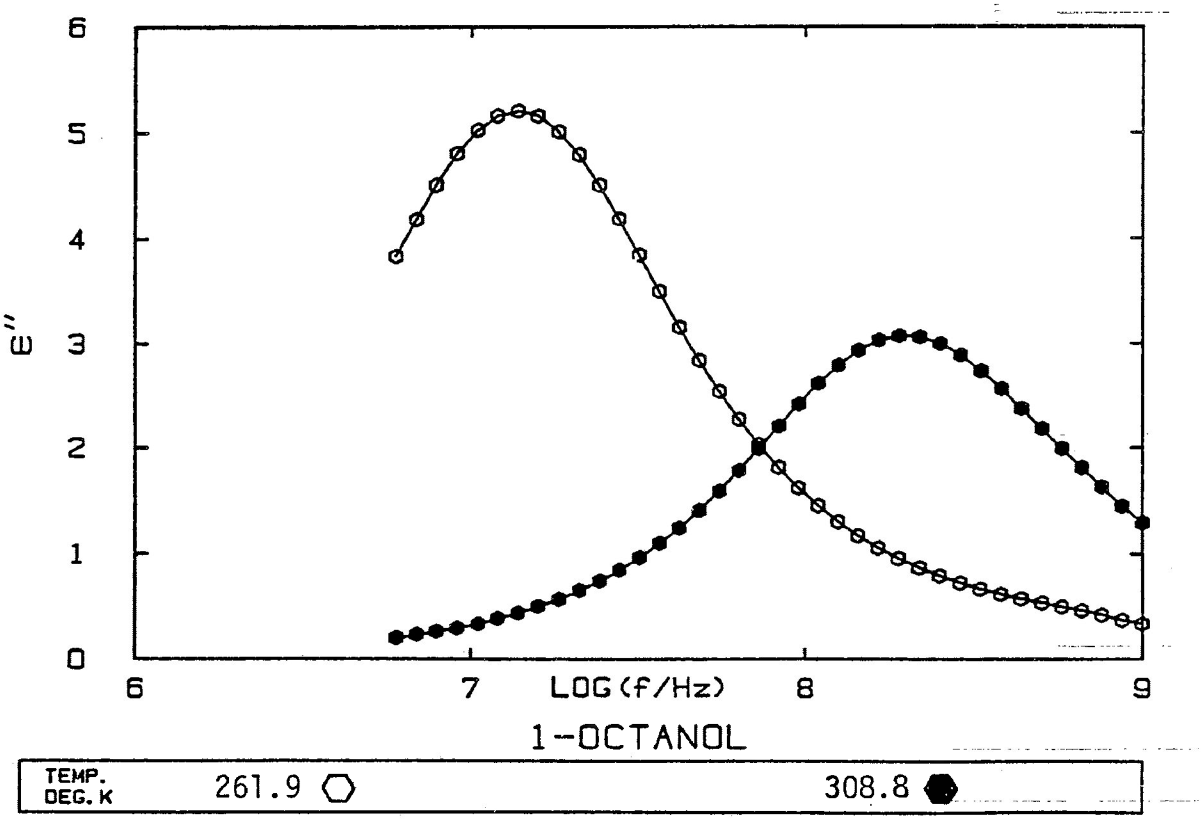


FIGURE III-4b: Dielectric loss factor, ε" versus log frequency for 1-octanol.

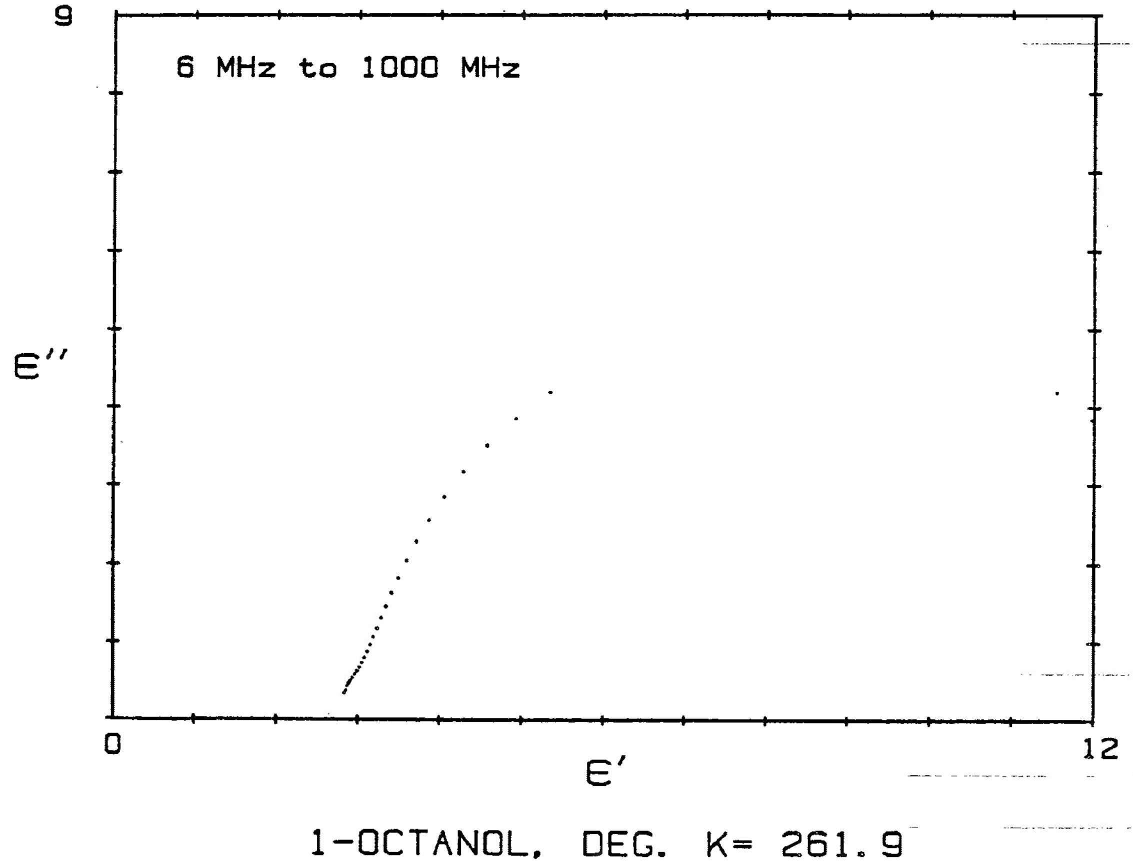


FIGURE III-4c: Cole-Cole plot for 1-octanol at 261.9 K.

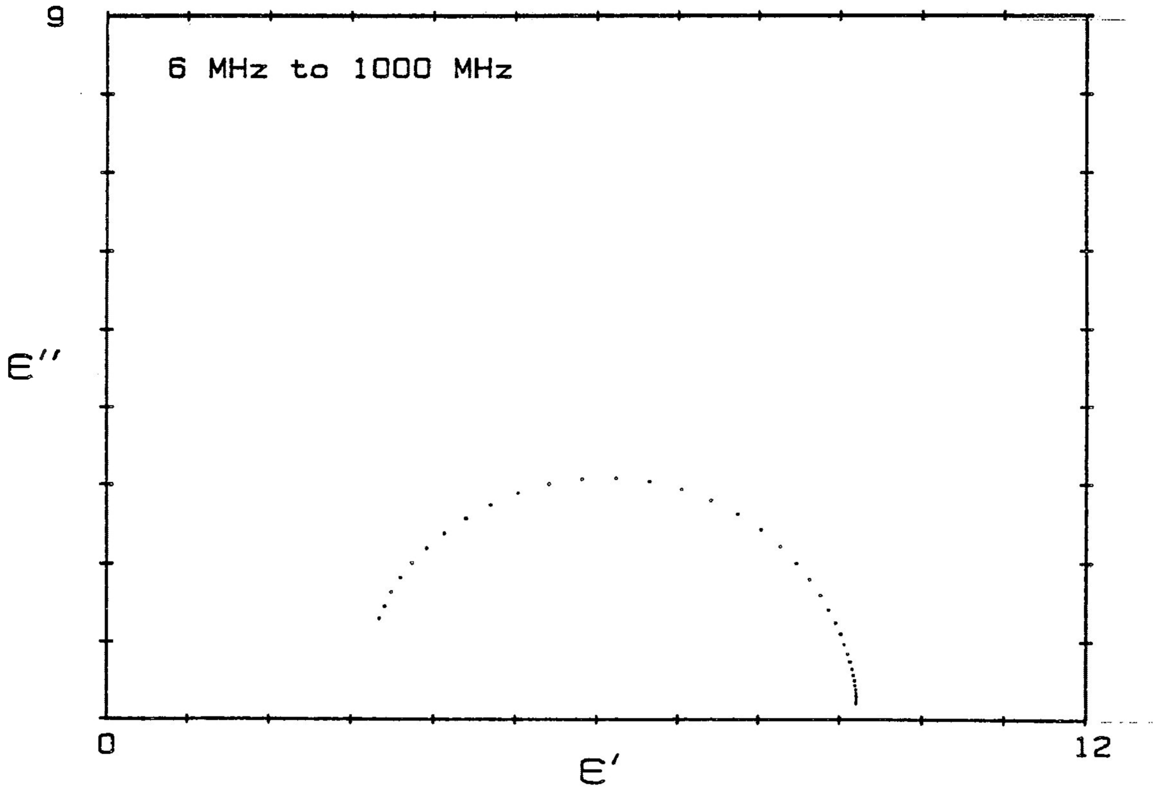


FIGURE III-4d: Cole-Cole plot for 1-octanol at 308.8 K.

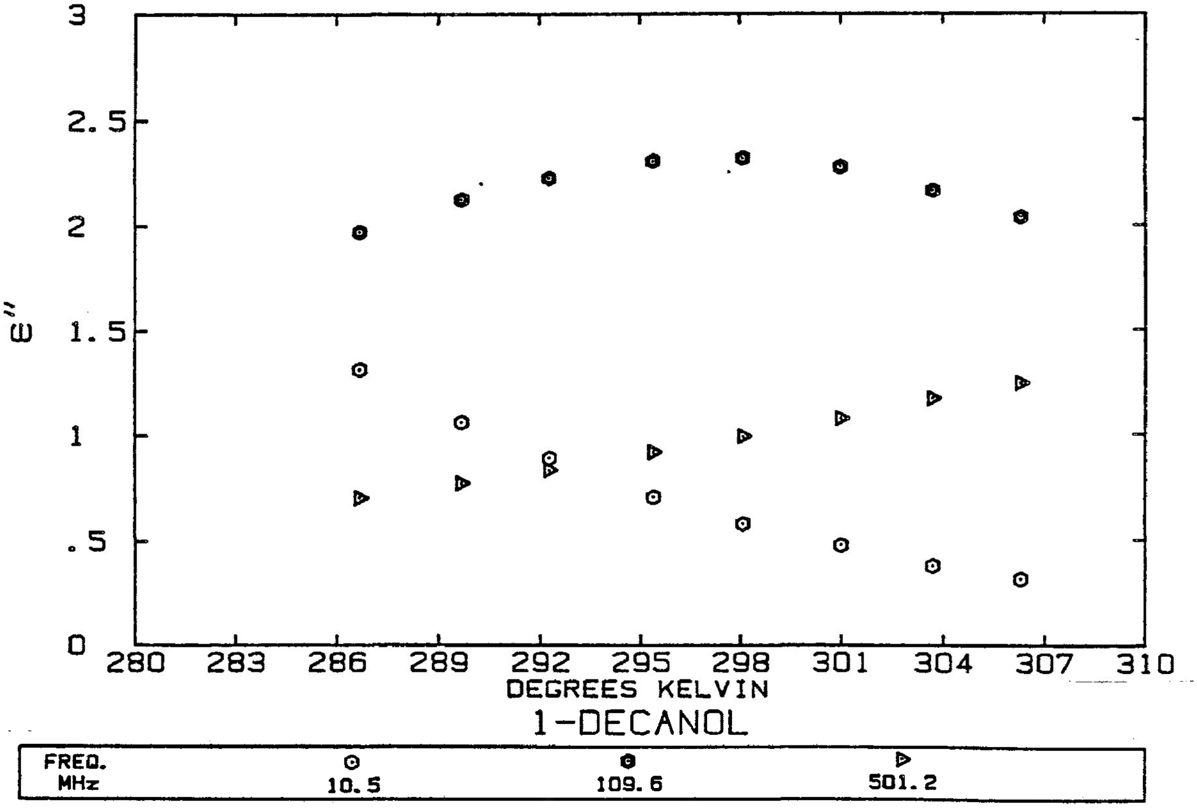


FIGURE III-5a: Dielectric loss factor, ε" versus temperature for 1-decanol.

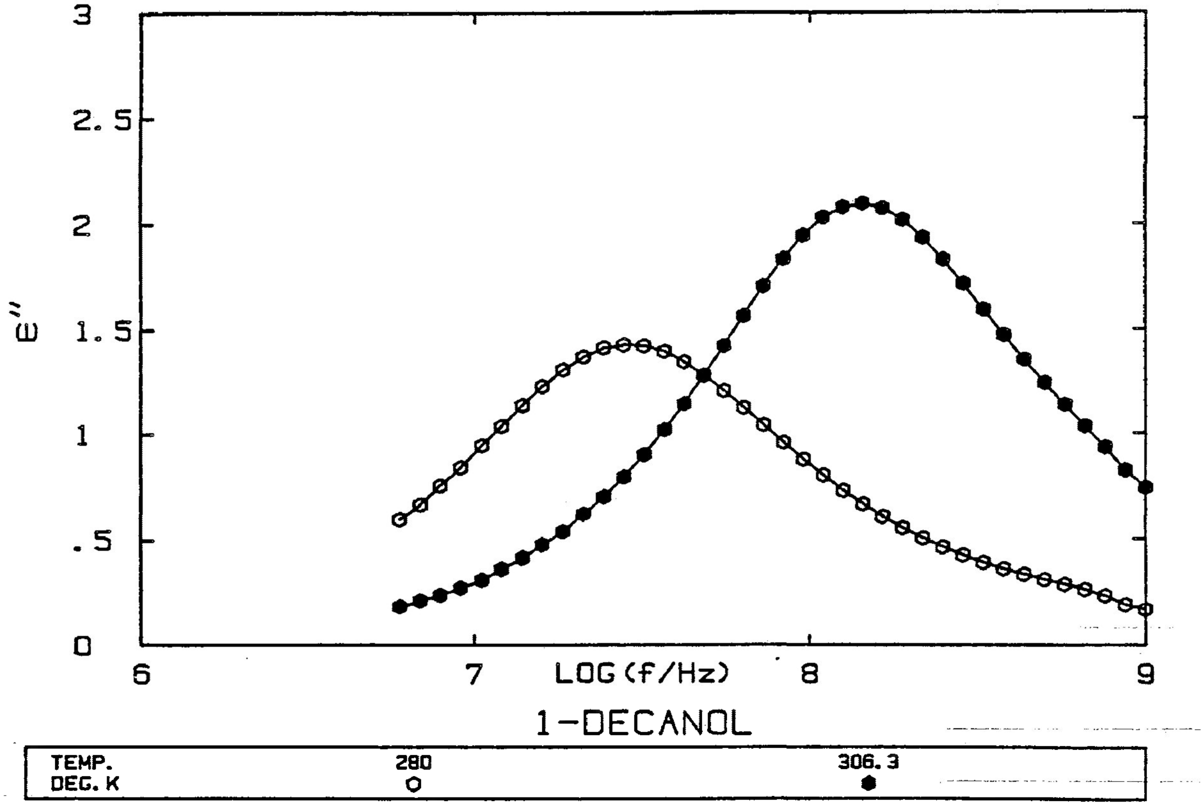


FIGURE III-5b: Dielectric loss factor, ε" versus log frequency for 1-decanol.

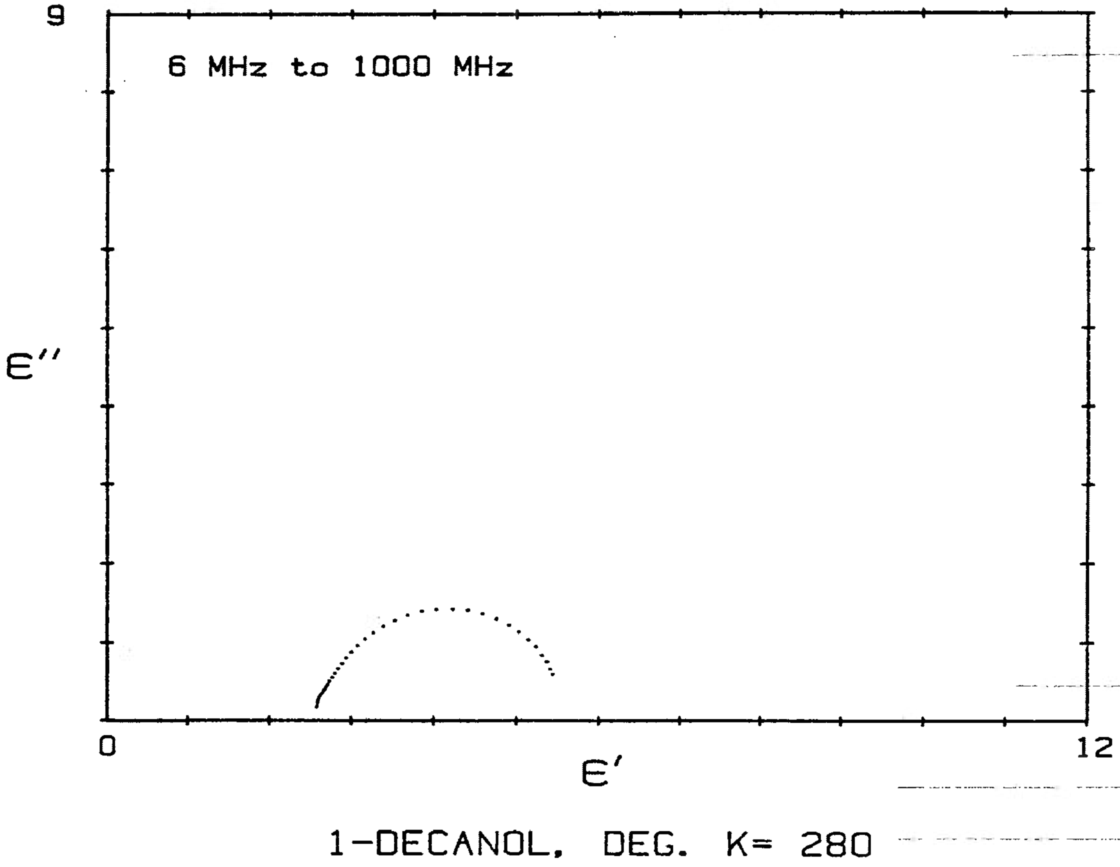


FIGURE III-5c: Cole-Cole plot for 1-decanol at 280 K.

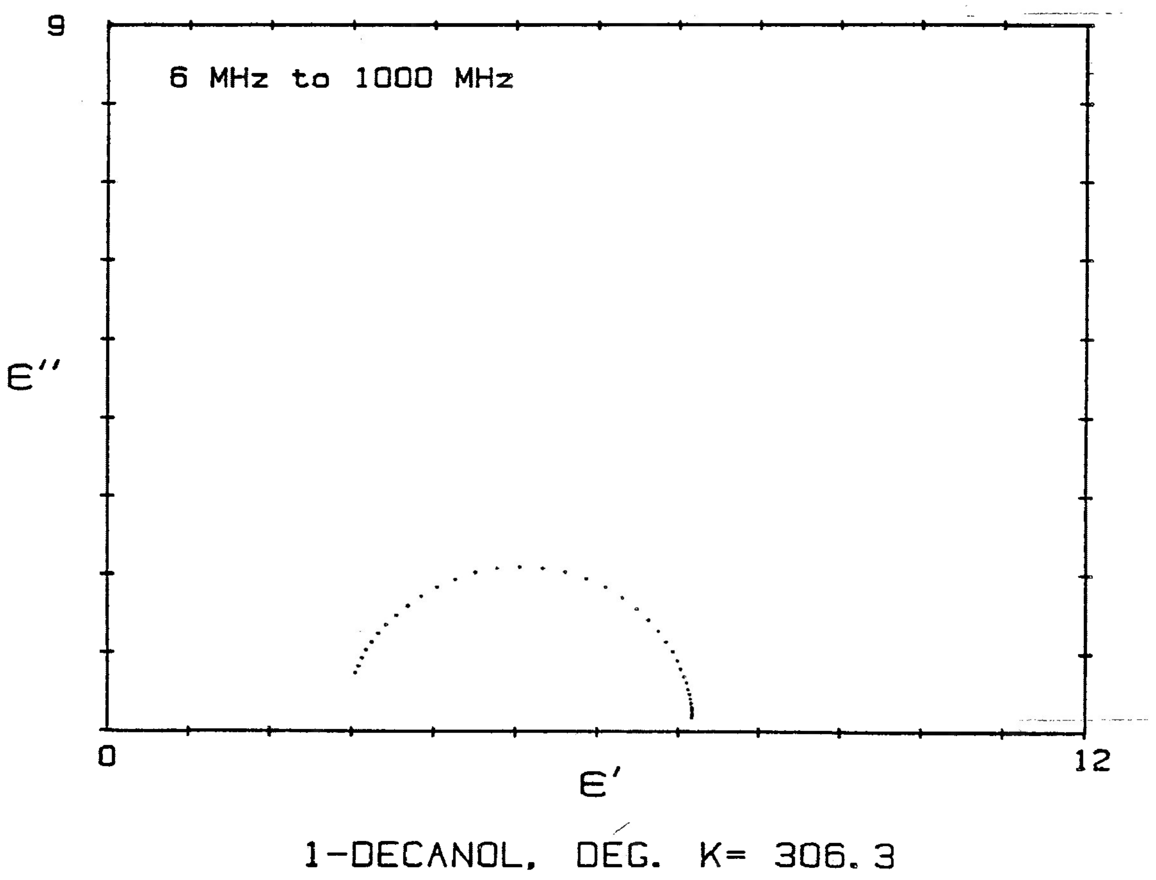


FIGURE III-5d: Cole-Cole plot for 1-decanol at 306.3 K.

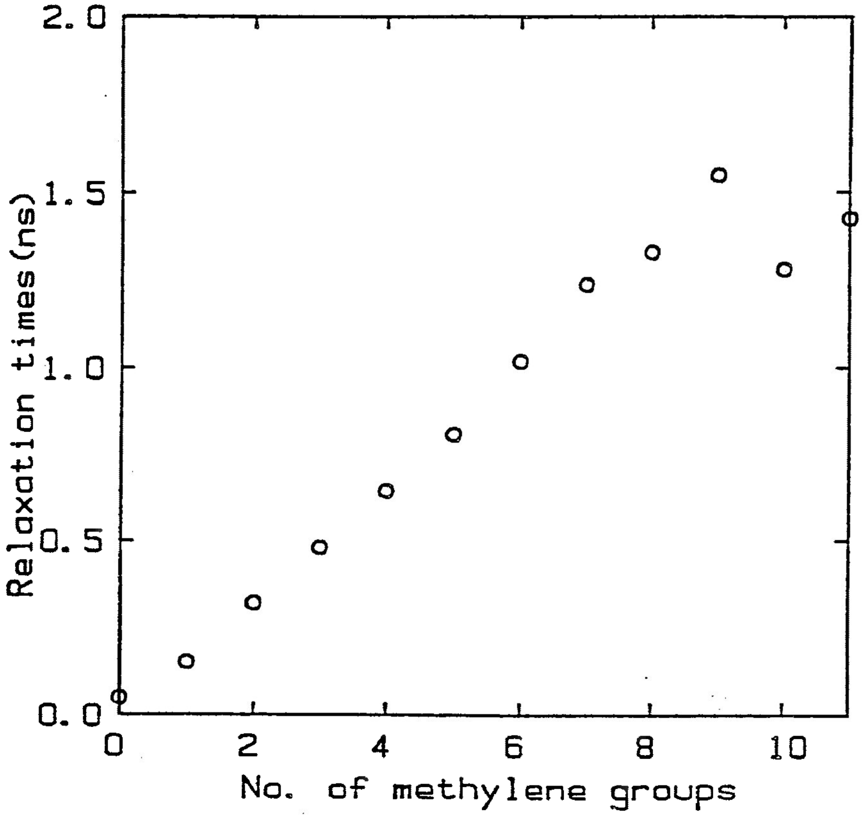


FIGURE III-6a: Relaxation time, τ_1, at 300 K as a function of the number of methylene groups (n) in the general formula, $CH_3(CH_2)_nOH$ for the liquid 1-alkanols.

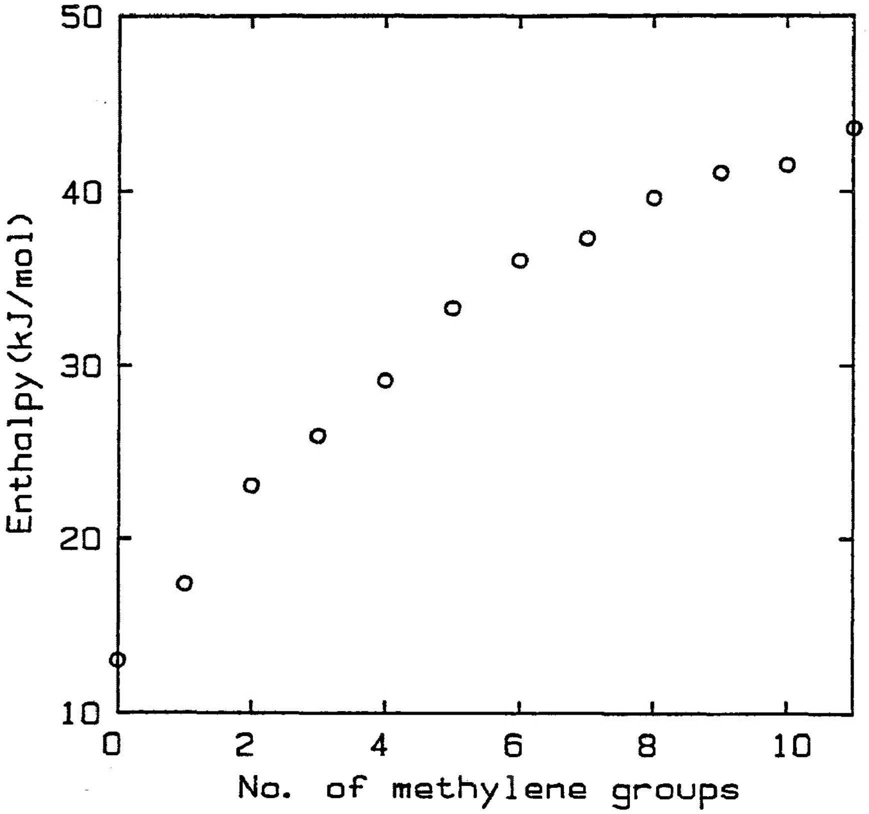


FIGURE III-6b: Enthalpy of activation, ΔH_E, as a function of the number of methylene groups for the liquid 1-alkanols.

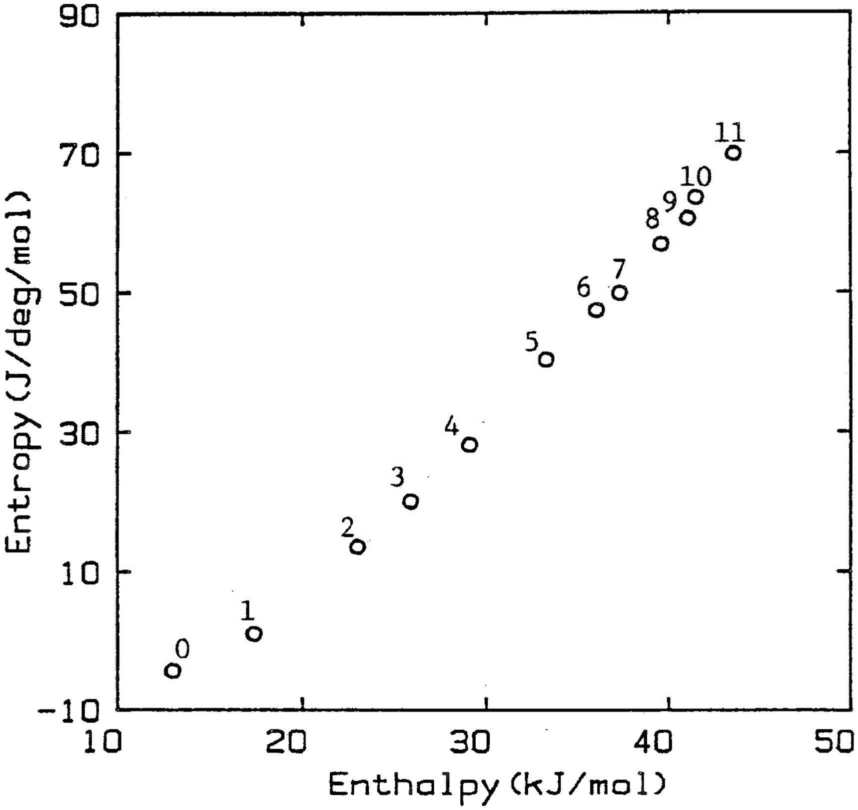


FIGURE III-7: Plot of entropy of activation, ΔS_E, versus enthalpy of activation, ΔH_E, for the liquid 1-alkanols. The numbers indicate the values of n in the general formula, $CH_3(CH_2)_nOH$.

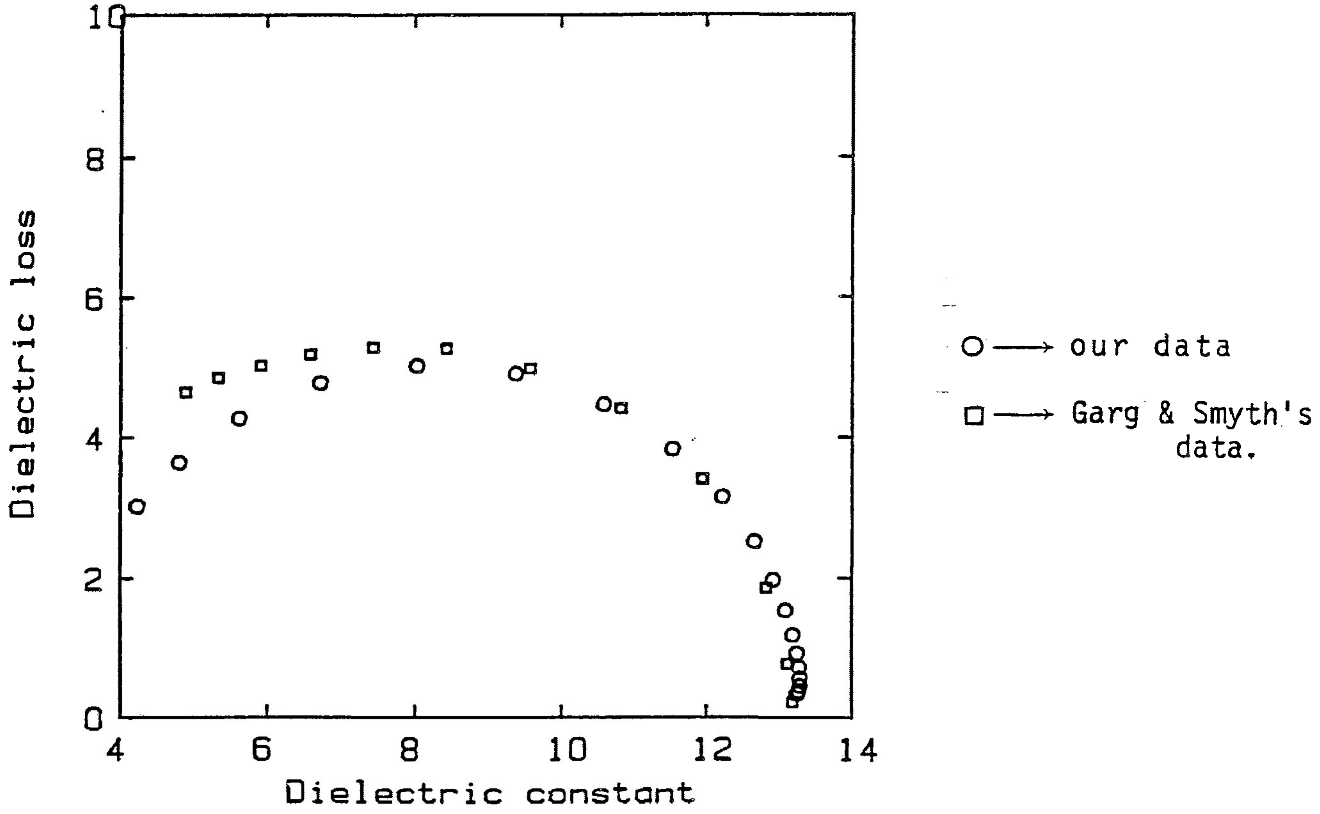


FIGURE III-8a: Cole-Cole plot for 1-hexanol at 293 K.

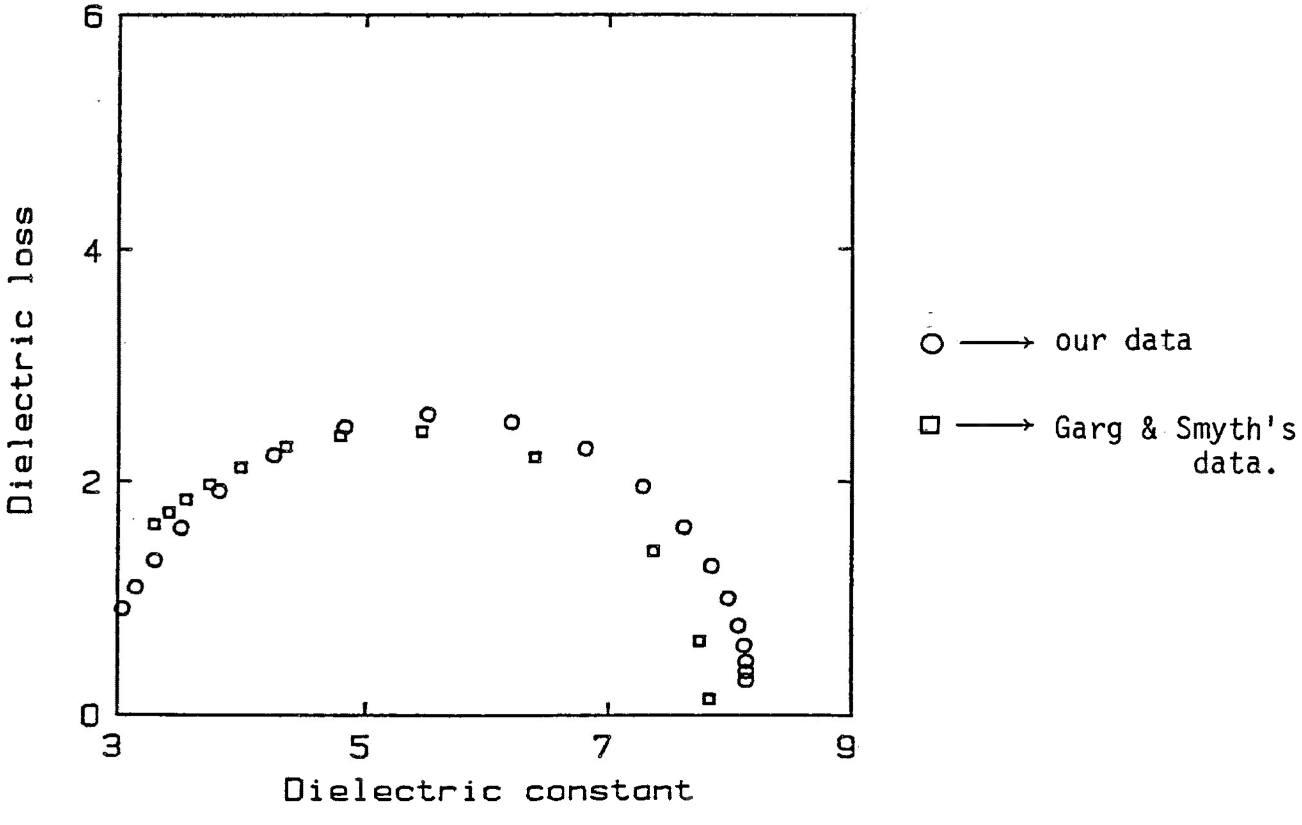


FIGURE III-8b: Cole-Cole plot for 1-decanol at 293 K.

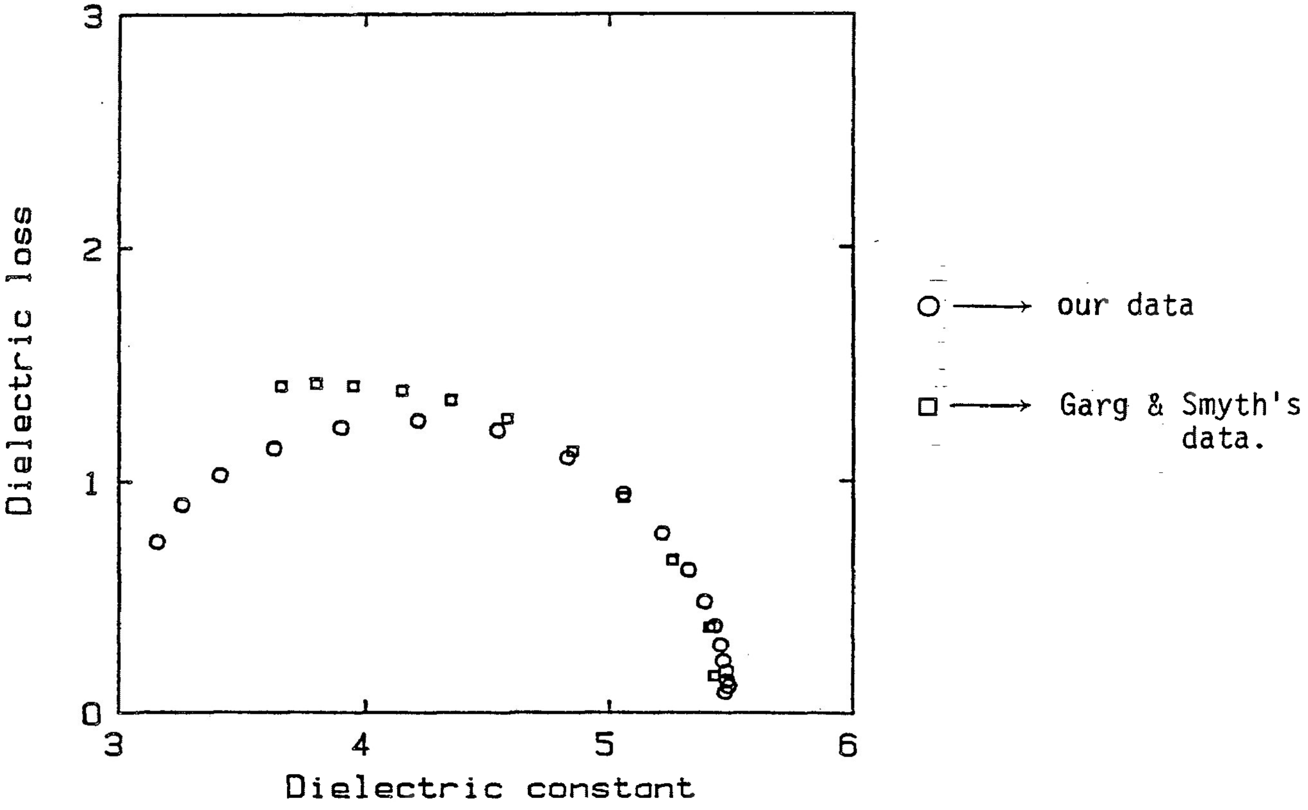


FIGURE III-8c: Cole-Cole plot for 1-dodecanol at 313 K.

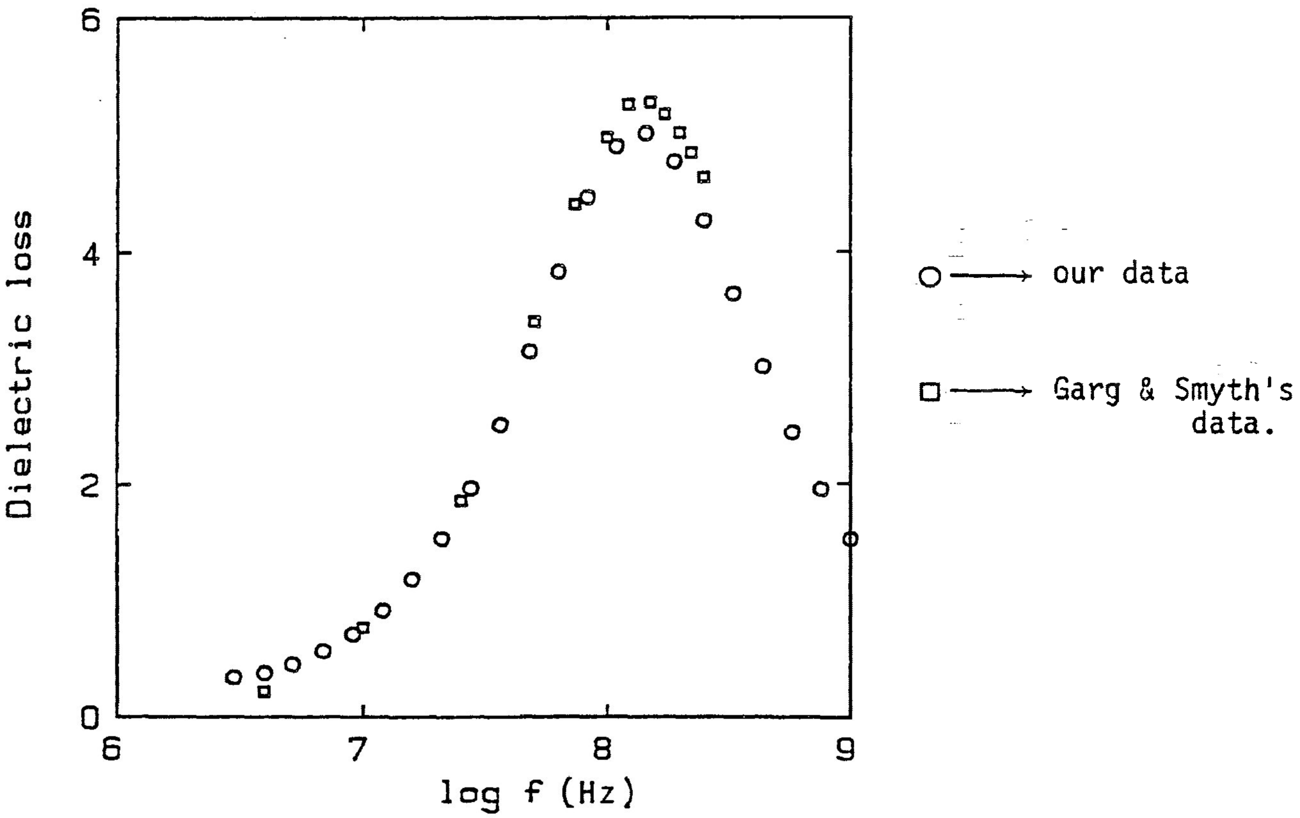


FIGURE III-9a: Dielectric loss factor, ε'' versus log frequency for 1-hexanol at 293 K.

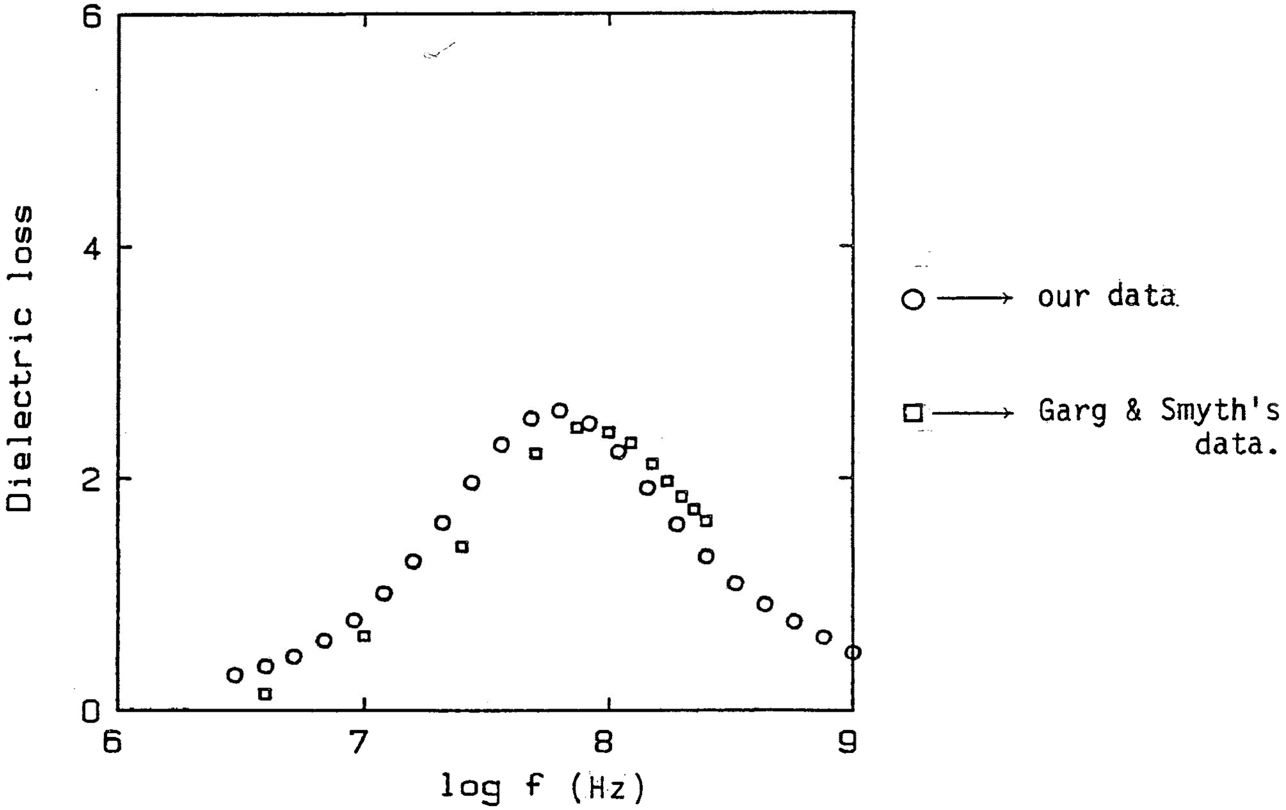


FIGURE III-9b: Dielectric loss factor, ε" versus log frequency for 1-decanol at 293 K.

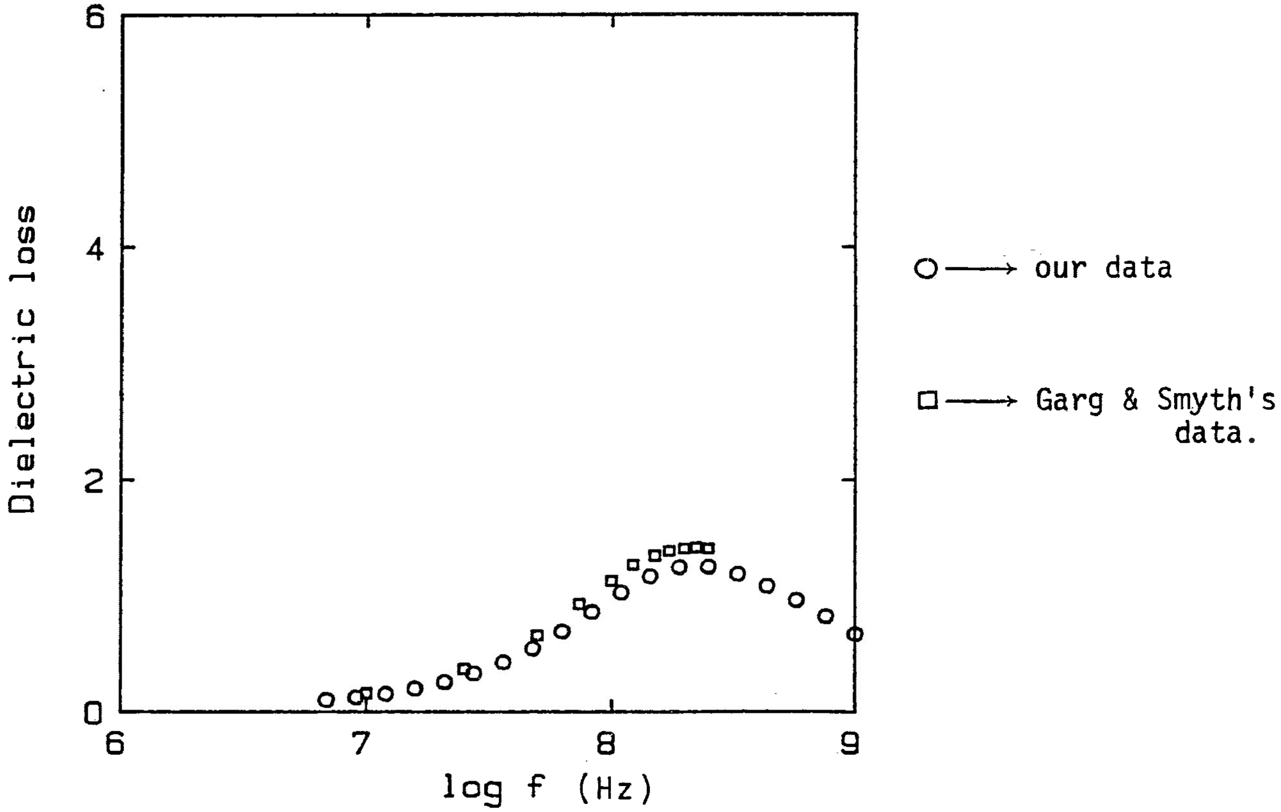


FIGURE III-9c: Dielectric loss factor, ε" versus log frequency for 1-dodecanol at 313 K.

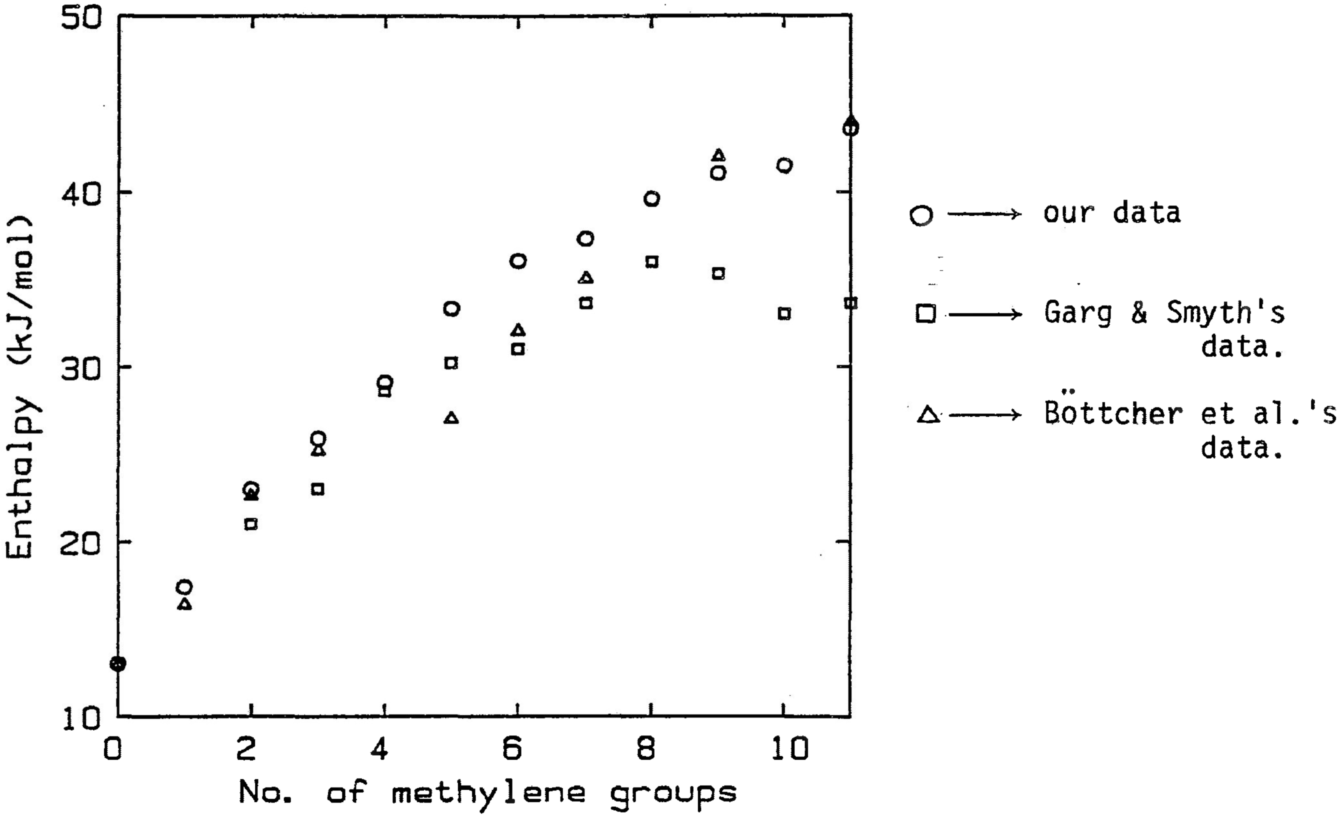


FIGURE III-10: Enthalpy of activation, ΔH_E, as a function of the number of methylene groups for the liquid 1-alkanols.

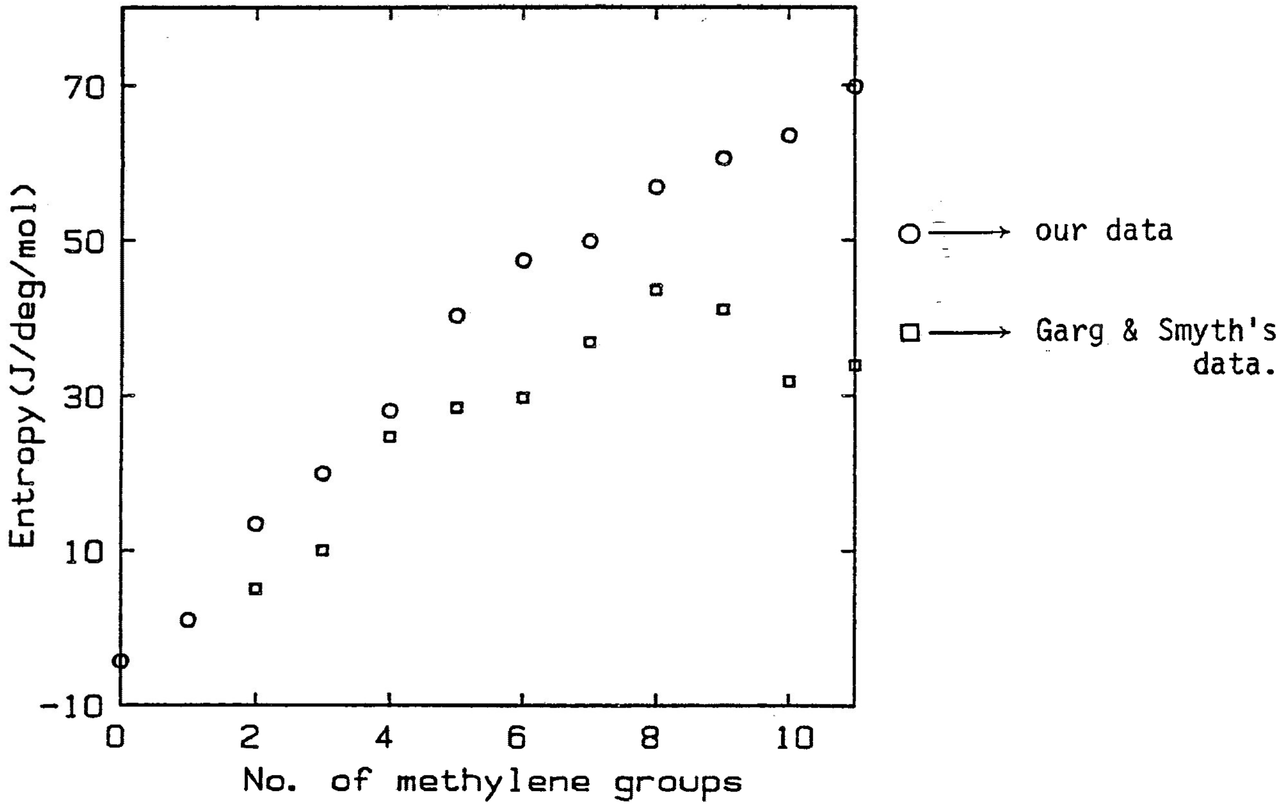


FIGURE III-11: Entropy of activation, ΔS_E, as a function of the number of methylene groups.

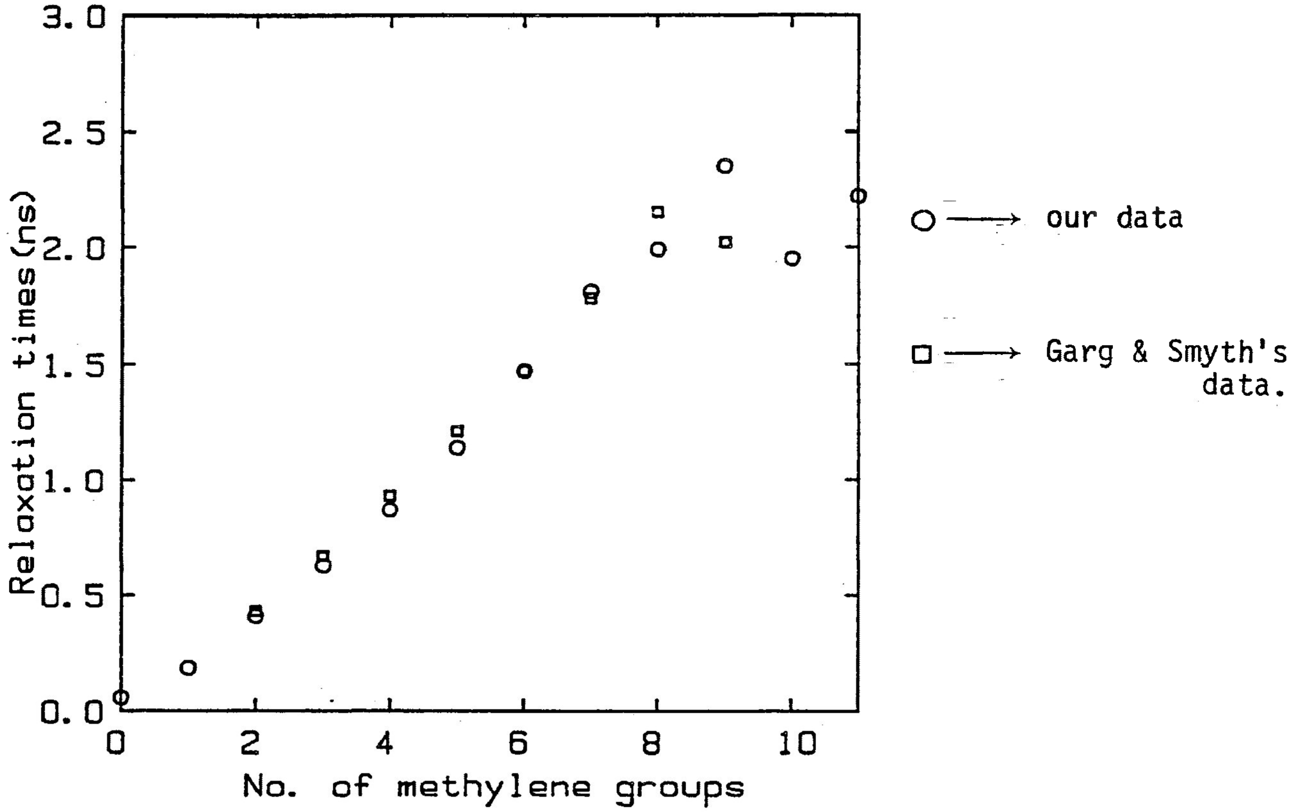


FIGURE III-12: Relaxation time, τ_1, at 293 K as a function of the number of methylene groups.

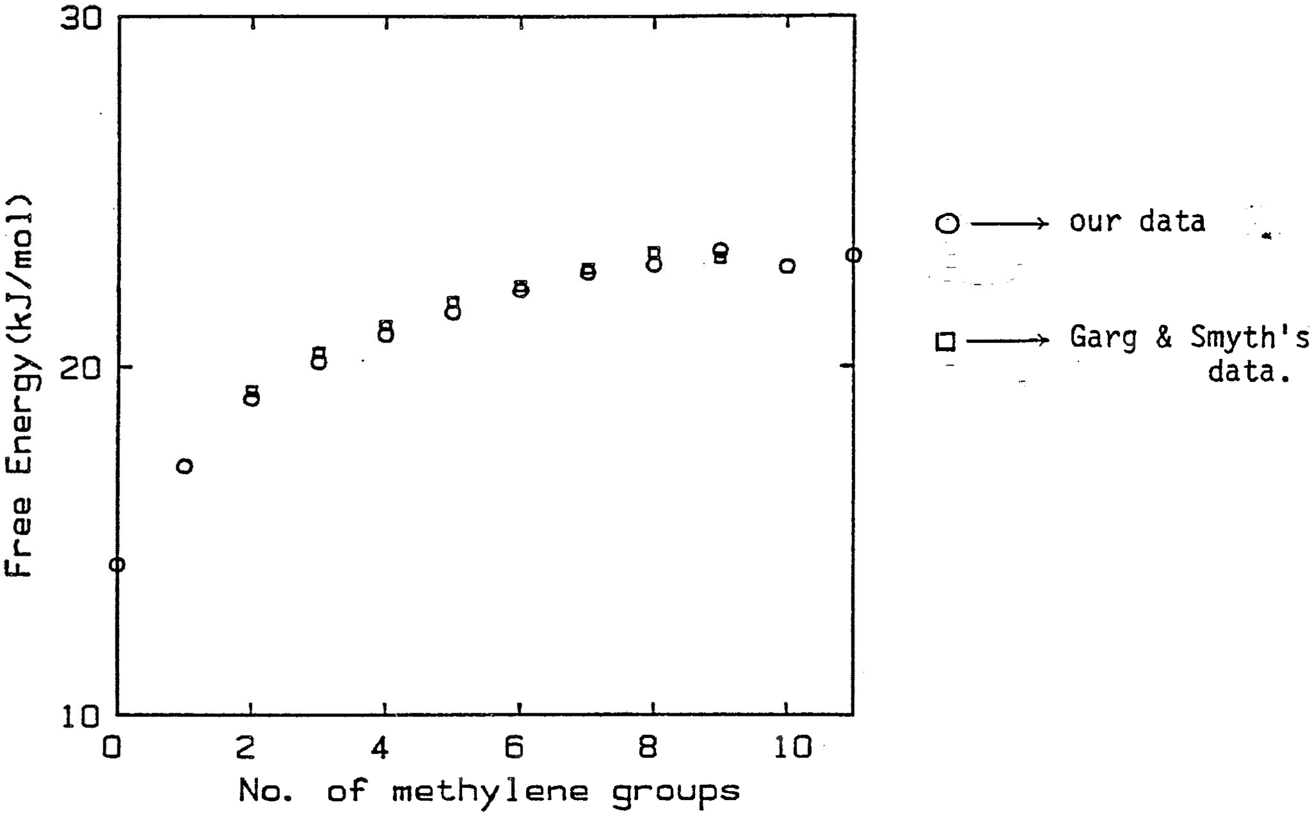
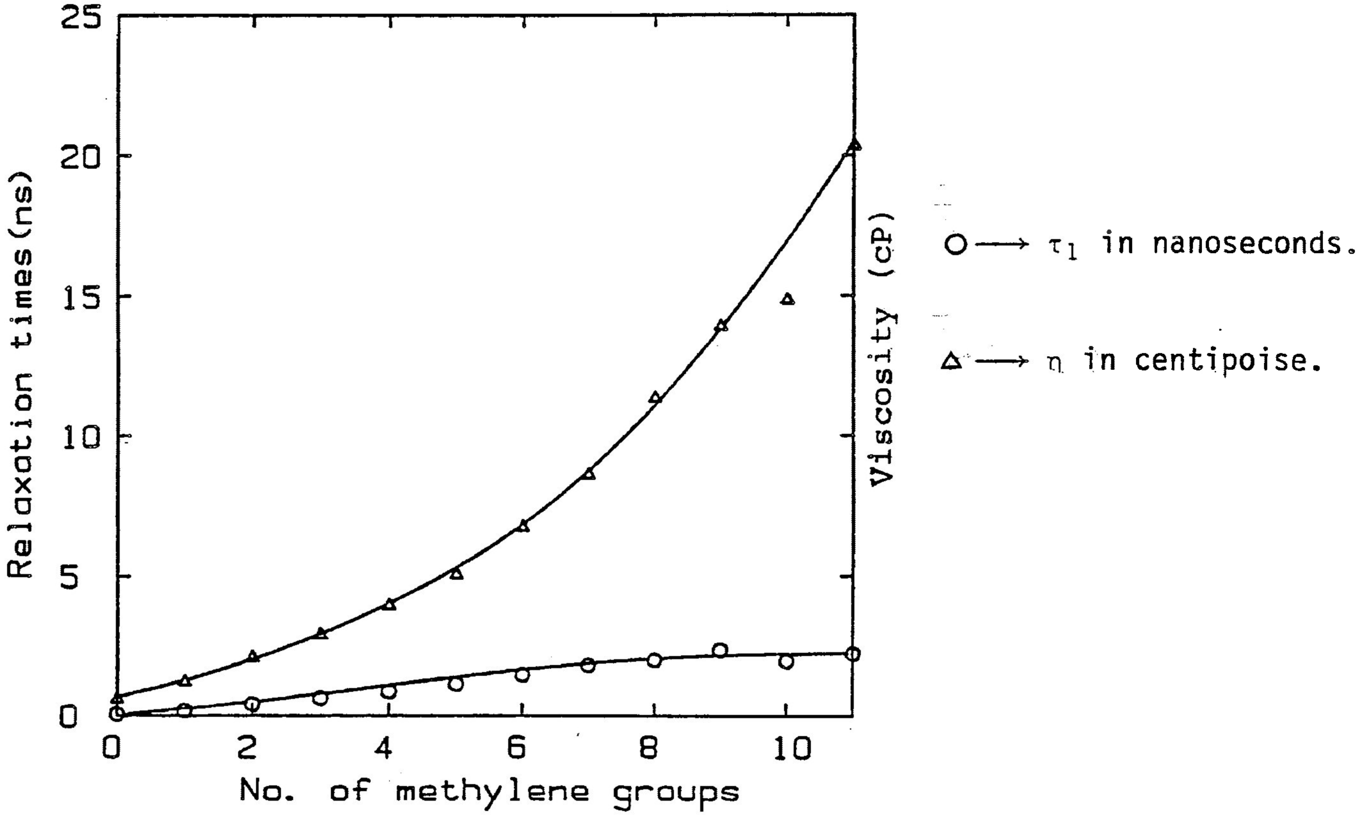


FIGURE III-13: Free energy of activation, ΔG_E, at 293 K as a function of the number of methylene groups.



<u>FIGURE III-14a</u>: Principal relaxation time, τ_I, and macroscopic viscosity, η, at 293 K as a function of the number of methylene groups (n) for the liquid 1-alkanols.

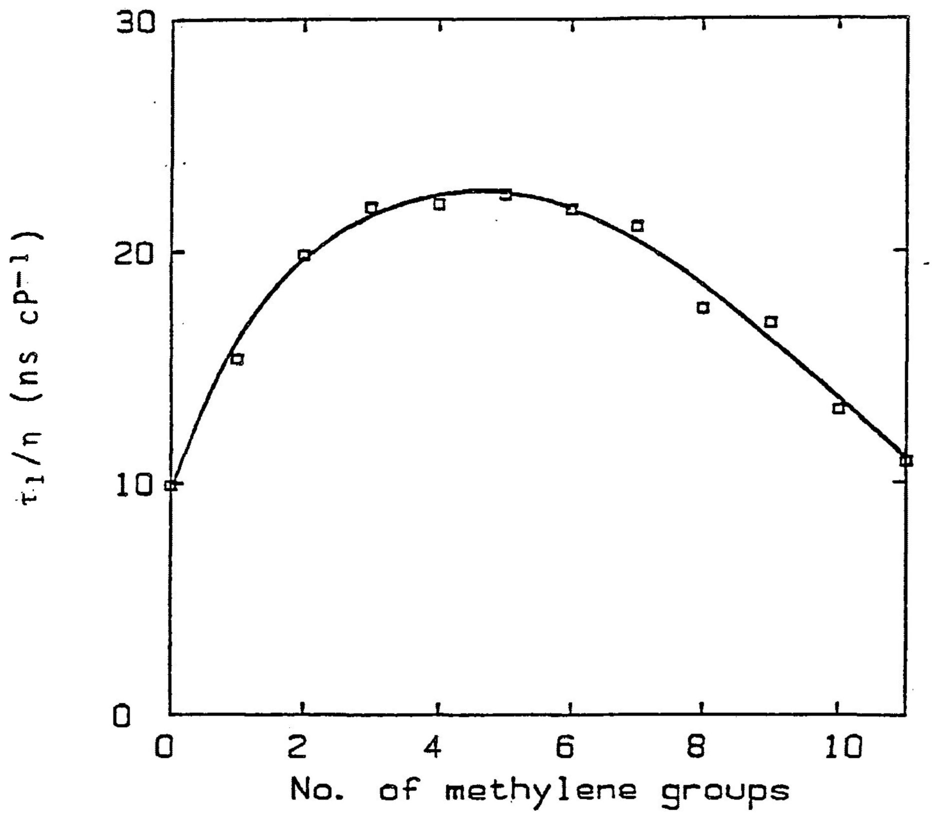


FIGURE III-14b: τ_1/η (ns cP^{-1}) at 293 K as a function of the number of methylene groups for liquid 1-alkanols.

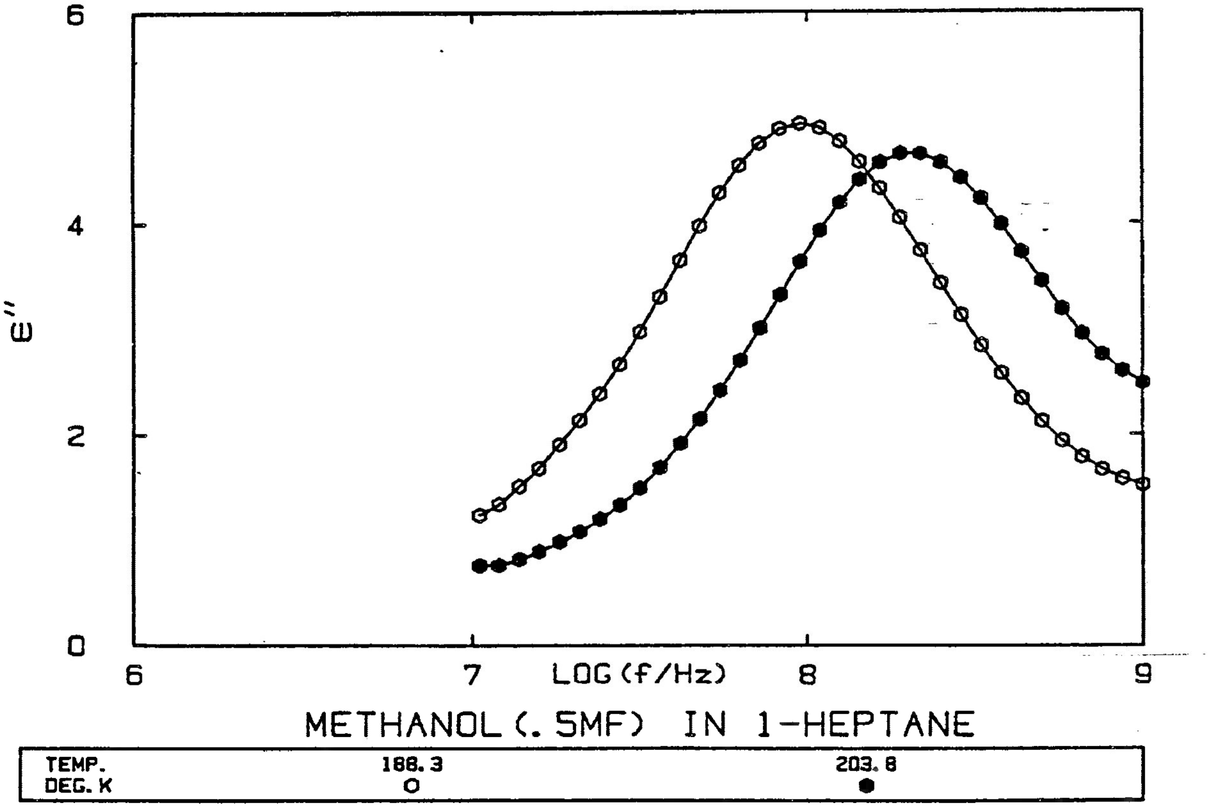


FIGURE IV-1: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of methanol in 1-heptane solution.

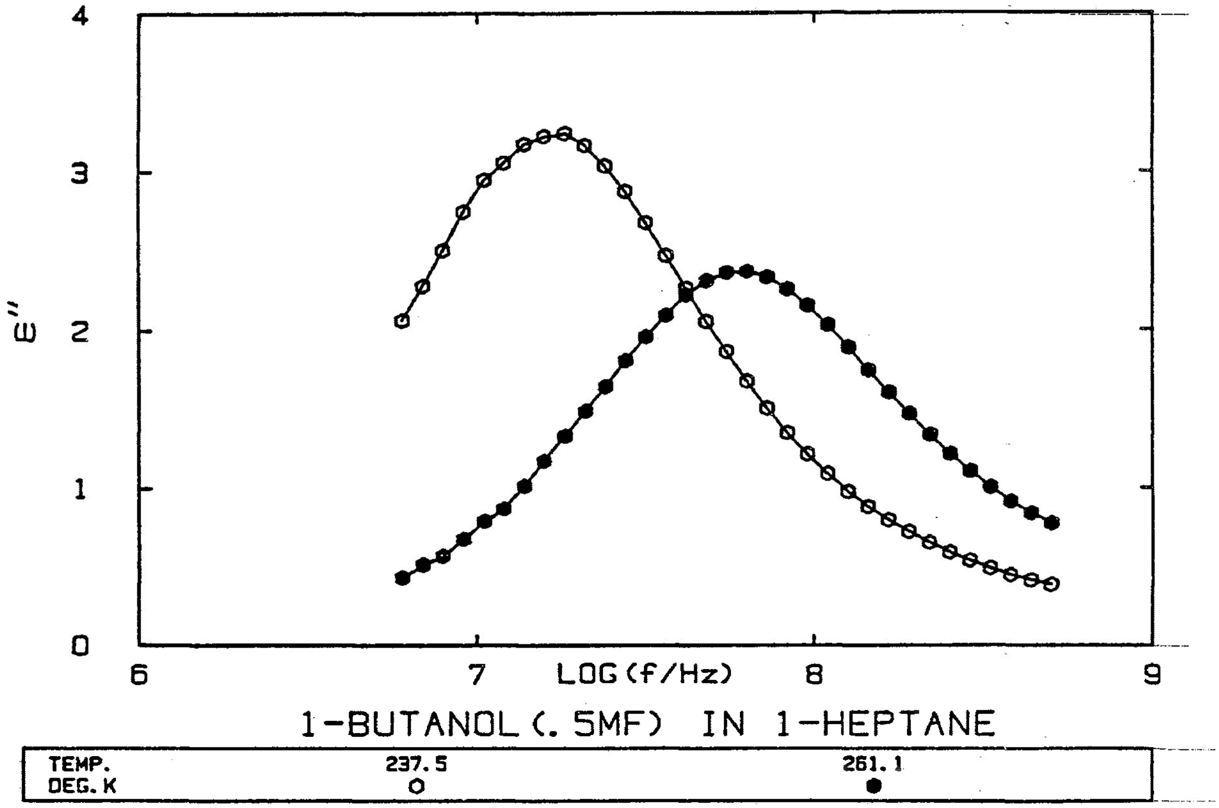


FIGURE IV-2: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-butanol in 1-heptane solution.

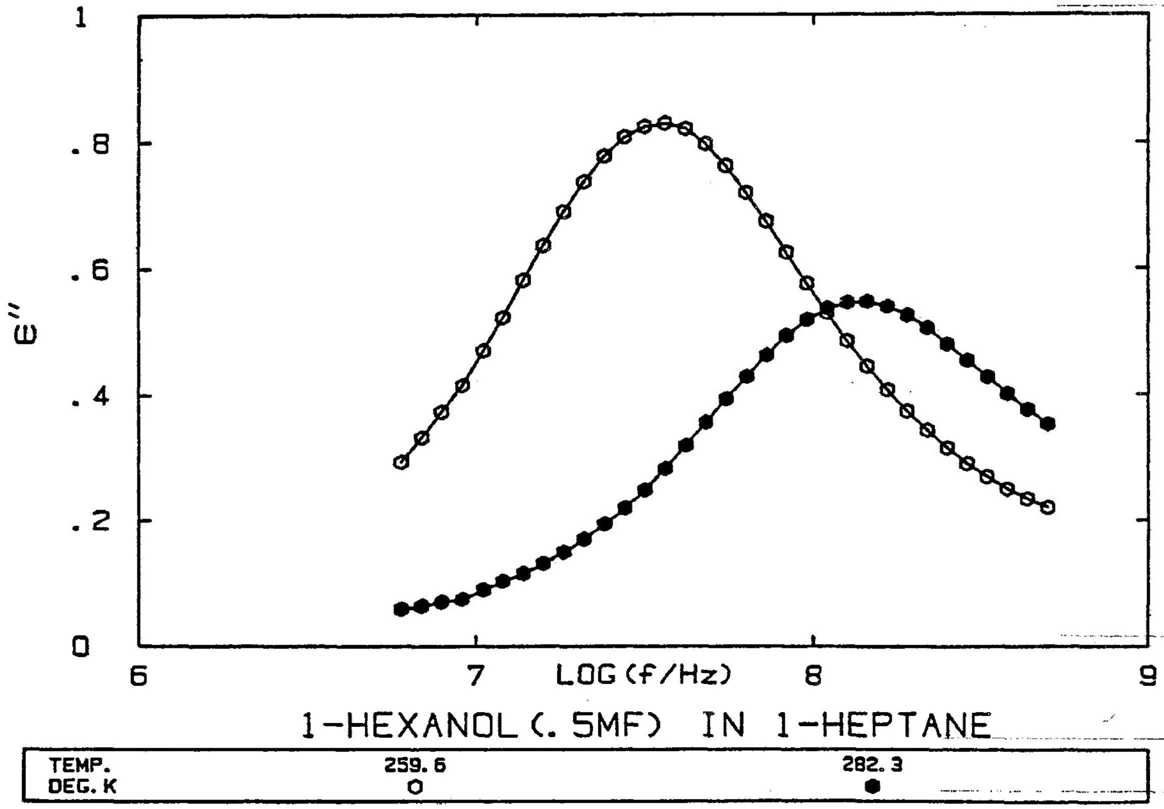


FIGURE IV-3: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-hexanol in 1-heptane solution.

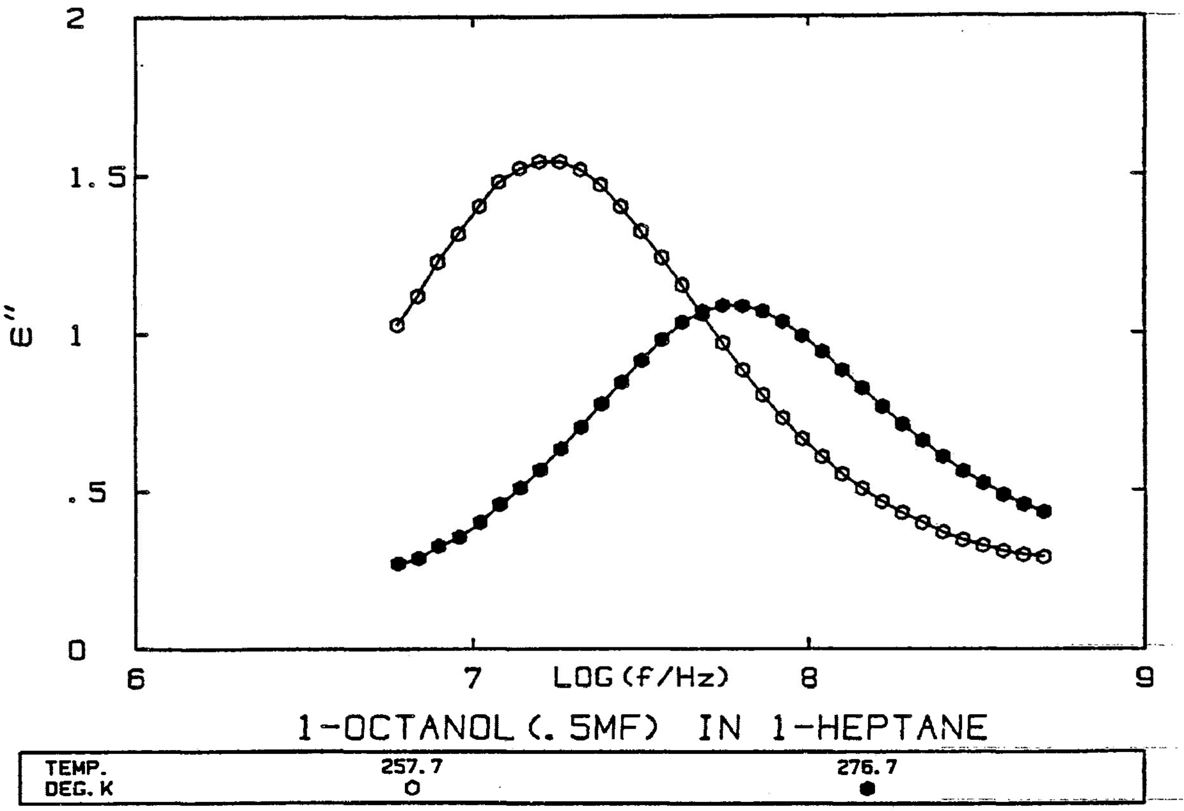


FIGURE IV-4: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-octanol in 1-heptane solution.

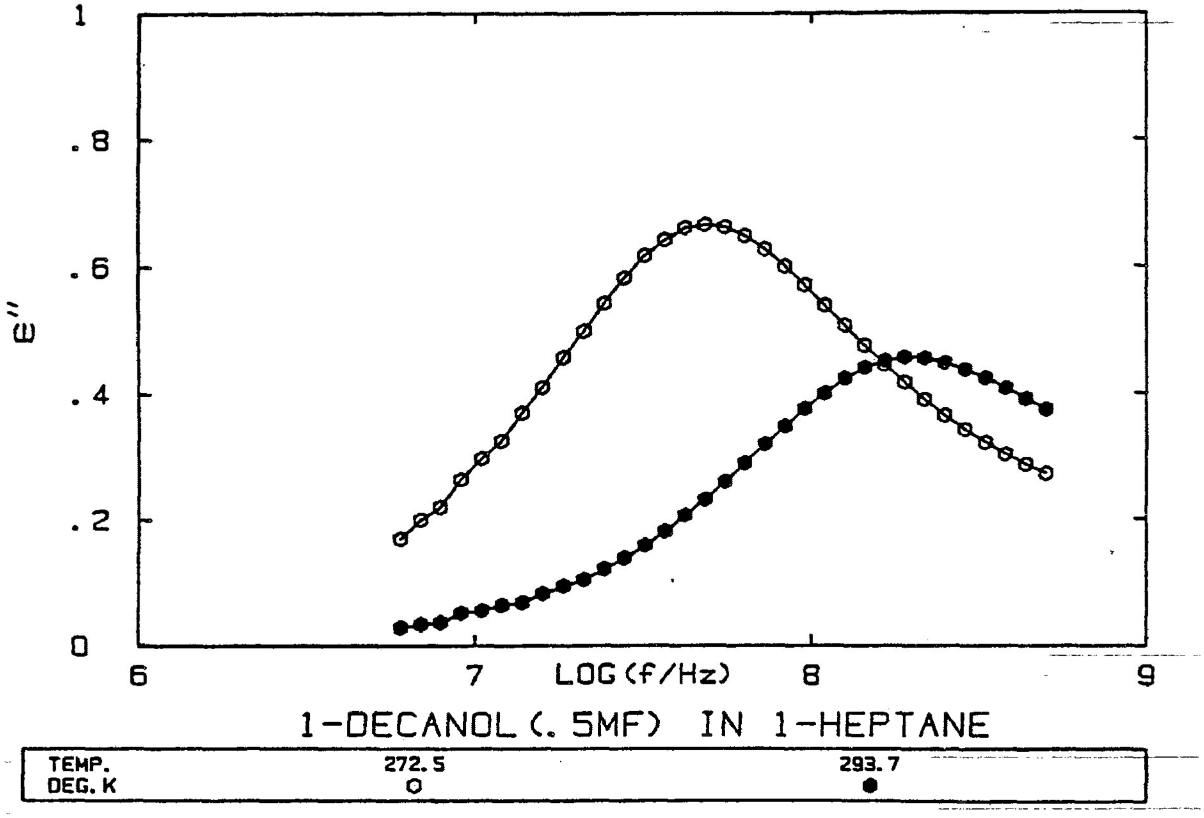


FIGURE IV-5: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-decanol in 1-heptane solution.

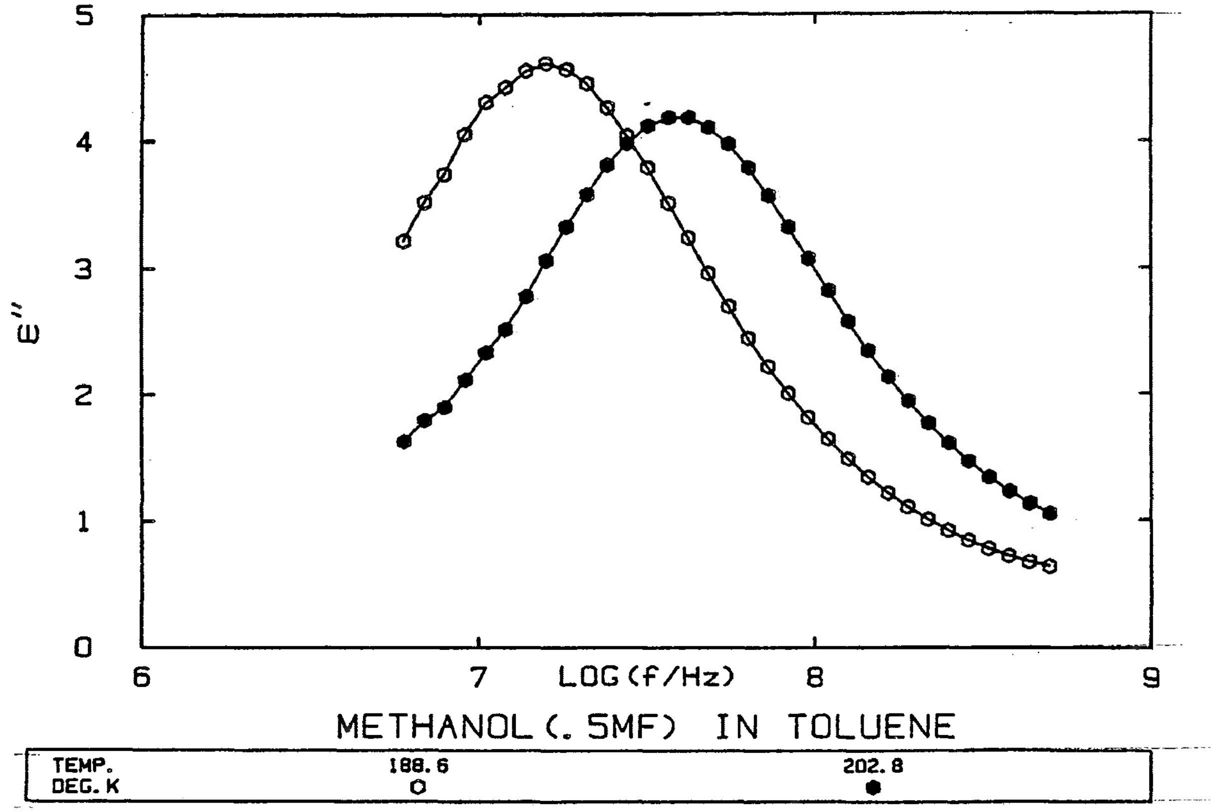


FIGURE IV-6: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of methanol in toluene solution.

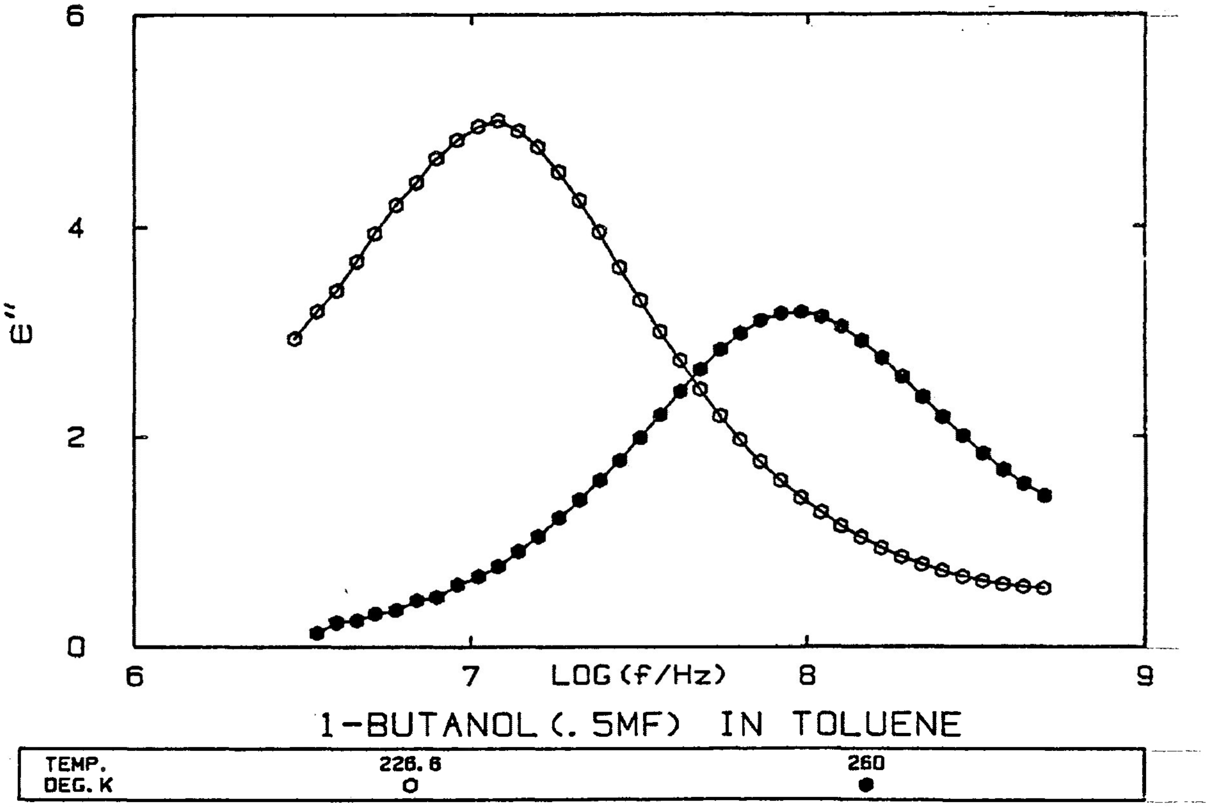


FIGURE IV-7: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-butanol in toluene solution.

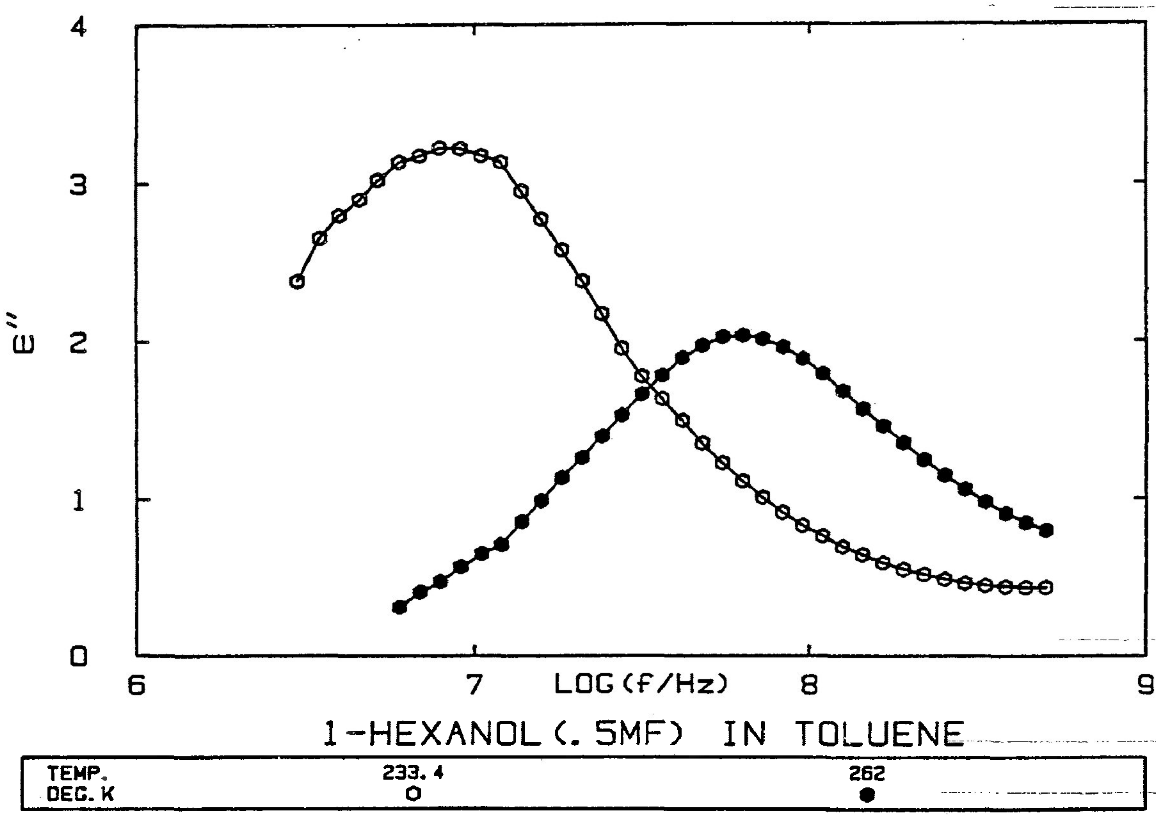


FIGURE IV-8: Dielectric loss factor, ε'' versus log frequency for 0.5 mole fraction of 1-hexanol in toluene solution.

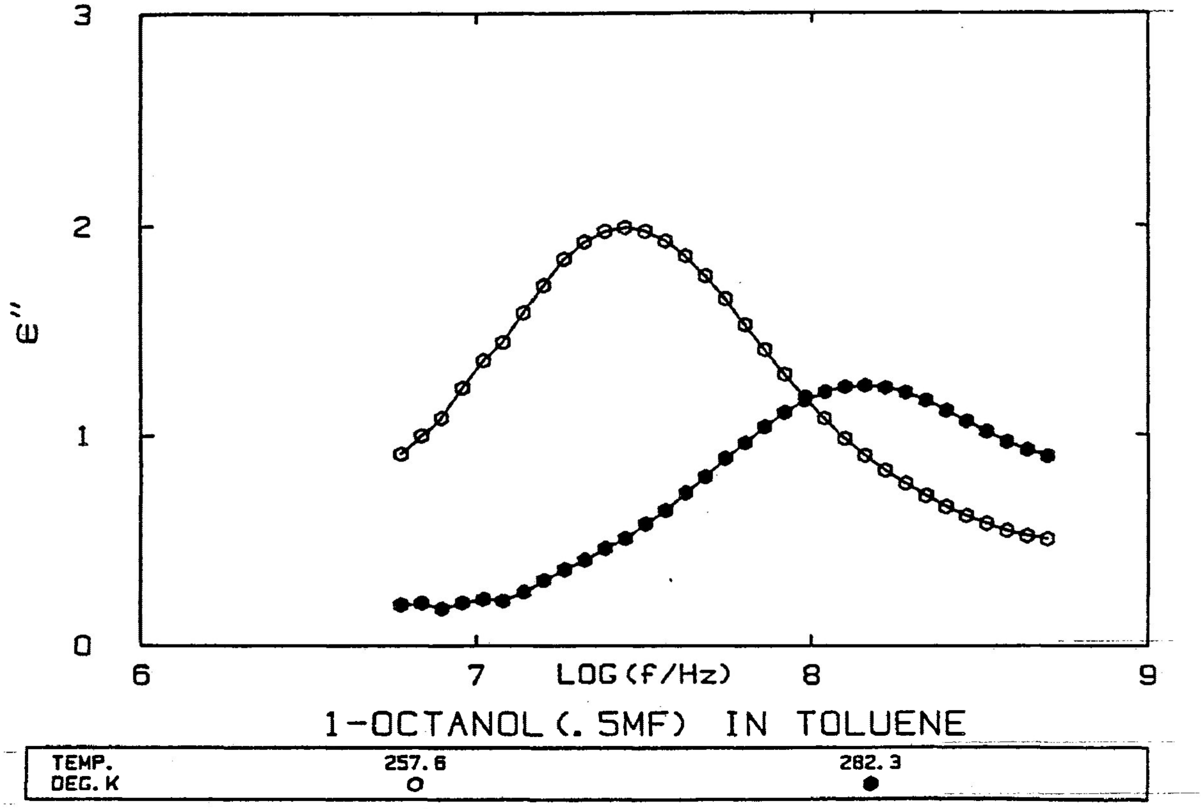


FIGURE IV-9: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-octanol in toluene solution.

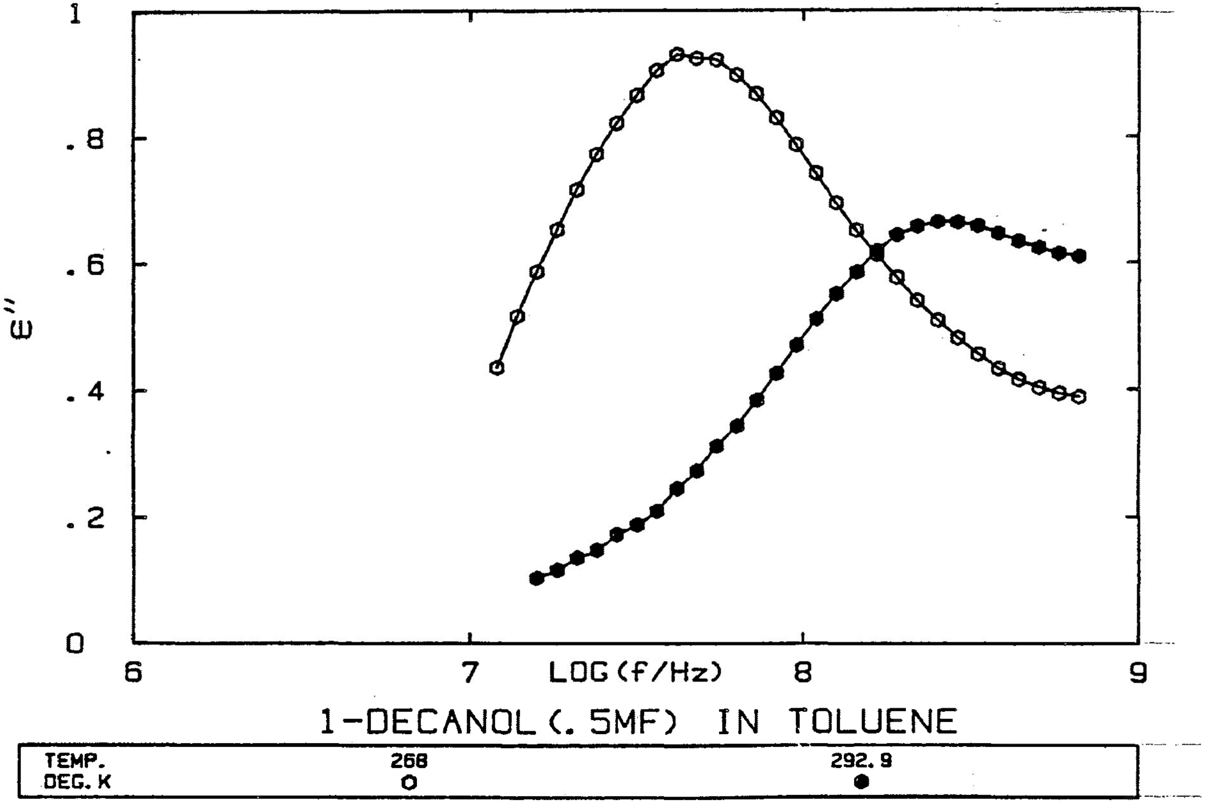


FIGURE IV-10: Dielectric loss factor, ε'' versus log frequency for 0.5 mole fraction of 1-decanol in toluene solution.

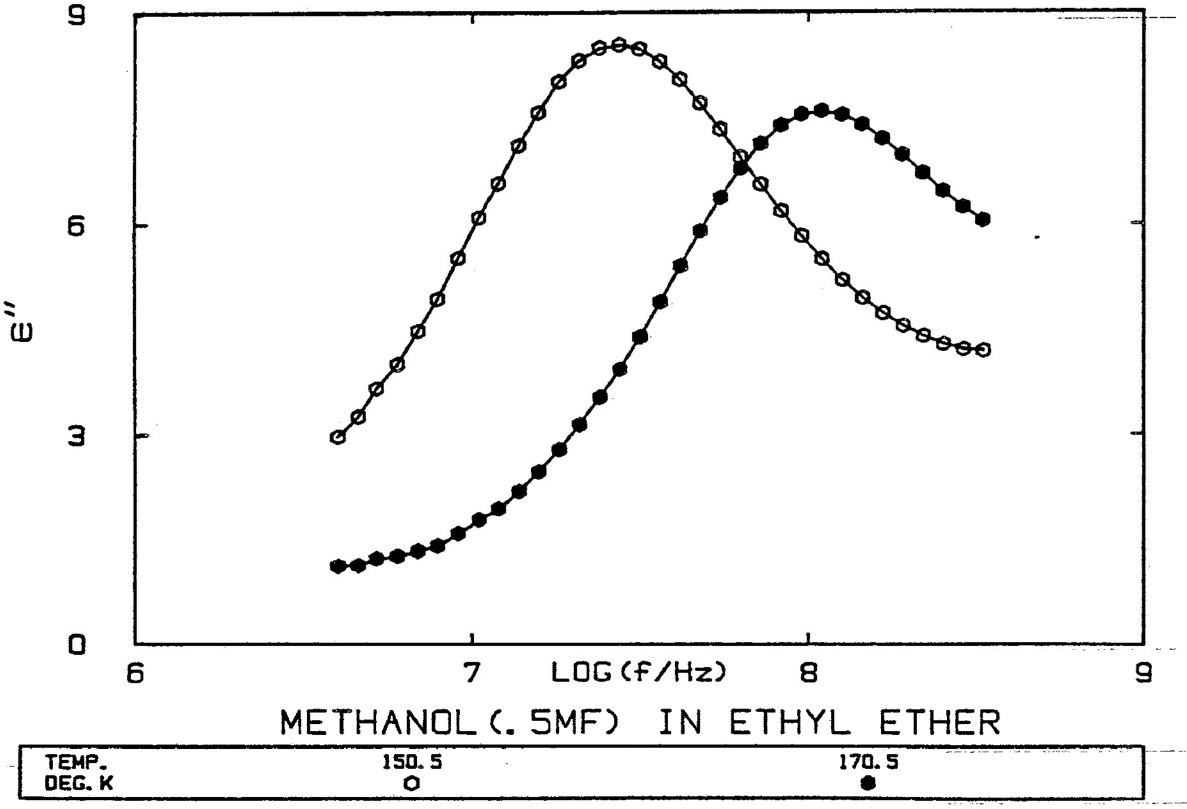


FIGURE IV-11: Dielectric loss factor, ε'' versus log frequency for 0.5 mole fraction of methanol in ethyl ether solution.

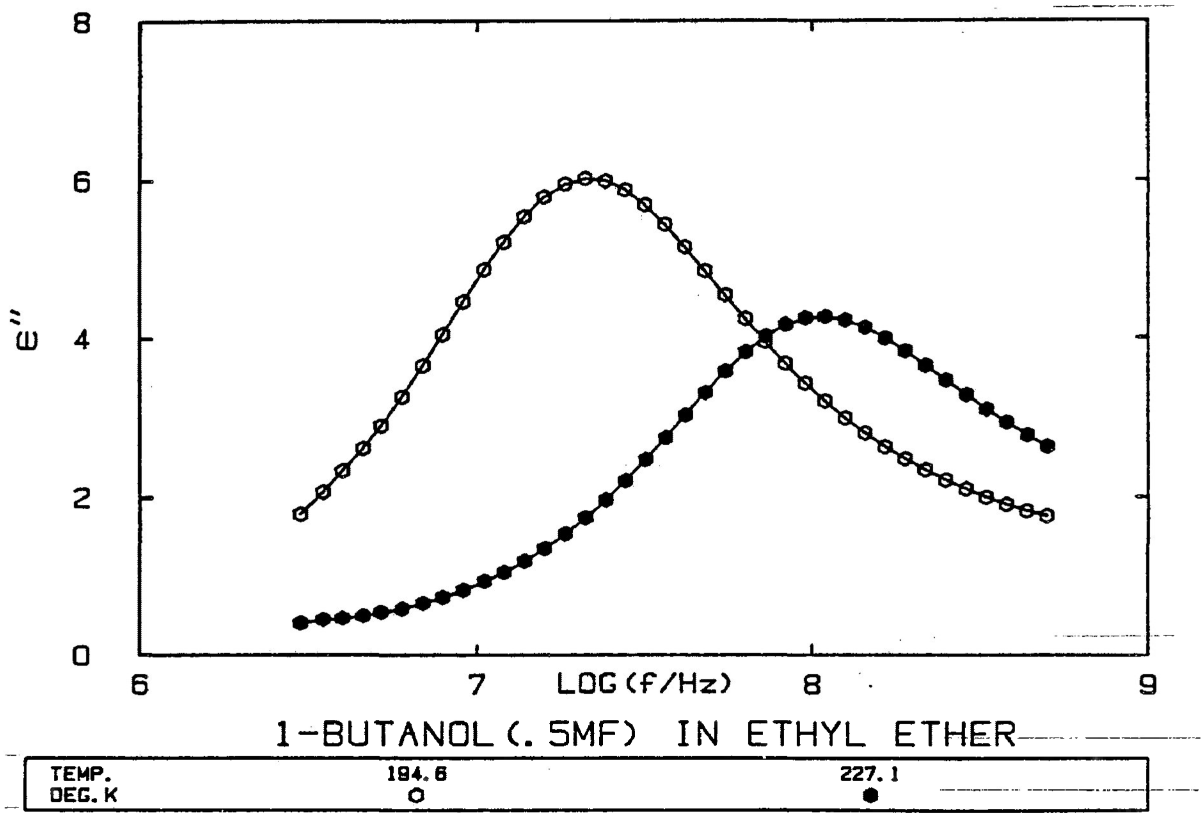


FIGURE IV-12: Dielectric loss factor, ε'' versus log frequency for 0.5 mole fraction of 1-butanol in ethyl ether solution.

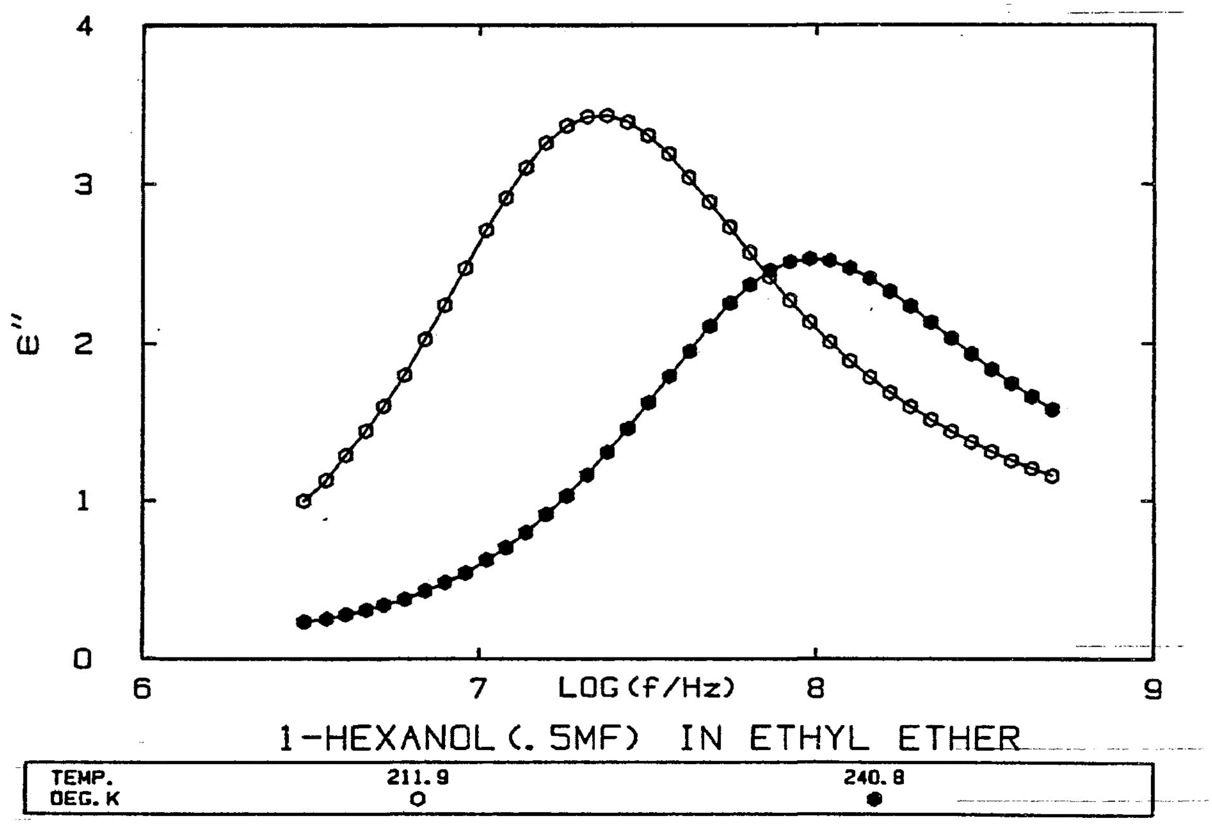


FIGURE IV-13: Dielectric loss factor, ε'' versus log frequency for 0.5 mole fraction of 1-hexanol in ethyl ether solution.

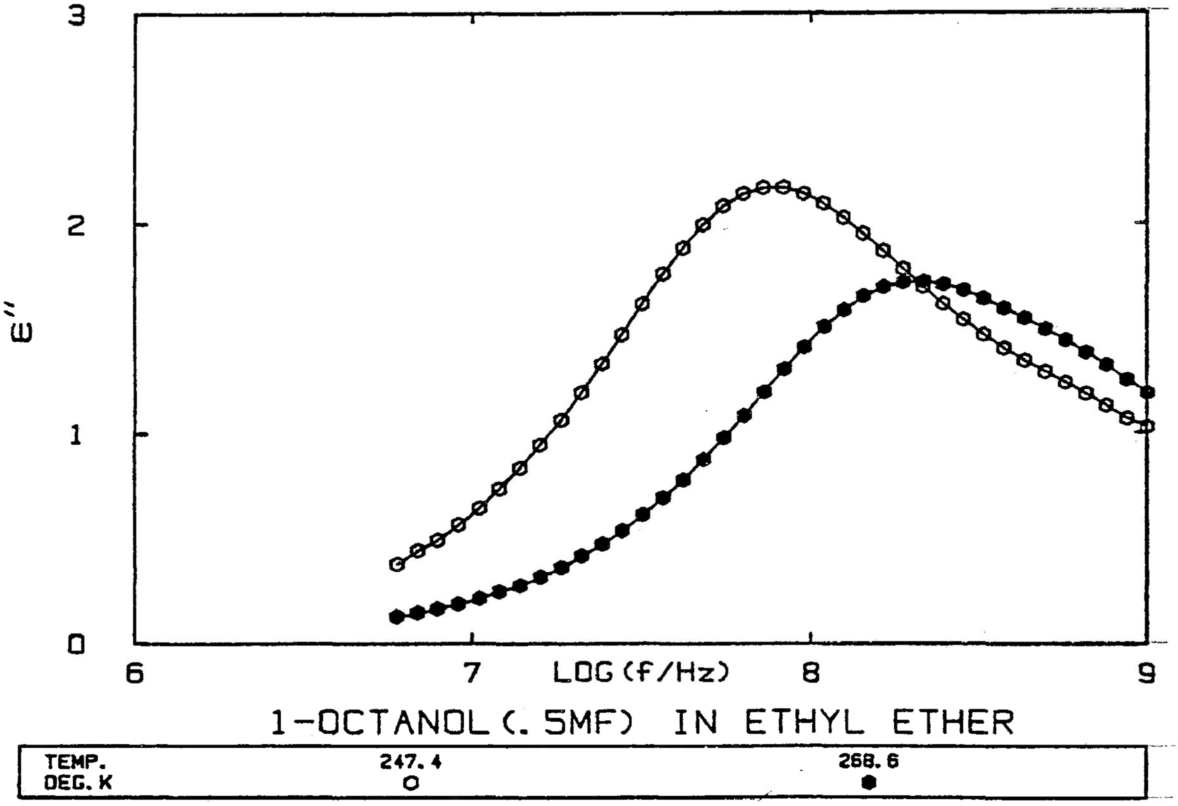


FIGURE IV-14: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-octanol in ethyl ether solution.

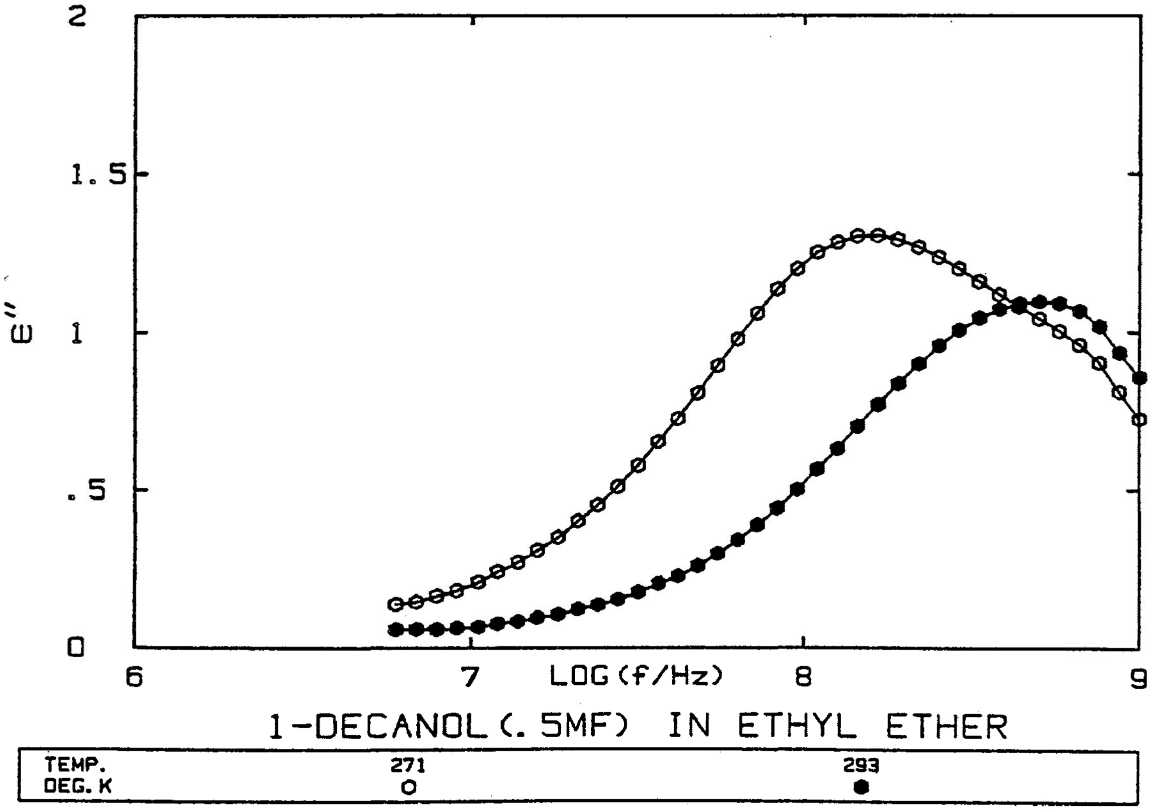


FIGURE III-15: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of 1-decanol in ethyl ether solution.

Solid lines from Figures IV-16 to IV-19 represent the corresponding theoretically calculated τ_1 values using Equation 6 of Chapter IV.

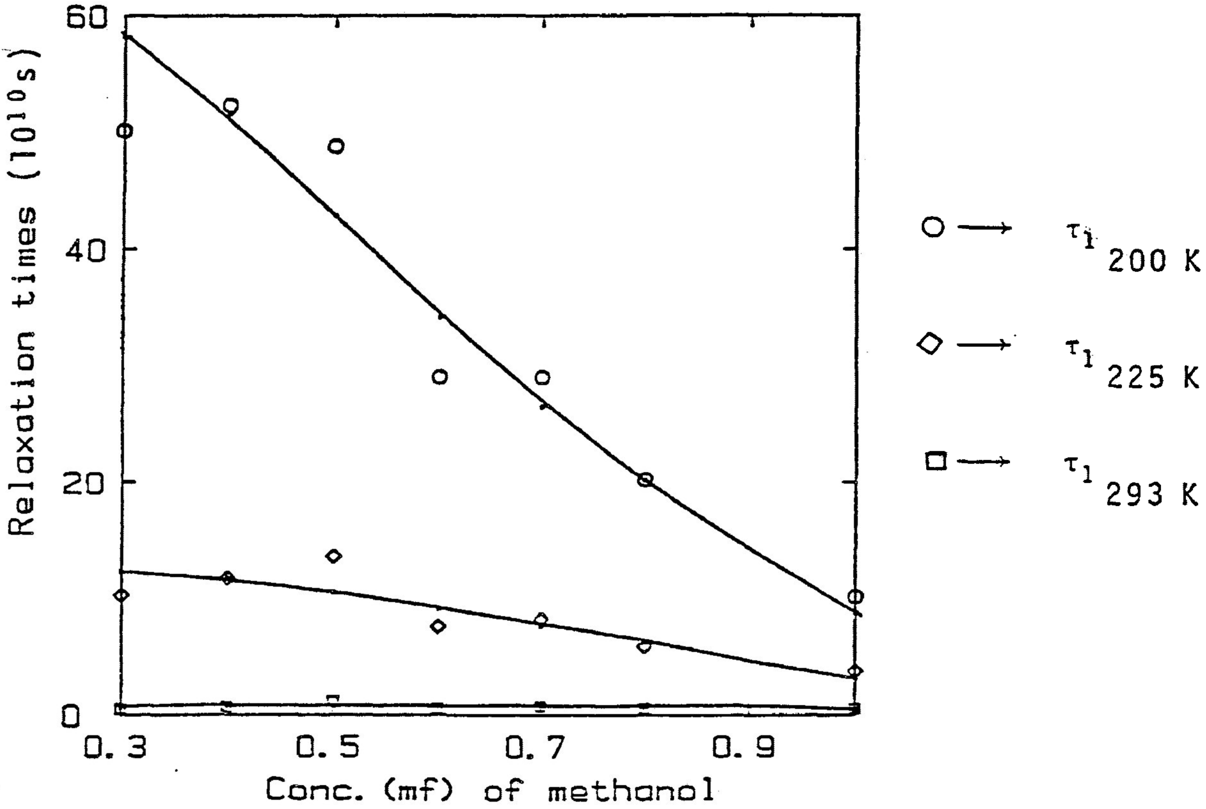


FIGURE IV-16a: Principal relaxation times, τ_1 versus mole fraction of methanol, in toluene solution.

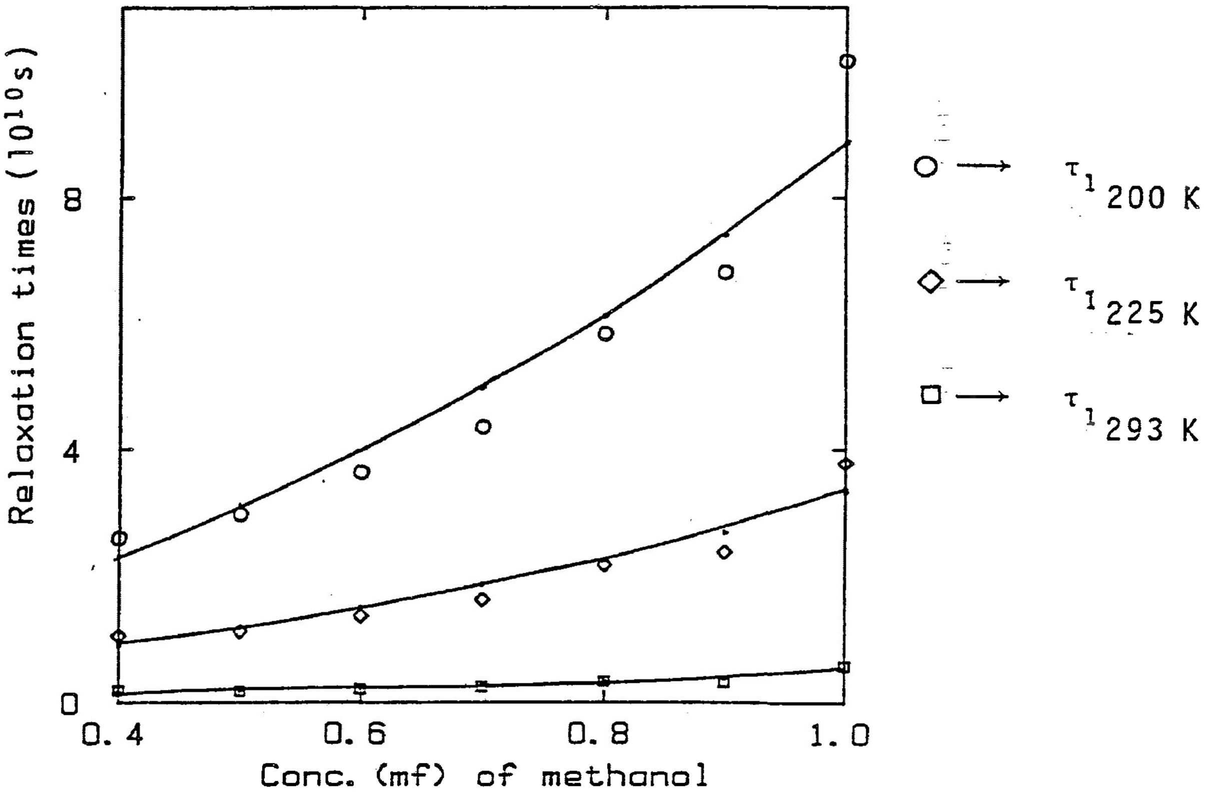


FIGURE IV-16b: Principal relaxation times, τ_1 versus mole fraction of methanol, in ethyl ether solution.

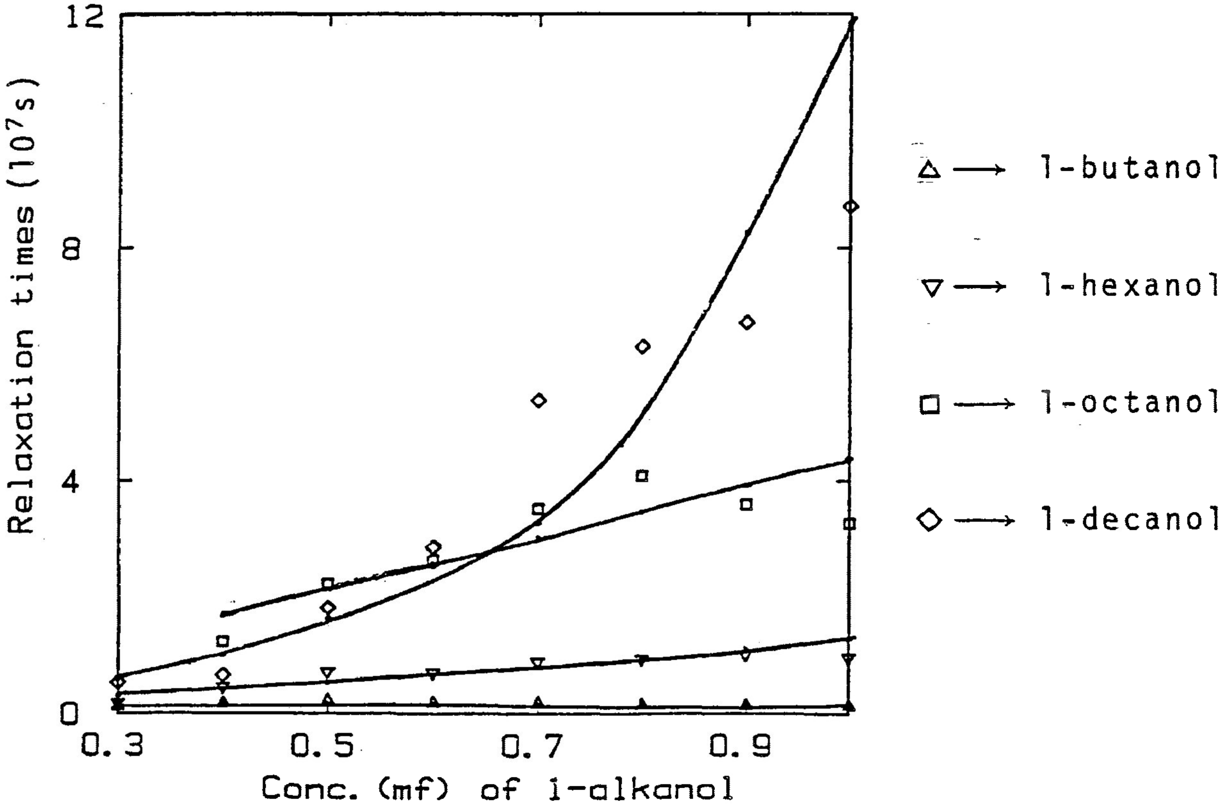


FIGURE IV-17a: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in 1-heptane solution at 200 K.

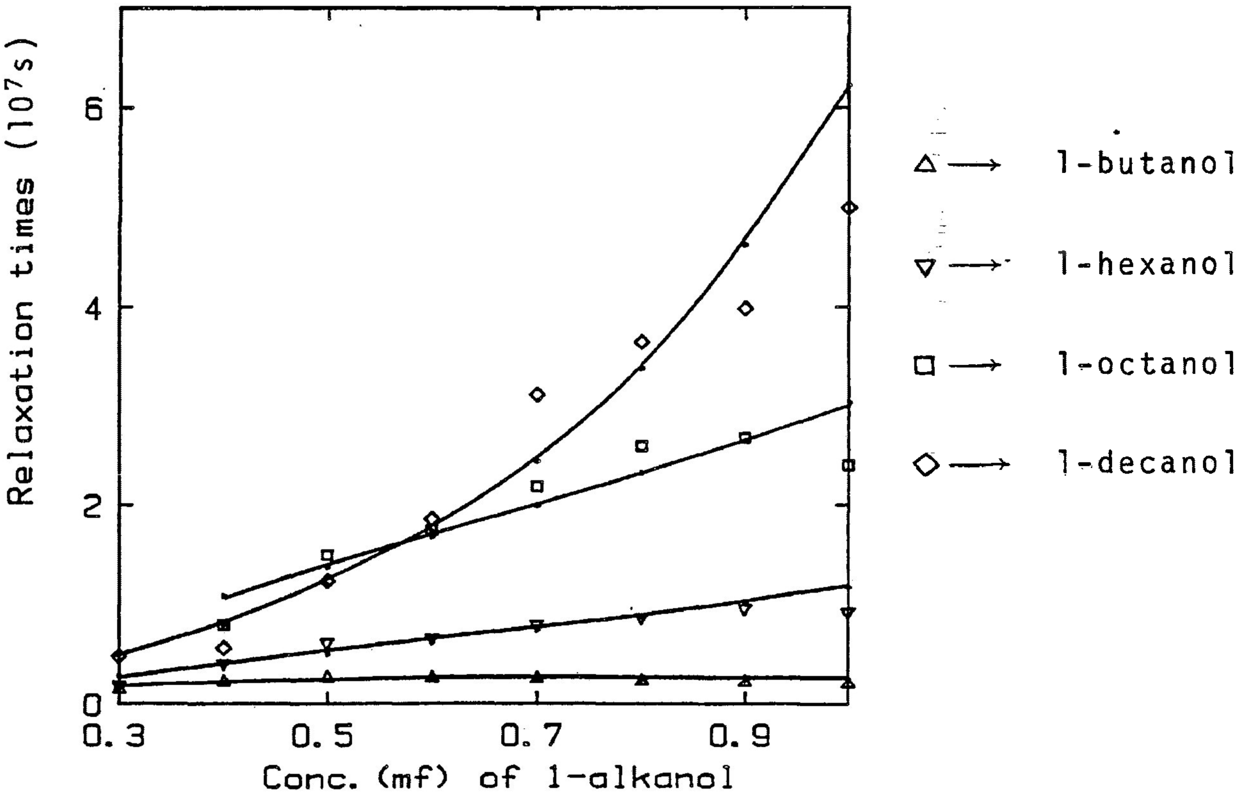


FIGURE IV-17b: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in 1-heptane solution at 225 K.

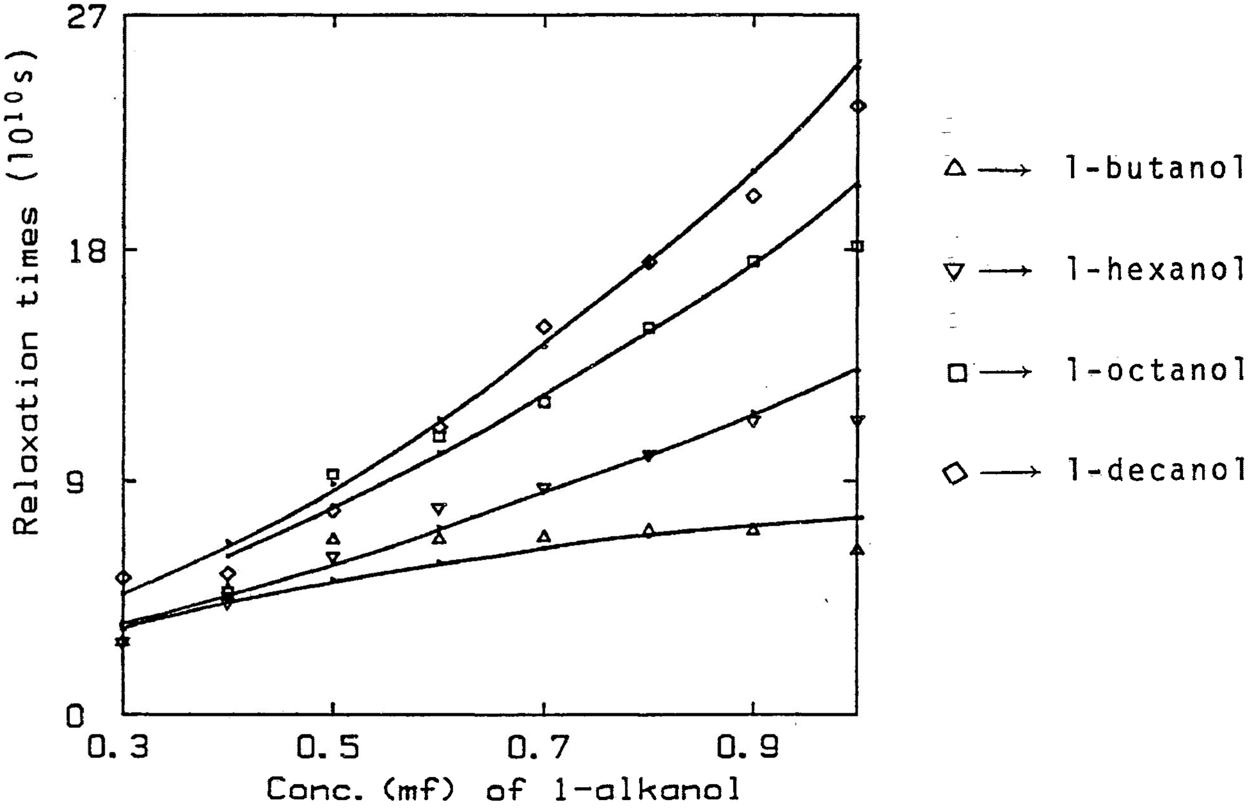


FIGURE IV-17c: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in 1-heptane solution at 293 K.

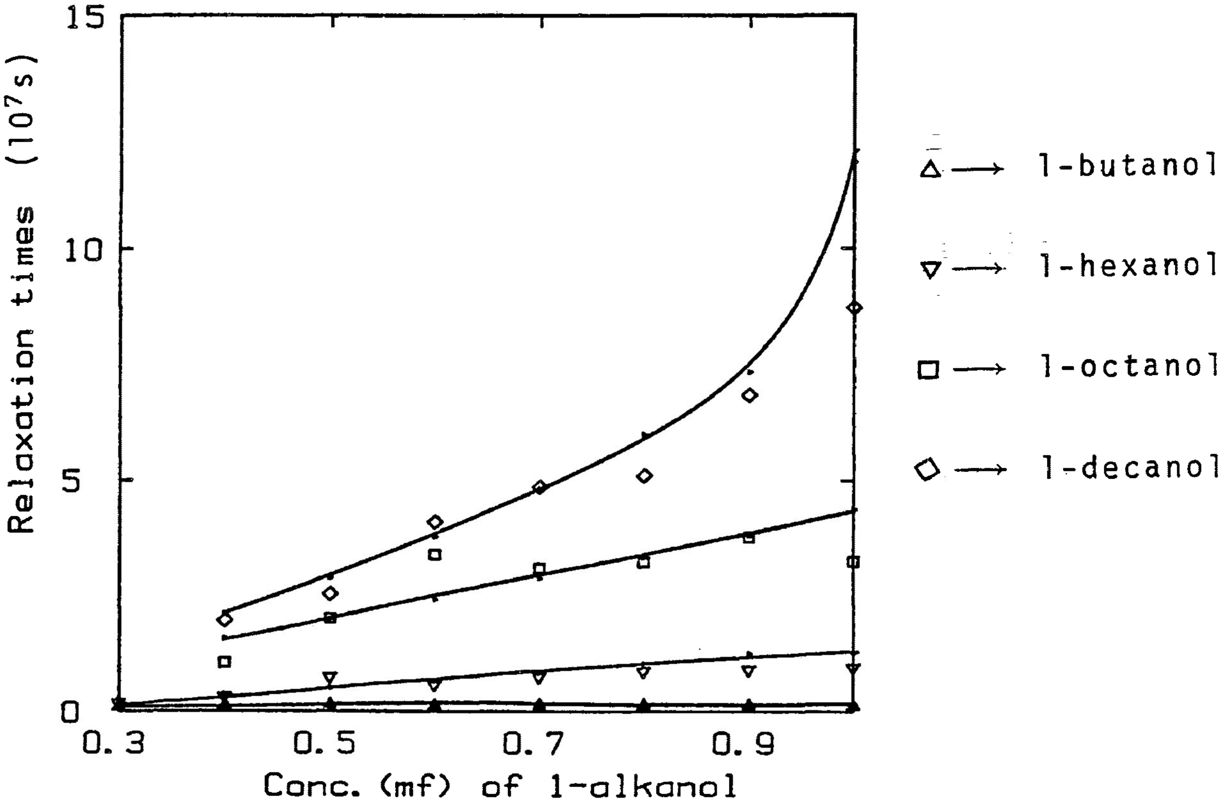


FIGURE IV-18a: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in toluene solution at 200 K.

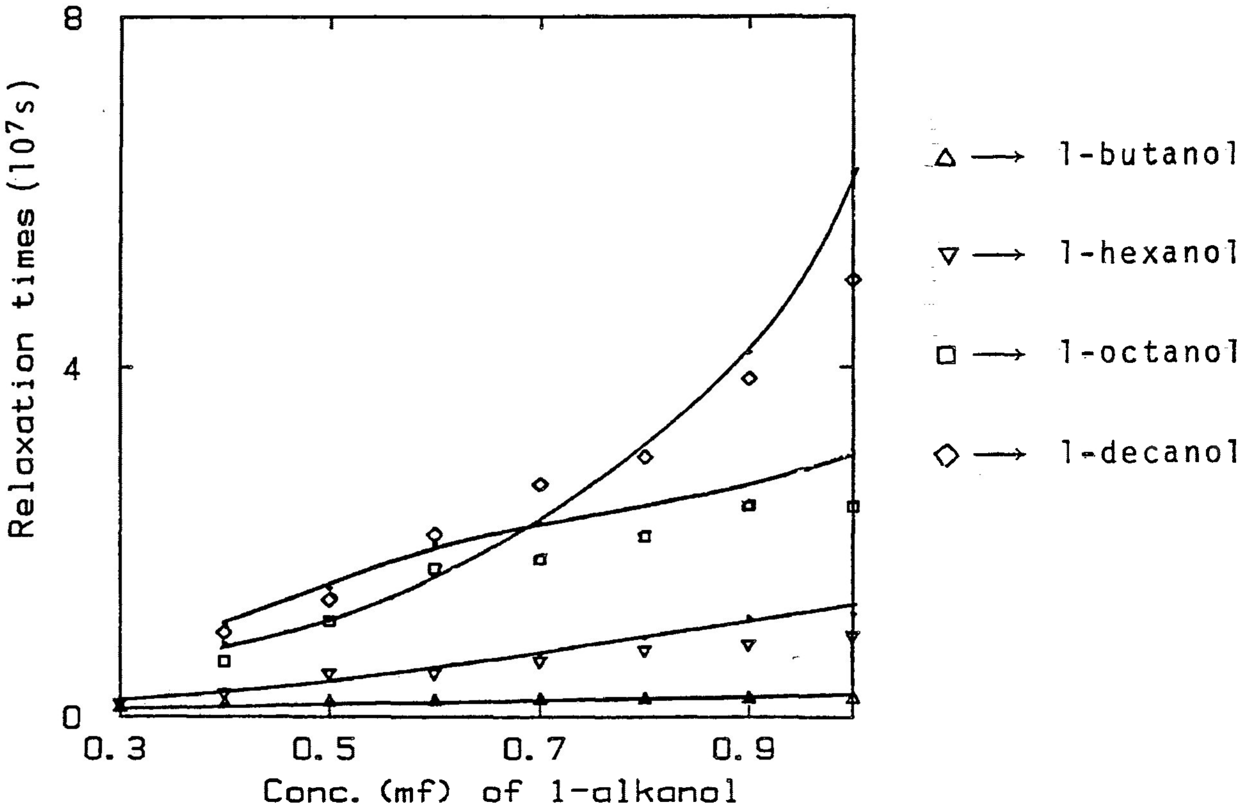
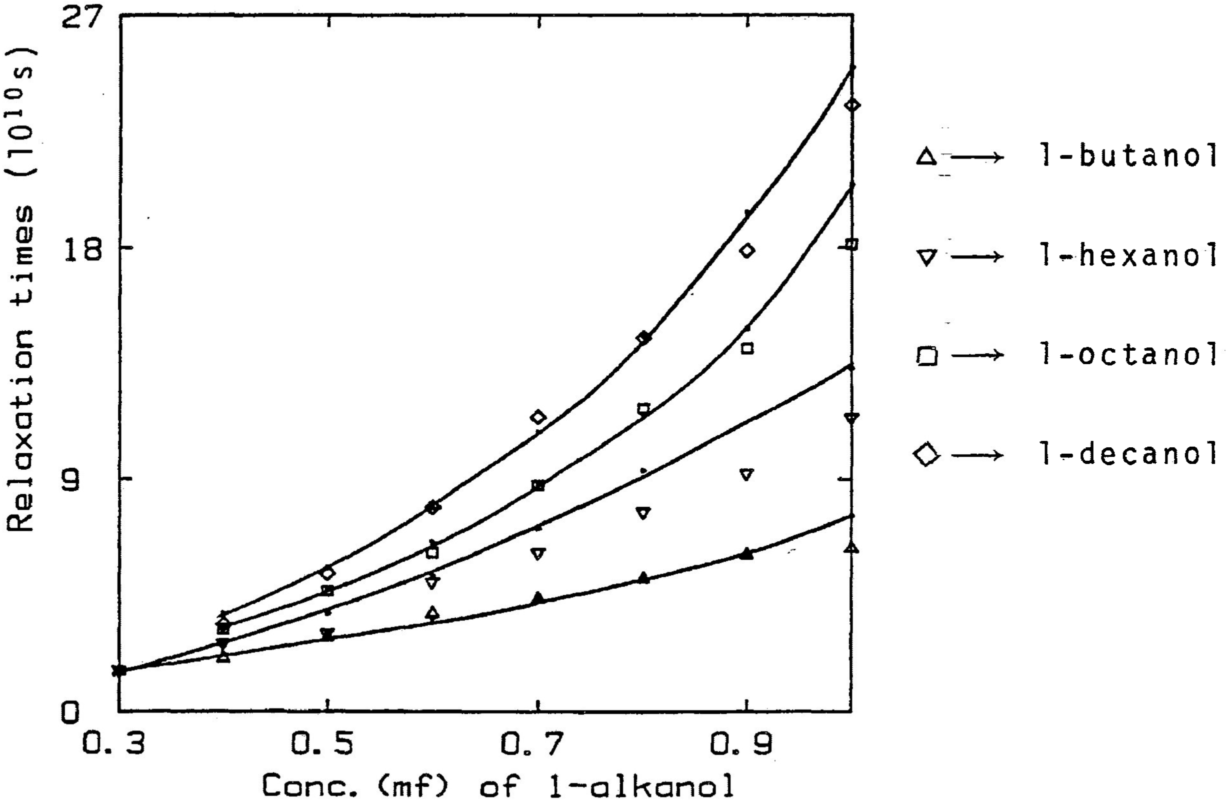


FIGURE IV-18b: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in toluene solution at 225 K.



<u>FIGURE IV-18c</u>: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in toluene solution at 293 K.

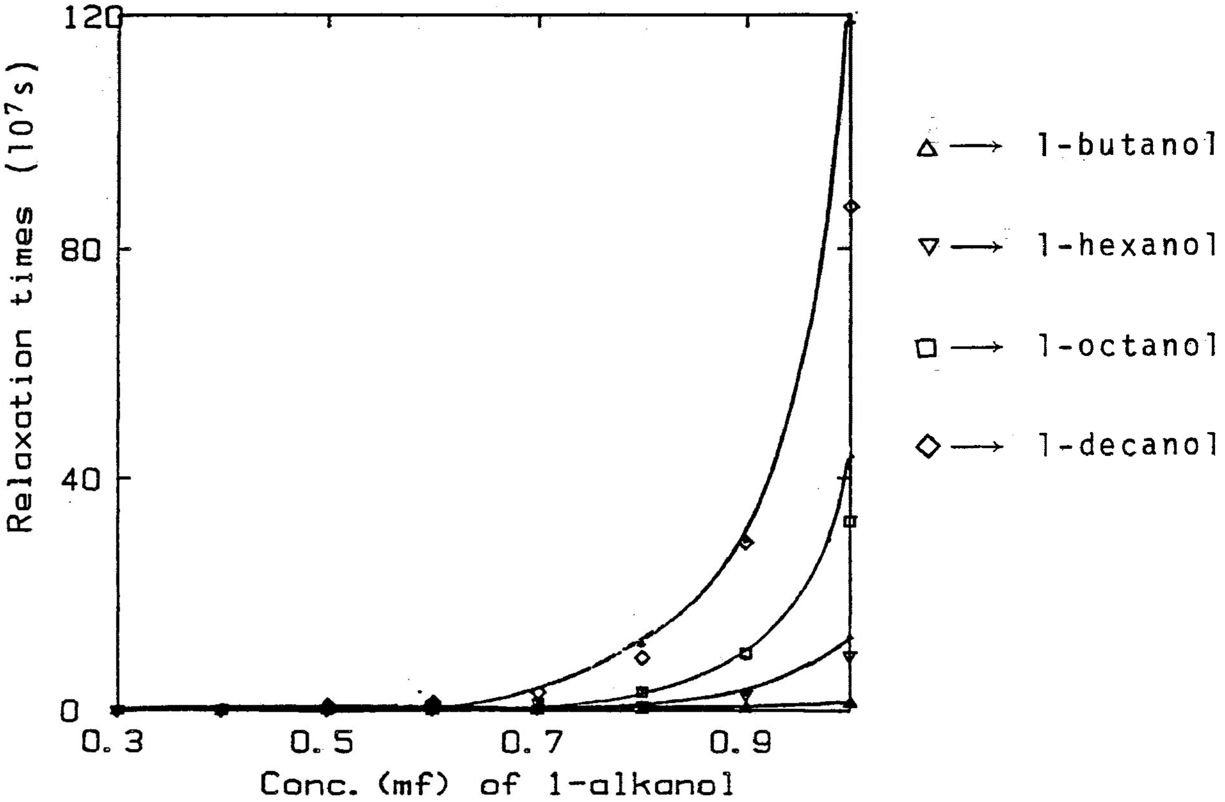


FIGURE IV-19a: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in ethyl ether solution at 200 K.

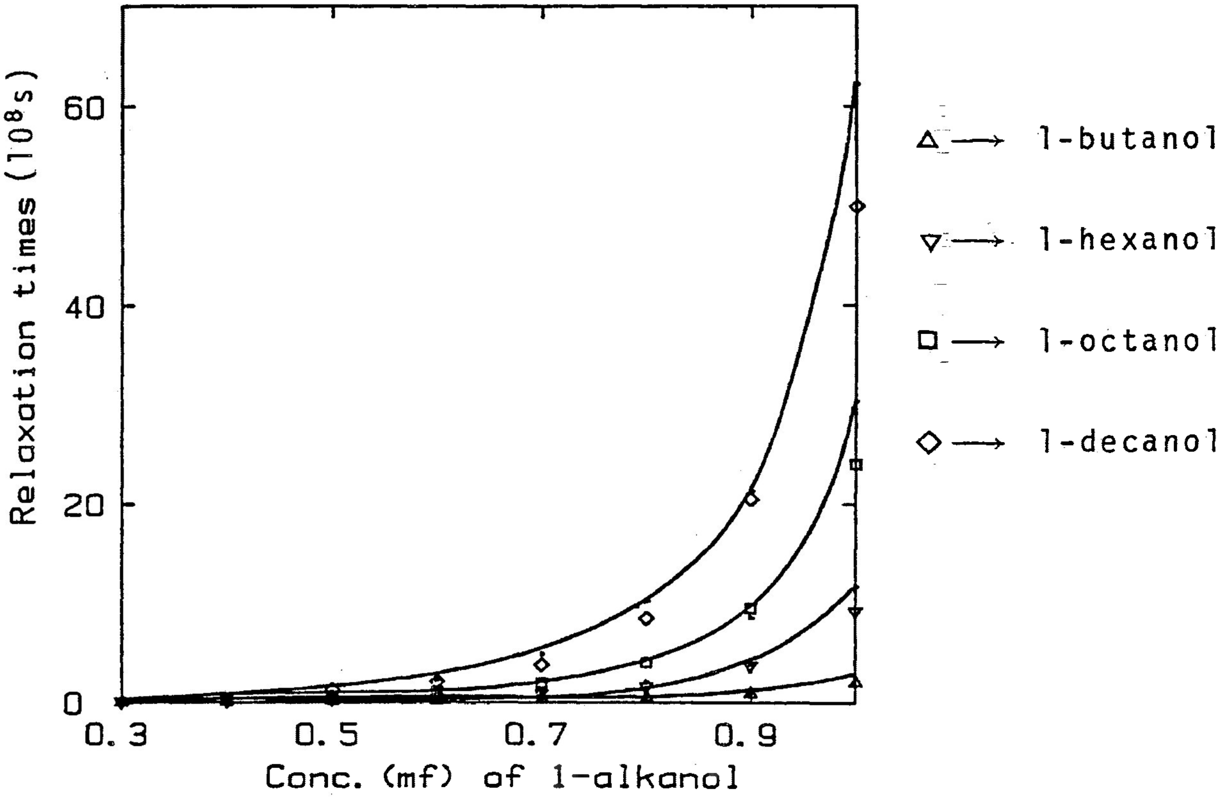


FIGURE IV-19b: Principal relxation times, τ_1 versus mole fraction of 1-alkanol, in ethyl ether solution at 225 K.

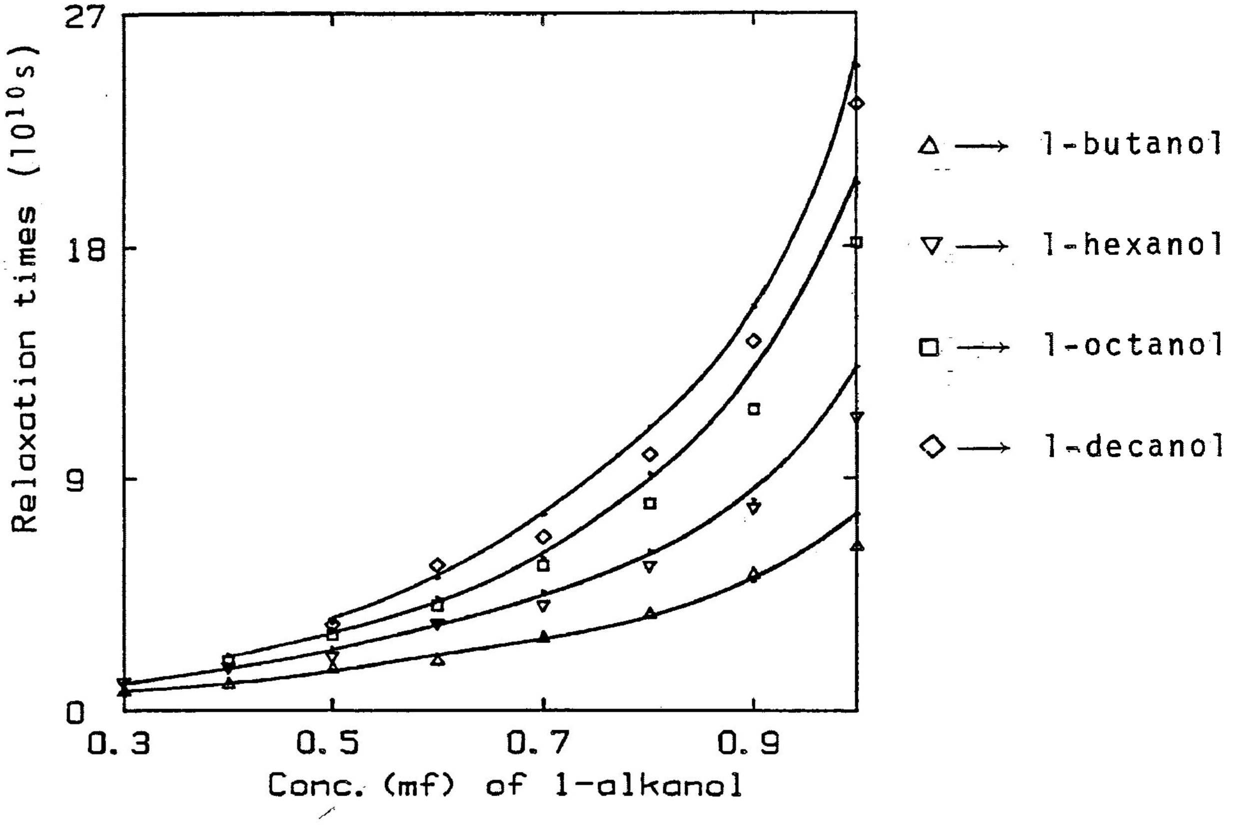


FIGURE IV-19c: Principal relaxation times, τ_1 versus mole fraction of 1-alkanol, in ethyl ether solution at 293 K.

Solid lines from Figures IV-20 to IV-22 represent the corresponding least square fittings for the experimental data points.

The symbols used for different alcohols from Figures IV-20 to IV-23 are:

△ ⟶ Methanol
▽ ⟶ 1-Butanol
□ ⟶ 1-Hexanol
◇ ⟶ 1-Octanol
○ ⟶ 1-Decanol

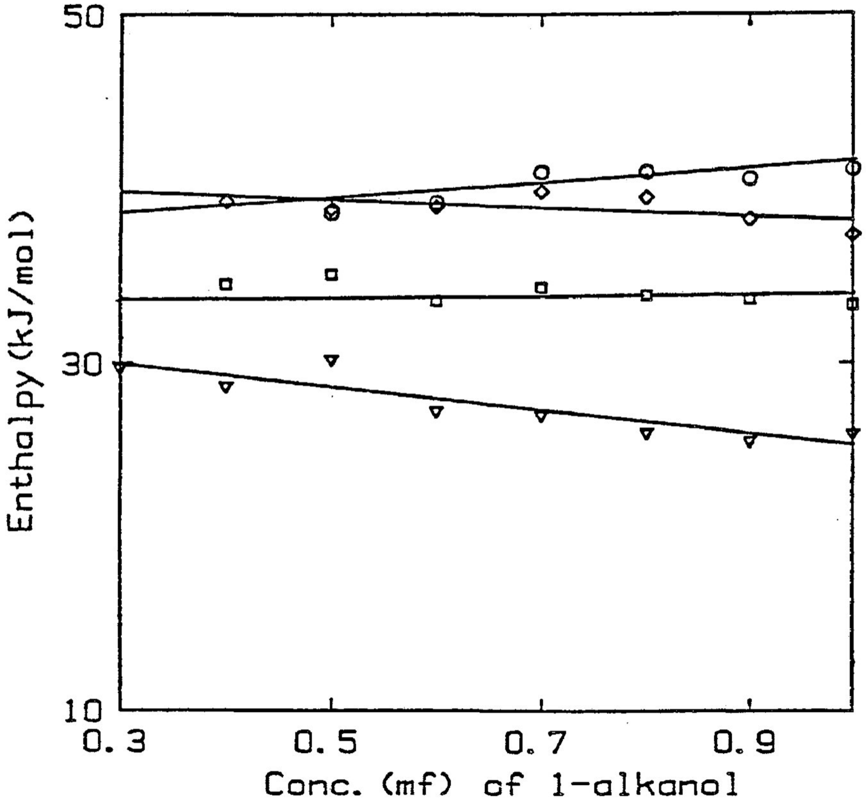


FIGURE IV-20a: Enthalpy of activation (ΔH_E) as a function of alcohol mole fraction, in 1-heptane solution.

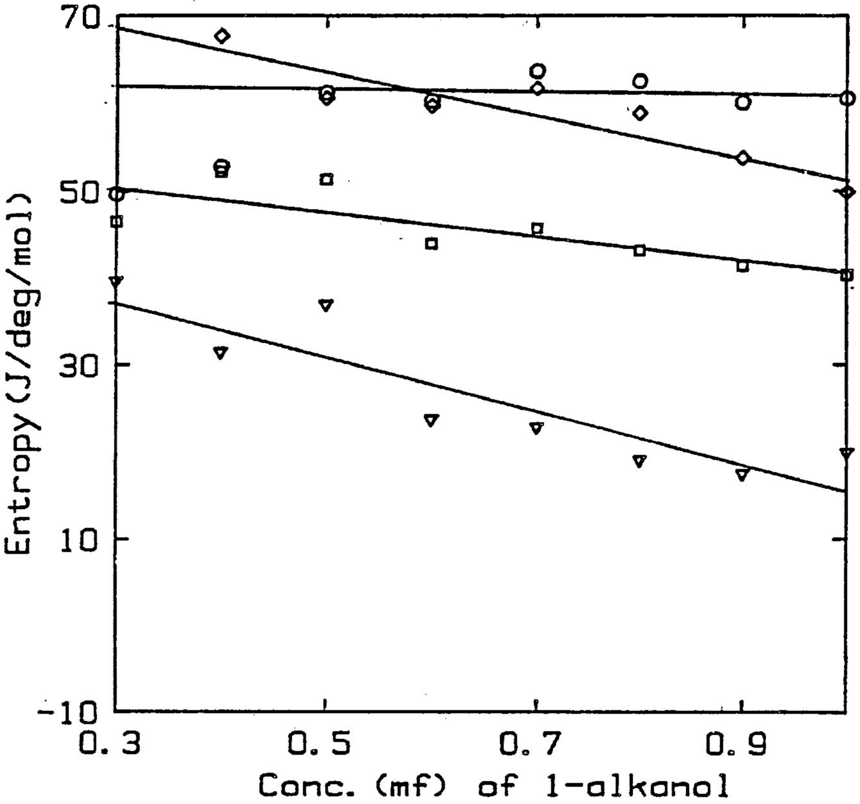


FIGURE IV-20b: Entropy of activation (ΔS_E) as a function of alcohol mole fraction, in 1-heptane solution.

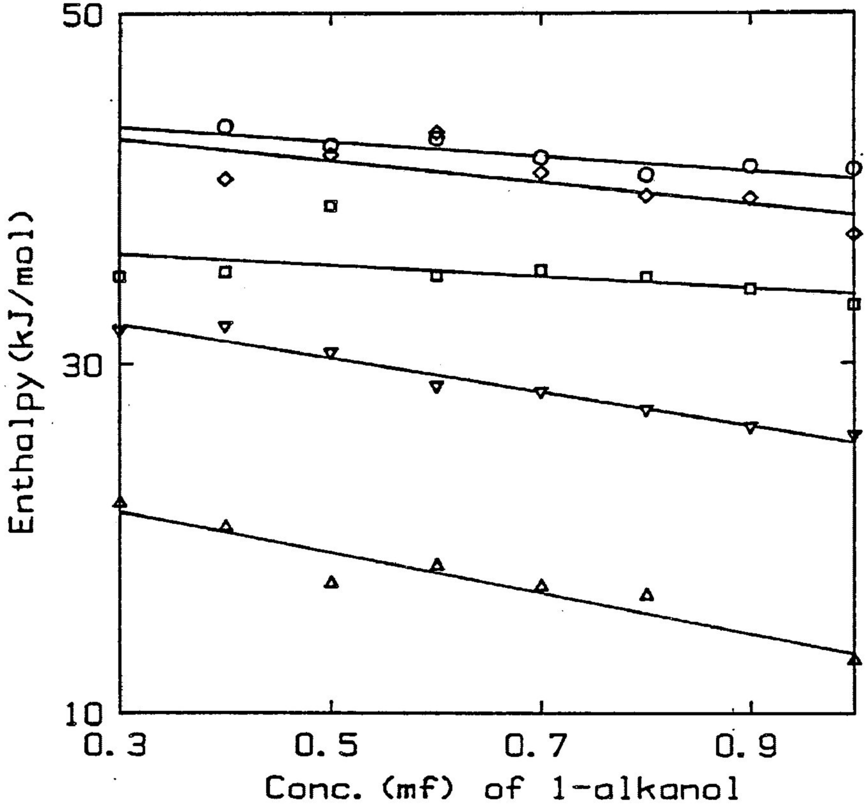


FIGURE IV-21a: Enthalpy of activation (ΔH_E) as a function of alcohol mole fraction, in toluene solution.

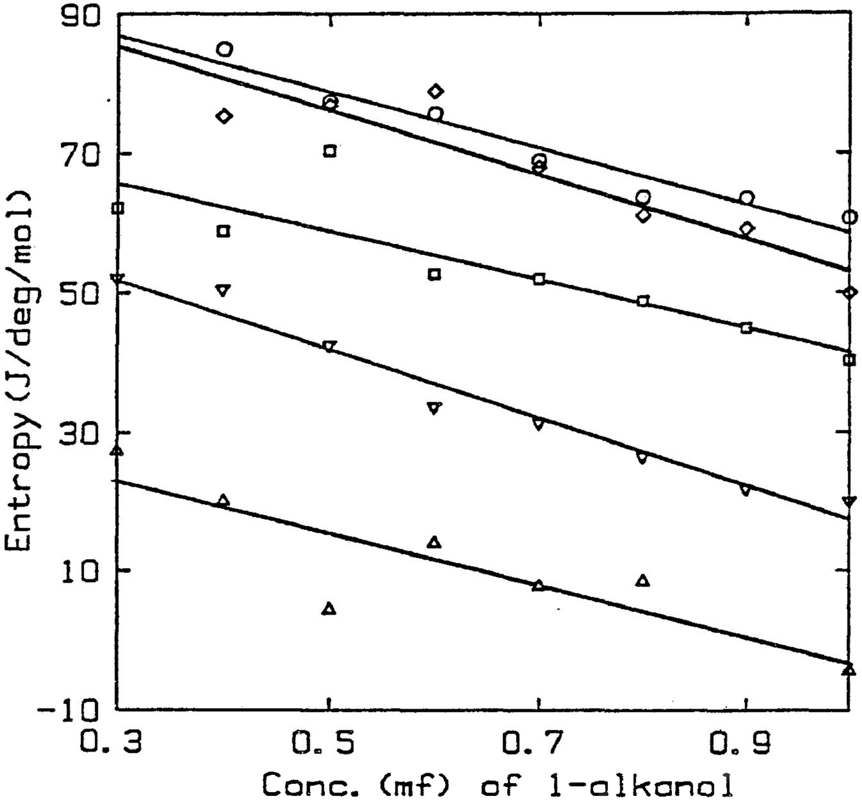


FIGURE IV-21b: Entropy of activation (ΔS_E) as a function of alcohol mole fraction, in toluene solution.

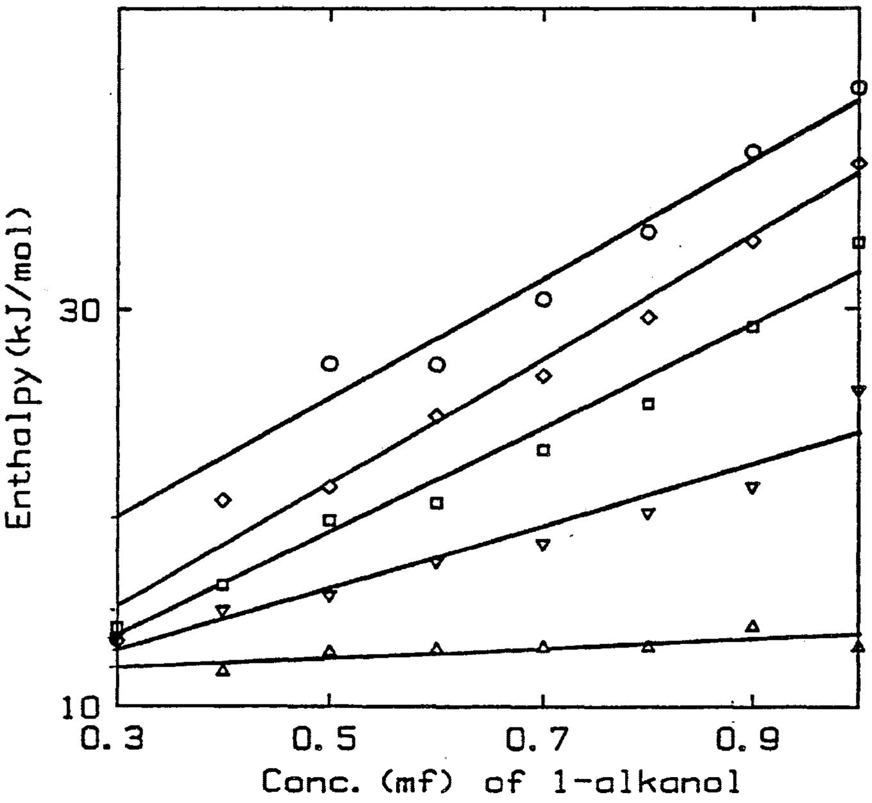


FIGURE IV-22a: Enthalpy of activation (ΔH_E) as a function of alcohol mole fraction, in diethyl ether solution.

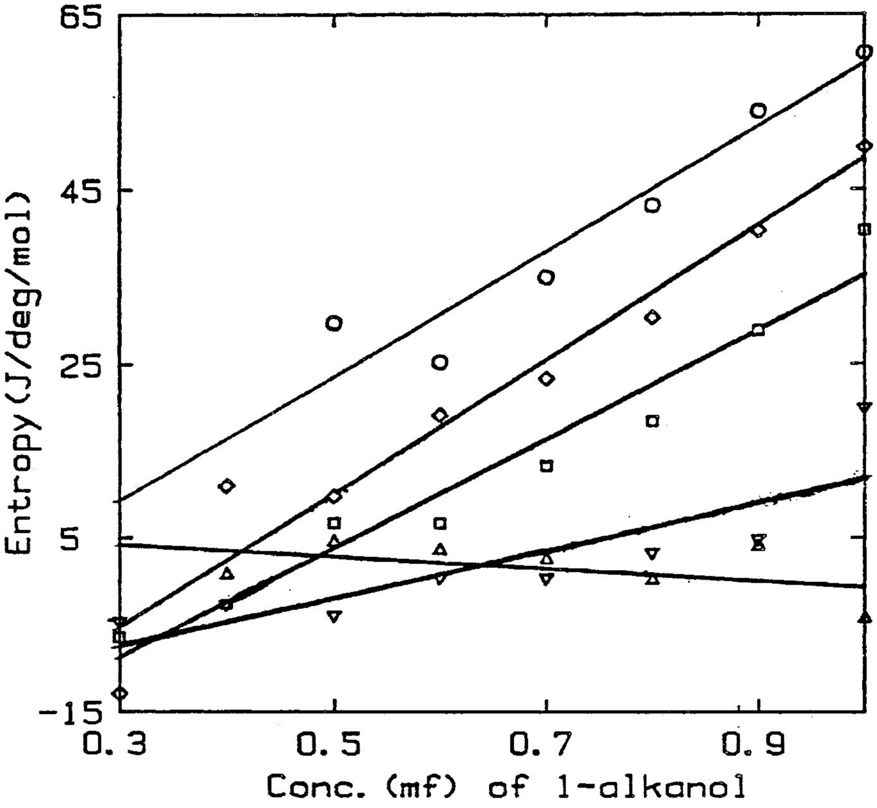


FIGURE IV-22b: Entropy of activation (ΔS_E) as a function of alcohol mole fraction, in diethyl ether solution.

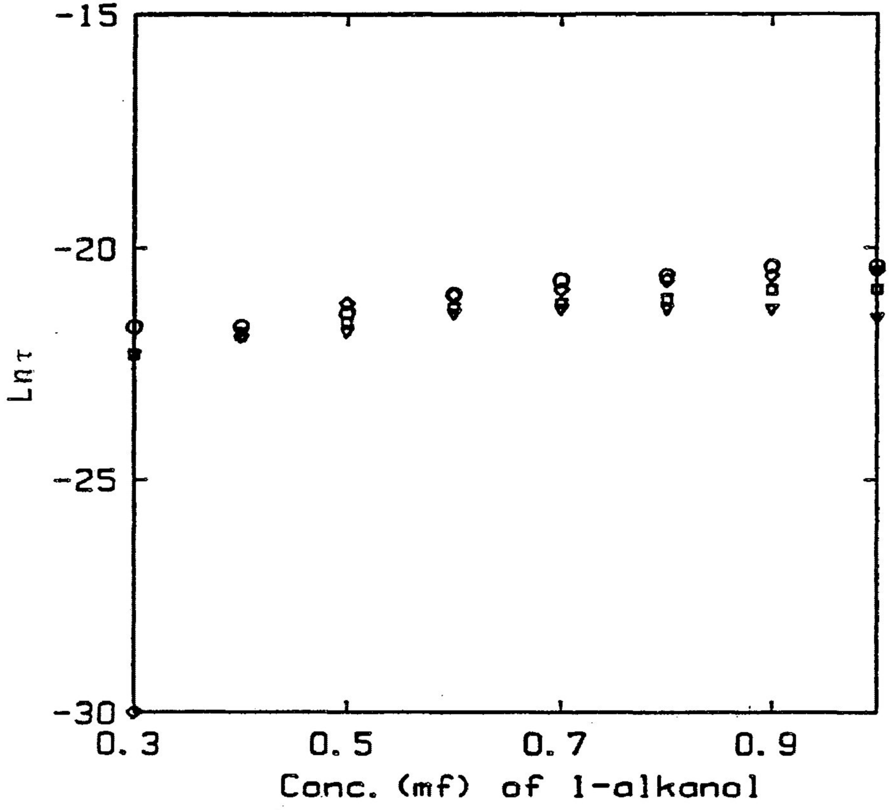


FIGURE IV-23a: Lnτ as a function of alcohol mole fraction, in 1-heptane solution at T = 300° K.

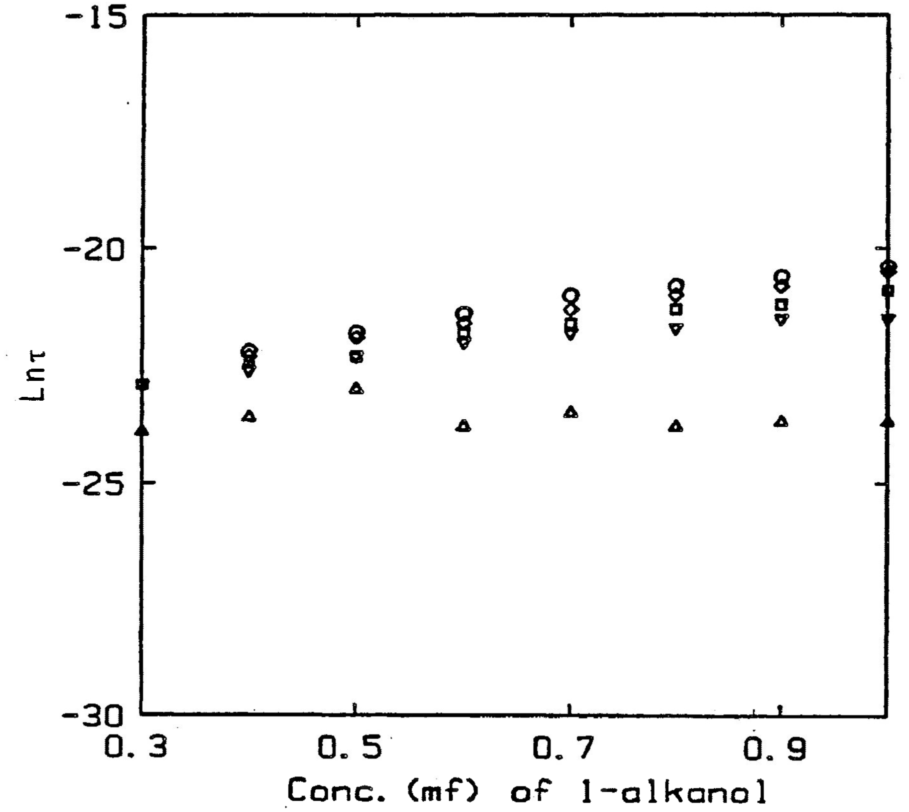


FIGURE IV-23b: Lnτ as a function of alcohol mole fraction, in toluene solution at T = 300°K.

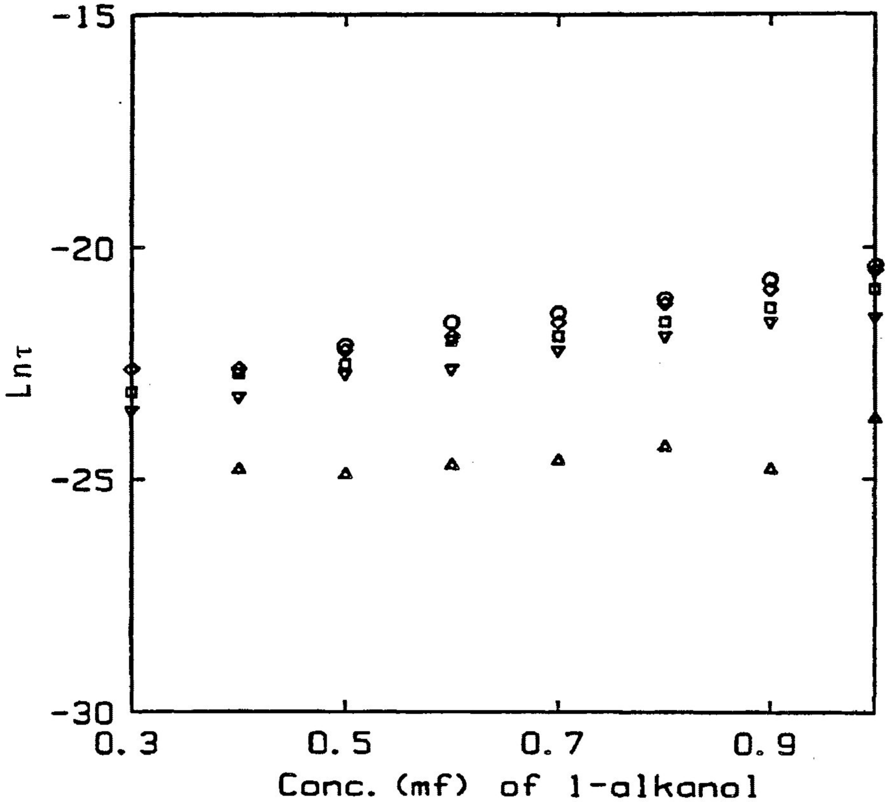


FIGURE IV-23c: Lnτ as a function of alcohol mole fraction, in diethyl ether solution at T = 300^{0}K.

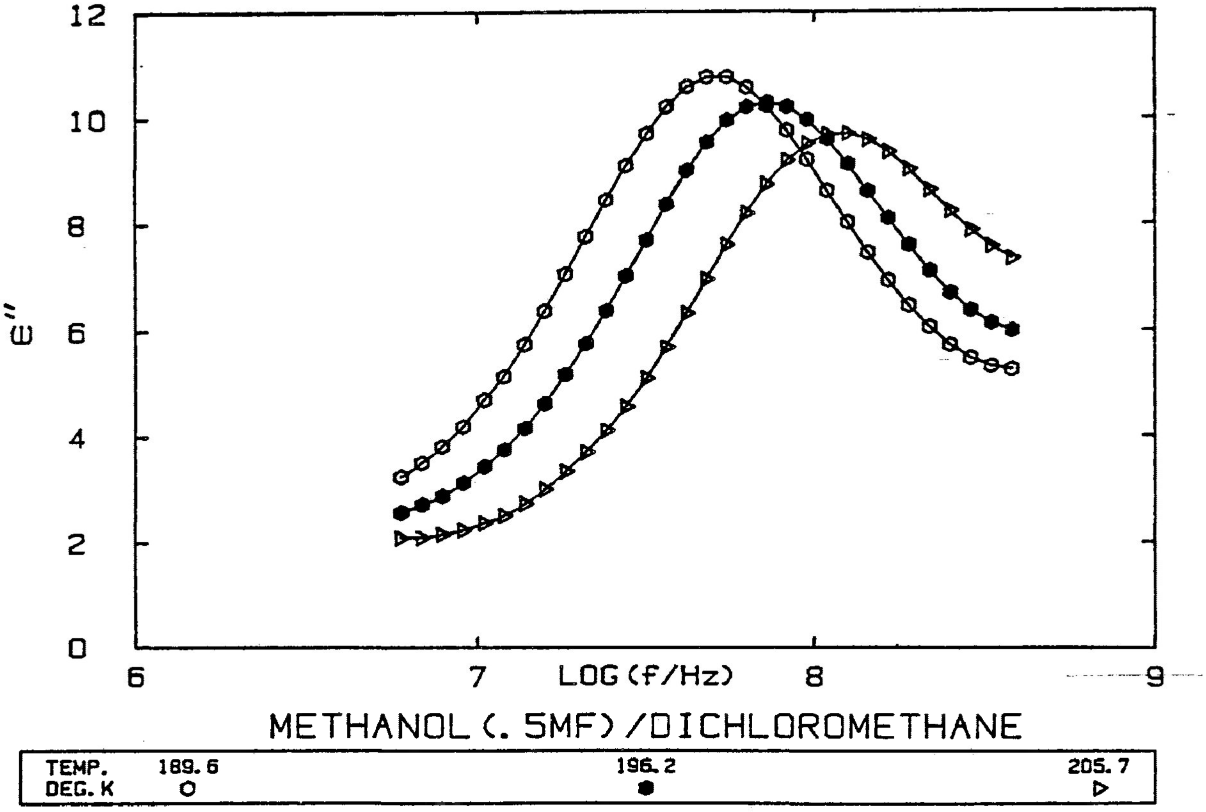


FIGURE V-1a: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of methanol in dichloromethane solution.

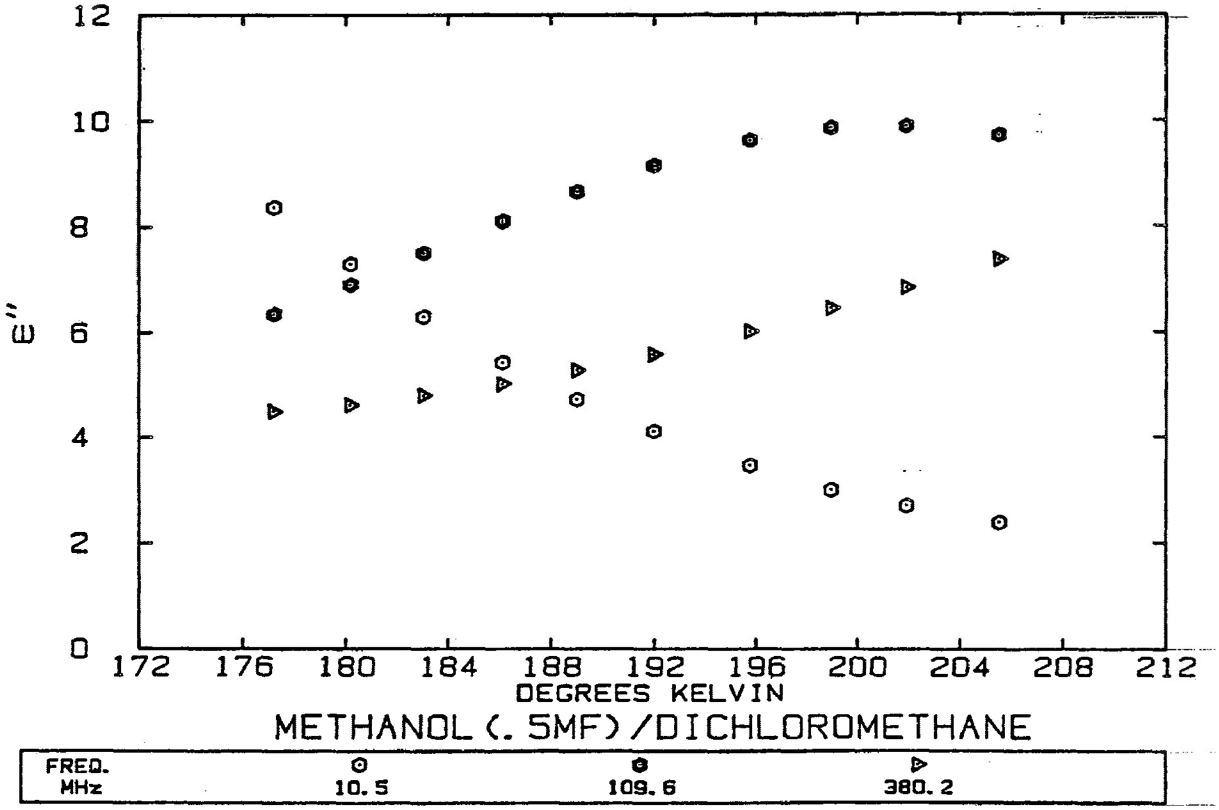


FIGURE V-1b: Dielectric loss factor, ε" versus temperature (°K) for 0.5 mole fraction of methanol in dichloromethane solution.

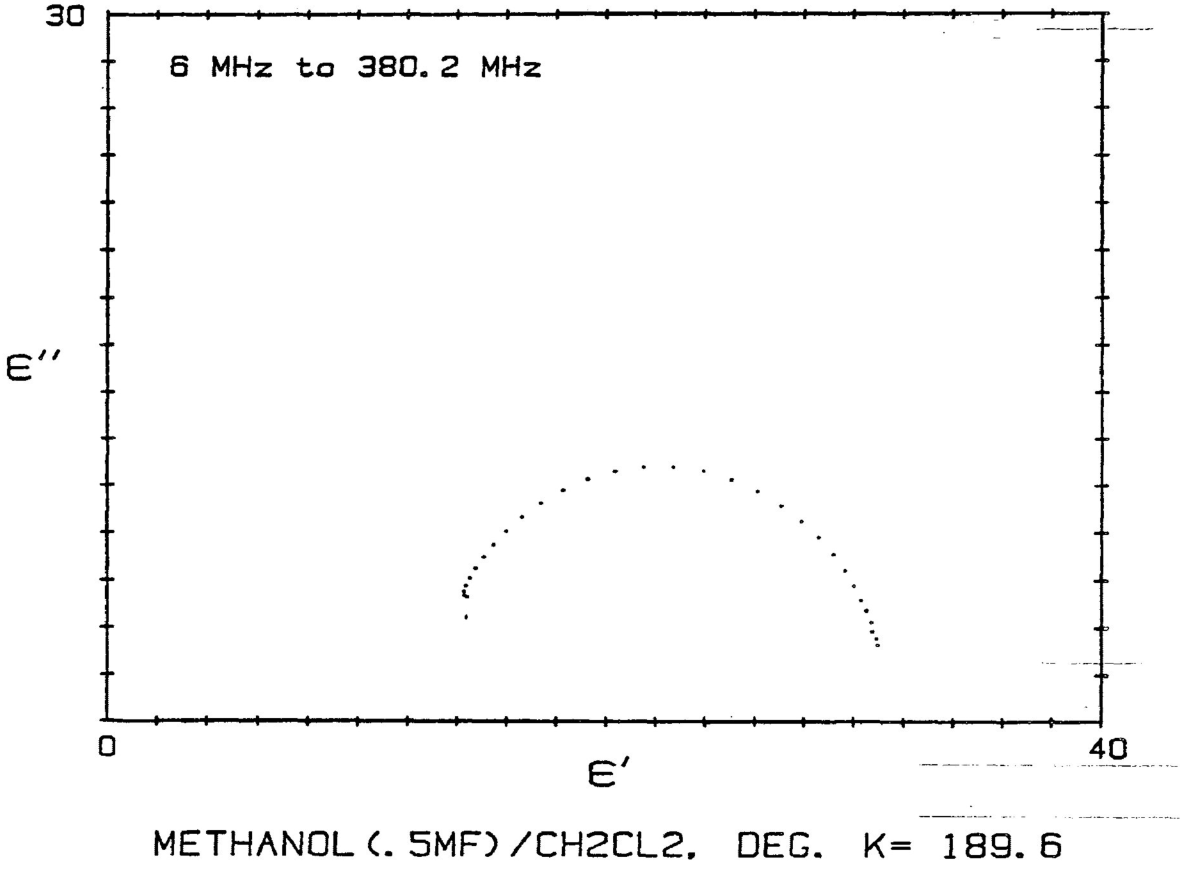
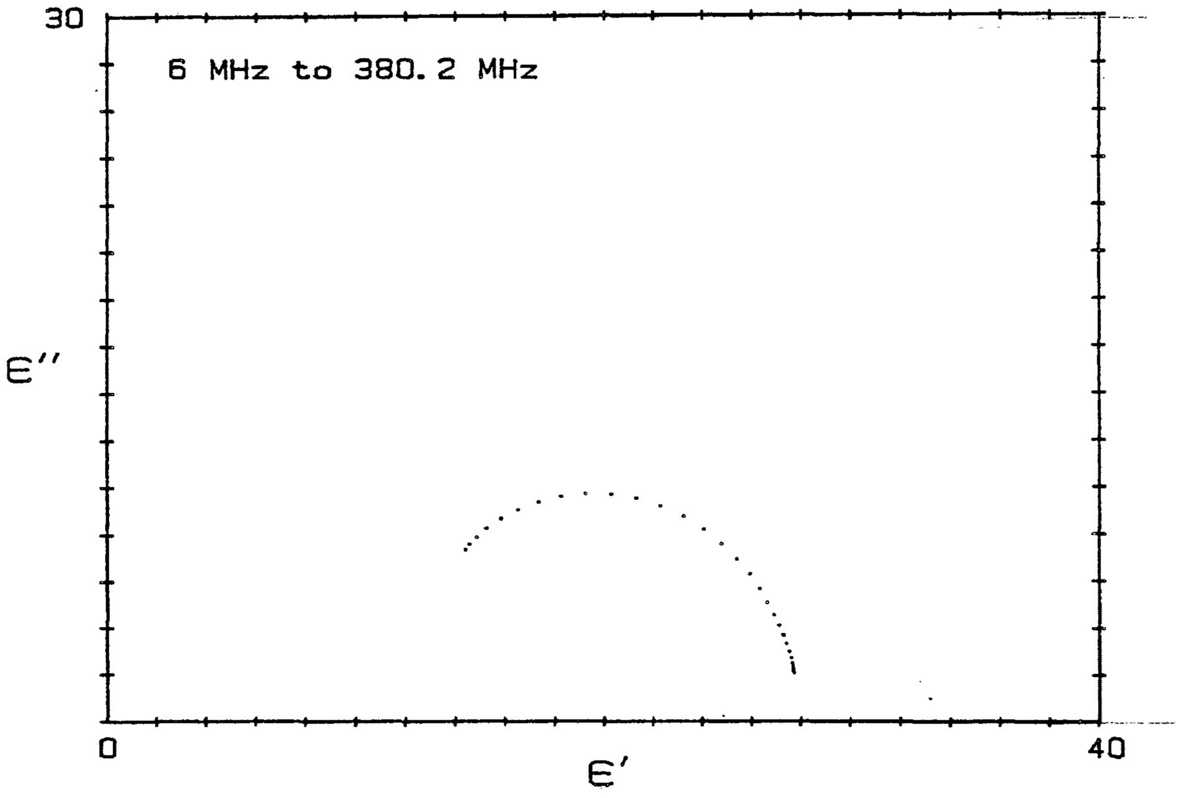


FIGURE V-1c: Cole-Cole plot for 0.5 mole fraction of methanol in dichloromethane solution at T = 189.6^{0}K.



METHANOL (.5MF)/CH2CL2, DEG. K= 205.7

FIGURE V-1d: Cole-Cole plot for 0.5 mole fraction of methanol in dichloromethane solution at T = 205.7°K.

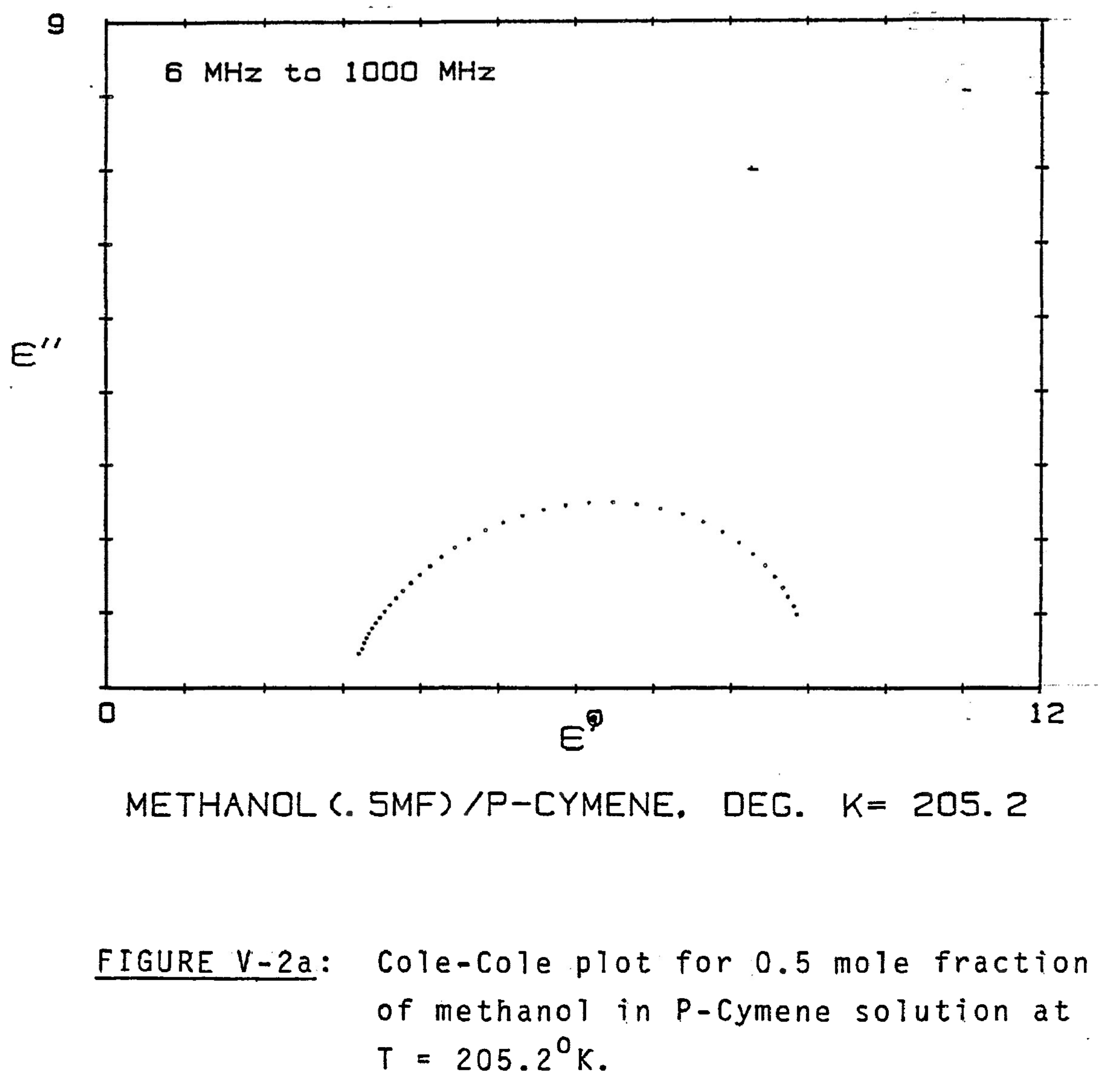


FIGURE V-2a: Cole-Cole plot for 0.5 mole fraction of methanol in P-Cymene solution at T = 205.2^{o}K.

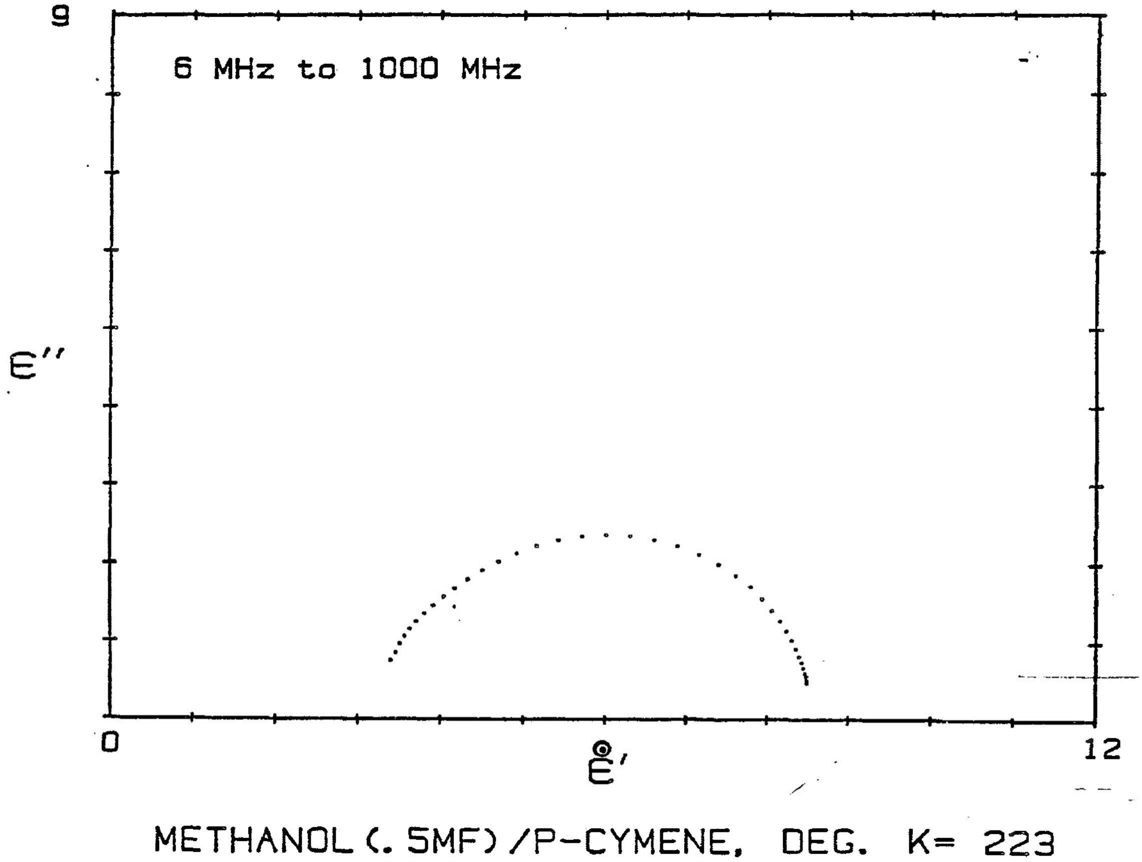


FIGURE V-2b: Cole-Cole plot for 0.5 mole fraction of methanol in P-Cymene solution at $T = 223^{0}K$.

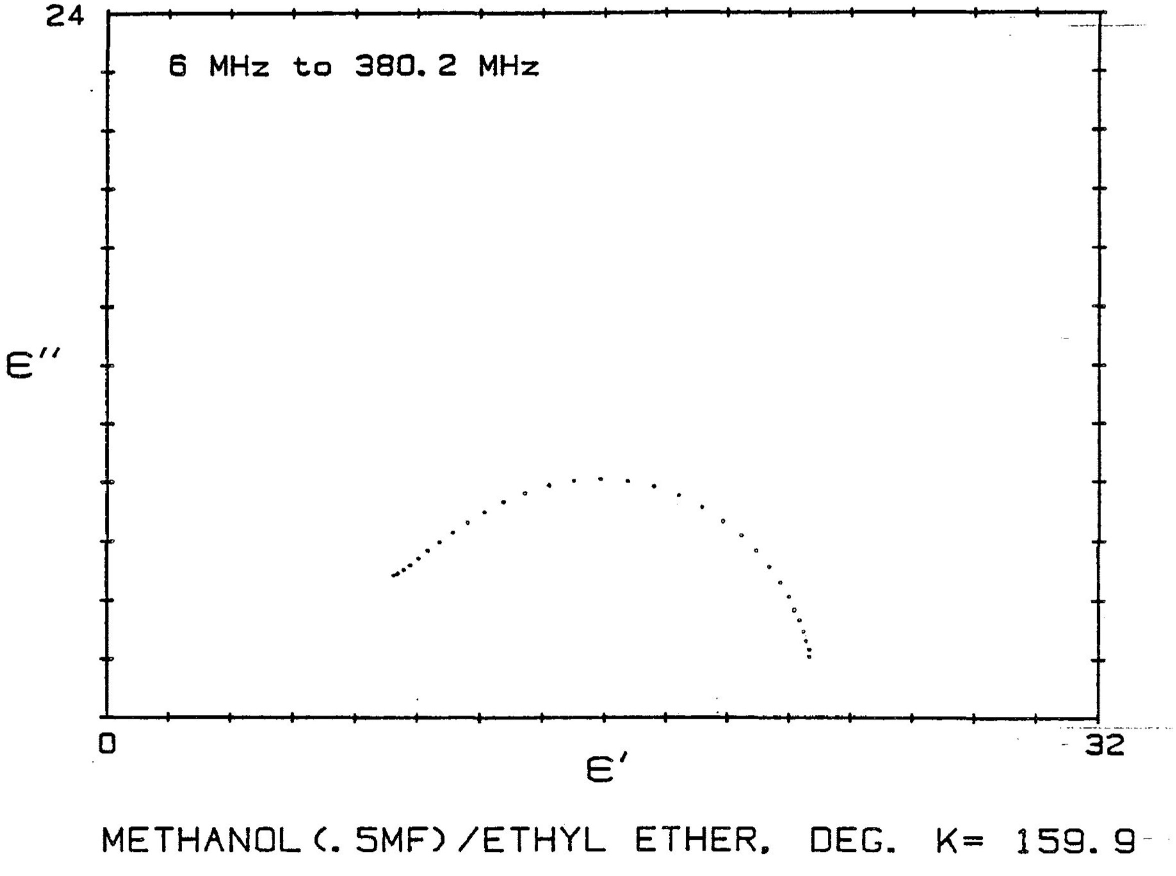


FIGURE V-3a: Cole-Cole plot for 0.5 mole fraction of methanol in diethyl ether solution at T = 159.9°K.

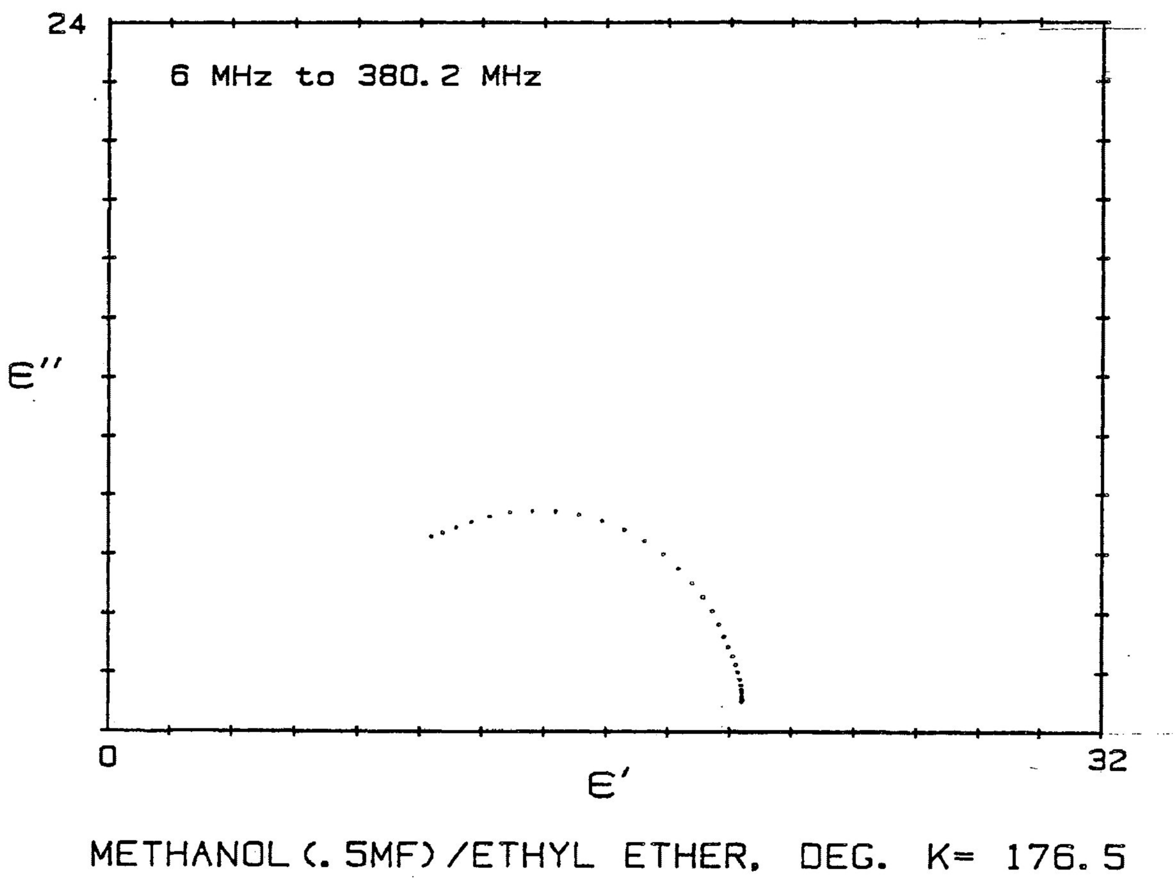


FIGURE V-3b: Cole-Cole plot for 0.5 mole fraction of methanol in diethyl ether solution at T = 176.5°K.

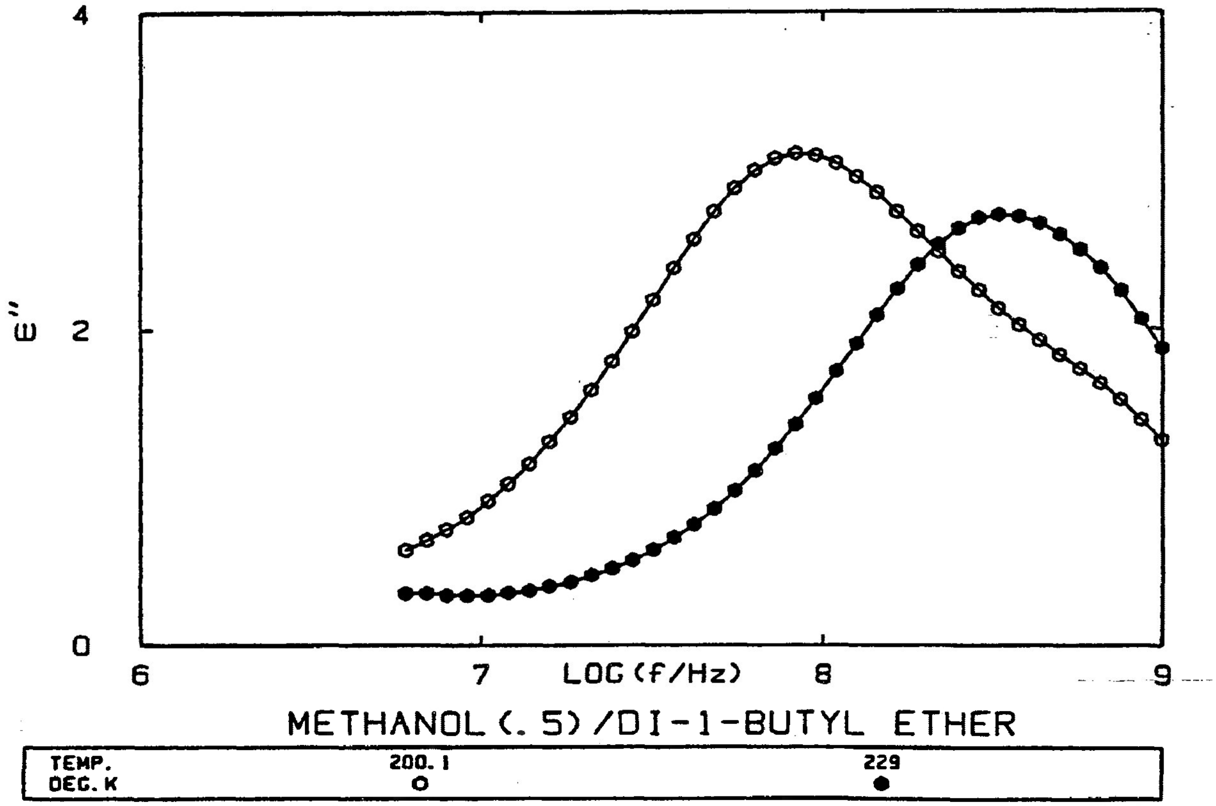
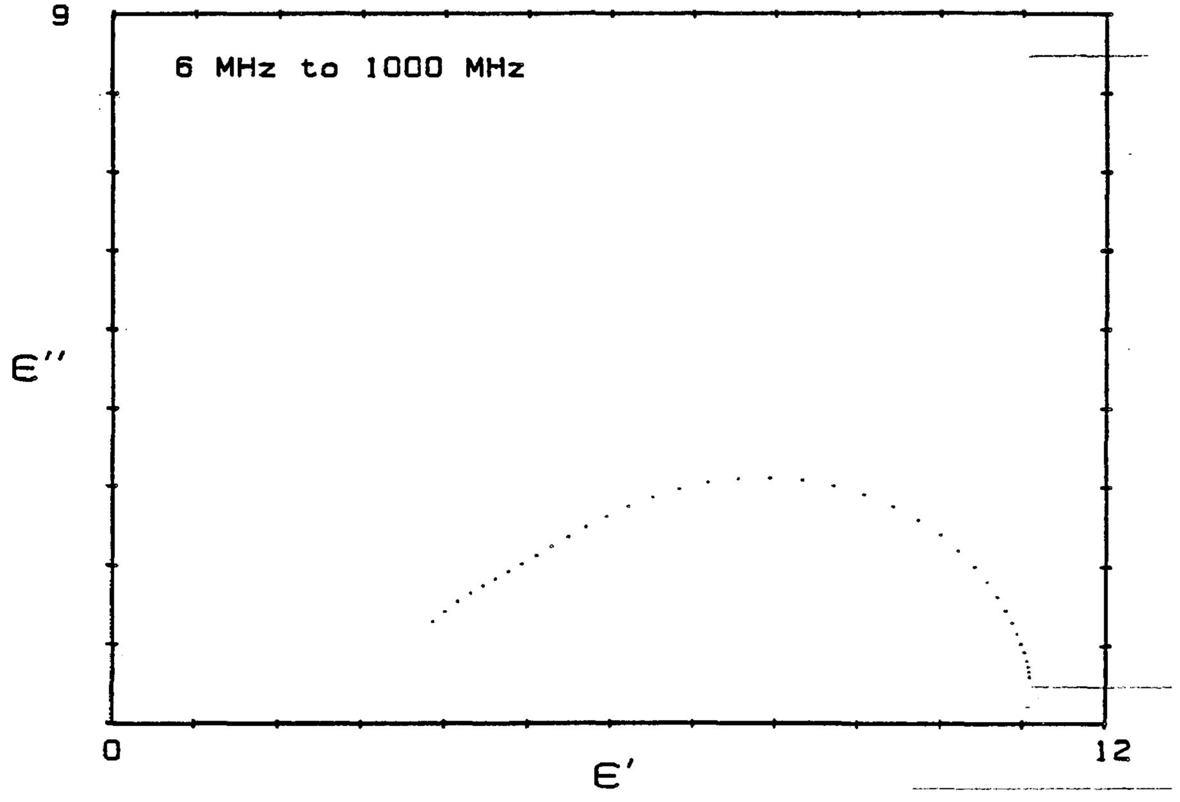
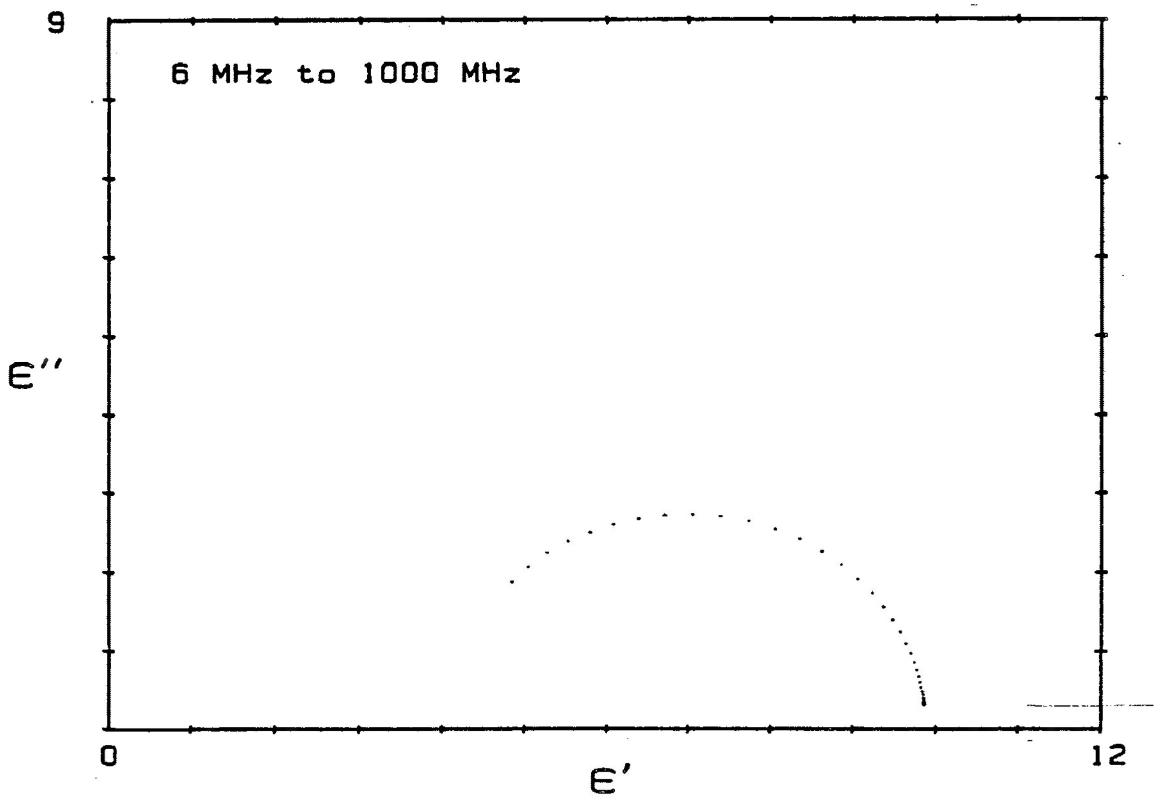


FIGURE V-4a: Dielectric loss factor, ε" versus log frequency for 0.5 mole fraction of methanol in di-n-butyl ether solution.



METHANOL (.5)/DI-1-BUTYL ETHER, DEG. K= 200.1

FIGURE V-4b: Cole-Cole plot for 0.5 mole fraction of methanol in di-n-butyl ether solution at 200.1 K.



METHANOL (.5)/DI-1-BUTYL ETHER, DEG. K= 229

FIGURE V-4c: Cole-Cole plot for 0.5 mole fraction of methanol in di-n-butyl ether solution at 229 K.

The symbols used for methanol in different solvents from Figures V-5 to V-8 are:

- △ ⟶ Methanol in P-cymene
- ▽ ⟶ Methanol in toluene
- □ ⟶ Methanol in dichloromethane
- ◇ ⟶ Methanol in diethyl ether
- ○ ⟶ Methanol in di-n-butyl ether
- ▷ ⟶ Methanol in pyridine

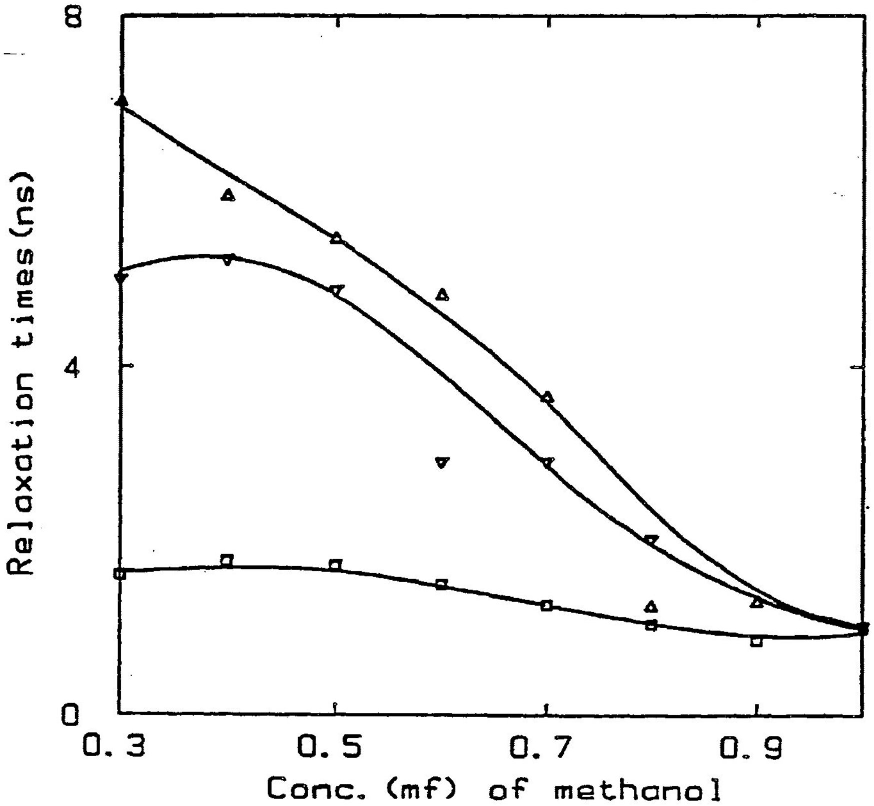


FIGURE V-5a: Relaxation times (τ_1) versus mole fraction of methanol, in different weakly interacting solvents at 200 K.

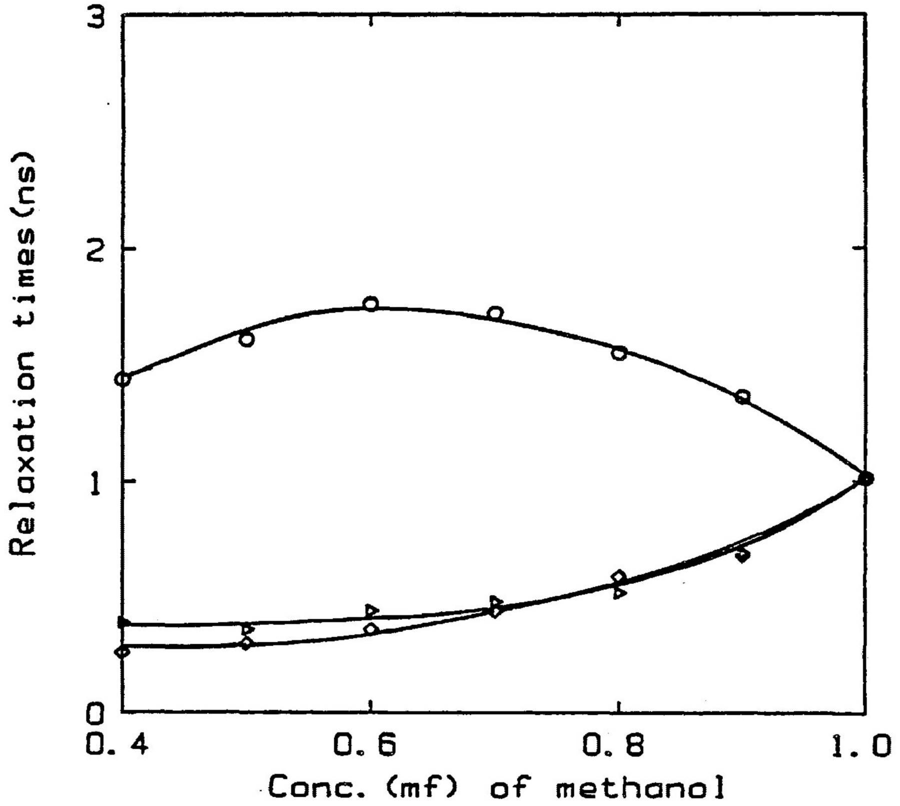


FIGURE V-5b: Relaxation times (τ_1) versus mole fraction of methanol, in different strongly interacting solvents at 200 K.

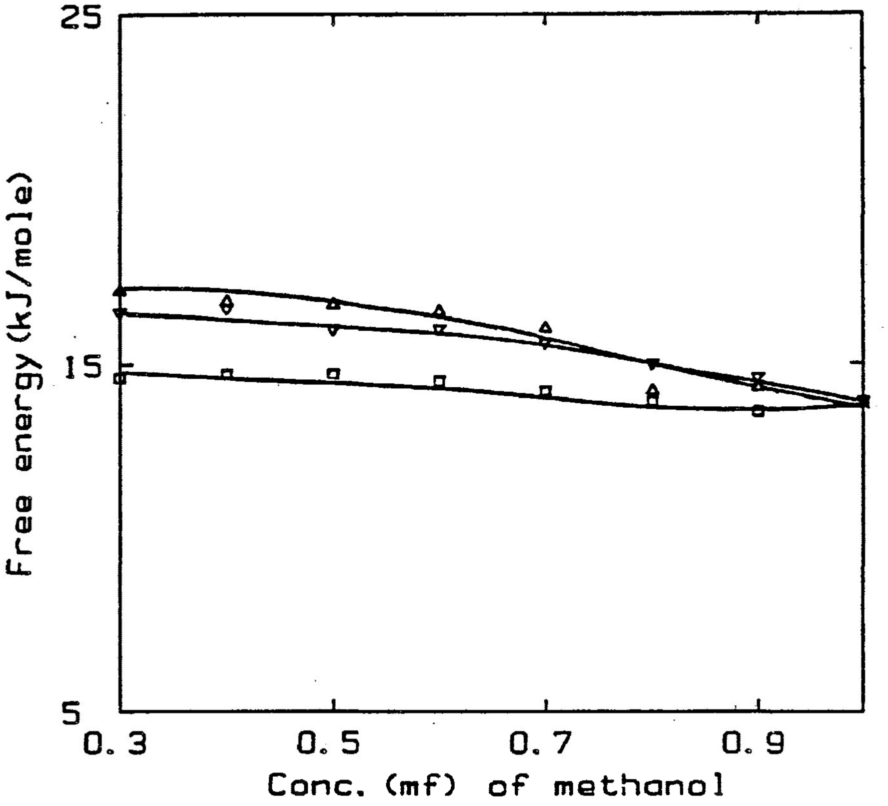


FIGURE V-6a: Free energy of activation (ΔG_E) versus mole fraction of methanol, in different weakly interacting solvents at 200 K.

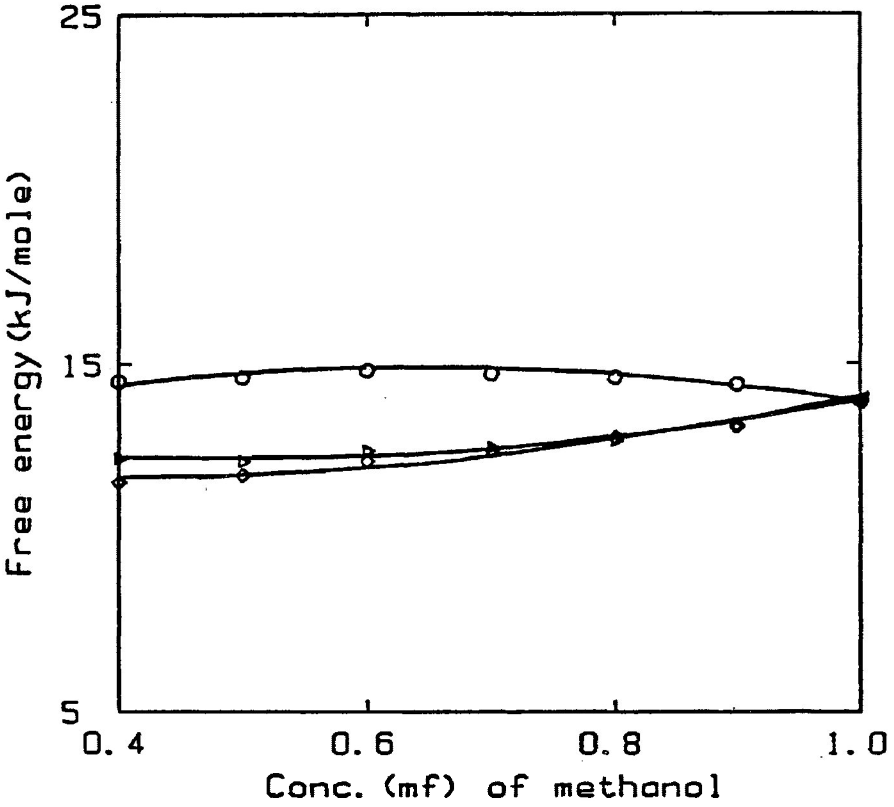


FIGURE V-6b: Free energy of activation (ΔG_E) versus mole fraction of methanol, in different strongly interacting solvents at 200 K.

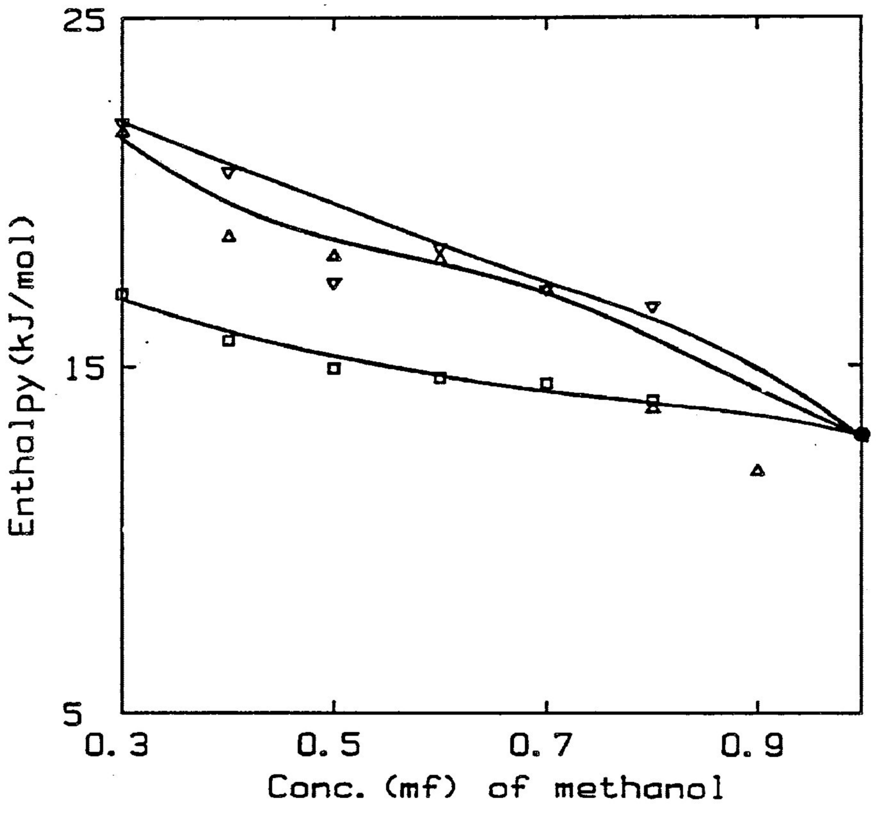


FIGURE V-7a: Enthalpy of activation (ΔH_E) versus mole fraction of methanol, in different weakly interacting solvents.

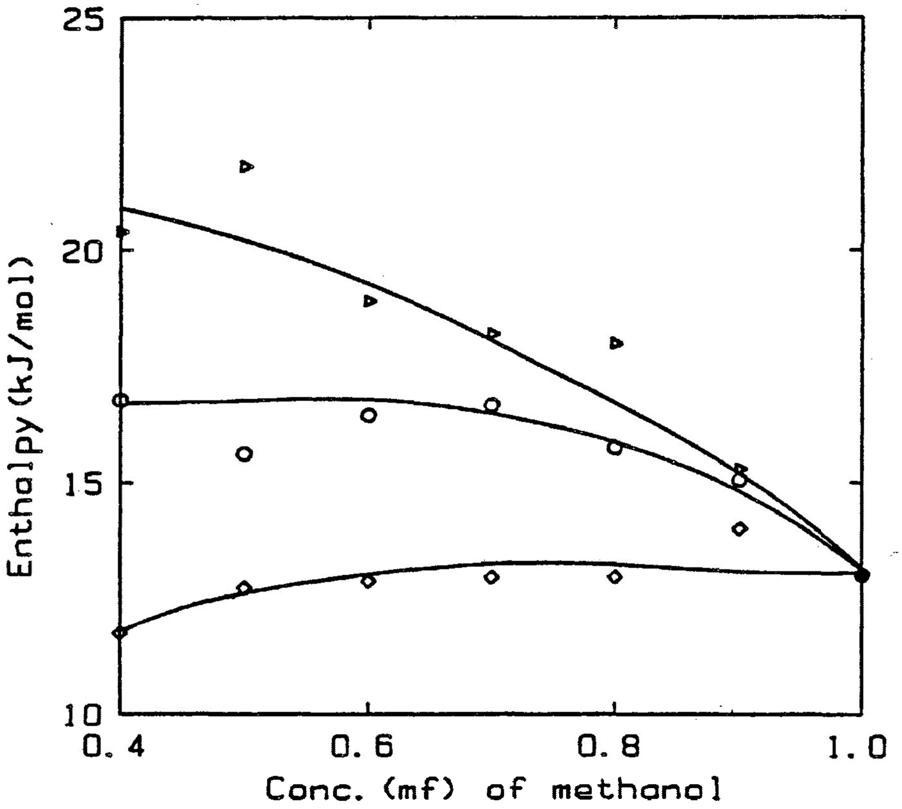


FIGURE V-7b: Enthalpy of activation (ΔH_E) versus mole fraction of methanol, in different strongly interacting solvents.

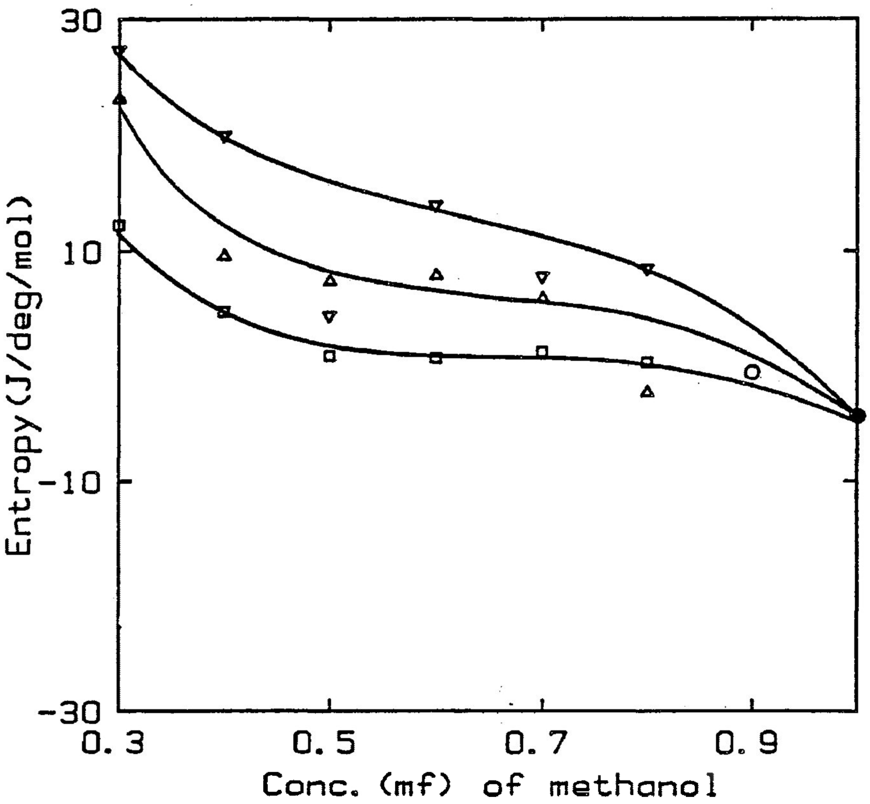


FIGURE V-8a: Entropy of activation (ΔS_E) versus mole fraction of methanol, in different weakly interacting solvents.

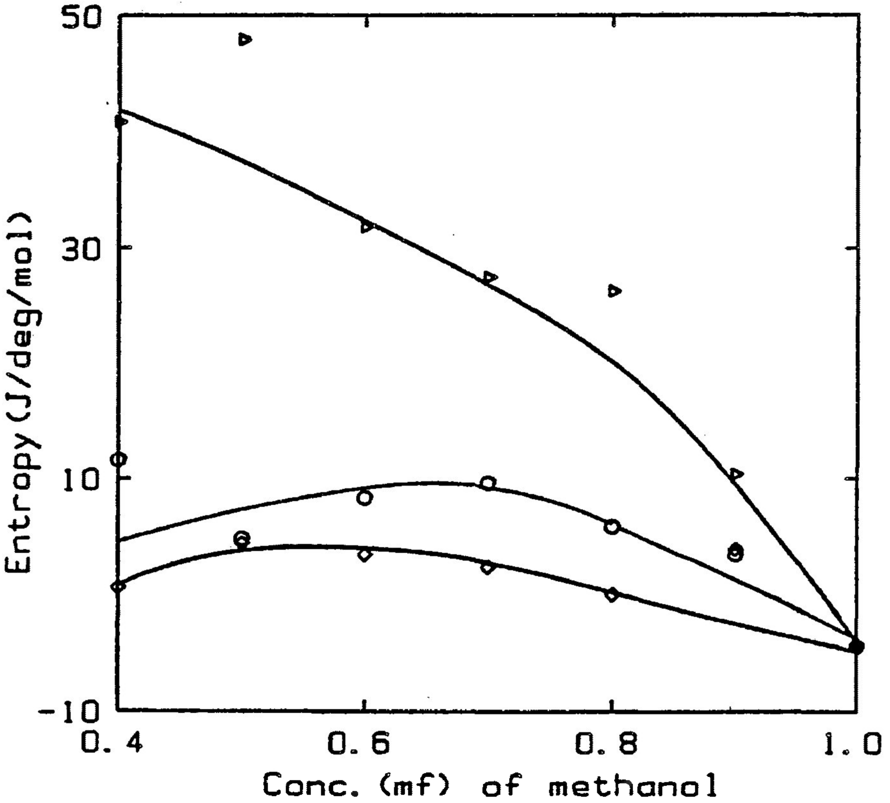


FIGURE V-8b: Entropy of activation (ΔS_E) versus mole fraction of methanol, in different strongly interacting solvents.

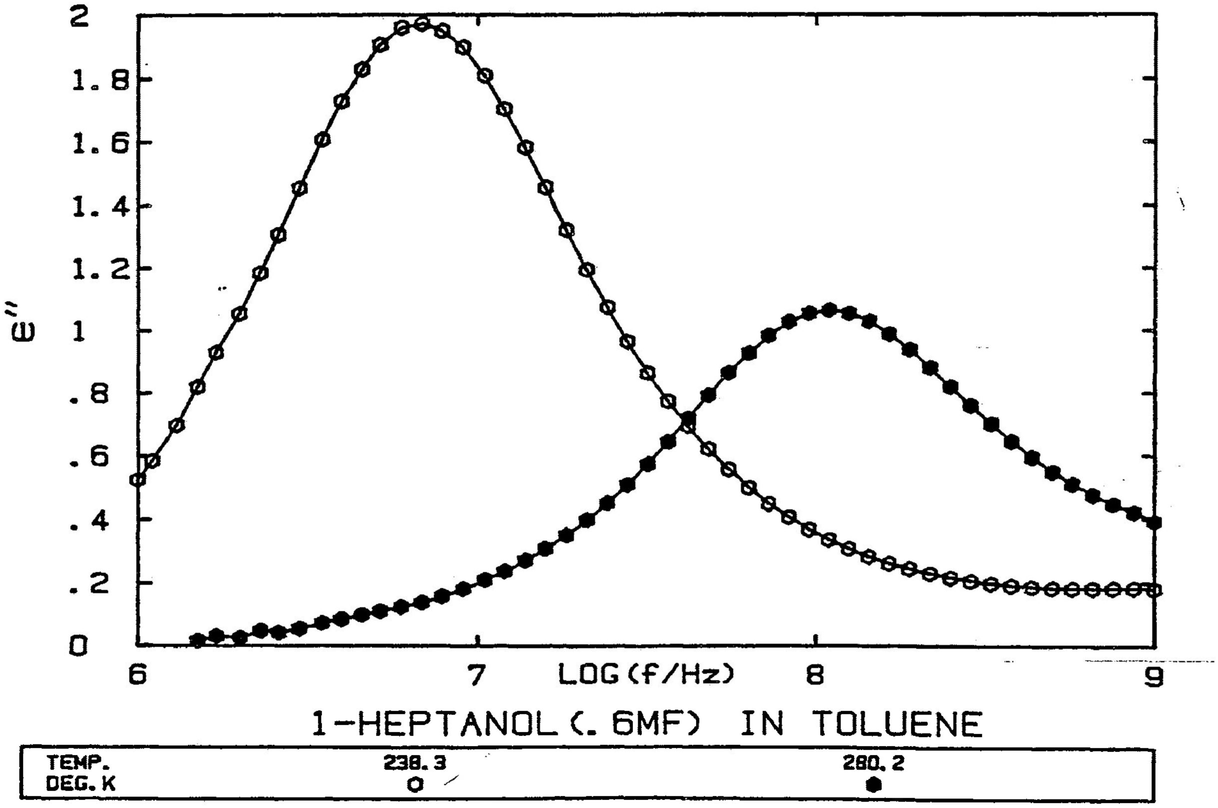
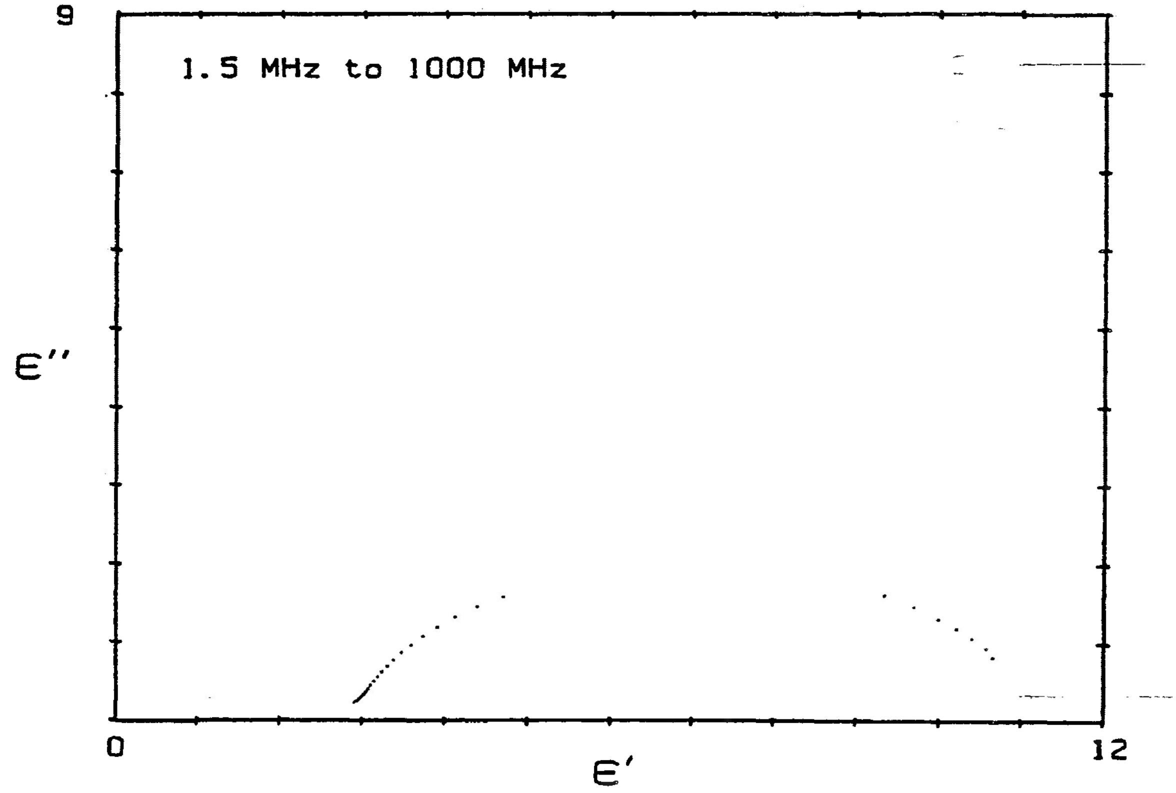
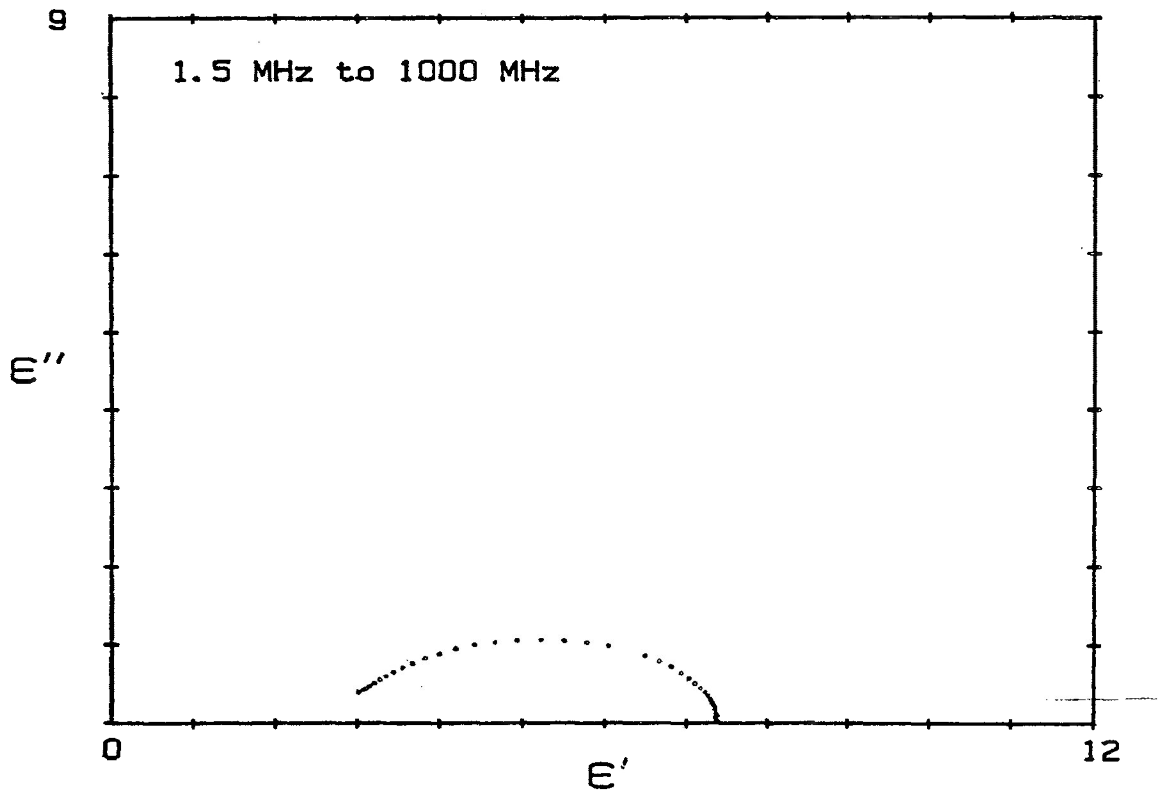


FIGURE VI-1a: Dielectric loss factor, ε'' versus log frequency for 0.6 mole fraction of 1-heptanol in toluene solution.



1-HEPTANOL (.6MF) IN TOLUENE. DEG. K= 238.3

FIGURE VI-1b: Cole-Cole plot for 0.6 mole fraction of 1-heptanol in toluene solution at 238.3 K.



1-HEPTANOL (.6MF) IN TOLUENE. DEG. K= 280.2

FIGURE VI-1c: Cole-Cole plot for 0.6 mole fraction of 1-heptanol in toluene solution at 280.2 K.

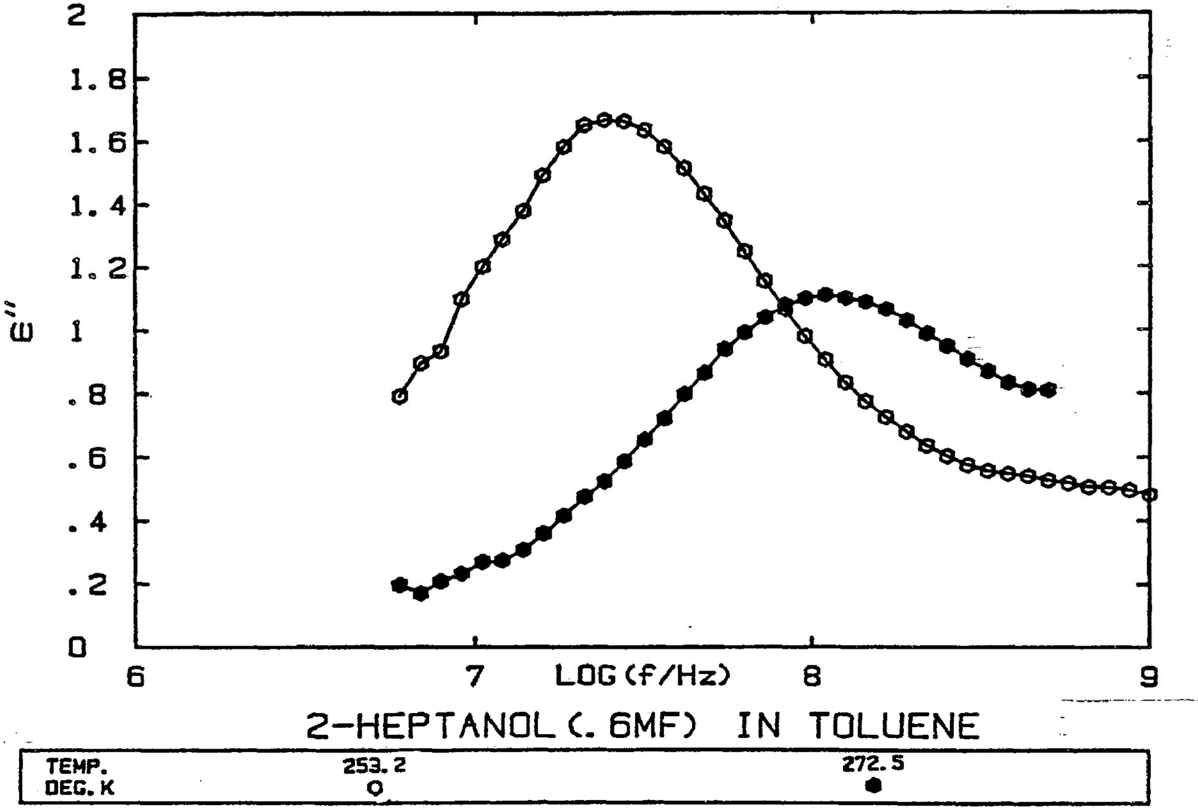


FIGURE VI-2a: Dielectric loss factor, ε" versus log frequency for 0.6 mole fraction of 2-heptanol in toluene solution.

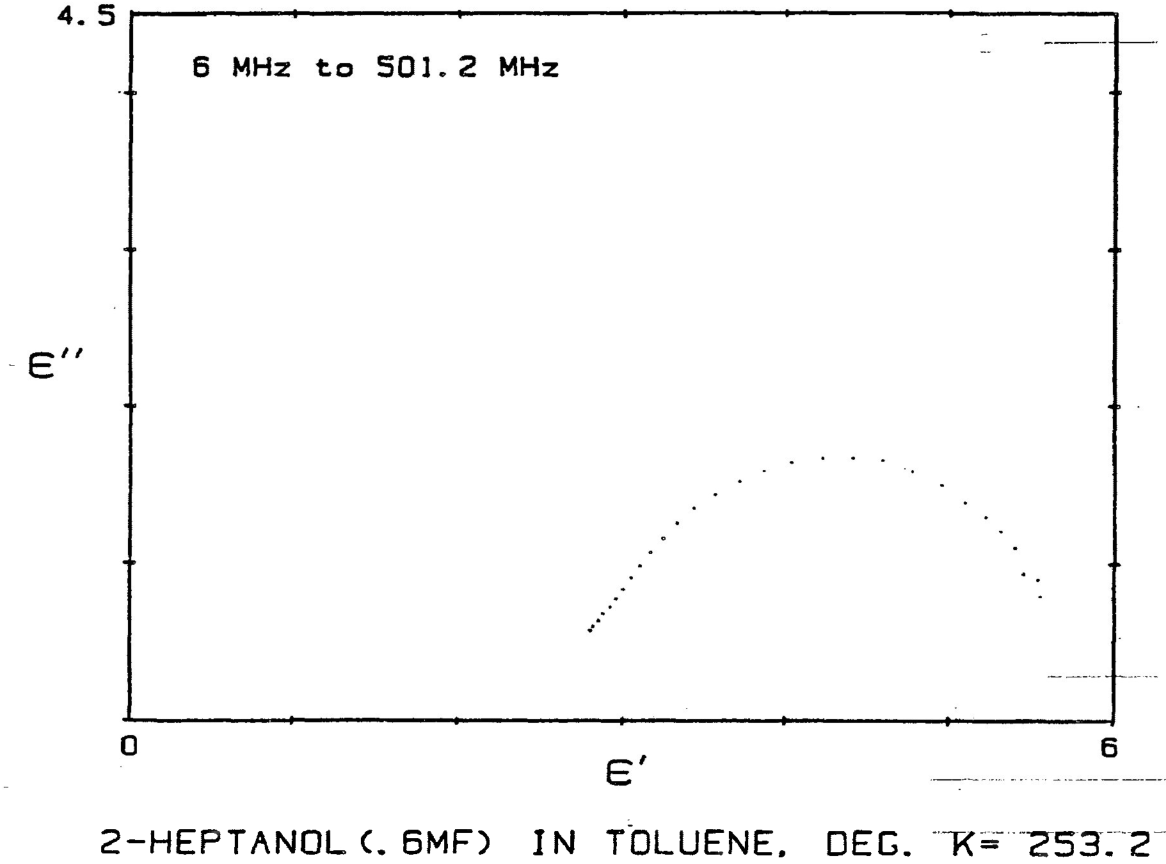
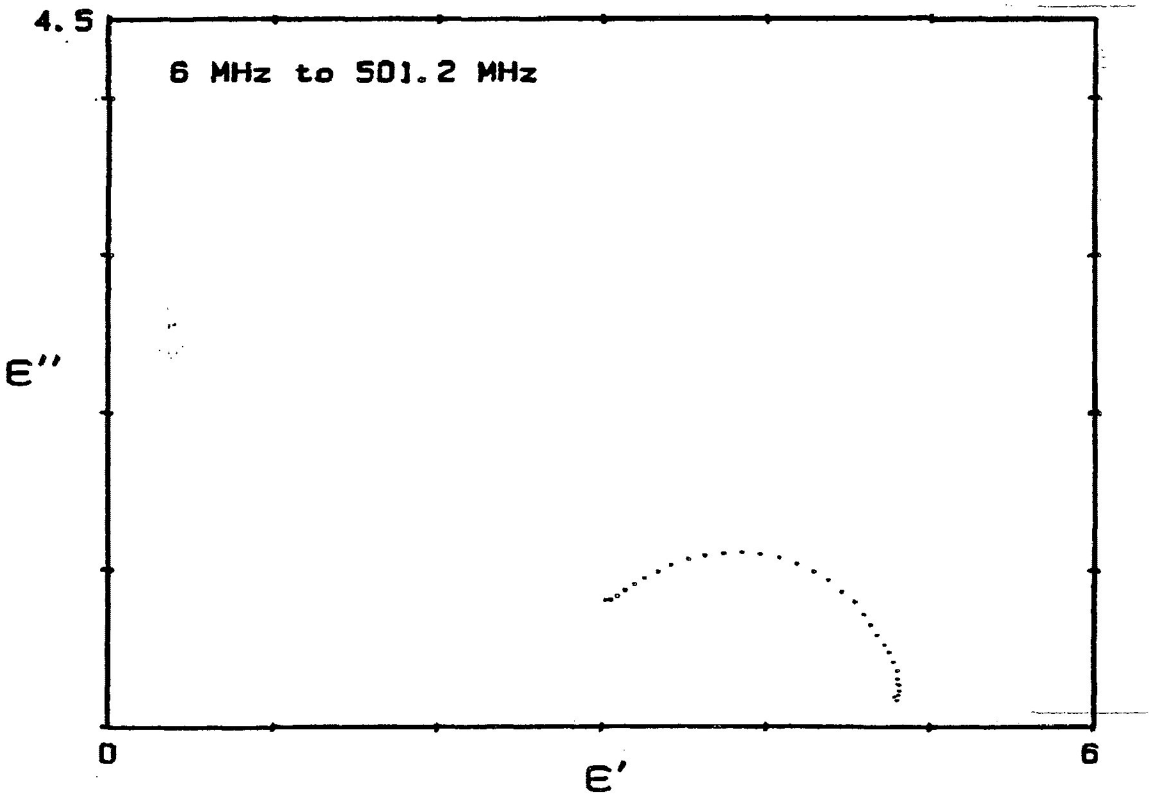


FIGURE VI-2b: Cole-Cole plot for 0.6 mole fraction of 2-heptanol in toluene solution at 253.2 K.



2-HEPTANOL (.6MF) IN TOLUENE, DEG. K= 272.5

FIGURE VI-2c: Cole-Cole plot for 0.6 mole fraction of 2-heptanol in toluene solution at 272.5 K.

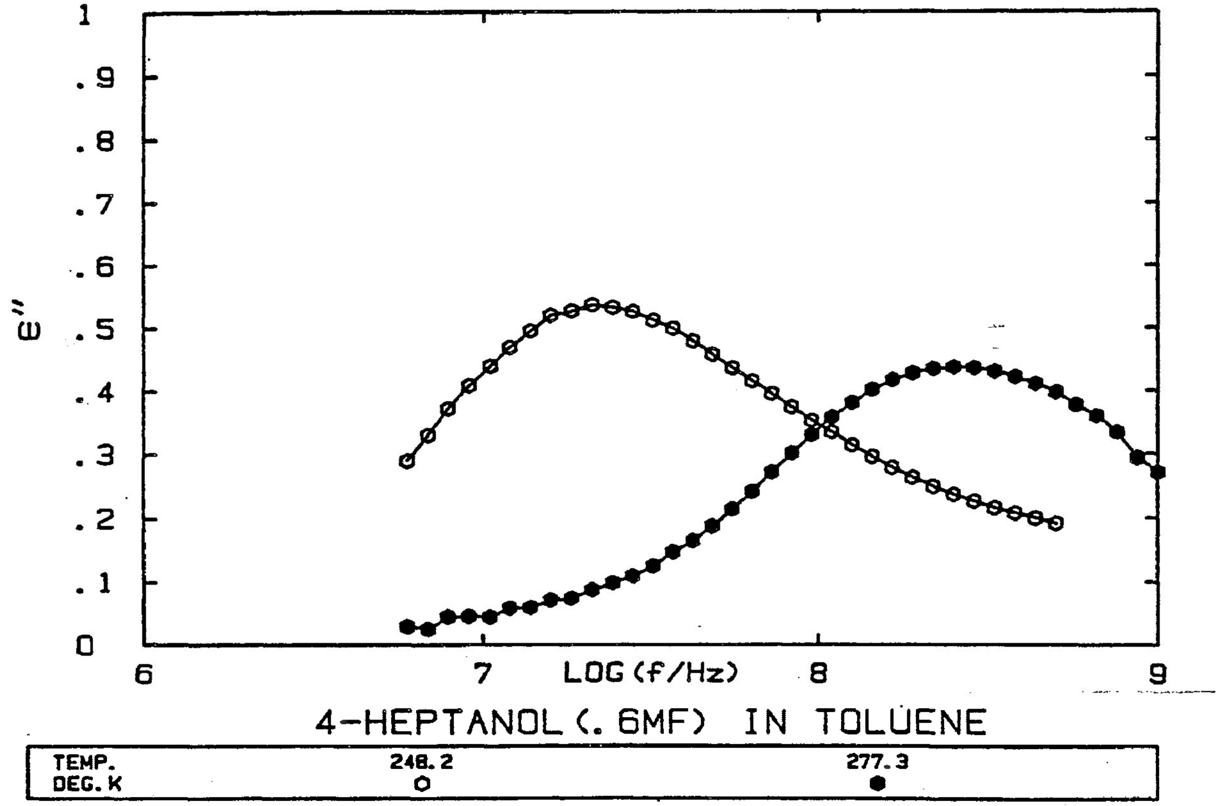
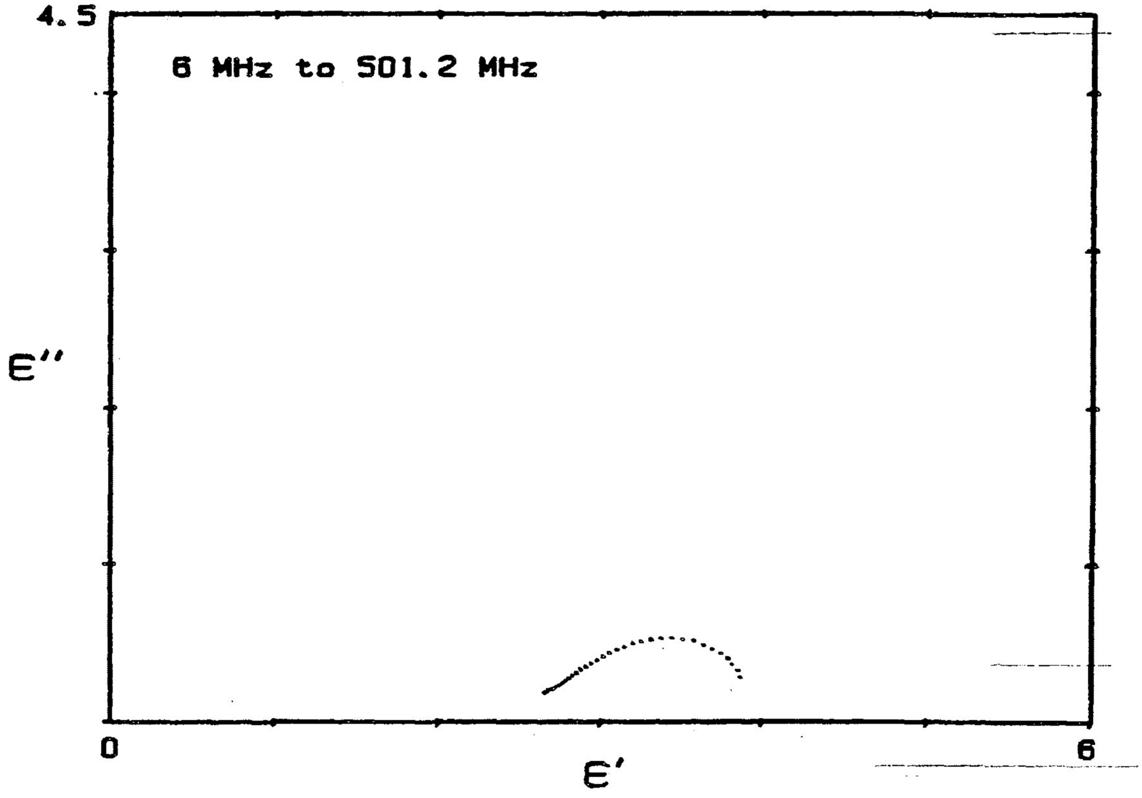
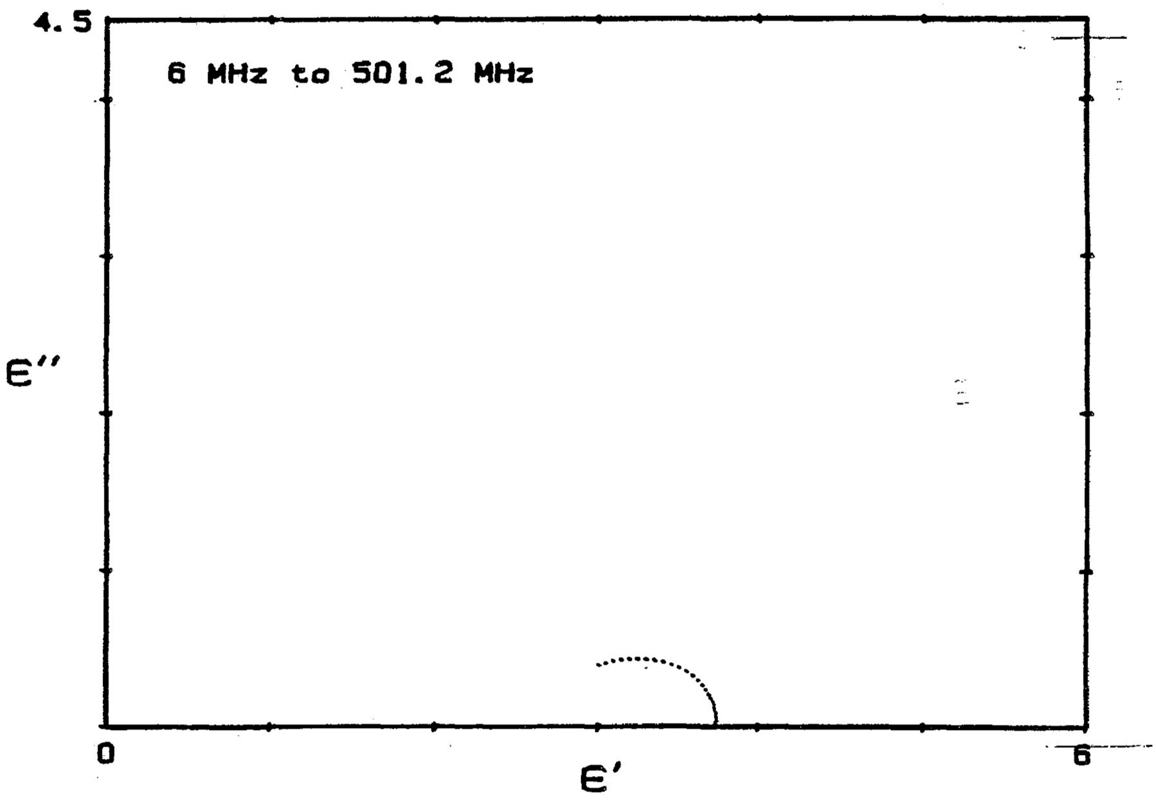


FIGURE VI-3a: Dielectric loss factor, ε″ versus log frequency for 0.6 mole fraction of 4-heptanol in toluene solution.



4-HEPTANOL (.6MF) IN TOLUENE, DEG. K= 248.2

FIGURE VI-3b: Cole-Cole plot for 0.6 mole fraction of 4-heptanol in toluene solution at 248.2 K.



4-HEPTANOL (.6MF) IN TOLUENE. DEG. K= 277.3

FIGURE VI-3c: Cole-Cole plot for 0.6 mole fraction of heptanol in toluene solution at 277.3 K.

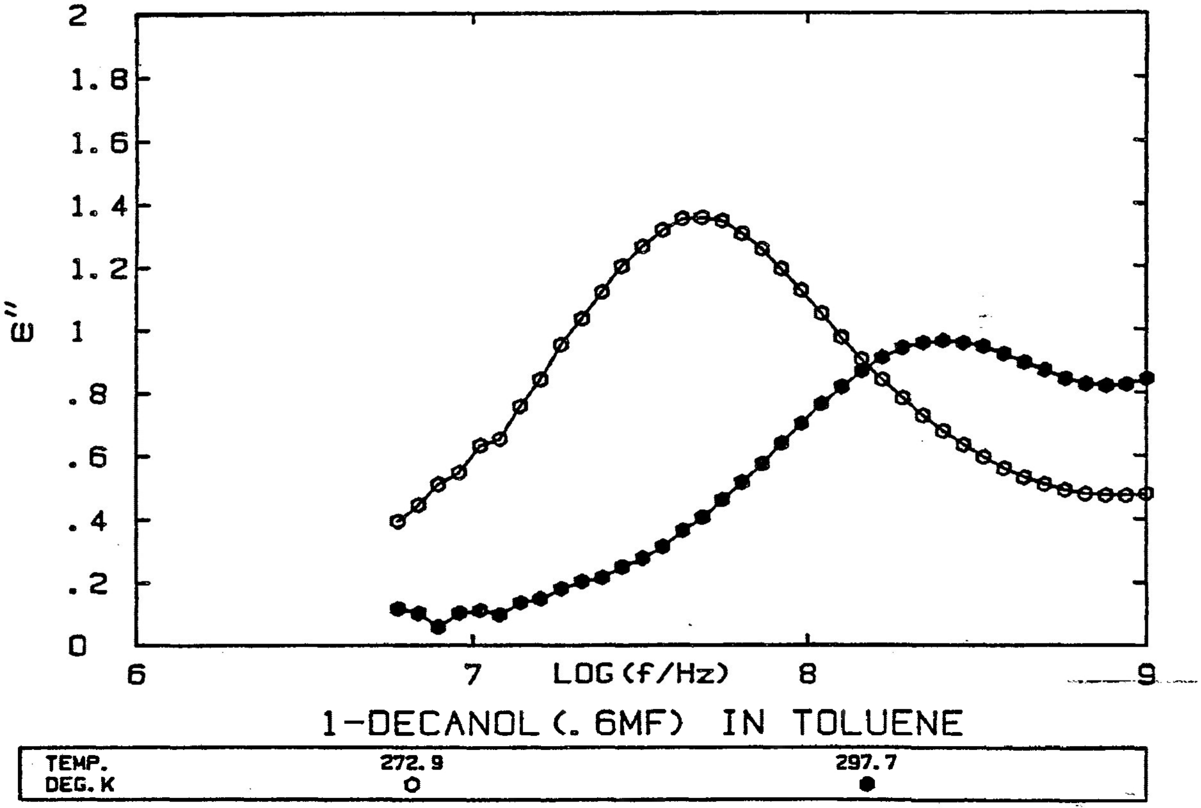
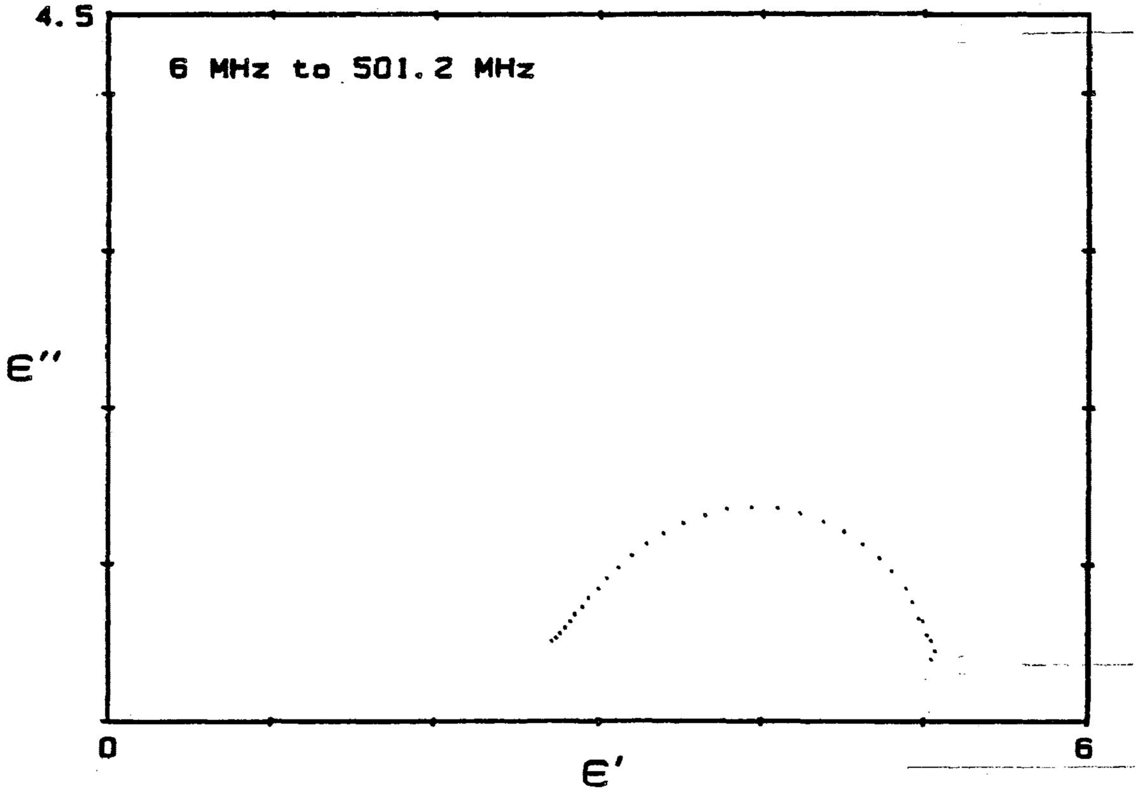


FIGURE VI-4a; Dielectric loss factor, ε" versus log frequency for 0.6 mole fraction of 1-decanol in toluene solution.



1-DECANOL (.6MF) IN TOLUENE. DEG. K= 272.9

FIGURE VI-4b: Cole-Cole plot for 0.6 mole fraction of 1-decanol in toluene solution at 272.9 K.

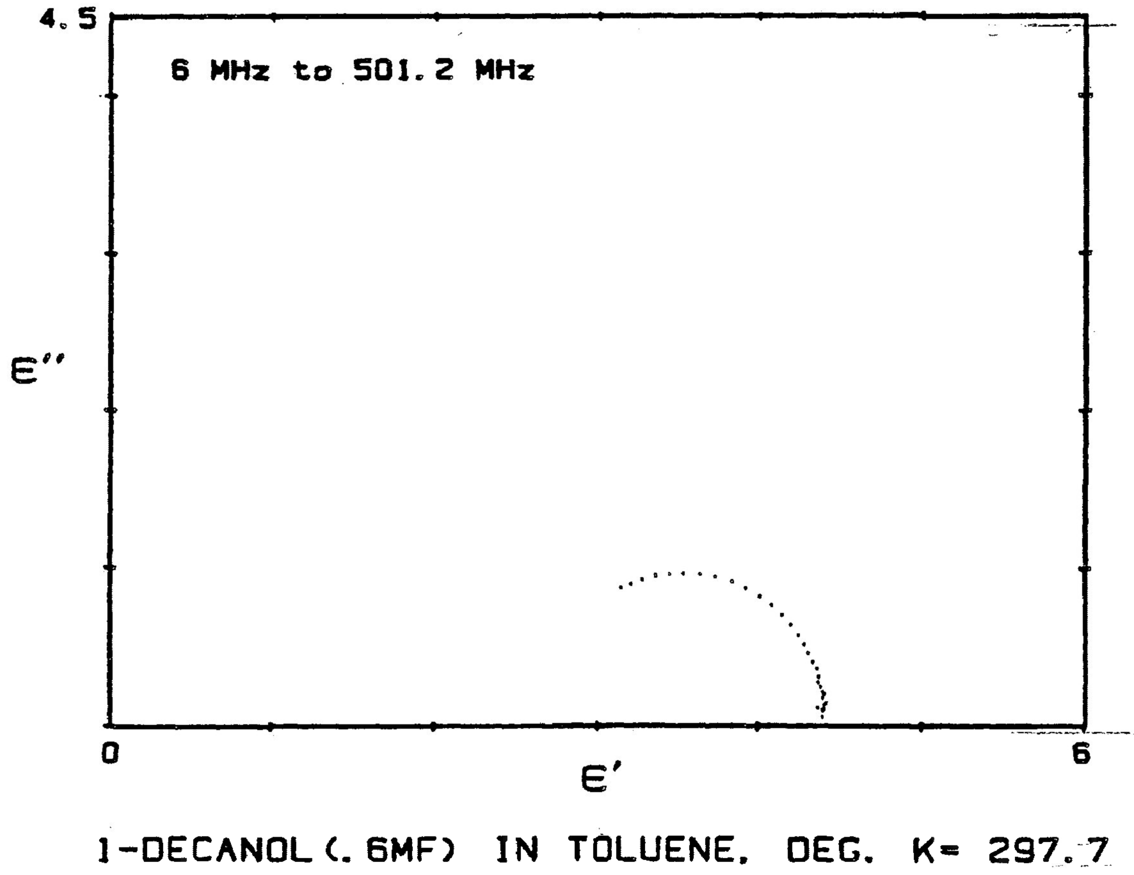


FIGURE VI-4c: Cole-Cole plot for 0.6 mole fraction of 1-decanol in toluene solution at 297.7 K.

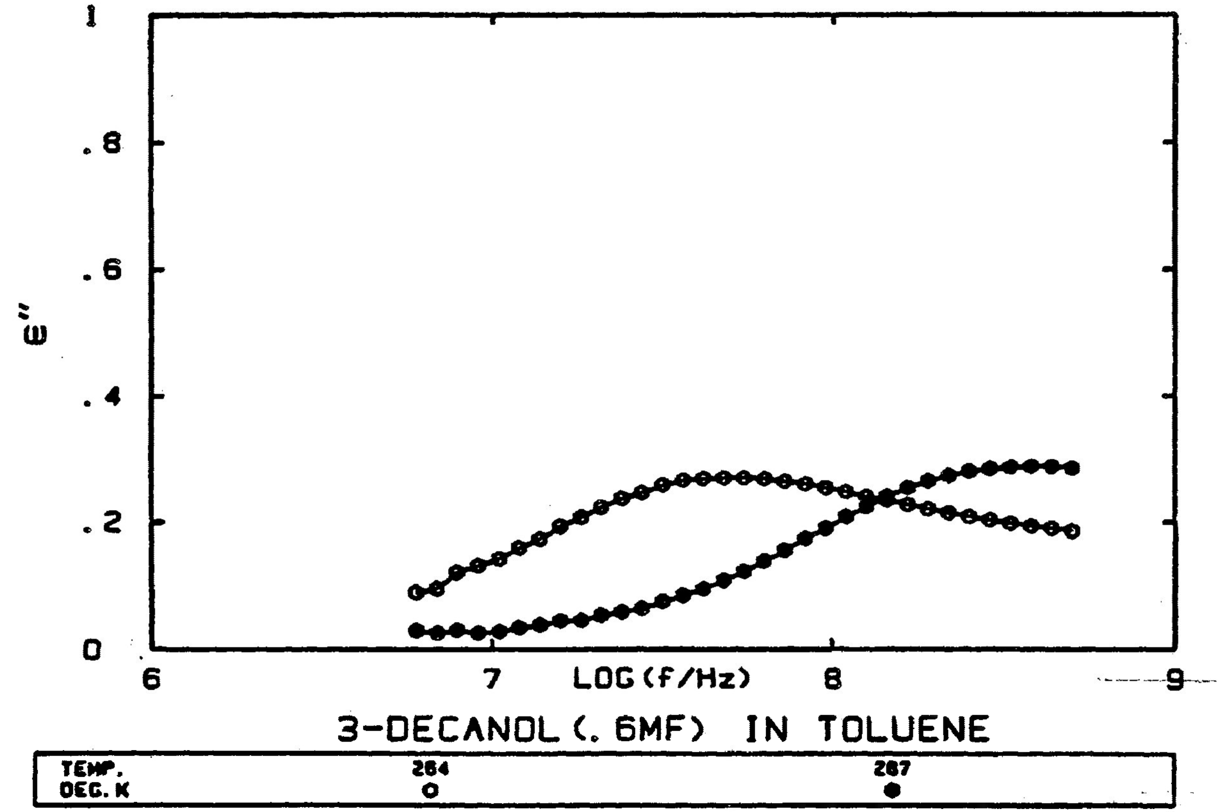


FIGURE VI-5: Dielectric loss factor, ε'' versus log frequency for 0.6 mole fraction of 3-decanol in toluene solution.

The symbols used for different alkanols in toluene from Figures VI-6 to VI-9 are:

△ ⟶ 1-alkanol
▽ ⟶ 2-alkanol
□ ⟶ 3-alkanol
◇ ⟶ 4-alkanol

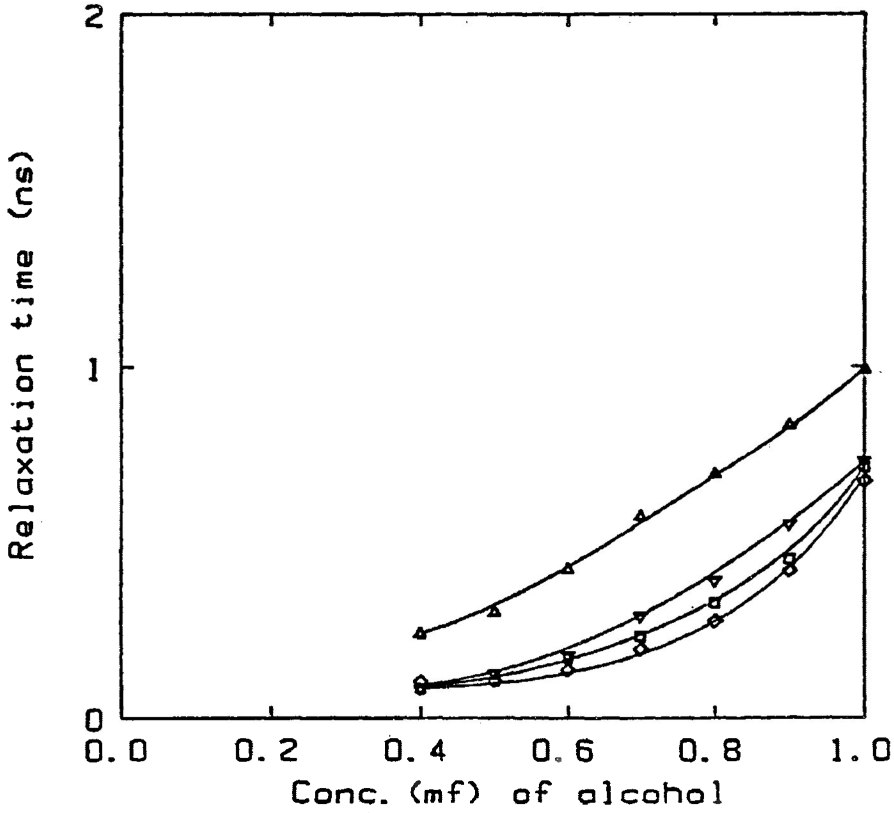


FIGURE VI-6a: Relaxation times (τ_1) versus mole fractions of 1-,2-,3- and 4-heptanols, in toluene solution at 300 K.

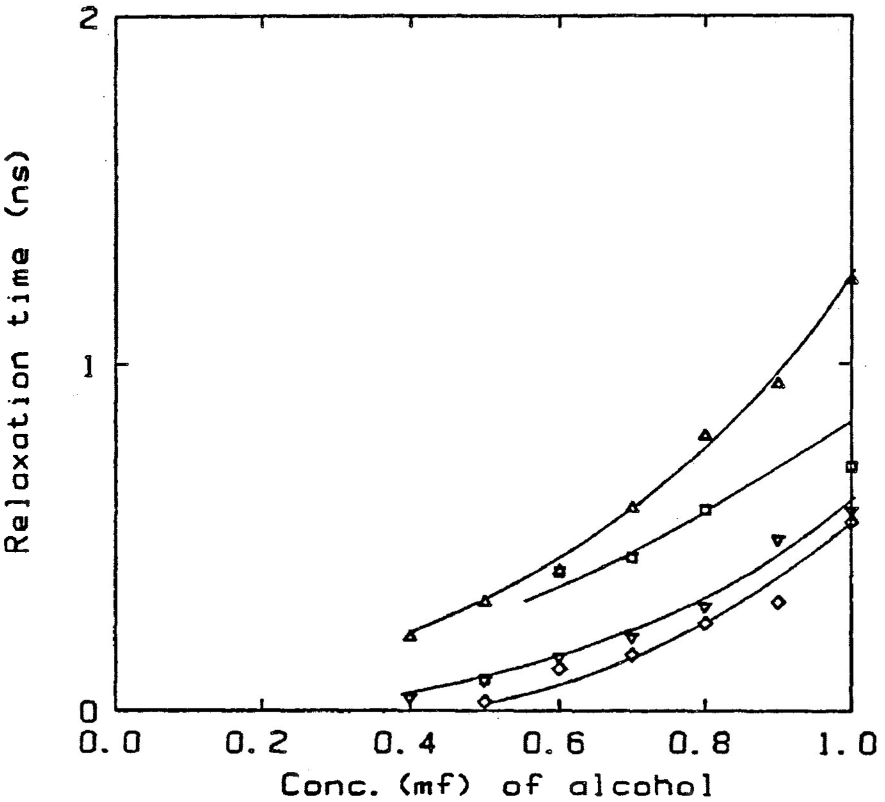


FIGURE VI-6b: Relaxation times (τ_1) versus mole fractions 1-,2-,3- and 4-octanols, in toluene solution at 300 K.

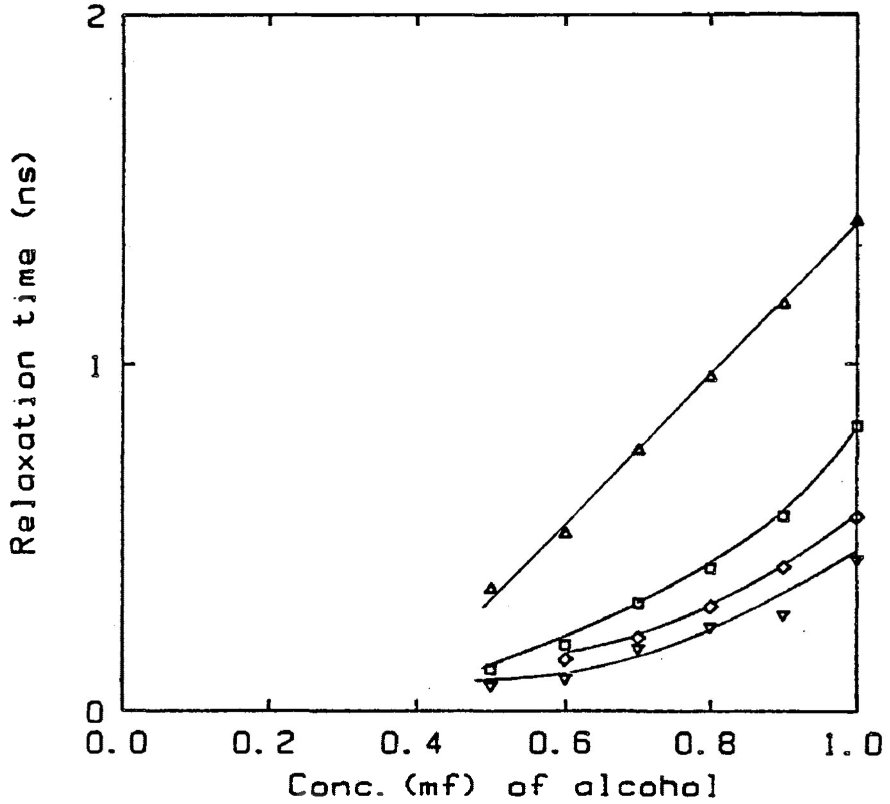


FIGURE VI-6c: Relaxation times (τ_1) versus mole fractions of 1-,2-,3- and 4-decanols, in toluene solution at 300 K.

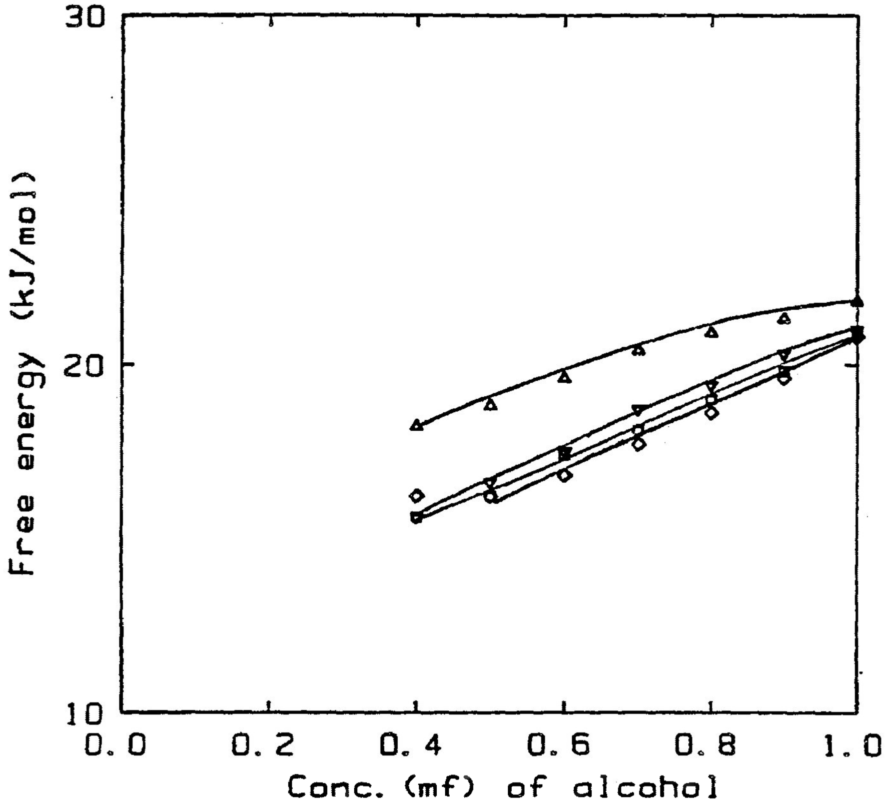


FIGURE VI-7a: Free energy of activation (ΔG_E) versus mole fraction of 1-,2-,3- and 4-heptanols, in toluene solution at 300 K.

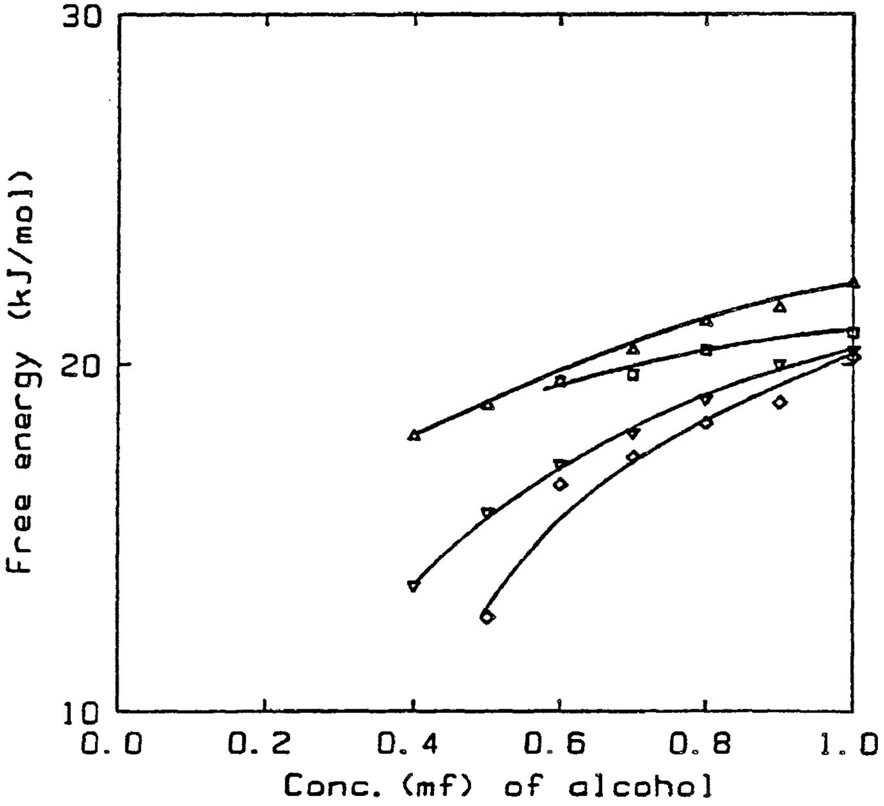


FIGURE VI-7b: Free energy of activation (ΔG_E) versus mole fraction of 1-,2-,3- and 4-octanols, in toluene solution at 300 K.

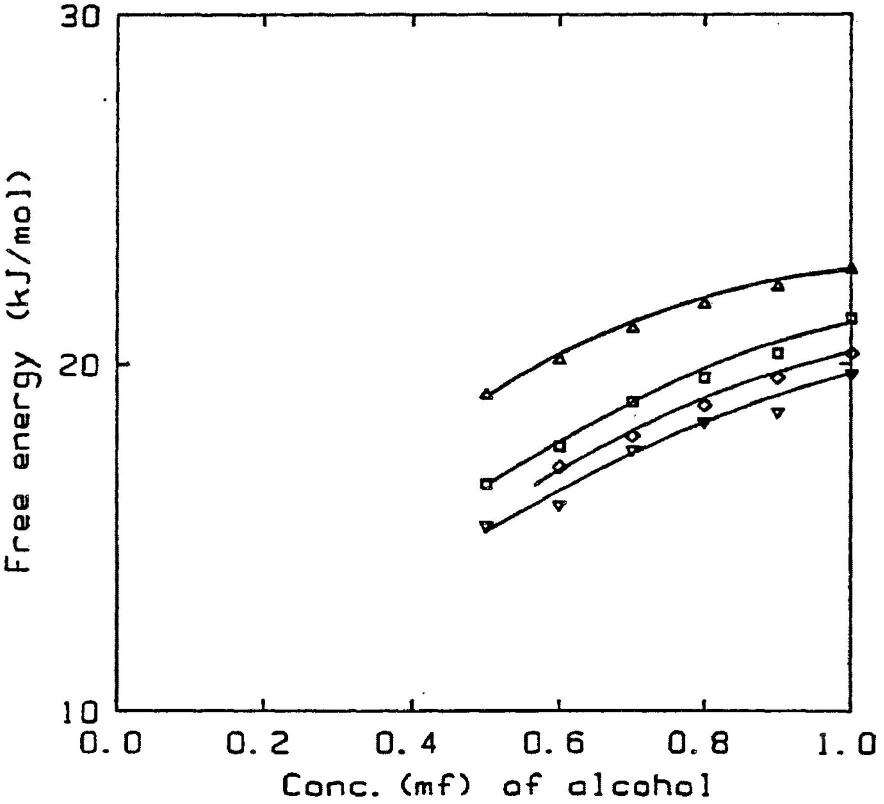


FIGURE VI-7c: Free energy of activation (ΔG_E) versus mole fraction of 1-,2-,3 and 4-decanols, in toluene solution at 300 K.

Solid lines from Figures VI-8a to VI-8c represent the corresponding least square fittings for the experimental data points.

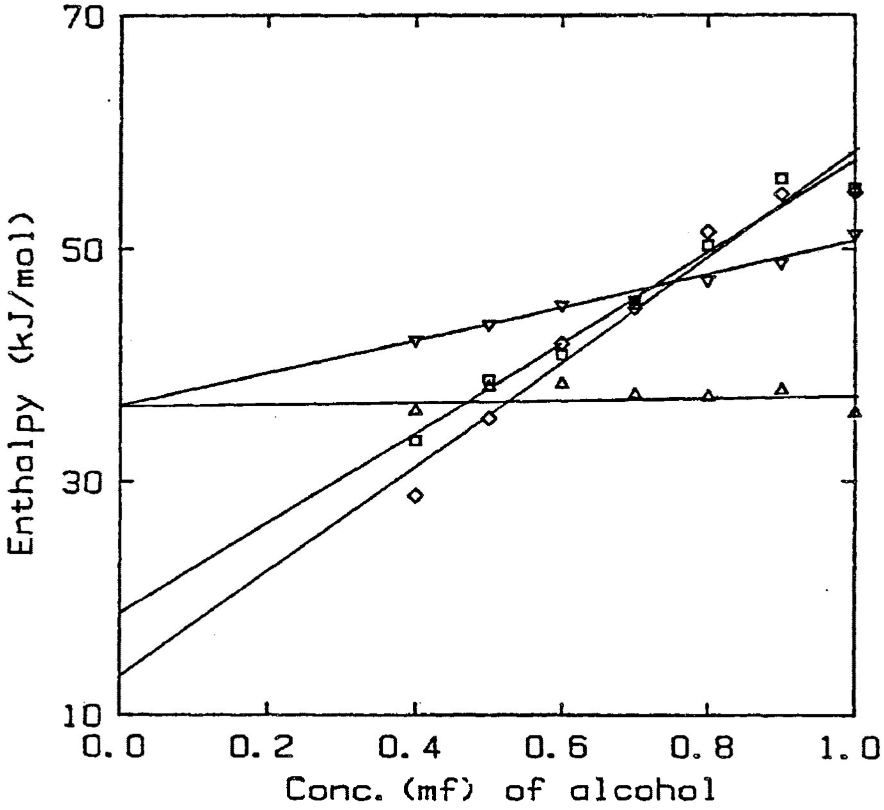
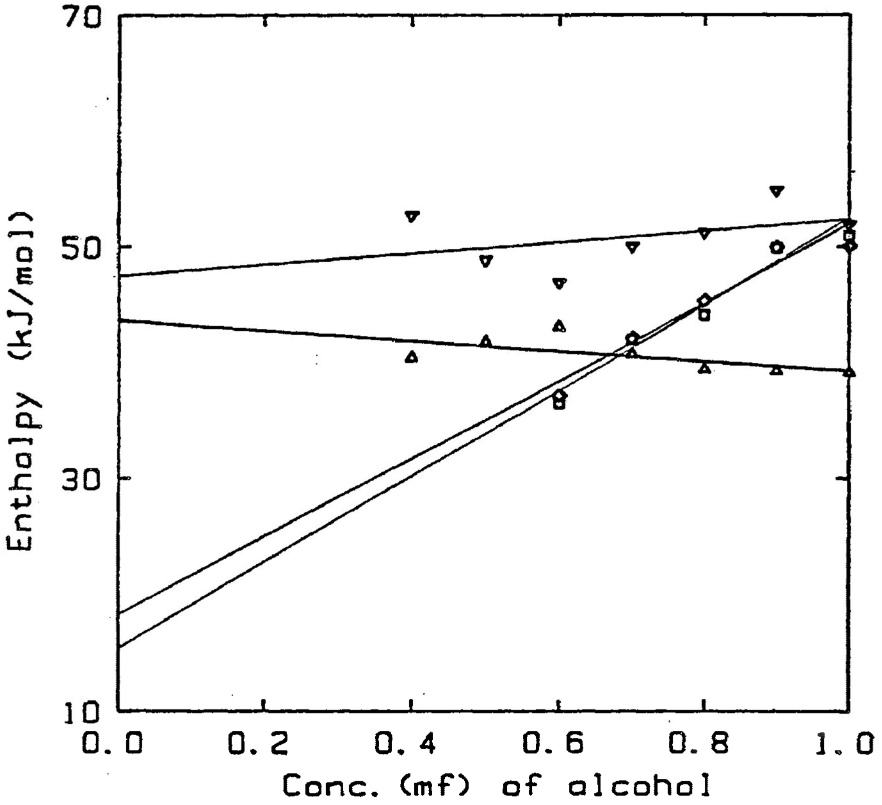


FIGURE VI-8a: Enthalpy of activation (ΔH_E) versus mole fraction of 1-,2-,3- and 4-heptanols, in toluene solution.



<u>FIGURE VI-8b</u>: Enthalpy of activation (ΔH_E) versus mole fraction of 1-,2-,3- and 4-octanols, in toluene solution.

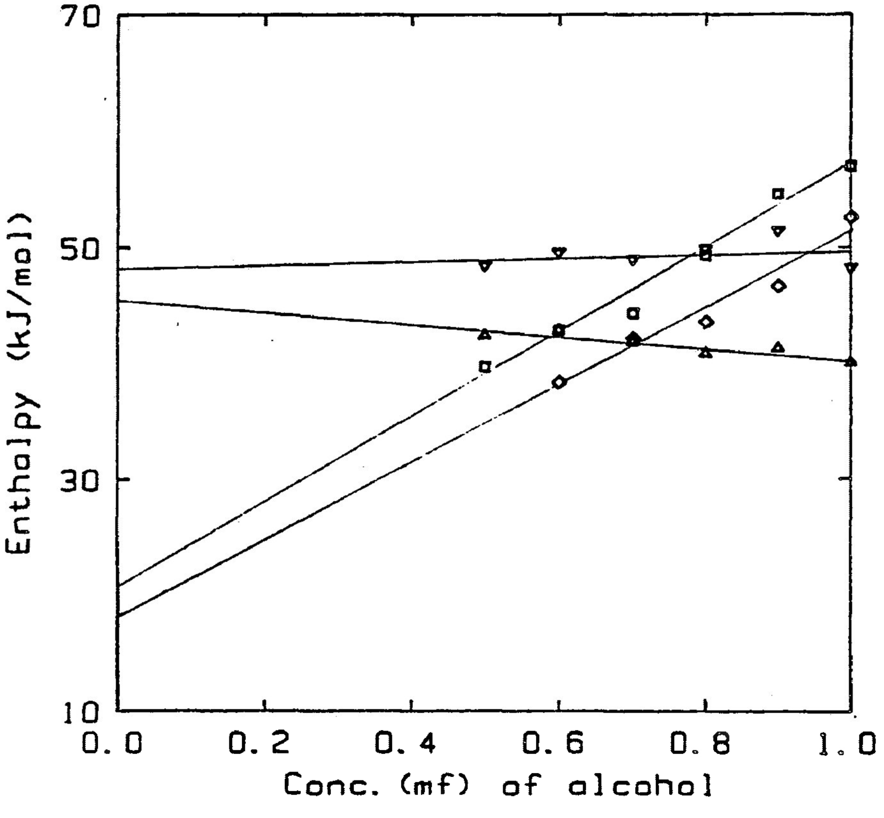


FIGURE VI-8c: Enthalpy of activation (ΔH_E) versus mole fraction of 1-,2-,3-4-decanols in toluene solution.

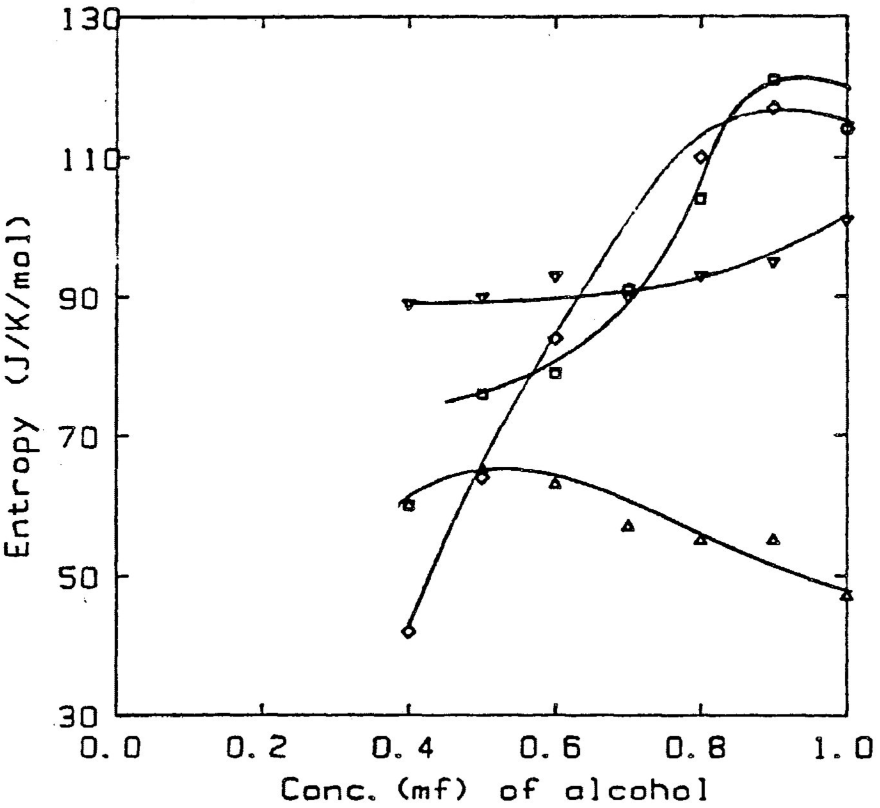


FIGURE VI-9a: Entropy of activation (ΔS_E) versus mole fraction of 1-,2-,3- and 4-heptanols, in toluene solution.

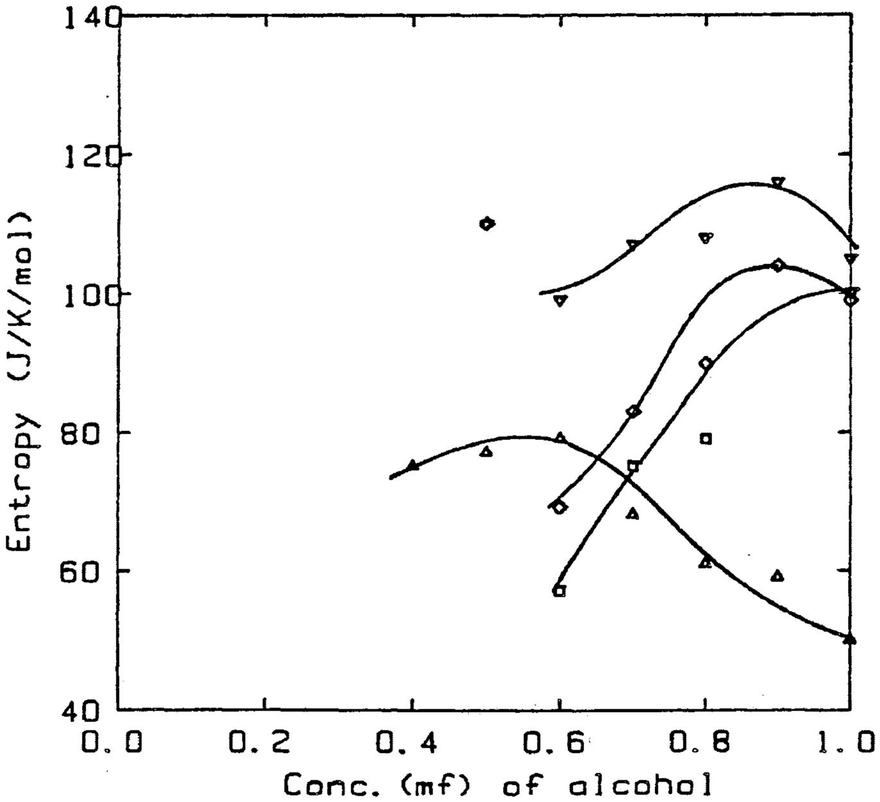


FIGURE VI-9b: Entropy of activation (ΔS_E) versus mole fraction of 1-, 2-, 3- and 4-octanols, in toluene solution.

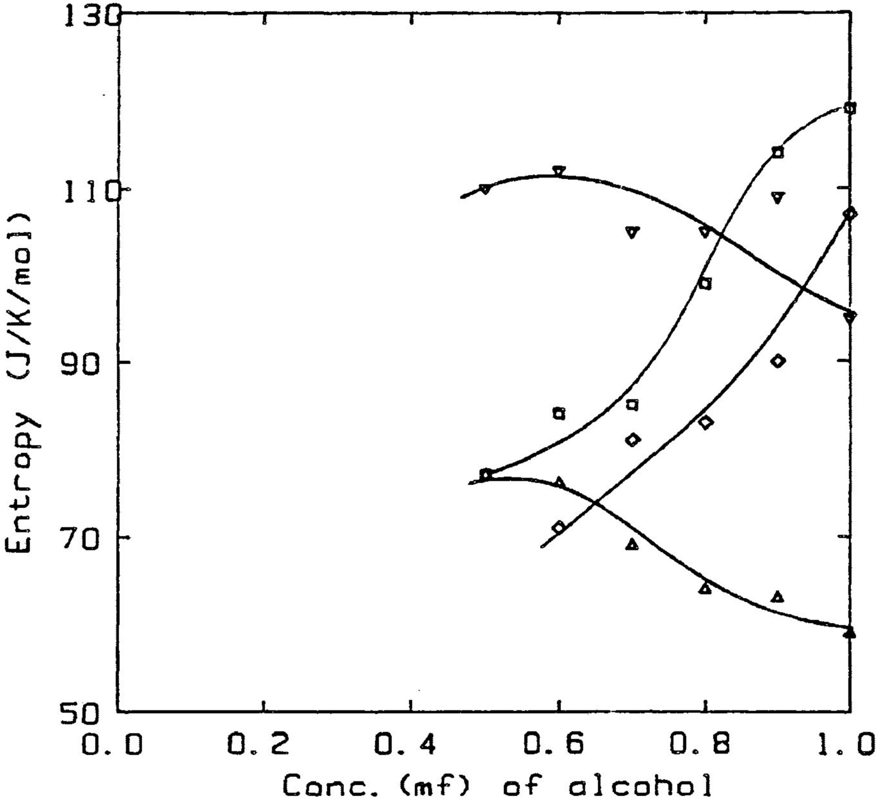


FIGURE VI-9c: Entropy of activation (ΔS_E) versus mole fraction of 1-,2-,3- and 4-decanols, in toluene solution.

A study of the enthalpies of activation (ΔH_E) of the first dispersion region.

(*i*) 1-alkanols in n-heptane:

When the alcohol concentration is increased from 0.3 to 1.0 MF for 1-butanol in n-heptane the enthalpy of activation (ΔH_E) changes only very slightly. Similar behaviour is noticed for 1-hexanol and 1-octanol, except for 1-decanol whose energy barrier goes up from 34 to 41 kJ mol^{-1} with the increase in alcohol concentration.

(*ii*) 1-alkanols in toluene:

For methanol in toluene, the enthalpy of activation (ΔH_E) increases from 13 kJ mol^{-1} to 22 kJ mol^{-1}. When the alcohol concentration is decreased. The same type of behaviour is also prevalent for 1-butanol in toluene where a difference in energy barrier of ~6 kJ mol^{-1} is noted between the pure and diluted states of alcohol. This difference, however, is only 1 to 3 kJ mol^{-1} when the behaviour of long chain alcohols in toluene is studied.

(*iii*) 1-alkanols in diethyl ether:

A different kind of behaviour is observed for these systems. There is hardly any change in enthalpy of activation (ΔH_E) for methanol (which has no chain at all) when its concentration in diethyl ether is increased from 0.3 MF to 1.0 MF. For the other 1-alkanols with chains, the ΔH_E values increase steadily with the increase in alcohol concentration in diethyl ether.

It is interesting to note that as the chain length is increased, the energy barriers (ΔH_E) increase, especially at high alcohol concentration. However, at low alcohol concentrations, i.e. at 0.3 MF, an energy barrier (ΔH_E) of ~13 kJ mol^{-1} is observed for all the alcohols, which is in fact, equivalent to the energy barrier of pure methanol. A similar kind of trend, i.e. the linear increase in ΔH_E with the