PART II

Dielectric Studies of Molecular Interactions in Amphiphilics in Solution State
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MOLECULAR CORRELATION FACTOR OF DIELECTRIC POLARIZATION OF AMPHIPHILICS IN THE SOLUTION STATE

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CHAPTER - V

MOLECULAR CORRELATION FACTOR OF DIELECTRIC POLARIZATION OF AMPHIPHILICS IN THE SOLUTION STATE

5.1. Introduction:

This chapter describes a quantitative measurement of the dielectric constants of amphiphilic molecules in the solution state. From a phenomenological approach of the Kirkwood correlation factor, the correlation of the molecular orientation of the amphiphilic molecules in the solution state is studied.

The structure of the film and the orientation of the hydrophobic tails were a matter of intensive studies through π-A isotherms. Many experimental methods are also available to characterize the degree of ordering. However, the relative instability of the films precludes intrusive techniques. Further, the assumption of a model is a prerequisite to interpret the results. Hence computer simulation modelling has come to stay[1]. Molecular dynamics simulation has been used for hydrocarbon chains[2]. Simulation studies on alkane crystals have shown that a model which includes the hydrogen atom
interactions is necessary for the accurate description of solid structures[3,4]. Major weakness of such models is that they do not include the head group structure and dipolar interactions. The proximity of the head group to each other in a two dimensional array means that these interactions may have an effect on the structure and dynamics. A model for the study of equilibrium dipole patterns in a monolayer was recently presented. [5]

Another simplified way of tackling the dipolar interactions is to consider the two dimensional array in the classical approximation potential [6] Wu, Chen-Xu et. al., [7] calculated the dielectric constant of a monolayer with dielectric anisotropy on a material surface. A monolayer of constituent rod-like molecules with a permanent dipole moment not parallel to the molecular long axis is assumed to form an infinite two-dimensional array. These dielectric anisotropic monolayer films degenerate into dielectric isotropic films with an apparent electronic polarizability,

\[ \alpha' = (\alpha_\pi + \alpha_\perp) / 2 \] 
(5.1)
in the first approximation. If the molecular area \( A < \sqrt{3} \frac{A^*}{2} \), where 
\( A^* = \pi l^2 \) where \( l \) is the length of the rod like molecule, the molecules turned out to be uniaxial, with an approximate dipole moment \( \mu \cos \theta_D \), where \( \theta_D \) is the tilt angle. It was found that the polarity of the additional relative dielectric constant produced by the coupling between the orientational distribution and the dielectric anisotropy of molecules is negative, whereas it is positive in the case in which the molecules are close to the critical area \( A_0 \). In spite of such successful predictions, it is true that the theoretical treatments do not address itself readily with the practical problems. The parameters required are very large for a meaningful interpretation. The next best approach is to investigate experimentally, the dipolar interactions in a more or less similar situation. For example, charaterization of waters of hydrophobic hydration through dielectric relaxation studies becomes possible with elastic protein based polymers because they exhibit a phase transitional behavior.[8,9] The solution curve \( \varepsilon'' \) vs frequency showed interesting characteristics representing the water interaction with the protein based polymers.

The earliest approach to study the solute-solvent interactions and their manifestations on the dipolar character of the species is through the
Kirkwood – Fröhlich relation [10]. For large biological molecules the Kirkwood correlation factor which describes the orientational correlation between one molecule and a certain number of other molecules is taken as unity. [11] However, for smaller molecules, like amphiphiles, this assumption is not adequate to describe the dipolar interactions. Comparatively few studies have been done regarding the Kirkwood correlation factor of amphiphilic molecules in interacting and non-interacting solvents. We report here, our static dielectric studies of several amphiphiles in dioxane. As a solvent, dioxane molecules do not associate among themselves but can act as proton acceptor, whose H-bonding character is close to that of water at least in two dimensions.

2 Theoretical considerations of Static Permittivity of Liquids:

The electric permittivity called as dielectric constant is a characteristic quantity easy to measure and which can give considerable information about the structural properties of polar fluids. The molecular dipole moment from the measured dielectric constant of the bulk material depends on its molecular interactions with their neighbours. The effect of these interactions in bulk can be theoretically raced to the effect of the internal field upon the dipoles. The Debye’s treatment[12] of the dipole moment of the molecule neglects the local
Directional forces exerted by the neighbouring molecules and the local field.

Onsag[13] improved this treatment by incorporating the local field due to long range interactions. In this model, a polar molecule of a species in a solution is viewed as a point dipole of moment $M_i$ in a spherical cavity of radius $a_i$. The mutual influence of permanent dipoles of their neighbourhood makes an assembly of dipoles, permanent or otherwise, as a co-operative phenomenon. The effective field acting on a dipole is generally not the externally applied field, but is augmented by a reaction field $R$. The ideal dipole in a molecule could be taken to be in the centre of a spherical cavity surrounded by other particles and the reaction field is proportional to the total electric moment and depends on the instantaneous orientation of the molecules.

If $\varepsilon_0$ is the permittivity of the liquid at static frequencies and $\varepsilon_\infty$ is that at optical frequencies, then Onsagar showed that,

$$R = \frac{4}{3} \frac{\pi N_A \varepsilon_\infty}{V} \left( \frac{2 \varepsilon_0 - 2}{2 \varepsilon_0 + \varepsilon_\infty} \right) \left( \frac{\varepsilon_\infty + 2}{3} \right) p_i \quad (5.2)$$

where $p_i$ is the dipole moment of the species in vacuum, $N_A$ is the Avagadro number and $V$ is the volume.
When Onsagar’s expressions for the internal and the directional fields are introduced into the fundamental equation of Debye, we get [14],

\[ p_i^2 = \frac{9kT}{4\pi N_A} \cdot \frac{V}{\varepsilon_0 (\varepsilon_x + 2)^3} \left( \varepsilon_0 - \varepsilon_x \right) \left( 2\varepsilon_0 + \varepsilon_x \right) \]

(5.3)

For non-associated polar liquids, \( p_i \) is the dipole moment of the \( i^{th} \) species in the gaseous state (\( \mu \)).

The configurational potential energy of a simple liquid is described by a Lennard – Jones potential. Attractive forces, dipole-dipole interactions and other slowly varying interactions play a role in the structure of the liquids. The modern theories of liquids [15,16] show that the repulsive inter-molecular forces dominate the structure of most dense fluids. In the case of such fluids, which are described correctly by a harsh repulsion in the van der Waals picture, the dielectric constants in the continuum approach lead to the Onsagar equation (Eq 5.2). An analysis of the reaction field in continuum models and molecular statistical theories was recently given [17].
The inadequacies of the Onsagar equation as applied to non-associated liquids have been found to arise from the assumption of a spherical shape for the molecules [18]. It is of course possible to calculate the size effect on the polarization of the dipolar molecules by considering them as ellipsoidal. Even then in many cases, the agreement between the experimental and the theoretical values of dipole moments is fortuitous. Hoye and Stell [19] and Chandler [20] had shown that the dielectric constant of a polar fluid can be expressed in terms of site-site distribution function. An analytical formulation of the dielectric constant of a dipolar hard-sphere using mean spherical approximation was given by Cummings and Blum [21]. But the methods cited above are unrealistic molecular models chosen for simplicity and convenience. Computer simulation studies have made considerable progress but that requires explicit considerations of a finite size medium with periodic boundaries for long range interactions [22,23].

In the case of associated liquids, it is almost impossible to account for their dielectric behaviour in the continuum approach and one has to recourse to the theories based on the statistical mechanical approach of dielectric constants. In the absence of a detailed theoretical
knowledge of intermolecular forces, the specific interactions of local order treated on the above approach must provide valid information on the structure of such liquids. Then a direct measurement of dielectric constants of the liquids is an experimental complement to the theory. Theoretical interpretations of the measured dielectric constants of associated liquids were enhanced by the Kirkwood's theory of dielectric polarization[24] which was later modified by Fröhlich [25]. The Kirkwood- Fröhlich treatment takes care of short-range correlations like hydrogen bonding through the introduction of the dimensionless correlation parameter g. The value of g which is always greater than zero is a macroscopic index of the average mutual orientations between dipolar molecules due to short-range interactions. The near impossibility of obtaining a theoretical knowledge of these interactions makes the experimental determination of this parameter as more important.
5.3 Statistical Mechanical Considerations on static dielectric constants and Kirkwood's Correlation Factor

Considering a macroscopic cavity of volume $V$ containing $N$ molecules and if $E_0$ is the mean macroscopic fluid due to electric charges situated outside the volume under consideration, the average moment $<M_E>$ of the volume in the direction of the field is,

$$<M_E> = \frac{\int \cdots \int M_E \exp\left(-\frac{U(X,E_0)}{kT}\right) dX}{\int \cdots \int \exp\left(-\frac{U(X,E_0)}{kT}\right) dX} \quad (5.4)$$

where $<M_E>$ is the moment associated with the given values of $E$ and $U(X,E_0)$ is the total potential energy of the $N$ particles and $X$ is a set of co-ordinates allowing complete description of the system. The energy $U$ depends on all interactions of all particles with one another and also with the field $E_0$. The major difficulty in the problem is that such interactions are not completely described.

The moment of the total volume is obtained by adding the moments of its $N$ molecules and this leads to
\[ M = \sum_{i=1}^{N} \left[ \mu_i + \alpha \left( E_0 - \sum_{k=1}^{N} T_{ik} \cdot m_{ik} \right) \right] \]  \hspace{1cm} (5.5)

where \( \mu_i \) is the permanent dipole moment of the isolated molecule, \( \alpha \) is the polarizability, taking care of the atomic and electric deformation polarization. The tensor product \( (T_{ik} \cdot m_{ik}) \) represents, in the first approximation, the field created by the \( k^{th} \) molecule in the region occupied by the molecule \( i \).

For a spherical volume surrounded by its own medium the boundary conditions lead to Onsagar's cavity field \( G' \) which could be substituted for \( E_0 \).

\[ G' = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} E_0 \]  \hspace{1cm} (5.6)

But the separation of the deformation effects from the orientation effects become difficult. Hence a mean effective or internal field \( (F) \) is defined as,

\[ F = E_0 - \sum_{k=2} \left\langle \left( T_{ik} \cdot m_{ik} \right)_E \right\rangle \]  \hspace{1cm} (5.7)
Combining equations (5.5) and (5.6)

$$\langle M_E \rangle = \sum_{i=1}^{N} \left[ \langle \mu_i \rangle_L + \alpha F_i \right]$$

(5.8)

In the continuum approach of Onsag, this internal field $F$ is split up into the cavity field $G'$ and the reaction field $R$. The reaction field exists even in the absence of the external field. Hence one should introduce the internal moment $p$ which is the sum of the moments of an isolated molecule and the moment due to the reaction field.

For a polar liquid, Kirkwood treated the orientation polarization by the consideration of statistical mechanics, leaving the deformation polarization to be described completely by empirical methods. The total potential energy $U$ is considered to be of two parts; (i) $U_1(X)$ due to dispersion forces which is practically independent of the field $E_0$ and (ii) $U_2(X,E_0)$ which is due to electrostatic interactions of the dipoles with the external field. Hence,

$$U(X, E_0) = U_1(X) + U_2(X,E_0)$$

(5.9)
and

\[ U_2 (X_2, E_0) = - \sum p_i E_0 \]  \hspace{1cm} (5.10)

where \( p \) is the internal moment (not \( \mu \)) of the set of non-deformable molecules, contained in the spherical cavity. Hence, if \( (p_i E_0/kT) \ll 1 \), the exponential in equation (5.4) could be expanded as power series, \( E_0 \) factorized out, and integration carried out easily.

When the sphere contains more than one molecule the value of \( p_i \) can be different from \( \mu_i \). However, if the number molecules introduced in the sphere increase beyond a particular minimum, \( p_i \) will be independent of \( N \) and the orientation effect of the representative molecule outside the cavity will completely disappear. Hence the deviations of \( p_i \) from \( \mu_i \) are the results of the molecular interactions. These short range ordering effects could then be studied by the Kirkwood Correlation Factor \( g \) which accounts for the deviations of \( p_i \) from \( \mu_i \).
Denoting the angle between the orientations of the $i^{th}$ and $j^{th}$ dipole by $\Theta_{ij}$, one could write,

$$\mu_i p_i = \mu^2 \sum_{j=1}^{N} \frac{\int \cos \Theta_{ij} \exp\left(-U_2 / kT\right) dx}{\int \exp\left(-U_2 / kT\right) dx}$$  \hspace{1cm} (5.11)

where $\mu$ is the dipole moment of the representative molecule in the gaseous state.

Defining 'g' as,

$$g = \sum_{j=1}^{N} \langle \cos \Theta_{ij} \rangle \frac{1}{\mu^2} \int W(X_i) \mu_i p_i dx$$  \hspace{1cm} (5.12)

where $W(X_i)$ is the statistical weight factor of the $i^{th}$ molecule and

$$\langle \cos \Theta_{ij} \rangle = \frac{\int \cos \Theta_{ij} \exp\left(-U_2 / kT\right) dX_i dX_j}{\exp\left(-U_2 / kT\right) dX_i dX_j}$$  \hspace{1cm} (5.13)

Here $U_2$ is the rotational intermolecular interaction energy of the molecule and $dX_i$ and $dX_j$ denote the coordinates of the $i^{th}$ and $j^{th}$ molecules. Hence from Onsagar's relation,
\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N}{3kT} \int \text{W}(x, \mu) \rho dX, \quad (5.14)
\]

\[
= \frac{4\pi N}{3kT} \rho \mu^2 \quad (5.15)
\]

Taking into account the deformation polarization, electronic as well as atomic,

\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N A \rho \mu^2}{3kTV} + \frac{4\pi N A \alpha}{3V} \quad (5.16)
\]

Fröhlich has chosen a model in which no such boundary effect need be considered. Treating the deformation polarization as a macroscopic phenomenon he was able to replace the molecules by a set of non-deformable point dipoles of moment \(p'\), placed in a continuous medium of dielectric constant \(\varepsilon_{\infty}\). He was able to show that this takes care of the deformation effects. The moment of spherical molecule is then,

\[
p' = \left[ \frac{\varepsilon_{\infty} + 2}{3} \right] \mu \quad (5.17)
\]

Hence one can obtain

\[
\frac{(\varepsilon_0 - \varepsilon_{\infty})(2\varepsilon_0 + \varepsilon_{\infty})}{3\varepsilon_0} = \frac{4\pi N A \rho}{3kTM} \langle p'M' \rangle \quad (5.18)
\]
where $M$ is the molecular weight and $M'$ is the moment of the spherical cavity placed in a continuous dielectric of moment defined by $p'$.

Therefore

$$
\langle p'M' \rangle = \frac{kT M}{4\pi N_a \rho} \frac{\left(\varepsilon_0 - \varepsilon_x\right)\left(2\varepsilon_0 + \varepsilon_x\right)}{\varepsilon_0}
$$

(5.19)

If the fundamental unit is the molecule itself, then,

$$
\langle \mu M' \rangle = g \mu^2 = \frac{9kT M}{4\pi N_a \rho} \frac{\left(\varepsilon_0 - \varepsilon_x\right)\left(2\varepsilon_0 + \varepsilon_x\right)}{\varepsilon_0\left(\varepsilon_x + 2\right)^2}
$$

(5.20)

The dimensionless parameter $g$ in equation (5.20) reflects the average mutual orientation correlation between the representative dipolar molecules and its neighbours. As per the equation (5.20), ‘$g$’ is always positive. The phenomenological generalization of the Kirkwood formula as above was further refined by many workers [26-28]. Though they provide necessary informations for a microscopic theory, the phenomenological expression given by equation (5.20) is essentially true for polarizable species [29].
5.4 Association in liquids and Kirkwood Correlation Factor

It is evident from equation (5.12) that $g$ describes something about the orientational ordering of the molecules in a liquid through the angular correlations of the neighbouring dipoles and hence a measurement of $\varepsilon_0$ would yield useful information about the structure of the liquid.

Oster and Kirkwood [30] showed how one could predict the structure of water from the determination of the values of $g$. Many authors have investigated the static dielectric behaviour of such associative liquids since then. An extensive review of the earlier work in this field was given by Böttcher [14] and the latter by Tjia [31]. From the variations of the values of $g$, in associated liquids, like monoalcohols, certain general conclusions were drawn regarding the influence of the multimers, the temperature and chain length. At high temperature and at infinite solution, Onsagar’s equation with $g = 1$ is valid. The $g$ factor appears not to be influenced by the occurrence of double or triple bond in the carbon chain [32].

The interpretation of the results was based on the fact that, if the interactions in the system result in an average orientation of the neighbours parallel to the orientation of the representative dipole, the average correlation is positive and $g > 1$. On the other hand, the anti-
parallel dipole orientation should lead to a negative correlation and $g < 1$. It was stressed by Tjia and then by Bordewijk et al., [33] that a value of 1 for $g$ factor does not imply in itself the absence of association between the molecules of the system.

The influence of the association by hydrogen bonds on the structure of liquids and its dielectric manifestations have been studied for a long time [14]. The monohydric alcohols, dihydric alcohols, the substituted phenols, the carboxylic acids and N-substituted amides are the most common associated liquids which have been studied by extensively. Reviews of previous work on the dielectric behaviour of alcohols have been published [34]. It has been realized that at least three types of multimers occur in these compounds. (i) The $\alpha$-multimers, dominating in pure compounds for which $g > 1$. (ii) the $\beta$-multimers dominating in solutions of normal alcohols, phenols and carboxylic acids in non-polar solvents at intermediate concentrations with $g < 1$ and (iii) the $\gamma$-multimers, whose presence is observed only at very low concentrations where the structure is again linear with $g > 1$.

5.5 Association in the liquid state of carboxylic acids and alcohols:

In the liquid state, majority of the carboxylic acids with low alkyl group are said to exist in dimeric form, open or closed. Eberson [35] has reviewed the various types of hydrogen bonding in carboxylic
acids. The theoretical PCIL0 studies of hydrogen bonding in carboxylic acids [36] have shown that the cis conformer is more stable than the trans conformer and the stability of cis increases with the increase of the alkyl group. In long chain acids, dimerization is weak.[37] The dielectric studies showed that [38] on dilution with non-interacting solvents, the Kirkwood correlation factor decreases indicating that the β-multimers with antiparallel dipoles are not broken while α-multimers, with parallel dipoles are more and more converted into β-multimers.

Regarding the structure of alcohols in the liquid form, it is widely accepted that it consists of winding chains with predominance of monomers forming an average of 2 hydrogen bonds. [39] On the contrary the water network has a 3D feature. Moreover, according to IR and NMR measurements water is supposed to contain a few percent of broken bonds at room temperature, with the consequence that partially unbonded, terminal OH groups are formed in the pure liquid. This seems not to occur in the alcohols. According to Symons and Co-workers [40-42] it determines a different situation when aprotic solvents are added to water or alcohol molecules. Hence the aprotic solvents attack directly the alcohol O-H groups. The NMR investigation of binary mixtures of 1-4 Dioxane with a series of alkyl alcohols showed the rupture of alcoholic chains with formation of dioxane –
alcohol adducts and smaller chains at least in low alkyl alcohols [43].

There are many dielectric studies of low alkyl chain alcohols in recent times. The dielectric behaviour and intermolecular association for octanol isomers was recently studied by Shinomiya [44]. The steric effects on the dielectric constants of alcohol mixtures was studied by Mandal and Walker [45]. Swain et al., [46] studied the dipolar interaction in binary mixtures of some higher order alcohols with polar liquids. Surprisingly, no systematic work seems to have been done in fatty alcohols.

5.6 Scope of the present work:

We report here, our dipolar interaction studies of several fatty acids and alcohols, in dioxane. The Kirkwood correlation factor was determined for the following systems.

1. Tetra decanol
2. Hexa decanol
3. Stearyl alcohol
4. Stearic acid
5. Arachidic acid
5.7 Experimental Techniques:

5.7(a) Dielectric constant measurements:

The dielectric constant was determined by the measurement of the capacity of a cylindrical cell (with and without liquid) at 1 KHz by a digital KEITHLEY 3330 LCZ meter. The temperature was maintained constant with ± 0.5°C using a thermostat supplied by Ms. Raagaa Industries, Chennai. From the readings of LCZ meter, the dielectric constant was calculated using the calibrated data. The instrument was calibrated using standard liquids like benzene and toluene. The experimental arrangement is shown in Fig. (5.1).

(b) Calibration of LCZ meter:

Pure standard liquids mentioned above were introduced into the cell and the respective readings of the capacitance meter were noted, the temperature being maintained at 308K. The dielectric constants of these liquids at 308K were taken from Lange’s Handbook of Chemistry[47]. The calibration data are given in the following table.
Fig. 5.1 EXPERIMENTAL SET UP
<table>
<thead>
<tr>
<th>Liquid</th>
<th>Meter Reading R pF</th>
<th>Dielectric constant $\varepsilon_0$ at 308K</th>
<th>Mean $\Delta\varepsilon/\Delta R \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>96</td>
<td>1.0000</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>201</td>
<td>2.2540</td>
<td>12.00</td>
</tr>
<tr>
<td>Toluene</td>
<td>209</td>
<td>2.4221</td>
<td></td>
</tr>
</tbody>
</table>

The dielectric constant of the solution was calculated using the equation

$$\varepsilon_x = \varepsilon_s + (R_x - R_s)\frac{\Delta\varepsilon}{\Delta R}$$

(5.21)

where $\varepsilon_x$ and $\varepsilon_s$ are the dielectric constants of the solution and solvent respectively. $R_x$ and $R_s$ are the corresponding meter readings. The uncertainty in the measurement of $\varepsilon_x$ is $\pm 1.0\%$.

(c) Measurement of Refractive Index ($n_D$)

The refractive indices of the samples were determined using an Abbe's refractometer. The uncertainty in the measurement of the refractive index is $\pm 0.0002$. 
(d) Determination of Dipole Moment:

The dipole moment of a polar molecule may be computed from the solution data using various methods. Halverstadt and Kumler [48] assumed linear variation of dielectric constant and specific volume $V$ with concentration.

\[ \varepsilon_0 = \varepsilon_1 + \alpha w_2 \]  \hspace{1cm} (5.22)

\[ V = V_1 + \beta w_2 \]  \hspace{1cm} (5.23)

where $w$ is the weight fraction, $\varepsilon_0$ and $V$ are the dielectric constant and specific volume $(1/\rho)$ respectively and $\alpha$ and $\beta$ are constants. The subscripts 1 and 2 refer to the solvent and solute molecules.

\[ P_{2x} = \frac{3M_2\alpha V_1}{(\varepsilon_1 + 2)^2} + \frac{(M_2V_1 + \beta)(\varepsilon_1 - 1)}{(\varepsilon_1 + 2)} \]  \hspace{1cm} (5.24)

where $P_{2x}$ represents the limiting polarization at infinite dilution of the solute. The value of $P_{2x}$ should almost be equal to the value of the total polarization of the solute in the gaseous state, because the dipoles are sufficiently separated from one another by non-polar molecules. Halverstadt and Kumler obtained the value of $\varepsilon_1$ from the curve $\varepsilon_0$ vs $w_2$ for the solution by extrapolation of $w_2 \to 0$. The method has the
advantage that it places less weight on the actual measurements made on the pure solvents than on any other measurements.

In the expression for the limiting polarization,

\[ P_{2x} = \left( \frac{4\pi N_A}{3} \right) \left( \alpha + \frac{\mu_2^2}{3kT} \right) \quad (5.25) \]

the value of deformation polarization \( \alpha \) is substituted from Lorentz-Lorentz formula

\[
\frac{4\pi N_A \alpha}{3} = \left( \frac{n_{D_2}^2 - 1}{n_{D_2}^2 + 2} \right) \rho_2 = R_{D_2}
\]

(5.26)

On rearrangement the value of \( \mu_2 \) is obtained as follows.

\[ \mu_2 = \left[ \frac{9kT}{4\pi N_A} \left( P_{2x} - R_{D_2} \right) \right]^{\frac{1}{2}} \quad (5.27) \]

Substituting the values for the constants

\[ \mu_2 = 0.0128 \sqrt{(P_{2x} - R_{D_2})T} \quad (5.28) \]

The dipole moments of the solute molecules in very dilute solutions in Dioxane were obtained from equation (5.28). The values were found to be in good agreement with that reported in the literature.
(c) **Determination of Kirkwood correlation factor:**

The interaction between the polar solute and a non-polar solvent may be considered by a modification of the Kirkwood correlation factor which takes into account the interaction between solvent molecules among themselves. In a binary solution two kinds of units have to be considered (i) those of solvent, characterized by internal moment \( p_1' \) and (ii) those of solute having a moment \( p_2' \).

Equation (5.19) obtained by Fröhlich for pure liquids must be replaced by

\[
\frac{(\varepsilon_0 - \varepsilon_x) (2\varepsilon_0 + \varepsilon_x) T}{3\varepsilon_0} = \frac{4\pi}{3k} \left[ \langle p_1'M_1'^* \rangle N_1 + \langle p_2'M_2'^* \rangle N_2 \right] 
\]

(5.29)

where \( N_1 \) and \( N_2 \) are the number of polar units of solvent and solute per unit volume of the solution. \( M_1'^* \) and \( M_2'^* \) are the total moments of a sphere having a polar unit of solvent or solute located at its centre in a given configuration. \( p_1' \) and \( p_2' \) are the moments of the polar units of solvent and solute in these configuration. Introducing weight fractions, \( w_1 \) and \( w_2 \) in equation (5.29), we find
\[ B(T) = \frac{(\varepsilon_0 - \varepsilon,)(2\varepsilon_0 + \varepsilon,)}{3\varepsilon_0\rho} T \]  

(5.30)

\[ = \frac{4\pi N_A}{3k} \left[ \langle p'_1 M'_1 \rangle \frac{w_1}{M_1} + \langle p'_2 M'_2 \rangle \frac{w_2}{M_2} \right] \]  

(5.31)

where \( w_1, M_1 \) and \( w_2, M_2 \) are the weight fractions and molecular weights of the solvent and solute respectively, \( \rho \) is density of the solution.

In a dilute solution there are many more solvent-solvent contacts than solvent-solute contacts so that \( \langle p'_1 M'_1 \rangle \) may be assumed to be practically equal to its value in the pure state.

Hence

\[ B_1(T) = \frac{(\varepsilon_1 - \varepsilon_{1x})(2\varepsilon_1 + \varepsilon_{1x})}{3\varepsilon_1\rho_1} T \]

\[ = \left( \frac{4\pi N_A}{3kM_1} \right) \langle p'_1 M'_1 \rangle \]  

(5.32)

\( \rho_1 \) is the density at temperature \( T \) for solvent. Combining equations (5.31) and (5.32)

\[ B(T) - w_1 B_1(T) = \left( \frac{4\pi N_A w_2}{3kM_2} \right) \langle p'_2 M'_2 \rangle \]  

(5.33)
The moments $p_2'$ and $M_2^*$ as well as their scalar product, depend on mutual orientation of all the dipoles present in the chosen microscopic sphere. In a general manner, whatever be the nature of the polar unit, we have

$$M_2^* = p_2' + Z\langle p_1' \rangle$$  \hspace{1cm} (5.34)

where $Z$ is the number of solvent molecules in direct contact with polar unit of the solute. $\langle p_1' \rangle$ is the average moment of the solvent molecule in the direction of $p_2'$.

If $\gamma$ is the angle between the polar units of the solute and solvent molecules, the equation (5.34) is modified as

$$\langle p_2'M_2^* \rangle = \langle p_2'^2 \rangle \left[ 1 + \frac{Zp_1'}{p_2'} \langle \cos \gamma \rangle_2 \right]$$  \hspace{1cm} (5.35)

The average of the product must be taken over all co-ordinates describing configuration of the fixed polar unit. In a similar manner $\langle \cos \gamma \rangle_2$ is given by

$$\langle \cos \gamma \rangle_2 = \int \cos \gamma \exp(-U/kT)d\omega_1$$  \hspace{1cm} (5.36)

where $U$ is the total energy of interaction between polar unit 2 and the solvent and $\omega_1$ is the solid angle described by the rotation of polar
unit 1. The subscript 2 indicates that $<\cos\gamma>_2$ is a function of the coordinates of unit 2. In fact, the energy $U$ depends on the dipole moment $p_2$ and $\cos\gamma$.

If the average angular correlation between polar species is represented by $g$ then

$$\langle p'_2 M'_2 \rangle = g\langle \mu^2_2 \rangle \left[ \frac{\epsilon_{ix} + 2}{3} \right]^2$$

(5.37)

The definition of $g$ here is most general in the sense that it is a measure of the angular correlation of the dipole vector of the molecule with the neighbouring molecules in the solution while the effect of the short range correlation between solvent molecules are also accounted for. Combining equations (5.33) and (5.37) one can write

$$g = \frac{27kM_2}{4\pi N_A w_2 \mu^2_2 (\epsilon_{ix} + 2)^2} \left[ B(T) - w_1 B_1(T) \right]$$

(5.38)

5.8 Results:

The results of our investigations are given in Tables 5.1 to 5.5 and shown graphically in Figs. 5.2 to 5.6.
5.9 Discussion:

It is found that \( g \) decreases with increase of dilution and reaches a minimum for all fatty acids and alcohols. It again increases with further dilution. This is a common behaviour for most of the low alkyl chain alcohols. [49] The strength of clustering in alcohol/dodecane mixture was studied by Kroeger[50]. It was pointed by him, that the effective dielectric constant is a function of the cluster size and varies as the volume fraction. The hydrogen bonds of 1-Butanol is more effective than that of 1-Octanol. As the size of butanol is small, there are more molecules per average 1-Butanol cluster, he argued. These clusters in cyclohexane at low concentrations say \(< 0.1\) mole fraction showed antiparallel orientation [51]. One of the significant observations made by Magallanes et. al., [52] is that the relaxation times of n-decanol, n-heptanol and n-propanol in heptane systems show a linear dependence as a function of the number density for each system. For a particular value of the number density, the relaxation time has a value \( \tau_L \) common to all the systems. They have also noticed that a similar behaviour for several n-alcohol/cyclohexane systems and the limiting value \( \tau_L \) is the same irrespective of the alcohol or the non-polar solvent [53]. This behaviour was later confirmed by Thenappan[54] and Poongodi [55] through their studies of Kirkwood Correlation factor for several n-
alcohol/non polar solvent systems. Interestingly, such an effect is noticed in all the 5 fatty acids and alcohols in dioxane reported here and the value of g tends to unity and the critical number density of the polar molecules is $N_c = 12 \times 10^{20}$ dipoles/unit volume. Does it imply that the coupling between dipoles is weak enough and one can consider that there is no co-operation mechanism for dipole orientation at this concentration? Surprisingly we find the value of $N_c$ the same as reported by Magallanes for n-alcohols. This implies that the basic relaxation mechanism and the nature of bonding is the same for all alcohols including fatty alcohols. For fatty acids, $N_c$ is found to vary with the solvent, though it is the same in dioxane. For lower concentrations there appears to be a different kind of co-operation for dipolar interaction stimulated by the inversion of electrical moment leading to increased g. The process of proton migration in the bridge $\text{OH} \ldots \text{O}$ can be given by a quantum jump.

\[ \text{O-H} \cdots \text{O} \] 

\[ \text{O} \cdots \text{H-O} \]
In the lower concentration region the orientation polarization of the multimers is disturbed by thermal motion, whereas at higher concentrations, the molecules pass from a random distribution to a slightly ordered distribution. We also noted that the critical number density for phase reversal is a function of both temperature and the solvent. Keeping this $N_c$ in the solvent for spreading the monolayers, we observed that the spread is without defects and voids. The transferability is also enhanced.
Table 5.1 Kirkwood Correlation Factor for Tetradecanol in 1-4 Dioxane

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2&lt;/sub&gt; moles / l</th>
<th>ε&lt;sub&gt;o&lt;/sub&gt;</th>
<th>ε&lt;sub&gt;x&lt;/sub&gt;</th>
<th>ρ (gm/cc)</th>
<th>g</th>
<th>N X 10&lt;sup&gt;20&lt;/sup&gt; dipoles / unit volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.358</td>
<td>2.0079</td>
<td>1.023</td>
<td>2.51</td>
<td>2.0</td>
</tr>
<tr>
<td>0.4</td>
<td>2.430</td>
<td>2.0051</td>
<td>1.015</td>
<td>1.61</td>
<td>5.0</td>
</tr>
<tr>
<td>0.6</td>
<td>2.489</td>
<td>2.0008</td>
<td>1.007</td>
<td>1.30</td>
<td>7.0</td>
</tr>
<tr>
<td>0.8</td>
<td>2.549</td>
<td>1.9966</td>
<td>0.998</td>
<td>1.18</td>
<td>9.6</td>
</tr>
<tr>
<td>1.0</td>
<td>2.584</td>
<td>1.9909</td>
<td>0.991</td>
<td>1.08</td>
<td>11.8</td>
</tr>
<tr>
<td>1.2</td>
<td>2.703</td>
<td>1.9895</td>
<td>0.983</td>
<td>1.13</td>
<td>14.2</td>
</tr>
<tr>
<td>1.4</td>
<td>2.822</td>
<td>1.9881</td>
<td>0.975</td>
<td>1.18</td>
<td>16.4</td>
</tr>
</tbody>
</table>

Table 5.2. Kirkwood Correlation Factor for Hexadecanol in 1-4 Dioxane

<table>
<thead>
<tr>
<th>C&lt;sub&gt;2&lt;/sub&gt; moles / l</th>
<th>ε&lt;sub&gt;o&lt;/sub&gt;</th>
<th>ε&lt;sub&gt;x&lt;/sub&gt;</th>
<th>ρ (gm/cc)</th>
<th>g</th>
<th>N X 10&lt;sup&gt;20&lt;/sup&gt; dipoles / unit volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.406</td>
<td>2.0953</td>
<td>1.024</td>
<td>2.41</td>
<td>1.9</td>
</tr>
<tr>
<td>0.4</td>
<td>2.465</td>
<td>2.0938</td>
<td>1.011</td>
<td>1.28</td>
<td>4.6</td>
</tr>
<tr>
<td>0.6</td>
<td>2.537</td>
<td>2.0909</td>
<td>1.003</td>
<td>1.16</td>
<td>6.4</td>
</tr>
<tr>
<td>0.8</td>
<td>2.596</td>
<td>2.0880</td>
<td>0.992</td>
<td>1.00</td>
<td>9.0</td>
</tr>
<tr>
<td>1.0</td>
<td>2.644</td>
<td>2.0851</td>
<td>0.985</td>
<td>0.92</td>
<td>11.5</td>
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<tr>
<td>1.2</td>
<td>2.775</td>
<td>2.0837</td>
<td>0.976</td>
<td>0.98</td>
<td>14.0</td>
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<tr>
<td>1.4</td>
<td>2.906</td>
<td>2.0822</td>
<td>0.964</td>
<td>1.06</td>
<td>16.2</td>
</tr>
</tbody>
</table>
Table 5.3: Kirkwood Correlation Factor for Stearyl alcohol in 1-4 Dioxane

<table>
<thead>
<tr>
<th>$C_2$ moles / l</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_\infty$</th>
<th>$\rho$ gm/ce</th>
<th>$g$</th>
<th>$N \times 10^{20}$ dipoles / unit volume</th>
</tr>
</thead>
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<tr>
<td>0.2</td>
<td>2.513</td>
<td>2.0938</td>
<td>1.014</td>
<td>2.44</td>
<td>2.3</td>
</tr>
<tr>
<td>0.4</td>
<td>2.549</td>
<td>2.0924</td>
<td>1.002</td>
<td>1.45</td>
<td>4.5</td>
</tr>
<tr>
<td>0.6</td>
<td>2.608</td>
<td>2.0909</td>
<td>0.993</td>
<td>1.14</td>
<td>7.0</td>
</tr>
<tr>
<td>0.8</td>
<td>2.703</td>
<td>2.0895</td>
<td>0.984</td>
<td>1.09</td>
<td>9.4</td>
</tr>
<tr>
<td>1.0</td>
<td>2.810</td>
<td>2.0880</td>
<td>0.974</td>
<td>1.08</td>
<td>11.6</td>
</tr>
<tr>
<td>1.2</td>
<td>2.941</td>
<td>2.0866</td>
<td>0.965</td>
<td>1.15</td>
<td>13.8</td>
</tr>
<tr>
<td>1.4</td>
<td>3.084</td>
<td>2.0851</td>
<td>0.957</td>
<td>1.22</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Table 5.4: Kirkwood Correlation Factor for Stearic Acid in 1-4 Dioxane

<table>
<thead>
<tr>
<th>$C_2$ moles / l</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_\infty$</th>
<th>$\rho$ gm/ce</th>
<th>$g$</th>
<th>$N \times 10^{20}$ dipoles / unit volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.418</td>
<td>2.0121</td>
<td>1.030</td>
<td>1.88</td>
<td>2.5</td>
</tr>
<tr>
<td>0.4</td>
<td>2.489</td>
<td>2.0107</td>
<td>1.028</td>
<td>1.20</td>
<td>4.9</td>
</tr>
<tr>
<td>0.6</td>
<td>2.572</td>
<td>2.0093</td>
<td>1.026</td>
<td>1.01</td>
<td>7.4</td>
</tr>
<tr>
<td>0.8</td>
<td>2.656</td>
<td>2.0079</td>
<td>1.024</td>
<td>0.94</td>
<td>9.8</td>
</tr>
<tr>
<td>1.0</td>
<td>2.739</td>
<td>2.0065</td>
<td>1.022</td>
<td>0.91</td>
<td>12.2</td>
</tr>
<tr>
<td>1.2</td>
<td>2.894</td>
<td>2.0051</td>
<td>1.020</td>
<td>0.97</td>
<td>14.7</td>
</tr>
<tr>
<td>1.4</td>
<td>3.096</td>
<td>2.0036</td>
<td>1.018</td>
<td>1.08</td>
<td>17.1</td>
</tr>
</tbody>
</table>
Table 5.5. Kirkwood Correlation Factor for Arachidic Acid in 1-4 Dioxane

<table>
<thead>
<tr>
<th>C₂ moles /1</th>
<th>ε₀</th>
<th>εₓ</th>
<th>ρ</th>
<th>g</th>
<th>N X 10²⁰ dipoles / unit volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>2.430</td>
<td>2.0093</td>
<td>1.033</td>
<td>1.79</td>
<td>2.5</td>
</tr>
<tr>
<td>0.4</td>
<td>2.489</td>
<td>2.0079</td>
<td>1.031</td>
<td>1.13</td>
<td>4.9</td>
</tr>
<tr>
<td>0.6</td>
<td>2.584</td>
<td>2.0065</td>
<td>1.030</td>
<td>0.97</td>
<td>7.4</td>
</tr>
<tr>
<td>0.8</td>
<td>2.668</td>
<td>2.0051</td>
<td>1.028</td>
<td>0.90</td>
<td>9.8</td>
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<tr>
<td>1.0</td>
<td>2.763</td>
<td>2.0036</td>
<td>1.024</td>
<td>0.89</td>
<td>12.3</td>
</tr>
<tr>
<td>1.2</td>
<td>2.917</td>
<td>2.0022</td>
<td>1.020</td>
<td>0.96</td>
<td>14.5</td>
</tr>
<tr>
<td>1.4</td>
<td>3.096</td>
<td>2.0008</td>
<td>1.017</td>
<td>1.05</td>
<td>16.9</td>
</tr>
</tbody>
</table>
Fig. 5.2. Tetradecanol + 1-4 Dioxane
Fig. 5.3. Hexadecanol + 1–4 Dioxane
Fig. 5.4. Stearyl alcohol + 1,4-Dioxane.
Fig. 5.5. Stearic Acid + 1,4 Dioxane.
Fig. 5.6. Arachidic Acid + 1-4 Dioxane.
CHAPTER – VI

MICROWAVE DIELECTRIC RELAXATION STUDIES OF CERTAIN FATTY ACIDS AND ALCOHOLS

6.1 Introduction

6.2 Theoretical considerations on Dielectric relaxation

6.3 Relaxation time distribution in dipolar fluids

6.4 Experimental methods to determine relaxation times
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   b) Smyth method

6.5 Experimental set-up

6.6 Procedure

6.7 Determination of parameters from measured Dielectric constants
   (i) Cole–Cole plot
   (ii) Higasi’s method

6.8 Results

6.9 Discussion
CHAPTER VI

MICROWAVE DIELECTRIC RELAXATION STUDIES OF CERTAIN FATTY ACIDS AND ALCOHOLS

6.1. Introduction:

Dielectric relaxation measurements provide a complementary approach to the study of H-bonding. At very high frequencies, the dipolar molecules do not attain equilibrium with the applied field, the energy is absorbed and the dielectric permittivity decreases. Hence a study of dielectric relaxation would give information on the fluid structure. While the static dielectric constants could be related to the microscopic parameters through equations of equilibrium positions of the molecular dipoles, the relaxation phenomenon is understood by considering the manner in which these equilibrium positions are related.

6.2. Theoretical considerations on Dielectric Relaxation

For time varying fields, eqn. (5.3) must be replaced by a most general relation

\[ \langle M_x(t) \rangle = C \int \cdots \int M_x(t) \tilde{f}(X,E_x,t)dx \]  

(6.1)
where the distribution function $f(x, E_\omega, t)$ depends on the time $t$ through $t_{1, \omega}$. The distribution function must be such that

$$E_\omega = 0, \quad <M_E> = 0$$

For a static field,

$$<M_E> = C'E_0 \int \cdots \int M_i f(x)f_i(x)dx$$

(6.2)

where $f(x, E_0) = f_0(x) [1 + f_1(x)E_0 + \ldots]$ (6.3)

For a periodic field, one can write in analogy

$$f(x, E_\omega, t) = f_0(x) [1 + f_{1, \omega}(x) E_0 \exp (j\omega t) + \ldots + \ldots ]$$

(6.4)

to find an expression for $f_{1, \omega}$ a macroscopic method may be used. If $\tau$ is the relaxation time of macroscopic polarization, the rate at which the orientation polarization disappears may be given by a decay function $\phi(t)$, which is proportional to the well known experimental law namely,

$$\phi(t) = \exp (-t/\tau)$$

(6.5)

Hence the distribution function at a given time may be written as

$$f(x, E_\omega, t) = f_0(x) [1 + f_1(x)/[1 + j\omega t] E_0 \exp (j\omega t) + \ldots ]$$

(6.6)

where the periodic field is taken as equivalent to a continuous series of static fields, each being applied during a short interval of time $x$. Therefore,

$$f(x, E_\omega, t) = f_0(x) [1 + f_1(x)/(1 + j\omega t)] E_0 \exp (j\omega t) + \ldots ]$$

(6.7)
This leads to the relation

\[
\left(\varepsilon' - \varepsilon_\infty\right) = \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau^2} - j \frac{(\varepsilon_0 - \varepsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2}
\]  

(6.8)

where \(\varepsilon'\) is the dielectric constant at the angular frequency \(\omega\). The imaginary part is the dielectric loss factor \(\varepsilon''\) given by

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2}
\]  

(6.9)

which is the energy dissipated in the dielectric. If \(\varepsilon^*\) is the complex dielectric constant then

\[
\varepsilon^* = \varepsilon' - j \varepsilon''
\]  

(6.10)

Hence combining equations (6.8) and (6.9), Cole and Cole \[56\] obtained

\[
\left(\varepsilon' - (\varepsilon_0 + \varepsilon_\infty)/2\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2
\]  

(6.11)

Equation (6.11) represents the circle but, since all values must be positive, it gives a semicircle when \(\varepsilon''\) is plotted as ordinate against \(\varepsilon'\) as abscissa, the diameter of the semicircle lying on the abscissa axis. When the measured dielectric constants and losses of a material give such a semicircle they conform to the Debye theory and the material may be described as showing Debye behaviour.
For condensed systems like liquids, Equations (6.8) and (6.9) are not in agreement with the experimental data. The dispersion curves $\varepsilon'$ vs $\ln \omega$ are flatter than predicted and the loss factor $\varepsilon''$ is smaller and $\varepsilon''_{\text{max}}$ for liquids is less than $(\varepsilon_0 - \varepsilon_x) / 2$ as predicted by the theory. These discrepancies are explained as arising from the existence of a range of relaxation times rather than a single relaxation time. Hence equations (6.8) and (6.9) must be replaced by

$$\varepsilon' - \varepsilon_x = \int_0^\infty \frac{F(\tau) \, d\tau}{1 + \omega^2 \tau^2} \quad (6.12)$$

and

$$\varepsilon'' = \int_0^\infty \frac{F(\tau) \omega \tau \, d\tau}{1 + \omega^2 \tau^2} \quad (6.13)$$

where a description with one relaxation time is not sufficient, various authors have proposed different equations with adaptable parameters. Cole and Cole [56] proposed a semi-empirical formula in the case of associated liquids,

$$\varepsilon^* = \varepsilon' - j \varepsilon'' = \varepsilon_x + \frac{\varepsilon_0 - \varepsilon_x}{(1 + j \omega \tau)^{1-a}} \quad (6.14)$$

This leads to a depressed semi-circular arc function for the plot of $\varepsilon''$ vs $\varepsilon'$ (Fig. 6.1). Also a most frequently encountered experimental plot in
Fig. 6.1 Complex-Plane showing depressed circular arc

Fig. 6.2 Skewed-Arc representation in the complex plane
the complex-plane locus for associated liquids leads to a right skewed arc (Fig. 6.2), which may be represented by a function [57]

\[ \epsilon^* = \epsilon' - j \epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + j \omega \tau)^\beta} \]  (6.15)

A large variety of functions for the representation of distribution of relaxation time was proposed on empirical basis [14, 58]. When two or more distinct relaxation processes occur the absorption regions for the two processes overlap and an appreciable value of \( \alpha \) occurs.

6.3. Relaxation time distribution in dipolar fluids:

The dielectric relaxation dynamics of polar solvents is one of the most fundamental areas of research. The studies of the time dependent response to an externally applied long-wavelength time dependent field can provide useful informations. A large number of experimental studies have been carried out on dielectric relaxation in binary dipolar liquids.[59] The Debye theory of relaxation forms the backbone of continuum based theories suggested at later times [60-62].

6.4. Experimental methods to determine relaxation times:

a) Poley’s method

The method developed by Poley requires the determination of Standing Wave Ratios (SWRs) at various liquid lengths in steps of \( \lambda_d / \)
using a slotted line carriage. Here $\lambda_d$ is the wavelength of the microwaves in the dielectric medium. When an electromagnetic wave travelling in a medium is reflected at a plane boundary between two media, the complex reflection coefficient $\tilde{R}$ is given by

$$\tilde{R} = |R_0| \exp(-j2\phi)$$

where $2\phi$ is the phase angle and $|R_0|$ is the amplitude of the reflection coefficient. The terminating or the input impedance of the first medium can be written as

$$Z_0 = Z_1 \left[ \frac{1 + R_0}{1 - R_0} \right]$$

$Z_1$ being the characteristic impedance of the first medium. If the attenuation in the first medium can be neglected, the inverse standing wave ratio $\rho$ is given by

$$\rho = \frac{E_{\text{min}}}{E_{\text{max}}} = \frac{1 - |R_0|}{1 + |R_0|}$$

From equation (6.18) the reflection coefficient at the boundary of the two media can be written as

$$R_0 = \frac{Z_0 - Z_1}{Z_0 + Z_1}$$
For the short circuited termination

\[ Z_0 = Z_2 \tanh v_d L. \quad (6.20) \]

Hence

\[ R_0 = \frac{\left( \frac{Z_2}{Z_1} \tanh v_d L \right) - 1}{\left( \frac{Z_2}{Z_1} \tanh v_d L \right) + 1} \quad (6.21) \]

From equations (6.19) and (6.22) one can write for the inverse voltage

\[
\rho = \frac{1 - \left[ \left( \frac{Z_2}{Z_1} \right) \tanh v_d L \right] - 1}{1 + \left[ \left( \frac{Z_2}{Z_1} \right) \tanh v_d L \right]} \quad (6.22)
\]

The above relation can not be easily solved. However, if the SWR is plotted as a function of the length \( L \) of the liquid column, a curve results which exhibits successive maxima and minima tending towards a final value of \( \rho_\infty \) for a length of liquid column which is electrically infinite in length. The distances between the minima is equal to the value of \( \lambda_d/2 \). Introducing
\[
\tan \Delta = \frac{\varepsilon''}{\varepsilon' - \left(\frac{\lambda_0}{\lambda_c}\right)^2}
\tag{6.23}
\]

(where \(\lambda_c\) is the cut-off wavelength of the guide and \(\lambda_0\) is the free space wavelength of the microwave) as a waveguide loss tangent, analogous to the free space loss tangent

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]

it is possible to deduce the value of

\[
\tan \frac{\Delta}{2} = \frac{\alpha_d}{\beta_d} = \frac{\alpha_d \lambda_d}{2\pi}
\tag{6.24}
\]

from the ratios of the \(\rho\) values in the successive maxima. Denoting the SWR in the \(m^{th}\) and \(n^{th}\) maxima by \(\rho_m\) and \(\rho_n\), one can obtain, to a very close approximation.

\[
\rho_m = \frac{\tanh \left[ m \pi \tan \left( \frac{\Delta}{2} \right) \right]}{\tanh \left[ n \pi \tan \left( \frac{\Delta}{2} \right) \right]}
\tag{6.25}
\]

and

\[
\frac{\rho_m}{\rho_n} = \tanh \left[ m \pi \tan \frac{\Delta}{2} \right]
\tag{6.26}
\]
These two relations can be used to derive a set of curves for $\frac{\rho_m}{\rho}$ as functions of $\tan(\Delta/2)$ for which $\tan(\Delta/2)$ may be read off for any given measure SWR. With the data of $\lambda_d / 2$ and $\tan(\Delta/2)$, the required values of $\varepsilon'$ and $\varepsilon''$ are as follows:

$$
\varepsilon' = \left[ \frac{\lambda_0}{\lambda_e} \right]^2 + \left[ \frac{\lambda_0}{\lambda_d} \right]^2 \left[ 1 - \tan^2 \left( \frac{\Delta}{2} \right) \right] 
$$

(6.27)

$$
\varepsilon'' = 2 \left[ \frac{\lambda_0}{\lambda_d} \right]^2 \tan \left( \frac{\Delta}{2} \right) 
$$

(6.28)

The values of $\tan(\Delta/2)$ for the different ratios of $\rho_m$ and $\rho_n$ calculated from equation (6.26) are available [63], which are used in the present investigation. The measured value of $\rho$ are corrected for the wall losses outside the cell, losses at the termination and at the window. The value of $\rho$ is determined first at $d=0$, say it is $\rho_0$. Then the corrected value of $\rho$ will be

$$
\rho_{\text{corrected}} = \rho_{\text{measured}} - \rho_0 
$$

(6.29)
b) Smyth Method:

Smyth et. al., [64] have described a width at twice minimum SWR method suitable for the measurement of dielectric constant and dielectric loss of low loss liquids for the solutions of polar liquids in non-polar solvents. For short-circuited termination of dielectric lengths of integral multiples of $\lambda_d/2$ the inverse voltage SWR is given by

$$\rho_n = Z_2 \tanh(n\alpha_d \lambda_d / 2)$$  \hspace{1cm} (6.30)

where $Z_2 = \lambda_d/\lambda_g$. For small values of $\alpha$, that is, for low loss liquids this expression can be approximated as

$$\rho_n = Z_2 (n \alpha_d \lambda_d/2)$$

$$= n \alpha_d \lambda_d^2/2 \lambda_g$$  \hspace{1cm} (6.31)

The experimentally measured value of $\rho_n$ will include a factor $R_{sc}$ to account for the plunger resistance and other losses, then

$$\rho_{meas} = n\alpha_d \lambda_d^2/2 \lambda_g + R_{sc}$$  \hspace{1cm} (6.32)

The effect of the loss term $R_{sc}$ is eliminated by plotting several values of $\rho_{meas}$ vs $n$. The slope of this graph will give the value of $\alpha_d$ as below.

$$\alpha_d = \frac{2\lambda_g}{\lambda_d^2} \frac{d\rho_{meas}}{dn}$$  \hspace{1cm} (6.33)

The loss factor $\varepsilon''$ will then be given as
The expression for \( \varepsilon'' \) is given by

\[
\varepsilon'' = \left( \frac{1}{\pi} \right) \left( \frac{\lambda_0^2}{\lambda_d} \right) \alpha_d \\
= \left( \frac{1}{\pi} \right) \left( \frac{\lambda_0^2}{\lambda_d} \right) \left( \frac{2\lambda_0^2}{\lambda_d^2} \right) \frac{d\rho_{\text{meas}}}{dn}
\]

\[
\varepsilon'' = \frac{2}{\pi} \frac{\lambda_0^2 \lambda_\delta}{\lambda_d^3} \frac{d\rho_{\text{meas}}}{dn}
\]

(6.34)

The expression for \( \varepsilon' \) is given by

\[
\varepsilon' = \left( \frac{\lambda_0}{\lambda_c} \right)^2 + \left( \frac{\lambda_0}{\lambda_d} \right)^2
\]

(6.35)

6.5 Experimental Set-Up:

The apparatus used to measure the dielectric constant and dielectric loss of liquids at the X-band microwave frequency is schematically given in Fig. 6.3. Klystron (K-27) was used as the source of microwave power at 8.31 GHz and was operated by a well regulated power supply. A variable attenuator and a slotted line wave guide with a slit in the broad face to accommodate a probe were connected with a liquid cell. The signal from the Klystron was fed to the attenuator through a ferrite isolator so as to allow free passage of power in the forward direction but to attenuate strongly the reverse wave.
Fig. 6.3 EXPERIMENTAL SET UP
The X-band liquid cell was supplied by M/s. The Scientific Instruments Co. Ltd., India. The sample length of liquids is adjustable by the micrometer plunger assembly. The micro wave power is transmitted from the slotted line into the liquid through a teflon window which has negligible dielectric loss. The probe which is a crystal detector measures the micro wave power by reflecting the micro wave power by feeding the micro wave current to a sensitive galvanometer. The temperature of the liquid inside the cell was kept constant by circulating water around it from a thermostat.

6.6 Procedure:

Keeping the probe of the detector fixed at a particular position, the plunger is moved in the liquid cell and the detected output is fed to a sensitive galvanometer. The distance between successive minima which gives the value of \( \frac{\lambda_g}{2} \) is thus obtained. The liquid cell is now filled in with the given liquid. The plunger is moved up in the cell from the bottom of the cell. The distance between two successive minima (or maxima) is measured as \( \frac{\lambda_d}{2} \). The first minimum deflection is noted. The plunger reading corresponding to the double minimum
above and below the first minimum position \((n_1)\) is noted. Let the difference be \(\Delta x\). Then the inverse voltage SWR \(\rho_1\) is given by

\[
\rho_1 = \pi \frac{\Delta x}{\lambda_g}
\]

(6.36)

The value of \(\rho\) is corrected for the approximation involved in the derivation of the above equation using a correction curve. Then the plunger is moved to the next minimum position and the experiment is repeated to get \(\rho_2\) corresponding to the second minimum \((n_2)\). Similarly the values of \(\rho_3, \rho_4\) etc., are obtained for minimum deflections. From the plot of \(\rho_n\) with \(n\), \(d\rho/dn\) is found. The values of \(\varepsilon'\) and \(\varepsilon''\) are given by the Eqns. (6.35) and (6.34). The static values of dielectric constant \(\varepsilon_o\) for the solutions were measured at 1 KHz using KEITHLEY 3330 LCZ meter. The refractive indices were measured for the sodium D-line using an Abbe's refractometer.

6.7 Determination of Parameters from measured Dielectric Constants

(i) Cole-Cole Plot

The measured values of \(\varepsilon', \varepsilon'', \varepsilon_o\) and \(\varepsilon_x\) are to be fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter drawn through the centre from the \(\varepsilon_x\) point and the
Abscissa axis is equal to $\alpha \pi/2$. From the Cole-Cole arc, the relaxation time $\tau$ can be found using the equation

$$ (\omega \tau)^{1-\alpha} = v/u $$

where $\omega$ is the angular frequency of the microwave used and $\alpha$ is the distribution parameter.

(ii) Higasi's Method

Assuming $\varepsilon', \varepsilon_\alpha, \varepsilon_\infty$ and $\varepsilon''$ vary linearly with weight fraction $W_2$ of the solute, we have,

$$ \varepsilon_0 = \varepsilon_1 + a_0 w_2 $$
$$ \varepsilon' = \varepsilon_1 + a' w_2 $$
$$ \varepsilon'' = a'' w_2 $$
$$ \varepsilon_\infty = \varepsilon_1 + a_\infty w_2 $$

Higasi [65] has given the following relation for $\tau$ and $\alpha$

$$ \tau = \frac{1}{\omega} \left[ \frac{A^2 + B^2}{C^2} \right]^{-1/2(1-\alpha)} $$

$$ (1 - \alpha) = \frac{2}{\pi} \tan^{-1} \left( \frac{A}{B} \right) $$

where

$$ A = a''(a_0 - a_\infty) $$
$$ B = (a_0 - a')(a' - a_\infty) - a''^2 $$
$$ C = (a' - a_\infty)^2 + a''^2 $$

(6.38)

(6.39)

(6.40)
The Debye equation in terms of $a_0$, $a'$, $a''$ and $a$, yields two independent equations [66]

$$\tau(1) = \frac{a'}{\omega(a' - a_0)}$$  \hspace{1cm} (6.41a)

$$\tau(2) = \frac{a_0 - a'}{\omega a''}$$  \hspace{1cm} (6.41b)

$\tau(1)$ may be described as a sort of average dielectric relaxation time and $\tau(2)$ as the relaxation time for overall rotation of the molecules.

$$\sqrt{\tau(1)\tau(2)} = \tau_0$$  \hspace{1cm} (6.42)

may be called the mean relaxation time.

In the absence of facilities to measure $\varepsilon'$ through a wide range of frequencies the Higasi's method has been used for the calculation of $\tau$. This will enable one to study quantitatively the relaxation mechanisms involved in the case of fatty alcohols and acids. There are several methods for the separation and recognition of the Debye type components of the experimental absorption other than the methods suggested above [67-69]. But many of them have a limited usefulness because in a practical situation only relatively a small number of data points are obtained. Puranik et. al., [70] developed a
curve fitting technique directly to the standing wave pattern in dilute solutions.

It has been pointed out by Magyari and Liszi [71] that unless the relaxation times of particular processes are known, these methods will not be useful since a perfect fit can always be obtained with infinitely close components of relaxation time. They have developed a reliable method for a distribution of Fuoss – Kirkwood type [72] This method has several advantages, as the spectrum decomposition is made easier.

6.8. Results:

The values of measured dielectric constants at 1KHz ($\varepsilon_0$), at 8.31 GHz ($\varepsilon'$) and at infinite frequency ($\varepsilon_{\infty}$) for stearic acid, arachidic acid, tetradecanol and hexadecanol in dilute solutions of carbon tetrachloride are recorded in Tables 6.1 to 6.4. The values of the average relaxation time $\tau_0$, obtained from equations 6.41 and 6.42 are also tabulated.
Table: 6.1.
System: Stearic Acid in CCl₄

Values of Dielectric constant at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>ε₀</th>
<th>εₓ</th>
<th>ε'</th>
<th>ε''</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.2571</td>
<td>2.1185</td>
<td>2.2363</td>
<td>0.0415</td>
</tr>
<tr>
<td>0.02</td>
<td>2.2749</td>
<td>2.1170</td>
<td>2.2332</td>
<td>0.0436</td>
</tr>
<tr>
<td>0.03</td>
<td>2.2802</td>
<td>2.1156</td>
<td>2.2318</td>
<td>0.0462</td>
</tr>
<tr>
<td>0.04</td>
<td>2.2970</td>
<td>2.1141</td>
<td>2.2273</td>
<td>0.0485</td>
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</tbody>
</table>

Values of Higasi's parameter at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>A₀</th>
<th>aₓ</th>
<th>A'</th>
<th>a''</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>24.05</td>
<td>-7.00</td>
<td>13.65</td>
<td>20.75</td>
</tr>
<tr>
<td>0.02</td>
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<td>7.12</td>
<td>12.82</td>
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<tr>
<td>0.03</td>
<td>13.69</td>
<td>-3.25</td>
<td>4.38</td>
<td>8.88</td>
</tr>
<tr>
<td>0.04</td>
<td>12.75</td>
<td>-2.67</td>
<td>2.65</td>
<td>7.03</td>
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Values of Relaxation time, Shear viscosity and Activation energies at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>Relaxation Time t₀(ps) (Higasi)</th>
<th>ηₛ</th>
<th>ΔΓₑ</th>
<th>ΔFₑ</th>
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<tbody>
<tr>
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<td>0.9898</td>
<td>8.91</td>
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<td>16.9</td>
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<td>18.3</td>
<td>0.9707</td>
<td>9.55</td>
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<td>0.04</td>
<td>22.4</td>
<td>0.9570</td>
<td>10.30</td>
<td>19.56</td>
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Table: 6.2
System: Arachidic Acid in CCl₄

Values of Dielectric constant at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>ε₀</th>
<th>ε₁</th>
<th>ε²</th>
<th>ε³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.3229</td>
<td>2.1170</td>
<td>2.2762</td>
<td>0.0346</td>
</tr>
<tr>
<td>0.02</td>
<td>2.3806</td>
<td>2.1141</td>
<td>2.2904</td>
<td>0.0499</td>
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Values of Higasi's parameter at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>a₀</th>
<th>a₁</th>
<th>a²</th>
<th>a³</th>
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</thead>
<tbody>
<tr>
<td>0.01</td>
<td>63.28</td>
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<td>37.33</td>
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<tr>
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<td>21.42</td>
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Values of Relaxation time, Shear viscosity and Activation energies at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>Relaxation Time</th>
<th>τ(o) ps (Higasi)</th>
<th>ηₛ</th>
<th>ΔFₜ</th>
<th>ΔF_η</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>εp</td>
<td>KJ/mole</td>
<td>KJ/mole</td>
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<td>12.5</td>
<td>0.8944</td>
<td>6.61</td>
<td>19.31</td>
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<td>0.02</td>
<td>15.3</td>
<td>0.8657</td>
<td>8.96</td>
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Table 6.3  
System: Tetradecanol in CCl₄

Values of Dielectric constant at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>ε₀</th>
<th>εₓ</th>
<th>ε'</th>
<th>ε''</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.3094</td>
<td>2.1170</td>
<td>2.2530</td>
<td>0.0543</td>
</tr>
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<td>0.04</td>
<td>2.3126</td>
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<td>2.2484</td>
<td>0.0360</td>
</tr>
<tr>
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<td>2.3136</td>
<td>2.1025</td>
<td>2.2439</td>
<td>0.0361</td>
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Values of Higasi's parameter at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>a₀</th>
<th>aₓ</th>
<th>a'</th>
<th>a''</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>38.62</td>
<td>-5.96</td>
<td>16.92</td>
<td>20.88</td>
</tr>
<tr>
<td>0.04</td>
<td>19.92</td>
<td>-3.54</td>
<td>7.58</td>
<td>6.92</td>
</tr>
<tr>
<td>0.06</td>
<td>13.08</td>
<td>-3.75</td>
<td>4.36</td>
<td>4.51</td>
</tr>
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</table>

Values of Relaxation time, Shear viscosity and Activation energies at 303K

<table>
<thead>
<tr>
<th>X₂</th>
<th>Relaxation Time (τ(0)) ps (Higasi)</th>
<th>ηₛ</th>
<th>ΔFₜ</th>
<th>ΔFₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>16.1</td>
<td>0.9573</td>
<td>9.64</td>
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<td>0.9068</td>
<td>8.64</td>
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<tr>
<td>0.06</td>
<td>17.1</td>
<td>0.8942</td>
<td>8.72</td>
<td>19.36</td>
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</table>

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### Table 6.4
**System: Hexadecanol in CCl₄**

#### Values of Dielectric constant at 303K

<table>
<thead>
<tr>
<th>$X_2$</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_r$</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>2.3213</td>
<td>2.1170</td>
<td>2.2715</td>
<td>0.0926</td>
</tr>
<tr>
<td>0.04</td>
<td>2.3260</td>
<td>2.1141</td>
<td>2.2684</td>
<td>0.0838</td>
</tr>
<tr>
<td>0.06</td>
<td>2.3330</td>
<td>2.1112</td>
<td>2.2551</td>
<td>0.0729</td>
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#### Values of Higasi's parameter at 303K

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<tr>
<th>$X_2$</th>
<th>$a_0$</th>
<th>$A_2$</th>
<th>$a'$</th>
<th>$a''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>37.43</td>
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<td>19.83</td>
<td>-3.12</td>
<td>10.07</td>
<td>14.20</td>
</tr>
<tr>
<td>0.06</td>
<td>13.93</td>
<td>-2.39</td>
<td>5.18</td>
<td>8.19</td>
</tr>
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</table>

#### Values of Relaxation time, Shear viscosity and Activation energies at 303K

<table>
<thead>
<tr>
<th>$X_2$</th>
<th>Relaxation Time</th>
<th>$\eta_s$</th>
<th>$\Delta F_{\tau}$</th>
<th>$\Delta F_\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau(\sigma)$ ps (Higasi)</td>
<td>$\eta_s$ cp</td>
<td>KJ/mole</td>
<td>KJ/mole</td>
</tr>
<tr>
<td>0.02</td>
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<td>0.9421</td>
<td>10.16</td>
<td>19.45</td>
</tr>
<tr>
<td>0.04</td>
<td>14.2</td>
<td>0.9101</td>
<td>10.33</td>
<td>19.40</td>
</tr>
<tr>
<td>0.06</td>
<td>17.3</td>
<td>0.8629</td>
<td>10.88</td>
<td>19.39</td>
</tr>
</tbody>
</table>
9. Discussion:

As for the pure alcohols, there are three important motions which are responsible for the dispersion of relaxation time. (i) the hydrogen bonded dynamics of molecular aggregates (ii) the monomer rotation and (iii) the rotation of the terminal group. It was inferred by Smyth [73] that the first one leads to a dispersion of relaxation time around $\tau(1) = 500 \times 10^{-12} \text{ S}$/ the second one leading to a relaxation time $\tau(2) = 20 \times 10^{-12} \text{ S}$ and the rotational orientation of the non-hydrogen bonded OH group leading to a relaxation frequency $\tau(3) = 3 \times 10^{-12} \text{ S}$ while the first one predominates in pure alcohols, the other two relaxation times are recorded in dilute non-polar solvents.[74-78] All these studies showed the concentration dependence of relaxation time of alcohols. Magallanes [79] observed a constant macroscopic relaxation time for all alcohols at a critical number density of the dipoles. This result was confirmed by us even in the case of fatty alcohols and acids.

A study of the relaxation time observed in phenols gives certain significant conclusions. 2,6 Di–t–butyl phenol, a molecule with unhindered phenolic group, has been reported to have a relaxation time of 8.6 p sec in p-Xylene solution by Magee and Walker [80]. Smyth et. al., [81,82] showed that the presence of a freely rotating polar group,
whose moment component does not lie along the axis group rotation leads to lowering of relaxation times. On the other hand, the restricted rotation of the –OH makes the molecule less flexible and the mean relaxation time increases to the order expected of a rigid molecule. The hindrance to free rotation of the –OH group is expected to arise from the intermolecular hydrogen bonding. The –OH group relaxation time for several phenolic Mannich bases was found to be in the order of 10 p sec by Jeyaraj and Sobhanadri. [83]. This compares favourably with the relaxation time for intramolecularly bonded hydroxyl groups [84].

The long chain aliphatic alcohols have the possibility of bending, twisting and rotation with a characteristic τ for the several processes besides the average macroscopic distribution of τo. The average τo observed here for fatty alcohols is almost twice that for low CH₂ alcohols and increases with increase of concentration. Similar is the case of fatty acids. One of the reasons may be due to the greater volume swept by these molecules or the steric hindrance.

An important effect to be considered in long chain molecules is the friction. When a dipole in a cavity rotates, it induces polarization on the surrounding medium, but the response of the medium is not instantaneous. The dynamic polarization field is not the same as the static polarization field for a given orientation of the dipole. This results
in the creation of an electric field in the cavity which opposes the reorientation of the dipole and shows the reorientation process. This is added to the stokes viscous friction. The high \( \tau_o \) values reported here compared to normal alcohols and acids in such dilution may be due to this dynamical effect due to the dipoles. The average relaxation time observed here, agrees well with those reported by Sit et al., [85] for octyl alcohols.

Eyring [86] treated the dipolar rotation on the basis of a chemical rate process. The molecules are assumed to jump from one equilibrium position to another depending on the following factors: (i) the number of collisions that it makes with the neighbouring molecules, (ii) the entropy \( \Delta S_e \) which describes the disturbance of the local structure of the medium during orientation and (iii) the heat of activation \( \Delta H_e \) which is equal to the potential barrier separating the successive equilibrium positions. Using this concept a relation between the microscopic relaxation time and the free energy of activation is given as

\[
\tau = \frac{h}{kT} \exp \left[ \frac{\Delta H_e}{RT} \right] \exp \left( \frac{\Delta S_e}{R} \right)
\]

\[
= \frac{h}{kT} \exp \left( \frac{\Delta F_e}{RT} \right)
\] (6.43)
It was suggested by Bauer et. al., [87] that the activation energy is nearly equal to the energy necessary to break the hydrogen bonds. The results of Middelhoek and Bottcher [88] for structurally similar systems of alcohols could not explain Bauer's theory. Hence Dannhauser and co-workers [89] presumed that the rupture of hydrogen bonds is not the rate determining step, but it is the cooperative process of molecular reorientation of the temporarily unbonded molecule with its surroundings that determines the relaxation times. The viscosity of a liquid can be given by a similar rate process,

\[ \eta_s = \frac{N_A h}{V} \exp(\Delta H_\eta / RT) \exp(\Delta S_\eta / R) \]

\[ = \frac{N_A h}{V} (\Delta F_\eta / RT) \]  

(6.44)

where \( V \) is the molar volume of the liquid. We have calculated \( \Delta F_\tau \) and \( \Delta F_\eta \) for all the four systems reported in Tables 6.1 to 6.4. The entropy and enthalpy of activation for viscous flow, namely \( \Delta S_\eta \) and \( \Delta H_\eta \) need not necessarily be the same as those of dipolar processes. Mazid et. al., [90] made certain important observations on the effect of CH\(_2\) alkyl chain increments on the relaxation behaviour of several phenyl-alkyl ketones. The enthalpy of activation (\( \Delta H_\tau \)) for the molecular relaxation of a solute is the important parameter which is highly dependent on the
size of a particular type of solute molecule. However, increment of the alkyl chain changes $\Delta H_\tau$ only by a small amount about 1kJ/mole. It suggests that the relaxation processes are similar to the short chain polar head group and relatively independent of the number of alkyl group. Mc Crum, Read and Williams [91] accounts for certain relaxation processes in polymers to a ‘Crankshaft’ type motion. This type of motion would then in principle, be feasible for long chain fatty alcohols and acids. Again, if the $\Delta H_\tau$ values are close to the polar head group values, this type of motion is again negligible.

It is evident from Tables 6.1 to 6.4 that the molar activation of free energy for viscous flow $\Delta F_\eta$ is greater than $\Delta F_\tau$ the free energy of activation for dielectric relaxation. This is in agreement with the fact that the process of viscous flow involves greater interference by neighbours than does dielectric relaxation, as the latter takes place by rotation only, whereas the viscous flow involves both the rotational and translational forms of motion. It is further suggested that for non associated polar liquids the free energy of activation for rotation and for viscous flow would be

$$\Delta F_\tau \approx 0.5 \Delta F_\eta$$  \hspace{1cm} (6.45)

This is found to be true in our present studies.
CHAPTER – VII

STUDIES OF DIPOLAR INTERACTIONS OF AMPHIPHILES WITH PYRIDINE AS HOST MOLECULES

7.1 Introduction
7.2 Theoretical studies of H-bonded interactions
7.3 Experimental studies of dielectric polarization of proton Donor-acceptor complexes
7.4 Scope of the present study
7.5 Experimental
7.6 Principle of determination of the dipole moment of the complexes
7.7 Results
7.8 Calculation of dipolar increment
CHAPTER – VII

STUDIES ON DIPOLAR INTERACTIONS OF AMPHIPHILES WITH PYRIDINE AS HOST MOLECULES

7.1 Introduction:

In the last few years there has been a fascinating progress in the study of molecular interactions. From a theoretical point of view molecular interactions are classified as two types – long range interactions and short range interactions. In practice, however, the precise boundary between the two can not be pin pointed. Amongst aggregates, involving short range interactions, one can distinguish molecular complexes formed by H-bonds and electron donor-acceptor (EDA) complexes. [92] The most important characteristics of hydrogen bonds are

(i) An increase in the distance of A-H of the bonding atom and

(ii) An increase in the polarity of the bond which is quantitatively described by the enhancement of the dipolemoment brought by the formation of H-bonds
The value of $\frac{A\mu}{A\nu_{(A\cdots)}}$ is of the order of $10 \text{ D.} A^e$ for the O-H...N bonds [93] and even more for O-H...O=C bonds. The complexes that are formed could be classified as (i) weak and normal complexes between neutral molecules, (ii) the molecular ionic tautomeric complexes and (iii) strongly ionic molecular complexes. However most real systems lie between these extremes. A good survey of the literature regarding the theoretical and experimental studies could be found in several recently published books.[94,95] We have seen earlier that the hydrogen bond of the O-H group of an alcohol or a phenol brings the proton of this group in the vicinity of the oxygen atom of a neighbouring molecule for a larger fraction of the time which restricts the freedom of the O-H for free rotation as well as its movements to the other domains. Thermodynamically, this results in a reduction in entropy compared to the unrestricted random contacts of apolar liquids. The ‘structuring’ of the O-H...O bond results in the weakening of the O-H stretching vibrations, with a result that the corresponding bending vibrations shift to higher wave numbers and a new vibration band appears which governs the O...O interdistance. The motion of the three nuclei directly involved in the hydrogen bond are thus drastically perturbed. Hence it may be
inferred that the most important methods that will give direct information on the perturbing influence of the hydrogen bonds are (i) the spectroscopic vibrational frequency studies, (ii) the changes in the dipole moment on complexation and (iii) the chemical shift in NMR. Because of the fundamental role of hydrogen bonds in biological systems, much attention has been devoted to the relation between the proton affinity and the enthalpy of formation of the 'specific structures' especially for the systems like O-H...O=C. For examples, Zeegers-Huyskens [96] recently established a linear relation between the enthalpy of hydrogen bonding in solution (-ΔH) and the P.A, the difference in proton affinity between the acid and the base, the slope being -0.10 for complexes involving hydroxyl derivatives and carbonyl bases. Similar relations were also established between the change in dipole moment (Δμ) and (-ΔH) on H-bond formation between weak acids and bases.

7.2 Theoretical studies of H-bonded interactions:

The basic assumption in classical electrostatic theories is that the formation of a H-bond does not perturb the participating molecules. This is untenable and calls for a better treatment. Coulson [97] critically analysed hydrogen bonding on the basis of (i)
electrostatic interactions, (ii) delocalization effects, (iii) repulsive forces and (iv) dispersion forces. All the four effects have a simple physical model. Such a division of interaction is of course an artificial one, used for the sake of ease of computation and comprehension. Many improvements in the methods of computations of hydrogen-bonded energy have been made. The *ab initio* LCAO-SCF-MO calculations are found to be quite reliable in predicting the hydrogen bond energy and the relative orientations of the component molecules in the complex [98,99]. Morokuma's scheme of electron distribution analysis on the basis of M.O theory to decompose the interaction energy into various components is the most complete one [100]. The important conclusions arrived from his calculations are that,

(i) The polarization causes the most significant charge redistributions, though its contribution to the energy term is small.

(ii) The energy transfer interactions disturb the charge distribution of the other parts of the molecule and

(iii) The charge in dipole moment $\Delta \vec{\mu}_{CT}$ occurs along the H-bonded line though the same cannot be said for $\Delta \vec{\mu}_{(pol)}$. 
The major disadvantage of this method of approach is that $E_{1}$ is not a well defined quantity and is not applicable directly to complexes with geometries which differ appreciably from those of the isolated systems.

Schuster [101] analysed the discrepancies of the results by different methods. PCILO methods [102,103] were successfully used for the study of H-bonds of complex molecules in recent times. Because of the combination of CNDO/2 with perturbation theory and the inclusion of the configuration interaction, the PCILO methods lead to distinct improvement of results in H-bonded complexes.

Bratoz [104] brought out the similarities of the valence bond treatment and Mullikan's charge transfer theory [105] in relation to the stability of the donor-acceptor complexes. The contribution of the charge transfer term to the stabilization energy of the H-bond increases if one considers stronger H-bonds. Also it is well established that the properties of H-bonded systems depend on ionization potential of the electron donor molecules or the acidities or the basecities of the components. These observations suggest that Mullikan's C-T theory may very well describe the electronic ground
state of H-bonded complexes. Ratajczak [106] pointed out that the change of dipole moment obtained in H-bonded complexes could successfully be explained on the basis of C-T theory.

According to C-T theory,

$$\psi_N = a\psi_0 + b\psi_1$$

(7.1)

where $\psi_0$ and $\psi_1$ are the wave functions of a non bonded (X-H...Y) and dative (X-H...Y^+) states respectively. Applying variation method to eqn. (7.1), one can get the following relation,

$$aw_0 + bw_{01} = W_N (a+b.S)$$

(7.2)

where

$$W_0 = \langle \psi_0 | H | \psi_0 \rangle,$$

$$H_{01} = \langle \psi_0 | H | \psi_1 \rangle,$$

$$S = \psi_0 / \psi_1$$ and

$$W_N = \langle \psi_N | H | \psi_N \rangle \approx -\Delta H$$
if $\psi_N$ is a normalised function and the reference energy of the two separate solvated molecules is equal to zero.

For weak complexes $a \approx 1$, $bS \ll a$. Therefore equation (7.2) reduces to

$$W_0 = b\beta_{01} = -\Delta H$$  \hspace{1cm} (7.3)

where $H_{01}$ is replaced by $\beta_{01}$. It has been shown by Mullikan [105] that for weak complexes $\Delta \bar{\mu}_{CT}$ is given approximately by

$$\Delta \bar{\mu}_{CT} = b^2 \bar{\mu}_1$$  \hspace{1cm} (7.4)

where $\bar{\mu}_1 = \langle \psi_1 | H | \psi_1 \rangle$, which is the dipole moment of the dative structure. Combining eqns. (7.3) and (7.4) one finds that

$$-\Delta H = W_0 + \left[ \frac{\beta_{01} \Delta \bar{\mu}_{CT}}{\bar{\mu}_1} \right]^2$$  \hspace{1cm} (7.5)
In the case of simple systems the electrostatic contribution is greater than the CT contribution. The exchange repulsion terms at equilibrium geometry are nearly compensated by the attractive terms arising from charge transfer, polarization and dispersion forces and so the stability of the hydrogen bond complexes is essentially governed by the electrostatic interaction. The final theoretical conclusion appears to be that the hydrogen bond may be considered as a specific type of electron donor-acceptor interaction. Another important conclusion from the theoretical studies is that a redistribution of charge due to polarization and charge transfer effects accompanies the molecular interaction. This charge redistribution phenomenon can be related to the changes observed in various molecular properties like dipole moment, IR intensity, NQR, NMR of complex systems compared to those of isolated molecules.

7.3 **Experimental studies of dielectric polarization of proton donor-acceptor complexes:**

The determination of dielectric polarization is one of the most direct and promising methods that will give useful informations regarding short-range interactions. The earlier studies [107-111] on excess dielectric polarization arising due to H-bonded complexes
between a hydroxyl group and the lone pair of electrons in the nitrogen and carbonyl compounds, were mainly to explore the various structural models of complexation. Pioneering work in the area was done by Sobczyk and his co-workers [112] and Huyskens et. al., [113], who have established the existence of a critical region where the normal hydrogen bonded complexes would be in tautomeric equilibrium with proton-transfer complexes. The effect of environmental reaction field on such complexes were studied by Srinivasan[114]. The presence of higher order complexes a_m b_n on dielectric polarization was studied by Ratajczak and Oszust[115]. Proton magnetic resonance studies[116] and Nuclear Quadrupole resonance studies [117] were also made to deduce information on charge redistribution in hydrogen bonds. The work of Jadzyn and Malecki [118] established the fact that if H-bonded complex tends to be entirely neutral or completely ion pair, the H-bond becomes less polarizable, whereas the reaction field of the polar medium would make the H-bond highly polarizable.

Zeegers-Huyskens [119,120] studied the IR frequency shifts and intensity changes of the O-H bond of several phenols and alcohols on H-bonding with amines and concludes that in acids stronger than parachlorophenol, the mechanism may be described as a
complete proton transfer. Hall and Wood [121] studied 24 adducts of phenols and substituted pyridines, but the results were not conclusive on the nature of complexation Sabesan et. al. [49] studied the dipolar increment for the complexation of phenyl carbinol and Butan-1-ol with pyridine and found that only polarization mechanism dominates.

7.4 Scope of the present study

The objective of the present study is to investigate the nature of molecular interactions of fatty alcohols and acids with electron donors in dilute solutions. It is desired to look into the probable structure of the complexes formed from their dipole moments.

7.5 Experimental:

The purified samples (99.9 %) supplied by Aldrich was used. The solvents were purified by standard methods. The dielectric measurements were made with a digital KEITHLEY 3330 LCZ meter as detailed earlier. The dipole moment of the complexes were evaluated as follows.

7.6 Principle of determination of the dipole moment of the complexes:

Fröhlich [122] has given a theory to obtain the overall dipole moment $\vec{\mu}$ of a system of solute-solvent mixture. For a solution containing polar substances and an apolar solvent (subscript-s), this
quantity can be calculated from the dielectric constant \( \varepsilon_0 \) of the solution, the refractive index \( n_D \) for the sodium line of the solution and the refractive index \( n_{D_s} \) for the sodium line of the solvent as follows

\[
M^2 = \frac{9kT}{4\pi} V \left[ \frac{(\varepsilon_0 - n_D^2)(2\varepsilon_0 + n_D^2)}{\varepsilon_0(n_D^2 + 2)^2} - \frac{C_s}{C_s} \left( \frac{C_s - n_{D_s}^2}{\varepsilon_0(n_{D_s}^2 + 2)^2} \right) \right]
\]

(7.6)

\( C_s \) is the actual concentration of the apolar solvent and \( c_s \) is its concentration in the pure state. The last term is the correction for the internal refractive index as measured for the sodium line.

Considering a ternary mixture of the polar components A (alcohol) and B in an apolar solvent, A and B may be involved in H-bonding. In view of the mobility of the liquid phase, the relative orientation of A and B continuously vary. The dipole moment of the solution at a given time, assuming that the time interval is short enough to consider the orientation as fixed may be written as,

\[
M^2 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} N_{ij} \bar{\mu}_{ij}^2
\]

(7.7)

where \( N_{ij} \) is the number of \( ij \) ensembles.
Huyskens et. al., [123] showed that equation (7.7) can be written as,

\[ M^2 = \sum_{i=1}^{x} \sum_{j=0}^{y} iN_{ij} \left( \frac{\langle \mu_{ij}^2 \rangle - j \langle \mu_{ij}^2 / j \rangle}{i} \right) + n_B \langle \mu_{ij}^2 / j \rangle N_A \]  

(7.8)

Here \( \langle \mu_{ij}^2 / j \rangle \) is the mean share of the B molecules in the square of the total dipole moment of the entities. For tertiary amines and ketones as proton acceptors B, \( j \) is taken as 1, and \( \langle \mu_{ij}^2 / j \rangle \) is practically \( \langle \mu_{ij}^2 \rangle \).

The quantity \( \left( \frac{\langle \mu_{ij}^2 \rangle - j \langle \mu_{ij}^2 / j \rangle}{i} \right) \) represents the mean share of A molecule in the square of the dipole moment of the entities. The number of moles of the polar components are related to \( \mu_{ij} \) as

\[ n_A = \sum_{i=0}^{x} iN_{ij} / N_A \]  

(7.9)

and

\[ n_B = \sum_{j=0}^{y} jN_{ij} / N_A \]  

(7.10)

where \( N_A \) is the Avagadro number. Hence equation (7.8) can be written as
\[
\frac{M^2}{VN_A} = \langle \tilde{\mu}_{ab}^2 - \tilde{\mu}_b^2 \rangle C_A + \langle \tilde{\mu}_b^2 \rangle C_B \quad (7.11)
\]

where \( C_A \) and \( C_B \) are the formal concentrations in (mole dm\(^{-3}\)) of the proton donor and proton acceptor respectively.

Comparing equations (7.6) and (7.11)

\[
\langle \tilde{\mu}_{ab}^2 - \tilde{\mu}_b^2 \rangle \frac{C_A}{C_B} + \langle \tilde{\mu}_b^2 \rangle = \frac{9kT}{4\pi N_A} \left[ \frac{(\epsilon_0 - n_D^2)(2\epsilon_0 + n_D^2)}{C_B} - \frac{1}{C_S} \frac{1}{C_B} \left( \frac{\epsilon_0 - n_D^2}{2\epsilon_0 + n_D^2} \right)^2 \right]
\]

\[
= \Omega_B \quad (7.12)
\]

Here \( \tilde{\mu}_s \), \( \tilde{\mu}_b \) and \( \tilde{\mu}_{ab} \) are the dipole moments of the proton donor, proton acceptor and 1:1 complex respectively.

If the formal concentration \( C_B \) of the proton acceptor is far greater than the formal concentration \( C_A \) of proton donor such that

\[
C_B - C_A \gg K^{-1} \quad (7.13)
\]

where \( K \) is the equilibrium constant for 1:1 complexation and if the solvent has zero dipole moment then the equation (7.12) reduces to
\[ \Omega_B = \bar{\mu}_b^2 + (\bar{\mu}_{ab}^2 - \bar{\mu}_b^2) \frac{C_A}{C_B} \]  \hspace{1cm} (7.14)

So from the experimentally observed values of \( \varepsilon_0 \), \( n_D \), \( \varepsilon_s \) and \( n_{D_s} \), it is possible to obtain the values of \( \Omega_B \) for different \( C_A/C_B \) values. A curve is plotted with \( C_A/C_B \) along X-axis and \( \Omega_B \) along Y-axis. Intercept of the curve in Y-axis gives \( \bar{\mu}_b^2 \) and slope of the curve gives \( \bar{\mu}_{ab}^2 \).

It should be noted that if higher order complexes other than 1:1 like \( a_2 \), \( b_2 \), \( ab_2 \) are present, the curve is no longer a straight line. This serves as the criterion for choosing the proper concentration \( C_A \) and \( C_B \) of the proton donor and acceptor for 1:1 complexation.

7.7. Results:

The dielectric polarization studies were made in the present investigation for the following systems.

1. Tetradecanol + Pyridine in Benzene
2. Hexadecanol + Pyridine in Benzene
3. Stearic Acid + Pyridine in benzene
4. Arachidic Acid + Pyridine in benzene
The values of dielectric constants, refractive indices and densities measured at different concentrations of proton donor $C_A$ are recorded in Tables 7.1 to 7.4. The formal concentration of the proton acceptor is kept at 1 mole/l. The values of $\Omega_B$ computed with Eqn. 7.12 are plotted against $C_A/C_B$ and are shown in Figures 7.1 and 7.2. The very fact that the plot is a straight line in the entire region of concentrations studied, shows that only 1:1 complexation is dominant. The values of $\mu_b$ obtained from the intercept of the line in the graphical method is slightly different from that obtained from binary measurements. For internal consistancy in the calculations of $\mu_{ab}$, the graphical values of $\mu_b$ is used.
Table 7.1:
Values of Dielectric constant, Density, Refractive Index, Molar Volume and Ratio of Formal concentrations and $\Omega_B$

System: Tetradecanol + Pyridine in Benzene  \[ C_A = 0.0876 \text{ mole/l} \]

<table>
<thead>
<tr>
<th>$C_B$ (mole/l)</th>
<th>$\varepsilon_0$</th>
<th>$\rho$ Kg m$^{-3}$</th>
<th>$n_D$</th>
<th>$V \times 10^6$ m$^3$</th>
<th>$C_A/C_B$</th>
<th>$\Omega_B$ D$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>2.5634</td>
<td>876.15</td>
<td>1.487</td>
<td>90.32</td>
<td>0.21</td>
<td>6.97</td>
</tr>
<tr>
<td>0.81</td>
<td>2.8609</td>
<td>880.69</td>
<td>1.4875</td>
<td>89.85</td>
<td>0.11</td>
<td>6.31</td>
</tr>
<tr>
<td>1.23</td>
<td>3.1822</td>
<td>886.20</td>
<td>1.488</td>
<td>89.33</td>
<td>0.07</td>
<td>6.03</td>
</tr>
<tr>
<td>1.61</td>
<td>3.4678</td>
<td>890.10</td>
<td>1.489</td>
<td>88.95</td>
<td>0.05</td>
<td>5.81</td>
</tr>
<tr>
<td>2.03</td>
<td>3.8010</td>
<td>894.44</td>
<td>1.490</td>
<td>88.52</td>
<td>0.04</td>
<td>5.71</td>
</tr>
</tbody>
</table>
Table 7.2:
Values of Dielectric constant, Density, Refractive Index, Molar Volume
Ratio of Formal concentrations and Ω

System: Hexadecanol + Pyridine in Benzene  \( C_A = 0.1026 \text{ mole/l} \)

<table>
<thead>
<tr>
<th>( C_B ) (mole/l)</th>
<th>( \varepsilon_0 )</th>
<th>( \rho ) Kg m(^{-3})</th>
<th>( n_D )</th>
<th>( V \times 10^6 ) m(^3)</th>
<th>( C_A/C_B )</th>
<th>( \Omega_B ) D(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>2.5753</td>
<td>880.60</td>
<td>1.491</td>
<td>90.37</td>
<td>0.24</td>
<td>6.94</td>
</tr>
<tr>
<td>0.81</td>
<td>2.8490</td>
<td>883.89</td>
<td>1.4915</td>
<td>89.97</td>
<td>0.13</td>
<td>6.08</td>
</tr>
<tr>
<td>1.22</td>
<td>3.1465</td>
<td>886.19</td>
<td>1.492</td>
<td>89.71</td>
<td>0.08</td>
<td>5.79</td>
</tr>
<tr>
<td>1.63</td>
<td>3.4559</td>
<td>887.92</td>
<td>1.4925</td>
<td>89.56</td>
<td>0.06</td>
<td>5.63</td>
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<td>2.03</td>
<td>3.7891</td>
<td>891.08</td>
<td>1.493</td>
<td>89.18</td>
<td>0.05</td>
<td>5.61</td>
</tr>
</tbody>
</table>
Table 7.3:
Values of Dielectric constant, Density, Refractive Index, Molar Volume
Ratio of Formal concentrations and $\Omega_B$

System: Stearic Acid + Pyridine in Benzene $C_A = 0.1028$ mole/l

<table>
<thead>
<tr>
<th>$C_B$ (mole/l)</th>
<th>$\varepsilon_0$</th>
<th>$\rho$ Kg m$^3$</th>
<th>$n_D$</th>
<th>$V \times 10^6$ m$^3$</th>
<th>$C_A/C_B$</th>
<th>$\Omega_B$ D$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>2.3849</td>
<td>881.23</td>
<td>1.491</td>
<td>90.70</td>
<td>0.46</td>
<td>6.07</td>
</tr>
<tr>
<td>0.41</td>
<td>2.5039</td>
<td>882.11</td>
<td>1.492</td>
<td>90.53</td>
<td>0.25</td>
<td>5.54</td>
</tr>
<tr>
<td>0.62</td>
<td>2.6348</td>
<td>883.10</td>
<td>1.493</td>
<td>90.43</td>
<td>0.17</td>
<td>5.29</td>
</tr>
<tr>
<td>0.83</td>
<td>2.7760</td>
<td>885.74</td>
<td>1.494</td>
<td>90.18</td>
<td>0.12</td>
<td>5.22</td>
</tr>
<tr>
<td>1.02</td>
<td>2.9085</td>
<td>888.13</td>
<td>1.495</td>
<td>89.86</td>
<td>0.10</td>
<td>5.16</td>
</tr>
</tbody>
</table>
Table 7.4:
Values of Dielectric constant, Density, Refractive Index, Molar Volume
Ratio of Formal concentrations and $\Omega_B$

System: Arachidic Acid + Pyridine in Benzene $C_A = 0.0815$ mole/l

<table>
<thead>
<tr>
<th>$C_B$ (mole/l)</th>
<th>$\varepsilon_0$</th>
<th>$\rho$ Kg m$^{-3}$</th>
<th>$n_D$</th>
<th>$V \times 10^6$ m$^3$</th>
<th>$C_A/C_B$</th>
<th>$\Omega_B$ D$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>2.3730</td>
<td>880.99</td>
<td>1.492</td>
<td>90.50</td>
<td>0.40</td>
<td>6.05</td>
</tr>
<tr>
<td>0.40</td>
<td>2.5039</td>
<td>881.47</td>
<td>1.493</td>
<td>90.43</td>
<td>0.20</td>
<td>5.60</td>
</tr>
<tr>
<td>0.59</td>
<td>2.6348</td>
<td>883.27</td>
<td>1.494</td>
<td>90.27</td>
<td>0.14</td>
<td>5.45</td>
</tr>
<tr>
<td>0.80</td>
<td>2.7776</td>
<td>885.41</td>
<td>1.495</td>
<td>89.96</td>
<td>0.10</td>
<td>5.39</td>
</tr>
<tr>
<td>0.99</td>
<td>2.9085</td>
<td>887.21</td>
<td>1.496</td>
<td>89.80</td>
<td>0.08</td>
<td>5.29</td>
</tr>
</tbody>
</table>
Fig. 7.1. Variation of $\Omega_B$ with $C_A / C_B$
Stearic acid + Pyridine in Benzene

![Graph of Stearic acid + Pyridine in Benzene]

Arachidic acid + Pyridine in Benzene

![Graph of Arachidic acid + Pyridine in Benzene]

Fig. 7.2. Variation of $\Omega_B$ with $C_A / C_B$
7.8 Calculation of dipolar increment

The vector diagram for dipole moment of the complex and its partners and dipole increment is given in Fig. 7.3

When a proton donor of dipole moment \( \vec{\mu}_a \) forms a H-bond with a proton acceptor of dipole moment \( \vec{\mu}_b \), the direction of \( \vec{\mu}_a \) and \( \vec{\mu}_b \) with respect of A-H...B axis can be defined by \( \theta_a \) and \( \theta_b \) respectively. If \( \theta_a \) and \( \theta_b \) differ from zero, one can define the azimuthal angle \( \phi \) which describes the rotation position of \( \vec{\mu}_b \) around the hydrogen bond with respect to the plane formed by this bond and \( \vec{\mu}_a \). The formation of the H-bond is accompanied by the dipole moment of the nuclei involved in H-bonding and the displacement of the electron. As a consequence the dipole vector of the complex is different from the vector sum and may be given by a dipolar increment.

\[
\vec{\mu}_{ab} = \vec{\mu}_a + \vec{\mu}_b + \Delta \vec{\mu}
\]  

(7.15)

If a single H-bond is formed between the partners, it can be presumed that \( \Delta \vec{\mu} \) has the direction of the hydrogen bond.

The vector equation can be transformed in the form [124]
Fig. 7.3. Dipole moment $\mu_n$, $\mu_i$, and $\mu_c$ of the complex and of the partners. Dipole increment $\Delta\mu$. 
\[ \Lambda \mu = \sqrt{\mu_{ab}^2 - \mu_a^2 \sin^2 \theta_a - \mu_b^2 \sin^2 \theta_b - 2 \mu_a \mu_b \sin \theta_a \sin \theta_b \langle \cos \phi \rangle} \]

\[ - \mu_a \cos \theta_a - \mu_b \cos \theta_b \]

(7.16)

The mean value, \( < \cos \phi > \) was found to be zero for \( 0-H...N \) which means that all rotomers around the axis of the bond are equally possible.

7.9. Discussion:

In the range of concentrations we have chosen for \( C_B \), the plot of \( \Omega_B \) vs \( C_A/C_B \) is linear. We find that in \( C_B \) is for in excess of \( C_A \), where all the H-bonds are of \( O-H...N \) type in the ternary amine, the square of the dipolemoment of the complex remains almost unchanged. For pure alcohols, characterised by a long \( O-H...O \) chains, \( \mu_a^2 \) of one alcohol molecule is about 9 D² [125]. However, we find here that the contribution is much less for long chain fatty alcohols.
An important effect that would enhance the dipole moment of a complex is the ion pair formation. If a proton jump occurs in the \(\text{O-H...N}\) bond, this jump will be proportional to the ratio \(C_A/C_B\); according to the principle of random walk. The increase in \(\Omega_B\) as \(C_A/C_B\) increases may be attributed to this factor of displacement of charges. We find that \(<\mu_a^2>\) is a constant in tetradecanol and hexadecanol which shows that the proton jump is regular and is shared by all the alcohol molecules in the chain.

As for the carboxyl acids the hydrogen bonds formed is dictated by lone pair direction. This assumption may not be strictly valid for all systems[126]. However, it was shown by Schuster [127] that the potential energy is minimum when the hydrogen bond is directed along the lone pair direction. The \(\Delta\mu\), calculated for the most stable configuration is given in Table. 7.5 for all systems. The dipolar increment \(\Delta\mu\) for all the systems are small and negative. The classical explanation that the displacement of the position of the hydrogen atom on H-bonding would mean a positive \(\Delta\mu\) values. Even the proton jump would mean a significant increase in \(\Delta\mu\) values. This would mean that there is yet another effect. The Solvent Induced Medium Effect (SIME) advocated by Pan and Effio [128] may be one of the
plausible reasons. Thermodynamically, there is an increase in enthalpy due to the breaking of the solvent structure by the tertiary amine and the inert solvent. Simultaneously, there is a decrease in entropy because of the larger volume provided by the solvent environment. It is evident that the latter effect is considerable in these systems. Hence it may be concluded that in these systems, there is a weak complexation with polarization interactions coupled with a structure breaking mechanism by the mixed solvents.
### Table: 7.5 Values of Dipole moment, Dipole moment of Complexes, Bond angles and Dipolar Increment

<table>
<thead>
<tr>
<th>System</th>
<th>$\mu_a$</th>
<th>$\mu_b$</th>
<th>$\mu_{ab}$</th>
<th>$\theta_a$</th>
<th>$\theta_b$</th>
<th>$\Delta\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetradecanol + Pyridine in Benzene</td>
<td>1.67</td>
<td>2.32</td>
<td>3.54</td>
<td>43°</td>
<td>0°</td>
<td>-0.1878</td>
</tr>
<tr>
<td>Hexadecanol + Pyridine in Benzene</td>
<td>1.67</td>
<td>2.29</td>
<td>3.40</td>
<td>43°</td>
<td>0°</td>
<td>-0.3042</td>
</tr>
<tr>
<td>Stearic acid + Pyridine in Benzene</td>
<td>1.80</td>
<td>2.25</td>
<td>2.67</td>
<td>60°</td>
<td>0°</td>
<td>-0.9790</td>
</tr>
<tr>
<td>Arachidic acid + Pyridine in Benzene</td>
<td>1.80</td>
<td>2.27</td>
<td>2.74</td>
<td>60°</td>
<td>0°</td>
<td>-0.9138</td>
</tr>
</tbody>
</table>
GIST OF WORKDONE

The classical examples of amphiphilic molecules are the long chain fatty acids, amines and alcohols. In water, the hydrophilic end preferentially takes to H-bonding in water while the hydrophobic end preferentially resides in the air. The solubility of an amphiphilic molecule in water depends on the balance between the alkyl chain length and the strength of its hydrophilic head. The head group which is polar, enter into a strong molecular interaction with the substrate and is pinned to the surface through a chemical bond. The energy associated with such bonds are of the order of several K. Joule/mole. There is also a van der waals interaction of the alkyl chain, whose energies are about a few Joule/mole. The chain - chain interactions are mostly governed by it, even though a polar bulky group in the chain may give rise to stronger electrostatic interaction. For multi layers and self assembled multi layers, the interaction of the terminal group (CH₃ in alkyl chain) is also important. The physico chemical studies of amphiphiles are mostly related to the kinetics of the formation of monolayers and multilayers in various substrates and their stability criteria. Interesting materials were synthesized in recent times which show useful optical and electrical properties. By adding suitable side groups to selected molecules complex structures with totally different properties from the parent compound are achieved. The possibility of controlling the molecular orientation of amphiphiles to fulfil certain specific
functions is possible only if the fundamental nature of these interaction are fully understood. Hence, great importance is stressed in recent times to study the nature of intra and inter molecular interactions of amphiphiles. We have attempted to study systematically a set of simple amphiphilic molecules by an application of selected techniques.

In part I of the thesis, the pressure-area isotherm studies on the monolayers and L.B. multilayer films on glass and quartz substrates are reported. In part II of the thesis, the dielectric studies of the amphiphilic molecules in the solution state are reported.

Many experimental observations exist in the literature illustrating the importance of the study of spread monolayers. The so called Langmuir (L) films at the air – water interface is of technological concern as a precursor of Langmuir – Blodgett films. They also show interesting phase transitions in a two dimensional system. The $\pi$ -A isotherm is rich in information on the stability of the L films on a water sub-phase. $\pi$ is the difference between the surface tension of pure water and that of the water covered with a mono layer. A is the area per molecule of the film. As the spread amphiphilic molecules are compressed, a first phase transition from ‘gas’ state to ‘liquid’ state takes place. Further compression leads to a second transition from ‘liquid’ to ‘solid’ state. In this condensed phase, the molecules are closed and uniformly oriented. At these pressures, the transfer of mono layers from the water – air interface on to a solid substrate is done and a conventional Langmuir – Blodgett film is achieved. The transfer ratio depends on various
factors. Once the stability of the mono layers at the water – air interface has been fully understood the transfer process can be addressed. The stability of the mono layer(L) films depends on many factors like temperature, pH, compression speed, the nature of sub-phase and the conformation of chain of the amphiphilic molecules. Recently Vollhardt and Retter established a theoretical model for the nucleation and collapsing processes.

In our present study, we have investigated the \( \pi - A \) isotherm of the stearic acid, arachidic acid, and their esters with metallic ion substitution. Chapter 1 gives a general introduction to the study of Langmuir films and Langmuir – Blodgett films and their importance. Chapter 2 deals with our study of \( \pi - A \) isotherms. The detailed study of mono layer structure at the water surface is of great importance. It gives an idea of how these selected molecules organize into two dimensional structures and how structural changes occurred during the phase transition. We report our studies on the pressure-area isotherms for several amphiphilic molecules.

**KSV** 5000 L.B. film deposition unit consisting of a Langmuir trough, Wilhelmy balance, barrier driving system and a deposition system was used. The unit is menu driven. The barrier is controlled by a microstep driver stepper motor. The barrier smoothly moves on the surface of the subphase. The area of the spread film is computed automatically. The \( \pi - A \) isotherms of several amphiphiles are recorded. The parameters like pH, temperature, compression speed and the nature of the subphase were varied in each case and the profiles were discussed. In
addition π-A diagrams of mixed amphiphiles were also investigated. The influence of host amphiphiles on π-A diagram was investigated. The collapsing processes of the monolayers in the presence of organic additives with strongly interacting groups were also recorded. It was found that solubilization of the amine molecules influences the head group interactions of the amphiphiles resulting in significant modifications in the π-A diagram.

The hysteresis trace of π-A diagram gives important information on the relaxation mechanism of monolayers. If the polar head group in the amphiphile is properly anchored to the water surface, the attractive interaction between the long-chain tails generate the self assembly and the packing is maintained in several systems, even after several cycling processes. The hysteresis of π-A itself during the first cycle gives an idea of the relaxation of the monolayers. This aspect is also dealt with in Chapter 2.

When a substrate is moved through the monolayer at the water surface the monolayer can be transferred during immersion or emersion and is known as L. B. films. For very hydrophilic head groups, the Y-type deposition is the most stable mode, as the interaction between the adjacent layers are either hydrophobic-hydrophobic or hydrophilic-hydrophilic. The study of the deposition mechanism is very vital as it plays an important part in device applications. A large number of such studies were made. There are several methods to analyze the film properties. Many attempts have been made to determine the mono layer and multi layer
structures by means of electron diffraction, X-ray diffraction, Raman Scattering and other methods. A brief review of such methods of characterization is given. F.T.I.R. Spectroscopy has been widely used as it is sensitive to changes in the molecular conformation and easy to handle. One can use external reflection spectroscopy or attenuated total reflection spectroscopy, as they would give complementary data. In Chapter 3, we have reviewed the F.T.I.R. multiple internal reflection spectroscopy as applied to L.B. film characterization. Chapter 4 reports our experimental study on the transfer of mono layer onto substrates at different controlled conditions. The effect of pH of the substrate, temperature, the deposition rate etc., on selected amphiphiles were reported.

The molecular orientation in L.B. films of stearic acid, cadmium stearate, tetradecanol, hexadecanol and hexadecyl aniline were investigated from the analysis of the stretching vibrations. The interpretation of the I-R spectra of monolayers deposited on a substrate is generally based on the vibrational analysis of the chains and various other groups in the molecule with reference to the shift in frequencies and the change in intensities. One of the I-R spectral characteristics of solid n-paraffins is a band progression at 20 cm$^{-1}$ interval around 1200 cm$^{-1}$ due to twist and wag modes of the CH$_2$ groups in an all trans-conformation. The presence or absence of this series indicates the crystalline order. Similarly significant information is provided by the CH$_2$ scissoring vibrations at 1460 cm$^{-1}$. The splitting of this line is caused by the crystal field. Hence the arrangement of molecules in L-B films is interpreted from the characteristic spectra of this
We have reported in the present investigations, a study of the multiple internal reflection spectra of stearic acid, arachidic acid, tetra decanol, hexadecanol and hexadecyl aniline. L-B films were deposited on glass and quartz on one side using a double plate method. The Langmuir films were compressed to an optimum pressure for each system and this pressure was maintained during deposition by the servo system of KSV 5000.

The infrared spectra of the L-B mono layers and multi layers were obtained by using a Perkin Elmer FTIR spectrometer with MIR attachment. The band profiles were analyzed and interpreted.

For the past several decades, the dielectric constants and dielectric relaxation in organic materials, both solids and liquids have been a subject of studies. As for the amphiphilic substances on air-water interfaces are concerned, the theoretical model assume a priori a two dimensional dipole array. The cyclic symmetry of two dimensional mono layers enables one to use classical mean field theory to calculate the dielectric constant. The permanent dipole moment of the constituent molecules usually does not orient in the direction parallel to the molecular long axis. Further, one has to introduce an interaction parameter for mono layers on a water surface.

The structure and dynamics of LB films on substrates have also been done recently by a combination of energy minimization and molecular dynamics. However, these theories are inadequate due to the limited knowledge of the
polarization mechanism of amphiphilic molecules. The solution state problem may be stated as follows. If molecules possessing a permanent dipole moment $\mu$ are dispersed in a medium of permittivity $\varepsilon_r$, one can write

$$\frac{(\varepsilon_s - \varepsilon_r)(2\varepsilon_s + \varepsilon_r)}{\varepsilon_s} = \frac{Ng\mu^2}{\varepsilon_0 VKT}$$

The quantity $g$ known as the Kirkwood correlation factor which accounts for the fact that short range interactions between molecules may lead to a net polarization in the immediate environment of a given molecule. $g^{1/2}\mu$ is called the effective dipole moment of the molecule. Surprisingly, though data regarding the $g$ factor is available for bio-molecules, very little information is found in literature regarding amphiphiles in solution state. Similarly the computer simulation studies of translational ordering and orientational ordering of fatty acids on a surface gives some idea regarding the cooperative reorientation involving the average tilt and precessional angles. However these models are also defective in the sense that they do not include the head group structures and their dipolar interaction. For large bio molecules, the Kirkwood correlation factor of dielectric polarization is taken as unity. However for smaller molecules this assumption would not be legitimate. Comparatively, few papers have appeared even in the solution state of amphiphiles.

In the present study, reported in Chapter 5, a systematic investigation of the correlation factor $g$ for several fatty acids and alcohols is made. For obvious reasons of solubility problem, we have taken 1-4 Dioxane as the solvent since the
interaction between the functional groups of the amphiphilic compound and dioxane resembles that of water though not fully. The dipole orientation of the head groups is as important as the effect of viscous deformation at interfaces in L.B. films. We hopefully feel that our study of the solution state 'g' factor which describes the orientational correlation between one molecule and a certain number of neighbours,

\[ g_i = \sum_{j \neq i}^{n} \langle \cos \phi_{ij} \rangle \]

where \( \phi_{ij} \) denotes the angle between the dipoles i and j, n the number of particles embedded in a dielectric medium, give useful information on the orientational ordering of the amphiphiles and the affinity of these groups towards the environmental dipoles. A critical number density of the acids and alcohols where \( g \) is a minimum is obtained and the significance of it is discussed.

Dielectric relaxation measurements provide important information regarding the sizes of multimers in associated molecules with a dispersion of the frequencies of relaxation. The frequency dependent dielectric constant \( \varepsilon(\omega) \) of a structureless fluid of dielectric continuum is normally given by Debye's formula

\[
\varepsilon' - \varepsilon_\infty = \int_0^\infty \frac{F(\tau) \tau}{1 + \omega^2 \tau^2} \, d\tau
\]

\[
\varepsilon'' = \int_0^\infty \frac{F(\tau) \omega \tau^2}{1 + \omega^2 \tau^2} \, d\tau
\]
Amphiphiles have a more dielectric response. The Debye relaxation times are commonly associated with three important molecular motions (i) The hydrogen bonded dynamics of molecular aggregates (ii) The monomer rotation and (iii) The rotation of the head group. Further, the relaxation time depends on the surrounding environment of a molecule.

Comparatively few studies have been done regarding the complex permittivity measurements of amphiphilic molecules. Most of the measurements are confined to small biological molecules only. The dependence of the relaxation time on the molecular weight has been fairly established. The early measurement of the activation enthalpies of biological molecules also suggests that the breaking of hydrogen bond is involved in the dielectric relaxation process.

In our present study, the complex dielectric constants $\varepsilon'$ and $\varepsilon''$ at 8.31GHz were determined for several amphiphiles in CCl$_4$ using a X-band microwave bench. The relaxation time is obtained by using Debye's theory. The distribution parameters and the free energy of activation for dipolar and viscous forces have also been calculated. The results are presented in Chapter 6. The molecule is seen to take up a form in solution, which is more compact than the extended chain.

The hydrogen bond formation generally increases the distance of O-H···B accompanied by an enhancement of the dipolemoment $\Delta\mu$. The value of $\Delta\mu / \Delta r$ is of the order of 10 Debye / A$^0$ in O-H···N bonds and even greater in O-H···O=C.
bonds. The dipolar increment $\Delta \mu$ is in effect the vector difference between the dipole moment of the complex and the constituents.

$$\Delta \vec{\mu} = \vec{\mu}_{AB} - \vec{\mu}_A - \vec{\mu}_B$$

Recent studies on a variety of $\text{O-H-\cdots}\text{N}$ and $\text{O-H-\cdots}\text{O=C}$ type of interactions in a medium of non-polar solvents indicated that charge transfer effects, polarization effects and partial proton transfer effects are responsible for $\Delta \vec{\mu}$.

In the present study, the dipole moment of several complexes of fatty acids and alcohols with amino compounds in inert solvents are determined and reported. The predictions from the quantum mechanical $\text{ab initio}$ calculations were used for determining the most favoured equilibrium geometrical model for these complexes. The dipolar increments were calculated for the systems studied, by assuming free rotation of the polar group along the A-H-\cdots B axis. The results show that these dipolar increments are not certainly due to proton transfer or charge transfer complexation. A predominant polarization interaction does occur and the complexation is of 1:1 type.