CHAPTER X
INTRODUCTION

The investigations of Schallamach (1946) on the dielectric relaxation of binary mixtures of non associated polar liquids at frequency of 9 Mc/sec in the temperature range -150°C to 50°C indicated a single relaxation mechanism while the mixtures of an associated and a non associated liquid indicated two absorption maxima. In the case of ternary mixtures containing two non associated polar liquids in a suitable non-polar solvent it is therefore reasonable to expect that at low concentrations two peaks in the loss factor $\varepsilon''$ vs temperature curves should be observed as the separation of dipolar molecules of the two types is large. With the increase of concentrations the two peaks in $\varepsilon''$ vs temperature should move closer and at sufficiently high concentration when the molecules can interfere each other one peak should be observed. In the case of mixtures of associated polar liquids the loss factor curve is expected to depend on associativity of liquids.

Previous investigations of dipolar mixtures in the neutral solvent however indicated the distinctness of two maxima in the loss curve even in the case of very similar nitrobenzene and o-nitrotoluene. The results seem to indicate that mixture chosen do not tend to one relaxation time but each retain its own thus not in conformity with earlier investigations of Schallamach.

In view of these divergent opinion the present
investigations were undertaken to throw some light on the relaxation mechanism. The measurement has been extended to the case of ternary mixtures of chloroform and benzophenone in n-heptane where the polar compounds have sufficiently different relaxation time. Measurements have also been made in the cases of mixtures of chlorobenzene in nujol and bromobenzene in nujol.

The results of investigations of different workers indicate that the relaxation process is intimately connected with the dipole-dipole interaction. To understand the phenomenon we consider a dipole as an equivalent L.C.R circuit. The interactions between different circuits will be equivalent to the dipole-dipole interaction and will be represented by $M$'s the mutual-inductance terms in circuit equation. We may construct a lagrangian $L$ for such a system:

$$L = \frac{1}{2} \sum_j \dot{I}_j^2 + \sum_{j \neq k} \sum_{M_{jk}} I_j I_k - \sum_j \frac{I_j^2}{2C_j} + \sum_j E_j(t)I_j$$

and a dissipative force.

$$\mathcal{F} = \frac{1}{2} \sum R_j \dot{I}_j^2$$

Here $I_j$'s have been used as the generalised coordinates. The Lagrangian equations are

$$L_j \frac{d^2 I_j}{dt^2} + \sum_{j \neq k} M_{jk} \frac{d^2 I_k}{dt^2} + R_j \frac{dI_j}{dt} + \frac{I_j}{C_j} = E_j(t) + \frac{\dot{\omega}^2}{\omega^2} \cdot \mathcal{A}$$

These equations form the set of equations describing a system of mutually inductively coupled circuits. Here $I_j$'s are the currents, the $L_j$'s the self inductances, $M_{jk}$'s the mutual inductances, the $R_j$'s the resistances, the $C_j$'s the capacitances
and \( F_j \)'s the external e.m.f.s.

It can be noticed however that in the expression of the lagrangian the first two terms together constitute an arbitrary homogenous quadratic function of the generalised velocities. Such is always the form of kinetic energy \( T \) for systems where the constraints (holonomies) are independent of time. The coefficients \( L_j \) and \( M_{ij} \)'s are then equivalent to masses. The terms \( \frac{F_j}{2C_j} \) in the lagrangian can correspond to the potential energy of a set of springs or harmonic oscillators \( V = \frac{1}{2} K x^2 \) so that \( \frac{1}{C_j} \)'s represent the spring constants \( K_s \). Now taking the external e.m.f.s \( F_j \)'s as the driving forces and the resistances as the viscous forces we get a picture of a complicated system of masses on springs moving in some viscous fluid and driven by external forces.

The equation of motion for such a mechanical system is:

\[
\sum_j T_{ij} \dddot{q}_i + \sum_j f_{ij} \ddot{q}_i + \sum_j v_{ij} q_i = F_{oj} e^{-i\omega t} \quad \quad (2)
\]

where the driving forces are

\[
F_j = F_{oj} e^{i\omega t}
\]

If we now neglect the mutual inductances, i.e. the dipole-dipole interactions our equivalent circuit equation (1) becomes

\[
L_j \frac{d^2 I_i}{dt^2} + R_j \frac{dI_i}{dt} + \frac{I_i}{C_j} = E_j(t) \quad \quad (1a)
\]

Reading \( L, R, \frac{1}{C} \) and \( E_j \)'s as the inertial terms, viscous forces, spring constants and driving forces respectively the
the equation (1a) like the equation (1) can be written as
\[
\sum_j T_{ij} \gamma_j + \sum_j F_{ij} \dot{\gamma}_j + \sum_j V_{ij} \gamma_j = F_{0j} e^{-i\omega t} \quad \ldots \ldots \quad (2a)
\]

But here the inertial terms \(T_{ij}'\) contains only \(I\) and not \(M\) but \(T_{ij}\) i.e., the inertial term in equation (2) contain both \(L\) and \(M\). It seems that due to the dipole-dipole interaction the mass of the dipole appears to increase.

Let us consider the equation (2)
\[
\sum_j T_{ij} \gamma_j + \sum_j F_{ij} \dot{\gamma}_j + \sum_j V_{ij} \gamma_j = F_{0j} e^{-i\omega t}
\]
and try to seek a particular solution of the form

\[
\gamma_j = A_j e^{-i\omega t}
\]

This gives us a set of inhomogeneous linear equations for amplitude \(A_j\):
\[
\sum_j A_j (V_{ij} + \omega F_{ij} - \omega^2 T_{ij}) = F_{0j} = 0
\]

According to Cramer's rule

\[
A_j = \frac{D_j(\omega)}{D(\omega)}
\]

where \(D(\omega)\) is the determinant of the coefficients

\[
D(\omega) = \begin{vmatrix}
V_{11} - i\omega F_{11} - \omega^2 T_{11} & V_{12} - i\omega F_{12} - \omega^2 T_{12} \\
V_{21} - i\omega F_{21} - \omega^2 T_{21} & V_{22} - i\omega F_{22} - \omega^2 T_{22}
\end{vmatrix}
\]

In this determinant if we replace the \(J^{th}\) column by the set \(F_{01}, F_{02}, \ldots \), we get \(D_j(\omega)\) Now \(D\) is the determinant appearing in the secular equation. Hence its roots are \(\omega_1, \omega_2, \ldots, \omega_n\) which are complex angular frequencies of the free modes of vibrations.
Thus
\[ D(\omega) = G(\omega - \omega_1)(\omega - \omega_2) \cdots (\omega - \omega_n) \]
\[ = G_1 G_2 G_3 \cdots (\omega - \omega) \]

indicates product of all terms like \( (\omega - \omega_1) \) etc. and \( G \)
is an arbitrary constant. If \( D^*(\omega) \) and \( G^* \) be complex conjugateof \( D(\omega) \) and \( G \) respectively then writing
\[ \omega_i = \omega_s + i k_s = 2\pi \nu_s + i k_s \quad \text{and} \quad \omega_s = 2\pi \nu_s \quad \text{and} \quad \omega = 2\pi \nu \]
we get
\[ D^*(\omega) D(\omega) = G^* G_1 G_2 G_3 \left[ 4\pi^2 (\nu - \nu_s)^2 + k_s^2 \right] \]

If we now rationalize the denominator of \( A_3 \) we get
\[ A_3 = \frac{D_i(\omega) D_i^*(\omega)}{D^*(\omega) D(\omega)} = \frac{D^*_i(\omega) D(\omega)}{G^* G_1 G_2 G_3 \left[ 4\pi^2 (\nu - \nu_s)^2 + k_s^2 \right]} \]

Hence resonance will take place when \( \sqrt{\nu} = \nu_s \). This means that if the polar medium is placed under the influence of a high
frequency alternating field maximum absorption energy by the
medium will occur when frequency \( \omega_m \) of the applied field is
\( \omega_m = 2\pi \nu_s = \omega_s \)

In order to get the expression for \( \nu_s \) we consider the
equation (2) and put \( F_i = 0 \).

We get
\[ \sum_i T_{ij} \eta_j + \sum_j F_{ij} \eta_j + \sum_j V_{ij} \eta_j = 0 \]
and let us a solution \( \sin \omega_s t \eta_j = a_j e^{i \omega_s t} \) where \( \omega_s \) denotes
frequency of \( \nu_s \) mode of vibration of the system of dipoles.

We thus get:
\[ \sum_j V_{ij} a_j - i \omega_s \sum_j F_{ij} a_j - \omega_s^* \sum_j T_{ij} a_j = 0 \]
Here the indices \( i \) and \( j \) indicate \( i \)th and \( j \)th particle of the system while the index \( S \) denotes the \( S \)th mode of vibration of the system. Multiplying by \( \alpha_i^* \), the complex conjugate of \( \alpha_i \) and taking sum over all \( i \)'s we get

\[
\omega_s^2 \sum_{ij} T_{ij} \alpha_i^* \alpha_j + i \omega_s \sum_{ij} F_{ij} \alpha_i^* a_j - \sum_{ij} \nu_{ij} \alpha_i^* a_j = 0
\]

writing \( \alpha_i = \alpha_i^* + i \beta_i \) and \( \alpha_j = \alpha_j^* + i \beta_j \) we find

\[
\omega_s^2 \sum_{ij} T_{ij} (\alpha_i \alpha_j^* + \beta_i \beta_j) + i \omega_s \sum_{ij} F_{ij} (\alpha_i^* \alpha_j + \beta_i^* \beta_j) - \nu_{ij} (\alpha_i \alpha_j^* + \beta_i \beta_j) = 0
\]

Solution for \( \omega_s \) gives the real part of \( \omega_s \) as

\[
\omega_s^R = \frac{2 \pi \nu_s}{L} \sqrt{\frac{1}{2} \sum_{ij} T_{ij} (\alpha_i \alpha_j^* + \beta_i \beta_j)} - \frac{1}{4} \left[ \sum_{ij} F_{ij} (\alpha_i^* \alpha_j + \beta_i^* \beta_j) \right]^2
\]

and the imaginary part is

\[
K_s = -\frac{1}{2} \sum_{ij} F_{ij} (\alpha_i \alpha_j^* + \beta_i \beta_j)
\]

If we neglect the dipole-dipole interaction then remembering the meaning of \( T, F \) and \( V \) in the language of equivalent circuit problem we get after proper normalisation of the coordinates:

\[
\omega_s^R = 2 \pi \nu_s = \frac{1}{2} \frac{\sqrt{L}}{C} - \frac{1}{4} \frac{R^2}{L^2}
\]

i.e.

\[
\omega_s = \sqrt{\frac{1}{2} \frac{\sqrt{L}}{C} - \frac{1}{4} \frac{R^2}{L^2}} - i \frac{1}{2} \frac{R}{L}
\]

and

\[
\frac{R^2}{L^2} = \mathcal{J}_0^2
\]

writing \( \omega_s = \frac{1}{\sqrt{\frac{C}{L}}}, \omega_s = \frac{1}{2 \pi \sqrt{\frac{1}{CL}}} \)
If, however, the dipole-dipole interaction is taken into account, \( \bar{T}_{ij} \) will contain \( N_{ij} \) in addition to \( L_i \) that is \( \bar{T}_i \) is increased due to the dipole-dipole interaction and it is evident from equation (3a) and equation (3b) that the increase of \( \bar{T}_{ij} \) means decrease of frequency \( \sqrt{\frac{3}{r}} \). This means \( \omega_m \) the frequency of the applied field at which maximum absorption takes place decreases due to the dipole-dipole interaction. Now if \( \bar{T} \) is the relaxation time of the dipole then as \( \omega_m \bar{T} = \text{constant} \), relaxation time \( \bar{T} \) increases.

We can, therefore, say that the dipole-dipole interaction produces an effect equivalent to an increase of the mass of the dipole resulting an increase in the relaxation time of the polar molecules.

One of the purpose of the present investigation is to see how far the model of the dipole presented here can depict the relaxation process.

References