

Analysis of the Rule of Molecular Polarizability in the Study of the Dielectric Behavior of Liquids.

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ABSTRACT

In this work we present the rule of molecular polarizability in analyzing the dielectric behavior of liquid using the concept of macroscopic and submicroscopic polarization. The influence of complex susceptibility and polarizability of the dielectric nature of liquid with reference to a spherical specimen was generalized with non-vanishing dipole-dipole coupling. The variation of complex permittivity as a function of frequency relating relaxation time and polarization characteristics were analyzed with the graphs showing the parameters that yield good insights into the implication of the polarizability in the study of dielectric measurements of polar liquids.

(Keywords: polarization, relaxation time, dielectric, susceptibility, dipole moment, field)

INTRODUCTION

Dielectric polarization can be electronic, ionic, or orientational in nature if the gross feature such as interfaces and structural irregularities are ignored. The first and second of these denoted by P_c and P_i are caused by induced dipoles which give rise to dispersions within the ultra-violet and infra-red regions of the electromagnetic spectrum respectively.

The third term is denoted by P_p and is caused by permanent dipoles and gives rise to dispersion within the region of low frequencies up to frequencies close to infra-red within the frequencies at which dispersion caused by

permanent dipoles occurs. For electronic and those materials in which it exists, ionic polarization mechanisms are both fully operative (i.e. they have their low-frequency or static values) giving rise to completely real polarization components P_{es} and P_{is} . They have effect on specimen capacitance which is not within the scope of this paper. It is only the orientational polarization that is being considered. As a result, there is no need for the subscript P , which will not be used. The addition of the subscripts to any of the denoted symbols means the low-frequency or static value.

In this article, we present a simple model involving the orientational polarization in relation to applied dc field in a spherical specimen of liquid to study the effect of polarizability in analyzing the dielectric characteristics of liquid.

MACROSCOPIC AND SUBMICROSCOPIC POLARIZATION CONCEPTS

The steady-state orientational polarization P is generally related to an applied dc field E through the relationship :

$$P = \varepsilon_0 x E \quad (1)$$

(Grant et al., 1982) where ε_0 is the permittivity of free space and x is the orientational electric susceptibility of the material.

Considering E as a *phasor* representing an applied field of angular frequency ω , the orientational polarization is found not to be in

phase with E in the frequency range where dispersion caused by permanent dipoles occurs and is therefore complex, and written as \widehat{P} . The related susceptibility $\widehat{\chi}$ is also complex and is given as:

$$\widehat{P} = \varepsilon_0 \widehat{\chi} E \quad (2)$$

The complex polarizability of the entities giving rise to \widehat{P} is denoted as $\widehat{\alpha}$ and hence the orientational polarizations is given as:

$$\widehat{P} = N \widehat{\alpha} \widehat{E}_\eta \quad (3)$$

N being the number of density of molecule each having a permanent dipole moment μ and \widehat{E}_η is the field acting on the molecules.

The field was considered to be the same in each case (i.e., the local field or internal field). It is the sum of the applied field E and the field acting on the molecule caused by the dipole of all the other molecules denoted as E_μ . This is written as:

$$E_\eta = E + E_\mu \quad (4)$$

The two fields are out of phase with each other (Calderwood, et al., 2007). The electronic and ionic polarizabilities arise from spring-like mechanism while the orientational polarizability does not. In polar liquids, the molecules exhibiting such nature of polarizability have a permanent dipole moment μ invariant with variation of field for all realistic field magnitudes.

The Langevin theory of magnetic dipoles (Langevin, 1905) is applicable to the electric dipoles. The problem involved in ordering effect of the field energy and the disordering influence of thermal energy is such that each molecule with a permanent dipole moment μ makes a contribution to the polarization proportional to the field. However, Langevin failed to consider dipole-dipole interaction (i.e., he neglected E_μ) and hence the expression he obtained for polarization cannot be used without modification when such an interaction is significant. However, the expression for α_s derivable from his analysis,

$\frac{\mu^2}{3KT}$ still holds, where K is Boltmann's constant and T is the absolute temperature.

\widehat{P} can be expressed in terms of the macroscopic quantity $\widehat{\chi}$ by relationship using Equation (2) and in term of the submicroscopic quantity $\widehat{\alpha}$ by the relationship using Equation (3). The analysis of dielectric behavior are usually carried out in terms of electric susceptibility or permittivity, but (Scaife, 1963) clearly pointed out that the analysis in terms of polarizability especially with more than one orientational polarization mechanism present has some significant advantage as it can be observed. When characteristics are made more evident with elaborate understanding since molecular polarizability is a factor that determines them.

COMPLEX SUSCEPTIBILITY AND POLARIZABILITY

As observed by Scaife (1963), long-range dipole-dipole coupling vanishes in a dielectric hence his analysis of dielectric behavior in terms of polarizability was referred to in carrying out a research with reference to a spherical specimen. The shape of the specimen is generalized with non vanishing dipole-dipole coupling in this work. The result, as observed by Scaife, are found to be similar.

For orientational polarization, if we eliminate \widehat{P} in Equation (2) and (3) we obtain:

$$\frac{\widehat{E}_\eta}{E} = \frac{\varepsilon_0 \widehat{\chi}}{(N \widehat{\alpha})} \quad (5)$$

Derivations of $\widehat{E}_\eta = f(E)$ can be seen in detail in books written by Bottcher (1973) and Scaife (1998). However, because of the complexity and some restrictions on their applicability, for example to molecular shape, we employed the Lorentz technique which is one of the best-earliest known techniques for this type of problem (Lorentz, 1952).

This technique involves the process of obtaining an expression for $E_{\eta s}$ by calculation of the field $E_{\mu s}$ caused in a spherical virtual cavity by the

bound polarization charges on linear field E , taken to be unperturbed by the presence of the virtual cavity.

The field $E_{\mu s}$ is in the same direction as E and is given by:

$$E_{\mu s} = \frac{P_s}{3\epsilon_n} \quad (6)$$

(Lorentz, 1952).

The above Equation (6) which expresses $E_{\mu s}$ is in absence of the contribution made by the dipole within the spherical virtual cavity following Lorentz, we shall take the local field $E_{\eta s}$ to be given by:

$$E_{\eta s} = E + \frac{P_s}{(3\epsilon_0)} \quad (7)$$

In the case of an applied field, Equation (7) may be generalized to give:

$$\hat{E}_\eta = E + \frac{\hat{P}}{(3\epsilon_0)} \quad (8)$$

Substituting Equation (8) into Equation (3) for \hat{P} , we obtain:

$$\frac{\hat{E}_\eta}{E} = \frac{1}{1 - N\hat{\alpha}/3\epsilon_0} \quad (9)$$

and substituting in Equation (9) that of Equation (5), we have:

$$\hat{\alpha} = \frac{\epsilon_0}{N} \left(\frac{1}{1/\hat{x} + 1/3} \right) \quad (10)$$

At low frequency, Equation (10) becomes:

$$\hat{\alpha}_s = \frac{\epsilon_0}{N} \left(\frac{1}{1/\hat{x}_s + 1/3} \right) \quad (11)$$

and combining Equations (10) and (11), we obtain

$$\frac{\hat{\alpha}}{\alpha_s} = \frac{1 + x_0/3}{x_s/\hat{x} + x_s/3} \quad (12)$$

Generally, the relationship between $\hat{\alpha}$ and \hat{x} is given by Equation (12) and with the knowledge of frequency dependence of \hat{x} , the value of the frequency relation of $\hat{\alpha}$ will also be known.

For a dielectric material having a susceptibility with a single relaxation time τ_x , we have:

$$\frac{\hat{x}}{x_s} = \frac{1}{1 + i\omega\tau_x} \quad (13)$$

substituting this expression for $\frac{\hat{x}}{x_s}$ into Equation (12), we obtain:

$$\frac{\hat{\alpha}}{\alpha_s} = \frac{1 + x_{s/3}}{1 + x_{s/3} + i\omega\tau_x} \quad (14)$$

When the numerator and denominator of the above expression are divided by $\left(1 + \frac{x_s}{3}\right)$, and a polarizability time constant τ_α is given such that:

$$\tau_\alpha = \frac{\tau_x}{1 + x_s/3} \quad (15)$$

Equation (14) becomes:

$$\frac{\hat{\alpha}}{\alpha_s} = \frac{1}{1 + i\omega\tau_\alpha} \quad (16)$$

However, one expects that as a *dc* field dE is applied to the liquid containing low concentration of polar molecules in non-polar solvent in which $E_\mu \rightarrow 0$, the polarization P builds up with time to give the relation:

$$P = P_s (1 - e^{-t/\tau_\alpha}) \quad (17)$$

Thus, if we ignore thermal fluctuations, in this case, the time constant τ_α is a measure of the

rate at which a degree of polar molecular order is built up after dc field was applied to it.

To achieve this, the experimental data relating to dielectric relaxation in liquid solutions as published by Bucher and Barthel has not been defined (Buchner, et al., 2001). This in conjunction with Equations (15) and (16) would provide a useful and enough source of information for a detailed study of this concept. From Equation (2) one sees that the polarizability depends on the local field acting on the material dipoles, which depends on the polarization of the material and so on its susceptibility.

If we now denote the relaxation processes by subscripts 1 and 2, the former being the low frequency process, and the latter, the high frequency process, then:

$$\tau_{x2} = k_x \tau_{x1} \quad (18)$$

where k_x is a constant such that $0 < k_x < 1$. In the usual case where the strength of the higher frequency dispersion is less than that of the lower,

$$x_{s2} = \lambda_x x_{s1} \quad (19)$$

where λ_x is a constant such that $0 < \lambda_x < 1$ we now write:

$$x^1 = x_1^1 + x_2^1 \quad (20)$$

and putting $\omega\tau_{x1} = c_x$,

$$x^1 = \frac{x_{s1}}{1+c_x^2} + \frac{\lambda_x x_{s1}}{1+(\lambda_x c_x)^2} \quad (21)$$

Similarly,

$$x_s = x_{s1} + x_{s2} = x_{s1} (1 + \lambda_x) \quad (22)$$

The relationship between k_α and k_x can be obtained from Equation (15) as:

$$\frac{k_\alpha}{k_x} = \frac{x_{s1} + 3}{\lambda_x x_{s1} + 3} \quad (23)$$

While the relationship between λ_α and λ_x can be derived from Equation (11) and it is given by:

$$\frac{\lambda_\alpha}{\lambda_x} = \frac{x_{s1} + 3}{\lambda_x x_{s1} + 3} \quad (24)$$

From equations (23) and (24), it follows that:

$$\frac{k_\alpha}{\lambda_\alpha} = \frac{k_x}{\lambda_x} \quad (25)$$

RESULT AND DISCUSSION

This result as obtained in Equation (15) agreed with the previously result derived by Scaife for a spherical specimen. This explained how τ_α , the time constant, exhibited by very dilute solutions of polar molecules in a non-polar solvent for which dilute solutions $x_s \rightarrow 0$, related to the concentration-dependent parameters of time constant τ_x and static susceptibility x_s .

It is evident that Equation (16) has the same form as Equation (13), and it follows that for a material exhibiting a single relaxation time as analyzed by Cole and Cole (1941) varies with the angular frequency ω and the case of the corresponding susceptibility relation as in Equations (13) and (14) indicate that $\tau_\alpha \leq \hat{x}$.

The reason for this difference in the time constant governing \hat{x} and $\hat{\alpha}$ is that \hat{x} is related to the applied field E through the relationship of Equation (2) while $\hat{\alpha}$ is related to the local field E_η through the relationship Equation (2). The applied field is the actual field experienced by the dipole. Hence it seen that $\hat{\alpha}$ is more directly related to the field-related dynamics of the polar molecules of the liquid than \hat{x} .

The values of x_s for a liquid consisting of a non-polar solvent in which some polar molecules have been incorporated as a solute. A high concentration means that x_s is high and hence the dipole moment per unit volume is high and so high is the specimen polarization P .

It follows from Equation (5) that the field E_μ at each polar molecule produced by all the other polar molecules is high, so that the local field E_η has a large component due to E_η in addition to the field due to the applied field E so $\frac{\tau_\alpha}{\tau_x} \rightarrow 0$ if the concentration of the solute is low, then as $E_\mu \rightarrow 0, E_\eta \rightarrow E$ and so $\frac{\tau_\alpha}{\tau_x} \rightarrow 1$. This dependence of $\frac{\tau_\alpha}{\tau_x}$ on the value of x_s is observed from Equation (15).

It is evident that while τ_α is basic characteristic of the material dependent on the behavior of the dipole in applied field E, τ_x is determined partly by their behavior in the field E_μ resulting from the influence of the electric field of the dipoles on each other. Thus τ_x depends on the polarization characteristic of the material of the liquid which depend in turn on the concentration of the solute molecules in the non-polar solvent. The quantities τ_x and x_s can be conventionally measured directly and τ_α is the limiting value of τ_α for dilute solutions of the molecules in a non-polar solvent.

From Equation 23, we observe that in order to obtain the value of k_α from the knowledge of k_x , it is important to have a pre-knowledge of the values of λ_x and x_{s1} considering that polar liquids often exhibit two or more relaxation mechanisms, each of these mechanisms is assumed to have its dispersion strength. The reasons for the second dispersion were explained by Smyth (1955) and Bötcher, et al. (1978).

Figure 1 shows the polarizability α in relation to the susceptibility χ . Arbitrarily, the value of χ was denoted as χ_{s1} . The polarizability α was denoted as α'_{s2n} . The value of k_χ was different for each of the χ graphs. From the graphs, there is evidence of the magnification of high-frequency relaxation. The variation of α'_{s2n} with χ_{s1} explains

how high-frequency relaxation behave for three values namely, $\lambda_\chi = 0.25, 0.1,$ and 0.01 .

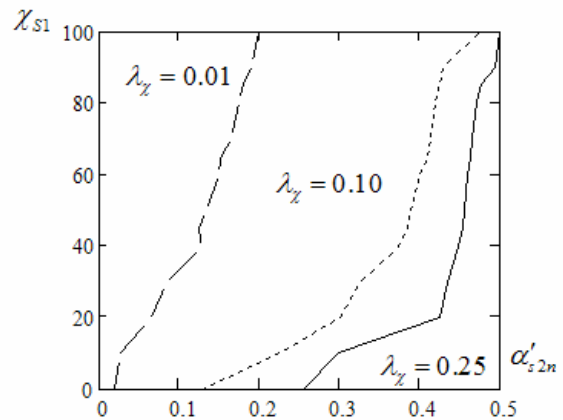


Figure 1: Graph of the Computed Variation of the Static Polarizability at Higher Frequency Relaxation with the Variation of the Susceptibility at given Ratio of the Strength of the Higher Frequency to Lower Frequency Dispersion.

Figure 2 presents the relation between χ'' and χ' for a chosen value of k_χ having a frequency related variable. This graphs behavior in the same manner as Figure 3 which result from evaluation of the equations (23) and (24) each being for a chosen value of k_χ and each having c_χ as the frequency related value.

Graph (a) is for $k_\chi = 0.1$. This curve lies very close to the horizontal axis. Curve (b) is for $k_\chi = 0.01$, where it is seen that the curve f moved slightly from the horizontal followed by curves (c) $k_\chi = 0.03153$ and curve (d) for $k_\chi = 0.001$. All of these curves were plotted for critical value of $\lambda_\chi = 0.25$.

Conclusion

The analysis showed the conditions to obtain polarization and susceptibility plots and that in view of the frequency analysis, α i.e. the polarizability is more important and useful than χ .

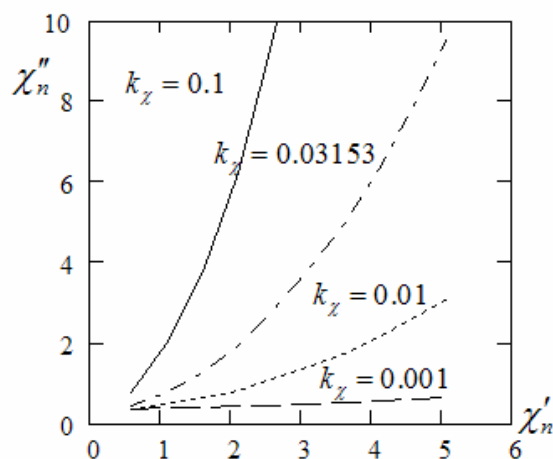


Figure 2: Graph of χ'' against χ' for the Dielectric Exhibiting Two Relaxation Times, when χ'' (Higher Frequency) is 0.25 (χ') (Lower Frequency) for the Range of Values of k_z .

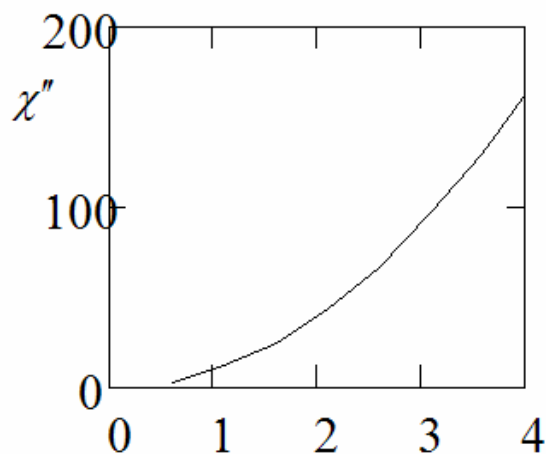


Figure 3: Graph of the χ'' against χ' for the Dielectric Exhibiting Two Relaxation Times at Higher and Lower Frequencies Respectively: $c_x = 1$ to 1000.

This is so because α magnifies the scale at high frequency and that the polarizability of the polar molecules provides the basic mechanism which brings about the polarization factor of the material.

Another important factor, apart from the applied field, is the time constant τ_α which determines the measure of the rate at which a polar molecular order is built up after the field application ignoring thermal fluctuations. While τ_α is a basic characteristic of the material dependent on the behavior of the dipoles, in their controllable applied field, τ_χ is determined by partly their behavior in a controlled field and partly by their behavior in the uncontrollable field resulting from the influence of the electric field of the dipoles on each other. Therefore τ_χ depends on the polarization of the specimen which depends, in turn, on the concentration of the solute molecules when they are subjected to a known and controllable applied field distinct from the effects ascribed to the internal field created by other polar molecules plays a vital role in addition to the applied field.

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