Dielectric relaxation phenomena of rigid polar liquid molecules under giga hertz electric field

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Abstract. The dielectric relaxation phenomena of rigid polar liquid molecules chloral and ethyltrichloroacetate \((j)\) in benzene, \(n\)-hexane and \(n\)-heptane \((i)\) under 4.2, 9.8 and 24.6 GHz electric fields at 30\(\textdegree\)C are studied to show the possible existence of double relaxation times \(\tau_2\) and \(\tau_1\) for rotations of the whole and the flexible parts of molecules. The probability of showing double relaxation is more in aliphatic solvents indicating their nonrigidity. The symmetric and asymmetric distribution parameters \(\gamma\) and \(\delta\) are obtained from \(\chi_{ij}/\chi_{0ij}\) and \(\chi''_{ij}/\chi_{0ij}\) at \(w_j \rightarrow 0\) where \(\chi'_{ij}\) and \(\chi''_{ij}\) are real and imaginary parts of the complex orientational susceptibility \(\chi_{ij}\) and \(\chi_{0ij}\) is the low frequency susceptibility which is real. \(\chi_{ij}\)'s are involved with the measured dielectric relative permittivities \(\epsilon'_{ij}, \epsilon''_{ij}, \epsilon_{0ij}\) and \(\epsilon_{\infty ij}\) of solutions. The theoretical weighted contributions \(c_1\) and \(c_2\) towards dielectric dispersions by Fröhlich’s method are compared with the experimental ones obtained from the graphical variation of \(\chi'_{ij}/\chi_{0ij}\) and \(\chi''_{ij}/\chi_{0ij}\) with weight fractions \(w_j\)'s at \(w_j \rightarrow 0\). The measured dipole moments \(\mu_2\) and \(\mu_1\) of the whole and the flexible part of a polar molecule in terms of the linear coefficients \(\beta\)'s of \(\chi'_{ij}\)'s with \(w_j\)'s and the estimated \(\tau_2\) and \(\tau_1\) reveal their associations with aliphatic solvents. The theoretical dipole moments \(\mu_{\text{theo}}\)'s from the available bond angles and bond moments of the substituent polar groups of the molecules with the estimated \(\mu\)'s suggest the mesomeric, inductive and electromeric effects in them under GHz electric field.

Keywords. Relaxation time; hf conductivity; dipole moment.

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1. Introduction

Dielectric relaxation studies of polar liquids in nonpolar solvents are of much importance as they provide interesting information of solute–solvent or solute–solute molecular association [1,2] under high frequency (hf) electric field. The associational aspects of polar liquids can, however, be inferred from the measured relaxation time \(\tau\) by Cole–Cole [3], Cole–Davidson [4] plot or by single frequency concentration variation method [5] and dipole moment \(\mu\) from the measured hf conductivity \(\sigma_{ij}\) and estimated \(\tau\) [6].

Srivastava and Srivastava [7] measured the real \(\epsilon'_{ij}\) and imaginary \(\epsilon''_{ij}\) parts of complex relative permittivity \(\epsilon_{ij}\) of chloral and ethyltrichloroacetate in benzene, \(n\)-heptane and \(n\)-hexane in 4.2, 9.8 and 24.6 GHz electric field by Smyth’s method [8] at 30\(\textdegree\)C. The polar
solutes (j) choral (CCl₃CHO) and ethyltrichloroacetate (CCl₃COOCH₂CH₃) were of pru-
ram grade of M/s. BDH, England, n-hexane and n-heptane from M/s. E Merck Darmstadt,
Germany. Both solutes and solvents were doubly distilled before making solutions of
varying concentrations called the weight fractions \( w_j \)'s of solutes which are defined as the
weight of the solute per unit weight of the solution up to four decimal places as shown
in table 1 in each solvent. The static relative permittivity \( \varepsilon_{0ij} \) at 100 KHz and refractive
index \( n_{Dij} \) of the solutions were measured. The purpose of this study was to observe the
solute–solvent or solute–solute molecular interactions. They, however, inferred that these
molecules may possess two or more relaxation processes towards dielectric dispersions.

Now a days, the usual practice is to study the dielectric relaxation processes in terms of
hf dielectric orientational susceptibility \( \chi^{ij}_0 \) rather than \( \varepsilon_0^{ij} \) or hf conductivity \( \sigma^{ij} \) [9,10].
\( \varepsilon_0^{ij} \) includes within it all the polarization processes while \( \sigma^{ij} \) is more linked to trans-
port of bound molecular charges. It is, therefore, better to work with susceptibilities
\( \chi^{ij} \)'s as they are concerned with orientational polarization. The dielectric susceptibilities
real \( \chi^{ij}_0(=\varepsilon^{ij}_0-\varepsilon_{mij}) \) and imaginary \( \chi^{ij}_i(=\varepsilon^{ij}_i) \) parts of complex dielectric susceptibility
\( \chi^{ij}_i(=\varepsilon^{ij}_i-\varepsilon_{mij}) \) and the low frequency dielectric susceptibility \( \chi^{ij}_0(=\varepsilon^{ij}_0-\varepsilon_{mij}) \) which
is real were derived from measured relative permittivities [7]. The experimental results
thus collected together are placed in table 1. One could not make a strong conclusion of
double relaxation phenomena of polar molecule in a nonpolar solvent based on the single
frequency measurement of relaxation parameters provided the accurate value of \( \chi^{ij}_0 \) in-
volved with \( \varepsilon_{0ij} \) and \( \varepsilon_{mij} \) is not available. The use of \( n^2_{Dij} \) for \( \varepsilon_{mij} \) [7] often introduces the
additional error in the calculation. Nevertheless, the data of table 1 are accurate up to 5%
for \( \chi^{ij}_0 \) and 2% for \( \chi^{ij}_i \) and \( \varepsilon^{ij}_0 \) respectively.

The nonspherical as well as nonrigid polar liquid molecules often possess two or more
\( \tau \)'s in GHz electric field for the rotation of different flexible polar groups attached to the
parent molecule and the whole molecule itself [11]. Bergmann et al [12], however, devised
a graphical method to obtain \( \tau_1 \) and \( \tau_2 \) for a pure polar liquid. The respective weighted con-
tributions \( c_1 \) and \( c_2 \) towards dielectric relaxations were also estimated in terms of \( \tau_1 \) and \( \tau_2 \).
A graphical method [13] was, soon employed from Fröhlich’s distribution function [14] to
get \( \tau_2 \) and \( \tau_1 \) of a pure polar solute. The methods indicate that a single frequency mea-
surement is not sufficient to have correct \( \tau_1 \) and \( \tau_2 \). Bhattacharyya et al [15] subsequently
attempted to get \( \tau_1 \), \( \tau_2 \) and \( c_1,c_2 \) for a polar molecule with \( \varepsilon',\varepsilon'',\varepsilon_0 \) and \( \varepsilon_m \) measured at
two different frequencies in GHz region. The graphical analysis made by Higasi et al [16]
on polar–nonpolar liquid mixture was, also a crude approximation.

Saha et al [6] and Sit et al [17] recently put forward an analytical method based on
single frequency measurement of relative permittivities \( \varepsilon^{ij}_0, \varepsilon^{ij}_i, \varepsilon^{ij}_{0ij} \) and \( \varepsilon^{ij}_{mij} \) of polar–
nonpolar liquid mixtures of different \( w_j \)'s at a given temperature to get \( \tau_1,\tau_2 \) and \( c_1,c_2 \)
respectively. Earlier investigation had been made on different chain-like polar molecules
like alcohols in nonpolar solvents [18,19] to see the double relaxation phenomena at three
different electric field frequencies in terms of relative permittivities. However, no such
study is made on the aforesaid rigid aliphatic polar liquid molecules in different solvents
under various electric field frequencies from measured \( \chi^{ij}_0 \)'s of table 1. Choral is widely
used in medicine as drug to induce sleep and relieving pain and in the manufacture of D.D.T.
as insecticides. Ethyltrichloroacetate, on the other hand, is used for artificial fragrance of
fruits and flowers.

Thus the object of the present paper is to detect the existence of double relaxation times
\( \tau_1 \) and \( \tau_2 \) due to rotation of the flexible part and the whole molecules themselves using