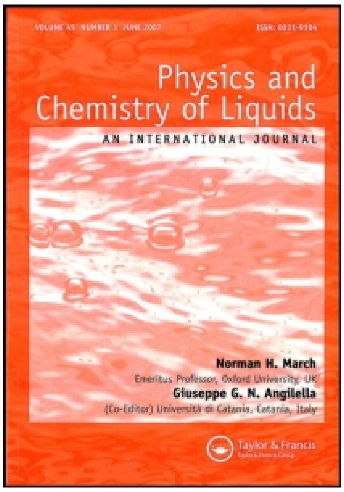

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Dielectric studies on some substituted indoles

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Dielectric studies on some substituted indoles

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Dielectric behavior of some substituted indole compounds, namely, 5-bromoindole, 5-methoxyindole, 5-fluoroindole, 2,3-dimethylindole, 2,5-dimethylindole at room temperature have been studied at two frequencies 8.55 and 9.65 GHz. These studies have been carried out in dilute solutions because such studies have the advantage over pure liquids that the strong dipole–dipole interactions in the dilute solution phase are much reduced.

Keywords: Dielectrics; Microwave; Dipole moment; Substituted indoles

1. Introduction

The dielectric behavior of a polar molecule is usually discussed in terms of its two molecular parameters, the electric dipole moment (μ) and dielectric relaxation time (τ) [1–12]. These parameters can be evaluated by measuring dielectric perimittivities (ε_s, ε_∞, ε', ε'') of polar dielectrics in pure liquid form or a set of graded dilute solutions of them in a non-polar solvent at static, optical and microwave frequencies. The values of μ and τ so determined help in drawing conclusions regarding the structure of molecules, nature of chemical bond, charge transfer complexations, inter and intramolecular interactions, hydrogen bonding, the nature of the orienting polar unit etc. Earlier work was reported recently along with effect of temperature and viscosity, by the authors, for different substituted benzenes [1–6]. The present article is a continuation of such work on a system of molecules which are less studied, namely indoles.

By assuming that the behavior of dilute solutions conform closely to that predicted by the Debye theory, the two parameters μ and τ can be evaluated by employing any of the procedures discussed in the literature [10–30]. Further, by carrying out the dielectric measurements on pure liquids at different frequencies it is possible to draw conclusions by using well-tested equations about whether the medium under study is associated with a single relaxation time, or a distribution around a most probable value

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or with more than one such distinct relaxation time corresponding to different dispersion regions.

To arrive at the values of μ and τ one can carry out dielectric measurements following concentration variation method at a single frequency or on a single appropriate concentration of it at several frequencies or at only two frequencies [10,11], not well separated by each other around the frequency corresponding to maximum absorption and determine the loss tangent. The latter method has a practical advantage in a situation where the quantity of the polar substance under investigation is not sufficient to prepare a set of varying dilute solutions in a non-polar solvent.

However, keeping all the above considerations in mind, despite a good deal of work has been reported in the literature [25–30] in this field in the last few decades, the authors believe that the phenomena of electric polarization and dielectric relaxation merit further study. Such studies warrant investigation on several other dielectric systems such as substituted indoles, on which the present article focuses.

In this work, dielectric measurements on a single weight fraction in benzene of 5-bromoindole, 5-methoxyindole, 5-fluoroindole, 2,3-dimethylindole, 2,5-dimethylindole at room temperature are carried out at two frequencies 8.55 and 9.65 GHz. The results are presented and discussed below.

2. Measurements and methods of evaluating μ and τ

The real (ε') and imaginary (ε'') parts of the complex dielectric constant ε^* were measured in a routine manner by employing Roberts and Von Hippel standing wave method [22] as modified by Dakin and Works [23] and is as already described in author's earlier work [1–4].

For the evaluation of μ, τ from single concentration two frequency measurements the loss tangent can be expressed as a fair approximation as

$$\tan\delta = \left[\frac{(\varepsilon'+1)^2}{\varepsilon'}\right]\left[\frac{4\pi CN\mu^2}{27VKT}\right]\left[\frac{\omega\tau}{1+\omega^2\tau^2}\right] \tag{1}$$

where, all the quantities in the equation have their usual meaning explained earlier [1–4]. The fact μ and τ are not frequency-dependent parameters and characteristics of the molecules, one can express the loss tangent measured at two frequencies ω_1 and ω_2 but at the same temperature T as,

$$\tan\delta_1 = A\mu^2\left[\frac{\omega_1\tau}{1+\omega_1^2\tau^2}\right] \tag{2}$$

and

$$\tan\delta_2 = B\mu^2\left[\frac{\omega_2\tau}{1+\omega_2^2\tau^2}\right] \tag{3}$$

where, $A = [(\varepsilon'+1)^2/\varepsilon'] \, [(4\pi CN\mu^2)/(27VKT)]$ at ω_1 and B is the same at ω_2. τ can be determined by the ratio of $\tan\delta_1$ and $\tan\delta_2$ while μ by the difference $\tan\delta_1 - \tan\delta_2$.

3. Results

The measured values of ε' and ε'' for a single weight fraction of each of the indole at room temperature and at 8.55 and 9.65 GHz frequencies are given in table 1. The molecular weight of each molecule is indicated under column 1 in parenthesis while the weight fraction chosen for the study, in the column 2 of this table. The values of μ and τ obtained are given in columns 7 and 8 of this table. Also given in this table are the estimated values of the molecular radii using the Debye's equation for $\tau = (4\pi r^3 \eta / KT)$ and also by atomic increment method as explained in the earlier article [5] assuming the shape of the molecule to be spherical. The estimated values of the polarizability (P) of each molecule following the additive rule for atomic refraction are given in column 11.

Referring to table 1 the observed values of the dipole moments of the substituted indole molecules are clearly of the right order in view of the fact that the dipole moments [25] of the parent molecule indole, the group moments of –Br, –F, $-OCH_3$ and $-CH_3$ being 2.11, 1.54, 1.46, 1.25 and 0.4 D, respectively. The dipole moments of the three monosubstituted indoles decrease from bromo- to methoxy- via fluoro-isomer and are in accordance with their group moments. The slightly higher moment in the case of bromo isomer may be due to its higher refraction [25]. Assuming that the indole moment acts along the line bisecting the nitrogen valence angle, the vector addition of moments gives the values 3.17, 3.11 and 2.94 D for bromo-, fluoro- and methoxy-indoles which are in fair agreement with the observed values. The observed increase in the moment from 2,3-dimethylindole to 2,5-dimethylindole may suggest that the $-CH_3$ group moment in the molecule acts away from the benzene ring of the indole structure. Further, it may be emphasized that the contribution by the resultant moment of two methyl groups in *ortho* position (2,3-dimethylindole) to the indole, dipole moment is small compared to that by the same substituents in *para* position as in the case of 2,6-dimethylindole and thus may support the inference arrived at earlier that the group moment of methyl radical acts away from the ring. In other words, the methyl-to-ring line is in the plus–minus direction of the dipole.

The relaxation time of a molecule in general depends upon several factors, such as molecular weight, polarizability, viscosity of the surrounding medium, nature and position of the orienting unit, steric effects, hydrogen bond effects, size, temperature and shape of the molecule under study. Further, it is a general observation that a substituted benzene molecule in benzene solution has a value ranging between 8–15 ps, this value is double for naphthalene substituted compounds and three times the value for three ring systems etc. In view of this, the observed τ values of all the compounds (in benzene solution) are clearly of the right order of magnitude.

It may be observed from table 1 that a common feature of all the molecules is that they contain rigid dipoles except in the case of 5-methoxyindole; the latter is excepted to make an inclination about 55° with the group bond. The observed τ values of all the molecules in general vary according to their molecular weights and polarizability values. The molecular weights of three mono-substituted indoles increase from fluoro- to bromo-indole via methoxy indole and the observed values of τ also follow this trend. However, as regards their polarizability values this trend does not seem to be followed. This can partly be due to the fact that because of the flexible nature of methoxy group, it is likely that there is a distribution of relaxation time around its most probable value. Further, the τ values of the two isomers of dimethylindoles differ outside the experimental errors ($\approx$10%) although they have equal values of molecular weights

Table 1. Dielectric measurements of some substituted indoles.

		Frequency of measurment (GHz)						Molecular radius in Å		
		8.85		9.65						
Compound	Wt fraction $C * 10^3$	ε'	$\varepsilon'' * 10^3$	ε'	$\varepsilon'' * 10^3$	τ (ps)	μ (D)	Atomic increment	Debye	Polarizability $P * 10^{24}$
5-Bromoindole MW 196.05	53.4	2.346	24.2	2.294	22.5	27.3	3.13	3.15	2.55	15.78
5-Methoxyindole MW 147.18	59.7	2.278	14.1	2.287	13.0	24.0	2.34	3.21	2.45	12.64
5-Fluoroindole MW 135.14	55.4	2.412	26.3	2.343	25.1	20.5	3.03	2.98	2.31	15.43
2,3-Dimethylindole MW 145.21	58.2	2.355	10.2	2.291	9.65	21.8	2.51	3.31	2.37	16.41
2,5-Dimethylindole MW 145.21	51.9	2.327	15.4	2.285	16.3	19.9	2.76	3.31	2.30	16.41

and polarizability values. It is likely that the two dipoles in *ortho* position introduce more restriction to free rotation of the molecule than in *para* position in the 2,5-dimethylindole molecules.

It may be observed from table 1 that the calculated molecular radii using observed τ and employing Debye's single relaxation time in a medium of viscosity η ($\tau = 4\pi\eta r^3/KT$) agree fairly well with those estimated by atomic increment method as explained in earlier work [5]. It is a general observation in the literature that the molecular volumes (or radii) estimated by Debye's relations are small compared to the actual volume of the molecules. Thus, it may be concluded that the observed dielectric absorption in all the cases of these molecules is due to the rotation of them as a whole but not due to segment, or part of the polar molecule, under investigation.

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