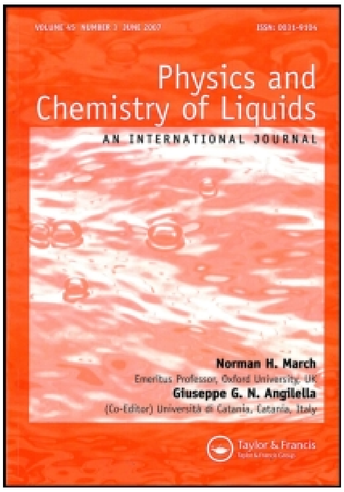

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Dielectric studies on some mesogenic, non-mesogenic and organic molecules

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Dielectric studies on some mesogenic, non-mesogenic and organic molecules

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Two important molecular parameters, namely, the dielectric relaxation time τ and electric dipole moment are highly useful in having insight into the molecular structure, size, shape, apart from the inter- and intra-molecular forces, etc. With these in view dielectric measurements in benzene at room temperature on the pure samples of *o*-ethyl phenol, 2-*n*-butylphenol, 4-*n*-butylphenol, 2,6-dimethoxyphenol and 3,4-difluorophenol were carried out at a frequency of 9.98 GHz by employing concentration variation method. Similar measurements, on a single weight fraction of each of them at 9.98 GHz and also at 8.74 GHz are carried out. Measurements on a single weight fraction in benzene of each of the liquid crystal samples, namely, EPCP.car (Butyl-*p*-(*p*-ethoxy phenoxy corbonyl)-phenyl carbonate), PPPB (*p*-pentylphenyl-*p*-propyl benzonate), EPAP.Hp (*p*-(*p*-ethoxyphenyl azo) phenyl heptenate) and EPAP. Und (*p*-(*p*-ethoxyphenyl azo) phenyl undecylenate were also carried out at the said two frequencies. Using the obtained values of ε', ε'' relaxation time and dipole moment were determined using different methods. The obtained results are compared with earlier results wherever available.

Keywords: dielectric relaxation; dielectric constant; polar solute, non-polar solvent

1. Introduction

The dielectric studies on aromatic molecules have been reported from our laboratory earlier [1–8] and others [9–40], as dielectric approach forms one of the powerful tools for the determination of molecular structure [9]. For example, in the case of some derivatives of sydnones rather high values of electric dipole moments could be explained in a satisfactory way by assigning cyclic meso-ionic structures rather than an improbable bicyclic structure. Two important molecular parameters, the dielectric relaxation time τ and electric dipole moment that are highly useful in having insight into the molecular structure, size, shape apart from the inter- and intra-molecular forces etc. By measuring the high frequency dielectric permittivity, ε', ε'' at different frequencies or at different temperatures, of pure liquids the relaxation time τ can be evaluated which will have the influence of intermolecular forces also. By measuring the high frequency dielectric permittivity, ε', ε'' different concentrations of a polar molecule in a non-polar solvent also

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give important information about molecular structure, size, shape apart from the inter- and intra-molecular forces, etc. Such studies have an advantage over pure liquids that the strong dipole–dipole interactions in dilute solution phase are greatly reduced and hence they permit one to study the effect of viscosity on the molecular parameters, in addition to the effect of temperature, only in the case of pure liquids.

The two molecular parameters μ, τ can be estimated by the concentration variation method either through Gopal Krishna method [32] or through slope methods due to Higasi [11], Higasi *et al.* [12] or through dielectric conductivity methods due to Acharya and Chatarjee [13] and Murthy *et al.* [8]. The method due to Jai Prakash [14] based on Frolich equation is another approach through which these quantities can be determined. All these methods assume that the behaviour of the dilute solutions conform closely to that predicted by the Debye theory [37]. However, instead of carrying out dielectric measurements on a set of graded concentrations of a polar solute molecule in a non-polar solvent, it is possible to carry out similar measurements on a single appropriate concentration at several frequencies [15,16], or at only two frequencies [28,29] around the frequency corresponding to maximum absorption and to determine the loss tangent (tan δ) from which both μ and τ can be evaluated. In particular, the latter method seems to be convenient in a situation where the polar substance under study is in solid phase at the temperature of measurement or the quantity is not enough, which is generally the case for liquid crystalline substances, to prepare a set of varying dilute solutions of it in a non-polar solvent. However, this procedure for the measurement of ε' and ε'' and evaluation of μ and τ values, there from, is not being widely used by the investigators. Therefore, the author feels, it is worthwhile to check the validity of this method by carrying out dielectric measurements on some polar molecules at a single frequency in the microwave region following the concentration variation method and also on a single arbitrary concentration of it that gives measurable maximum dielectric absorption at two different frequencies not well separated by each other and compare the results and draw conclusions on the basis of comparison of the results.

One of the measure concerns in the Debye theory is that it is an approximation in case of those molecules, which are not small in size where the shape of the molecules is assumed to be spherical. With this in view and in view of the considerations in the earlier paragraphs, dielectric measurements in benzene at room temperature on the pure samples of *o*-ethyl phenol, 2-*n*-butylphenol, 4-*n*-butylphenol, 2,6-dimethoxyphenol and 3,4-difluorophenol are carried out at a frequency of 9.98 GHz employing concentration variation method. Similar measurements, on a single weight fraction of each of them at 9.98 GHz and also at 8.74 GHz at the room temperature are carried out. Because of the want of enough quantity of the substance dielectric measurements only a single weight fraction in benzene of each of the liquid crystal samples, namely, EPCP.car (Butyl-*p*-(*p*-ethoxy-phenoxy corbonyl)-phenyl carbonate), PPPB (*p*-pentylphenyl-*p*-propyl benzonate), EPAP.Hp (*p*-(*p*-ethoxyphenyl azo)-phenyl heptenate) and EPAP. Und (*p*-(*p*-ethoxyphenyl azo) phenyl undecylenate) are carried out at the said two frequencies.

2. Methodology

The real and imaginary parts ε' and ε'' of the complex dielectric constant e^* ($=\varepsilon' - j\varepsilon''$) were measured by employing standing wave techniques as described earlier [1]. The static and optical permittivity of the solutes and solvents, were obtained in a routine way by using

Franklin oscillator set-up and Abbe's refractometer, respectively. The quantities X and Y required in the Gopal Krishna's method, the slopes a_0, a_∞, a' and a'', in the Higasi [11] and Higasi *et al.* [12] methods, the slope of $K'' \perp K'$ in the dielectric conductivity method to evaluate the molecular parameters μ and τ were determined by the appropriate linear plots of the dielectric parameters.

In case of Gopal Krishna method, the values of X and Y are given by,

$$X = \frac{(\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2)}{((\varepsilon' + 2)^2 + \varepsilon''^2)} \text{ and } Y = \frac{3\varepsilon''}{((\varepsilon' + 2)^2 + \varepsilon^2)}.$$

The values X and Y were determined for different weight fraction of a solute molecule W and the slopes of graph drawn X *versus* Y and X *versus* W yield $(1/\omega\tau)$ and $\{4\pi N\mu d/9\text{KTM}[1 + (\omega\tau)^2]\}$, respectively and from these μ and τ can be determined. Here d is the density of the solvent.

With very low dilution of solutes in non-polar solvents, in microwave conductivity approach, K' and K'' are defined as $(\omega\varepsilon''/4\pi)$ and $(\omega\varepsilon'/4\pi)$, respectively. With this,

$$\text{Slope of } K'' \textit{ versus } K' = \left(\frac{1}{\omega t}\right),$$

$$\text{The slope of } K' \textit{ versus } W = \frac{\omega N\mu^2 d(\varepsilon_o + 2)\omega\tau}{9\text{KTM}[1 + (\omega\tau)^2]},$$

from which μ and τ can be determined.

Higasi has proposed a method by which it is possible to examine whether the system under observation is of Debye-type or not even with dilute solution as in the present work. The results are obtained from the following equations:

$$\tau_o = \frac{1}{\omega}\left[\frac{A_2 + B_2}{C_2}\right]^{1/2(1-\alpha)} \text{ and } (1 - \alpha) = \frac{2}{\pi}\tan^{-1}\left(\frac{A}{B}\right),$$

with $A = a''\ (a_\text{o} - a_\text{d})$; $B = (a_\text{o} - a')\ (a' - a_\text{d}) - a''^2$ and $C = (a' - a_\text{d})^2 + a''^2$. Here, α is distribution parameter and τ_o is most probable or characteristic relaxation time for continuous distribution of relaxation times as defined by Cole–Cole in any dispersion region and a', a'', a_o and a_d are slopes of ε' versus W, ε'' *versus* W, ε_o *versus* W and ε_d *versus* W, respectively, with ε_o and ε_d being static dielectric constant and square of refractive index (of sodium D line), respectively of dilute solution having weight fraction W of solute in a solvent.

3. Experiment

The X band microwave setup was used to measure the dielectric constant and dielectric loss at 9.98 GHz as explained in our earlier work [1]. Microwave bench with necessary accessories supplied by Mrs Scanner Ltd, England was used to measure ε', and ε'' – the real and imaginary part of the dielectric constant. For the generation of microwave a gun oscillator supplied by Mrs Vidut Yantra Ltd, India operating in H_{01} mode was used instead of Klystron (R-302). The frequency 9.98 was fixed such that the intensity is maximum at the output. The technique adopted for these measurements was due to Wiffin and Thompson [29] modified later by Dekin and Works [31]. The static permittivities and the permittivities at optical frequencies were determined by usual manner (square of the refractive index of dilute solutions for sodium D-line), respectively, using Franklin oscillator and Abbe's refractometer. The chemicals used are of spectroscopic grade purity.

4. Results and discussion

In Table 1 a comparison of the dielectric parameters, μ and τ obtained from different methods is presented. The measured dielectric permittivities along with the determined μ and τ obtained from Wiffen and Thompson are presented in Table 2. In Figures 1–6, the plots for *o*-ethylphenol as solute molecule are presented. χ^2-test was applied for data and the errors estimated are within acceptable values. The typical value of the error for the one shown in the figures is around 3%.

The general observation from Tables 1 and 2 are presented in subsequent paragraphs. It is seen from Table 1 that there is a good agreement between τ values calculated from conductivity and Gopala Krishna's method while differing from the one obtained from Higasi *et al.*'s method. Further, the τ values obtained from this Higasi method differs and

Table 1. Values of μ and τ from different methods.

	Conductivity method		G.K. method		Higasi method		
Molecule	τ (ps)	μ (D)	τ (ps)	μ (D)	τ_o (ps)	μ (D)	α
o-Ethylphenol	2.7	1.72	2.9	1.70	5.6	2.28	0.67
2-*n*-Butylphenol	14.1	1.24	14.1	1.65	18.2	1.91	0.59
4-*n*-Butylphenol	6.3	1.51	6.7	1.38	7.6	2.04	0.23
2,6-Dimethoxyphenol	2.0	2.68	2.2	2.73	3.0	3.02	0.83
3,4-Difluorophenol	1.4	2.91	1.3	2.87	2.1	3.08	0.79

Table 2. μ and τ values by the method of Wiffen and Thompson.

				ε' and ε'' values at 8.74 GHz		ε' and ε'' values at 9.98 GHz			
Molecule	Weight fraction W	ε_o	$\varepsilon_\infty = n_d^2$	ε'	ε''	ε'	ε''	τ (P_S)	μ (D)
o-Ethylphenol	0.01404	–	–	2.3063	0.00762	2.2850	0.00851	3.1	1.70
2-*n*-Butylphenol	0.00921	–	–	2.2662	0.01402	2.2738	0.01427	15.4	1.65
4-*n*-Butylphenol	0.03014	–	–	2.2848	0.02207	2.2713	0.02400	7.2	1.38
2,6-Dimethoxy phenol	0.01129	2.4022	2.2617	2.2736	0.00869	2.3919	0.01039	2.8	2.73
3,4-Difluorophenol	0.02792	2.5386	2.2587	2.2809	0.02266	2.5103	0.02842	1.2	3.06
Butyl-*p*-(*p*-ethoxy phenoxy corbonyl)-phenyl carbonate	0.04432	2.6509	2.2533	2.2884	0.01385	2.2820	0.01562	200	2.41
p-Pentylphenyl-*p*-propyl benzonate	0.07166	2.6457	2.2688	2.3128	0.01620	2.3294	0.01846	180	1.94
p-(*p*-Ethoxyphenyl azo)-phenyl heptenate	0.04156	2.4698	2.2952	2.3444	0.01755	2.3564	0.01997	160	3.61
p-(*p*-Ethoxyphenyl azo)-phenyl undecylenate	0.03668	2.4357	2.2629	2.3135	0.01248	2.2921	0.01399	180	3.35

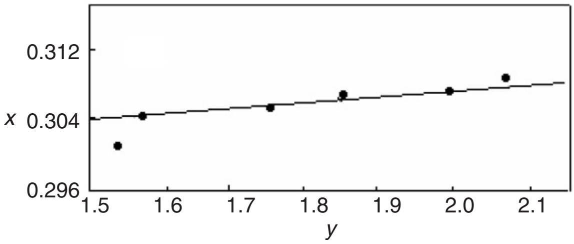

Figure 1. Plot of *X* *vs.* *Y* for *o*-ethylphenol.

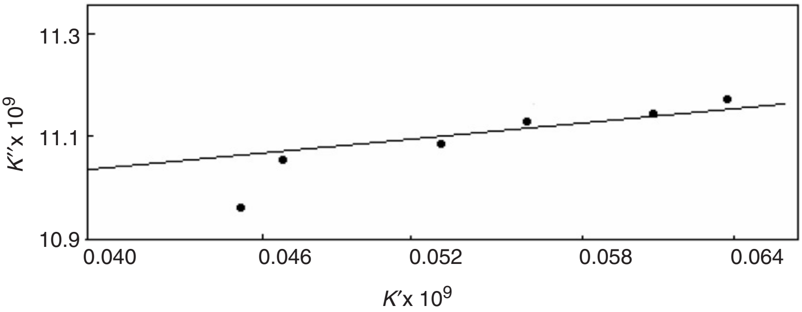

Figure 2. Plot of K' *vs.* K'' for *o*-ethylphenol.

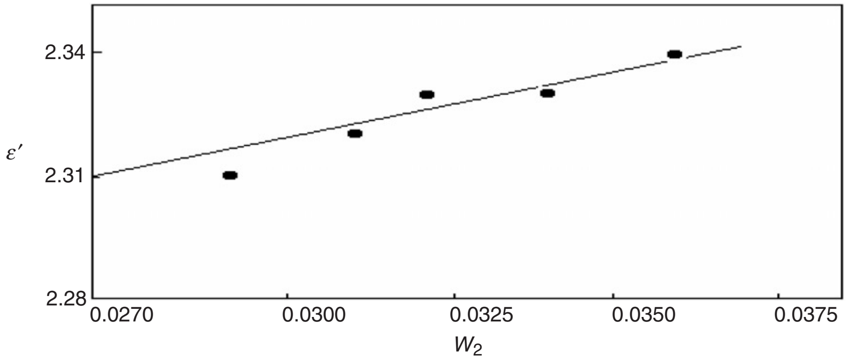

Figure 3. Plot of ε' *vs.* W_2 for *o*-ethylphenol.

the difference being well outside the experimental errors. Such a trend of variation is not unexpected because the former methods do not account for the distribution of the relaxation time whereas the latter does it. This is supported by the finite non-zero values of the distribution parameter α in all the cases as can be seen from this table.

As regards the dipole moment values of these molecules the agreement between the values obtained from Gopal Krishna and Higasi methods seems to be good if not better. A look at the last column of the Table 2 by two-frequency method tend to support that the μ values obtained are of right order. τ (1) values obtained by Higasi *et al.* [11] procedure compare well, except in the case of 2-*n*-butyl phenol with those determined by other procedures. The consistent larger τ values and higher μ values

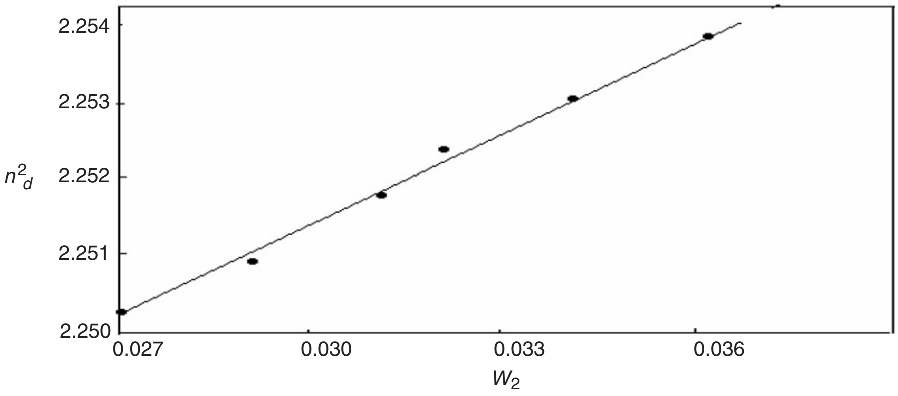

Figure 4. Plot of n_d^2 *vs.* W_2 for *o*-ethylphenol.

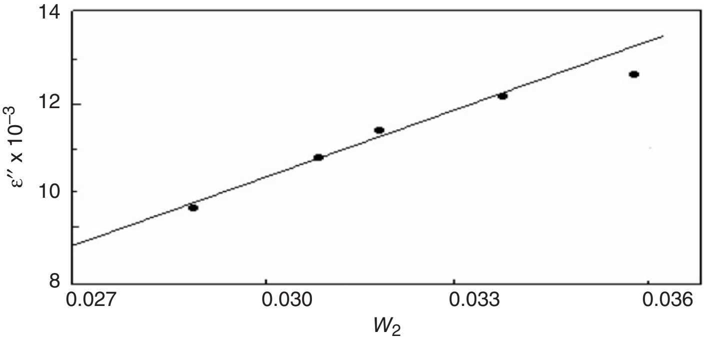

Figure 5. Plot of ε'' *vs.* W_2 for *o*-ethylphenol.

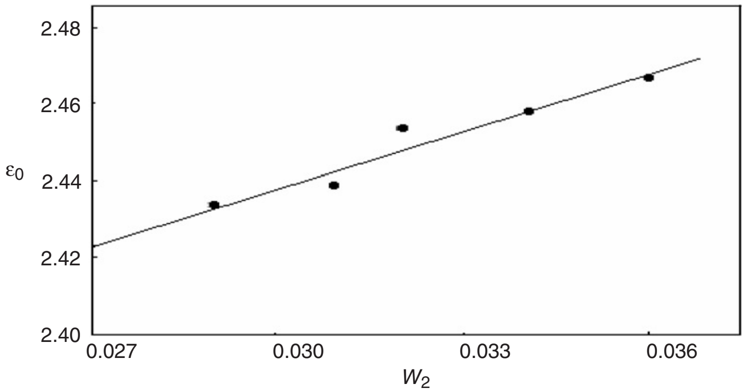

Figure 6. Plot of ε_o *vs.* W_2 for *o*-ethylphenol.

obtained in the case of Higasi procedure may partly be due to fairly large values of α around its most probable value which is not taken into account in the case of other methods. There may be some inherent inaccuracies in the determination of various slopes contradicting the requirements that these should be accurately determined.

The values of both 2-*n*-butyl, and 4-*n*-butyl phenols are longer compared to *o*-ethylphenol, which is consistent with their molecular weights. But the 2-butyl isomers have different values of τ, the difference being well outside the experimental errors, probably due to the change in the location of the dipole, another factor on which τ depends. The shorter relaxation times observed in case of 2,6-dimetoxy- and 3,4-difluoro-phenols seem to indicate that the restriction to free rotation of the methoxy and hydroxy group is not much. It is seen from Table 2 that for the substituted phenols the τ value obtained by the two-frequency-single-concentration procedure agrees quite well and is consistently closer to the τ values obtained from Gopal Krishna method. Judging from the μ values as determined by widely used Gopal Krishna method, it is seen that it decreases from 1.70 D for *o*-ethylphenol which is in excellent agreement with 1.69 D for this molecule reported in the literature [33], to 1.38 D for *n*-butylphenol via 1.65 D for 2-*n*-butylphenol. This may be partly due to possible inductive effects. The group moments of –OH, –OCH_3 and –F dipoles are reported to be in the order [33] 1.6 D, 1.25 D and 1.46 D, respectively, while their inclinations to the molecular axis in the order 62°, 55° and 0°, respectively. The observed value of 2.73 D and 2.87 D in case of 2,6-dimetoxy- and 3,4-difluoro-phenols, respectively, seems to be of right order of magnitude when compounded vectorially.

As regards the liquid crystalline molecules the values (Table 2) seems to be of right order in view of their chemical structures and the general observation made by Higasi [11] that two ring (benzene) systems would have τ values in the range of 16–30 ps and also these values lend support from the values of τ for some other thermo tropic nematic liquid crystals in their isotropic phase reported. For example the value of τ for p-azoxy anisole is in the range of 23–32 ps [41,42]. These values vary according to their molecular weights. For the two molecules EPAP.Hp and EPAP.Und the observed values in the present investigation seem to be larger. But such a situation is not uncommon in the literature. Since the τ values of these liquid crystal materials in their isotropic phase/dilute solution do not seem to have been reported in the literature as far as the author is aware. Therefore, it may be said that the values are of right order. But the observed values do not support this point and indicate that this method gives physically meaningless results. But, the ground state dipole moment values for these molecules determined by an independent method (modified Guggenheim) reported elsewhere [2] do not seem to contradict these values if not supporting them. Thus, it may be said that the single concentration – two-frequency method can serve as giving some qualitative trends. Further, in view of the several approximations made such as the molecule conform to Debye theory of single relaxation time and arbitrariness involved in selecting the single concentration, the results may be taken to give the results at least of right order of magnitudes.

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