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Dielectric behavior of some mesogenic-, non-mesogenic- and organic molecules

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Abstract

Dielectric behavior of some mesogenic and non-mesogenic compounds is presented and discussed from the data obtained using microwave frequency 9.98 GHz and 8.74 GHz by applying the Higasi method. The results are compared with earlier results obtained by different methods wherever available. 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 dilute solution phase are greatly reduced and also permit us to study the effect of viscosity on the molecular parameters, in addition to the effect of temperature only in the case of pure liquids.

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1. Introduction

Dielectric approach is a powerful tool for the determination of molecular structure [1–28]. 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 to these compounds rather than an improbable bicyclic structure [2–5]. The dielectric relaxation time τ and electric dipole moment μ are the two important molecular parameters that are helpful in understanding the structure, size, shape of the molecules: the inter-, and intra-, molecular forces etc. In particular the relaxation time τ can be evaluated by measuring the high frequency dielectric permittivity, ε', ε'' at either different frequencies, different temperatures, of pure liquids or at different concentrations of a polar molecule in a non-polar solvent. Such studies have the advantage over those on pure liquids that the strong dipole–dipole interactions in dilute solution phase are greatly reduced and they also permit us to study the effect of viscosity on the molecular parameters, in addition to the effect of temperature only in the case of pure liquids.

By assuming that the behavior of the dilute solutions conforms closely to that predicted by the Debye theory, the two molecular parameters μ, τ can be evaluated by the concentration variation method due to Gopalakrishna [6], slope methods due to Higasi [7], Higasi et al [8], dielectric conductivity methods due to Acharya and Chatarjee [9], Murthy et al [10], and also a method due to Jai Prakash [11] based on the Frolich equation. 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 [12,13], or at only two frequencies [14,15] 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 later method seems to be convenient in a situation where the polar substance under study is solid phase at the temperature of measurement or the quantity is not sufficient, to prepare a set of varying dilute solutions in a non-polar solvent which is generally the case for liquid crystalline substances.

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Table 1

Molecule	Conductivity method		Gopalkrishna method		Higasi method		
	$\tau(p_S)$	μ(D)	$\tau(p_S)$	μ(D)	$\tau_o(p_S)$	μ(D)	α
2-chloro thiophene	1.3	1.7	1.5	1.74	3.2	2.01	0.82
2-chloro-6-fluro benzaldehyde	6.1	2.82	6.9	3.26	13.1	3.74	0.51
p-flurophenyl acetonitrile	3.5	1.98	2.9	2.53	3.8	3.31	0.79
2-methyl benzoxazole	3.2	2.00	2.8	2.07	3.6	2.56	0.71
p-bromo-nitro benzene	5.8	1.38	7.5	2.10	8.7	2.92	0.82
Diphenyl sulfone	3.7	3.66	3.8	3.42	7.3	4.61	0.56

However, this procedure for the measurement of ε′and ε″ and evaluation of μ and τ values, therefrom, is 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 from each other and compare the results and draw conclusions on the basis of comparison of the results.

In view of the above considerations, dielectric measurements in benzene at room temperature on the pure samples of 2-chlorothiophene, 2-chloro-6-fluoro-benzaldehyde, *p*-fluorophenyl aceto-nitrile, 2-methyl benzoxazole, *p*-bromo nitrobenzene, *m*-bromo nitrobenzene and diphenyl sulfone are carried out at a frequency of 9.98 GHz employing the concentration variation method. Similar measurements, on a single weight fraction of each of them at 9.98 GHz and also at 8.74 GHz both at the room temperature are carried out. Because of the want of sufficient quantity of the substance dielectric measurements on a single weight fraction in benzene of each of the liquid crystal samples, namely, H_XOAB (4, 4′-Bis (hexyloxy)-azoxy benzene), H_POAB (4, 4′-Bis (heptyloxy)-azoxy benzene), POAB (4, 4′-Bis (pentyloxy)-azoxy benzene) and OBBA (4-*n*-octyloxy benzylidene-4-butyl aniline) are carried out at the chosen two frequencies and temperature.

2. Experiment and methodology

The real and imaginary parts ε′ and ε″ of the complex dielectric constant $\varepsilon^*(=\varepsilon'-j\varepsilon'')$ were measured by employing standing wave techniques as described earlier [16]. The static and optical permittivity of the solutes and solvents were obtained in a routine way by using a Franklin oscillator set-up and an Abbe refractometer, respectively. The quantities X and Y required in Gopalakrishna's method, the slopes a_0, a_∞, a' and a'' in the Higasi and Higasi et al 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 the Gopalkrishna method, the values of X and Y are given as follows,

$$X = (\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2)/((\varepsilon' + 2)^2 + \varepsilon''^2);$$

$$Y = 3\ \varepsilon' \ / \ ((\varepsilon' + 2)^2 + \varepsilon''^2)$$

The values X and Y were determined for different weight fractions of a solute molecule W and the slopes of the graphs X vs. Y and X vs. W yielding $(1/\omega\ \tau)$ and $(4\pi N\mu d/9KTM(1+(\omega\ \tau)^2))$, respectively, and from these μ and τ can be determined. d is the density of the solvent.

At 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

$$\text{slope of } K'' \ vs.\ K' = (1/\omega\tau)$$

$$\text{slope of } K' vs.\ W = (\omega N\mu^2 d(\varepsilon_o + 2)\omega\tau \ / \ 9KTM(1 + (\omega\tau)^2)),$$

μ and τ can be determined.

Higasi [7] has proposed a method, with which it is possible to examine whether the system under observation is of Debye

Table 2

Molecule	Weight fraction W	ε_o	$\varepsilon_\infty = n_d^2$	ε′ and ε″ values at 8.74 GHz		ε′ and ε″ values at 9.98 GHz		$\tau(p_S)$	μ(D)
				ε′	ε″	ε′	ε″		
2-chloro thiophene	0.01590	–	–	2.3511	0.008605	2.3361	0.009693	2.1	1.88
2-chloro-6-fluro benzaldehyde	0.00865	2.5172	2.2602	2.2981	0.02726	2.5488	0.03339	6.4	3.14
p-flurophenyl acetonitrile	0.01285	2.4751	2.2596	2.3971	0.1607	2.4463	0.01852	3.5	2.54
2-methyl benzoxazole	0.01214	2.3609	2.2593	2.2990	0.008737	2.2832	0.009836	2.8	2.19
p-bromo-nitrobenzene	0.01795	2.4188	2.2619	2.2828	0.01914	2.2670	0.02106	6.2	1.96
m-bromonitro benzene	0.01405	2.4846	2.2641	2.2704	0.03207	2.3522	0.03711	5.2	3.03
Diphenyl sulfone	0.01176	–	–	2.2324	0.02263	2.3075	0.02627	4.0	3.42
4,4′Bis(hexyloxy)-azoxy benzene	0.02070	2.5171	2.2598	2.3231	0.009418	2.2879	0.01051	11.0	4.91
4, 4′-Bis (heptyloxy)-azoxy benzene	0.03015	2.3990	2.2563	2.3132	0.009739	2.3322	0.01108	25.0	2.90
4, 4′-Bis (pentyloxy)-azoxy benzene	0.04593	2.4278	2.2599	2.2847	0.007012	2.2703	0.007906	3.0	4.98