

Relaxation behaviour of phenol and cresols in highly viscous media

MRADULA CHAUHAN, MRIDULA GUPTA, S K SAXENA*
and J P SHUKLA

Physics Department, Microwave and EPR Lab.
Lucknow University, Lucknow 226 007, India

*Present address: D B S College, Kanpur, India.

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Abstract. Dielectric relaxation times (τ) have been determined for phenol, *o*-cresol, *m*-cresol and *p*-cresol in solutions of *n*-heptane + paraffin oil of varying viscosities. Since, all the four systems contain an -OH group, capable of group rotation, the dielectric absorption was further resolved using Higasi, Koga and Nakamura method in terms of $\tau(1)$ and $\tau(2)$. In each case the dielectric relaxation time has been found to be maximum in the neighbourhood of 75% *n*-heptane+25% p.o. in the mixture. On further increasing the viscosity of the medium, the τ values shorten. The results obtained suggest the associative nature of the compounds investigated.

Keywords. Distribution function; dielectric dispersion.

1. Introduction

The influence of association by hydrogen bonding on the structure of liquids and their relaxation behaviour has been extensively studied by Pimental and McClellan (1960). Phenols are among the systems characterised by the self association due to hydrogen bonding. The dielectric technique has been applied by Magee and Walker (1966, 1971) for studying the associative nature of phenol at microwave frequency. The lengthening of the relaxation times in these systems has been attributed to either the solute-solute interaction or the hydrogen bonding of the solute molecule with the solvent (*p*-xylene).

Dielectric investigations of the associative type molecules in highly viscous media had been comparatively limited. Studies by Grubb and Smyth (1962) and Saxena *et al* (1980), on the relaxation behaviour of several molecules in dilute solutions in viscous media, show considerable deviation from the straight line characteristics between $\log \tau$ vs. $\log \eta$. The effect of macroscopic viscosity (η) on τ for a mixture of 1-butanol and 1-decanol in paraffin oil and *n*-heptane, has been studied by Srivastava and Crossley (1976a). In an attempt to extend these studies on the associative systems dielectric investigations were carried out on phenol, ortho-meta-and para-cresol molecules in dilute solutions of *n*-heptane + paraffin oil. The relaxation parameters were determined by using the methods of Gopala Krishna (1957), Higasi (1966) and Higasi *et al* (1971). The associative nature of the molecules has been discussed in terms of the observed relaxation parameters.

2. Experimental

The dielectric constant ϵ' and dielectric loss ϵ'' have been measured at x -band (9.8 GHz) and temperature 308 K by the technique of Roberts and von Hippel (1946), later modified by Dakin and Works (1947). The refractive indices (n_D) of different dilute solutions at optical frequency and static dielectric constant ϵ_0 at 300 kHz have been measured by Abbe's refractometer and RLO9 dipole meter, based on heterodyne beat principle respectively. The ϵ' and ϵ'' values were accurate upto $\pm 2\%$ and $\pm 5\%$ respectively. Average viscosity of the six solutions has been determined using Ostwald viscometer.

The chemicals phenol *o*-, *m*- and *p*- cresols have been obtained from BDH England. Solvent *n*-heptane and paraffin oil have been obtained from Sarabhai chemicals and Liberty Pharmaceuticals, respectively.

Five solvents of varying viscosity have been prepared in the following percentage by volume (i) pure *n*-heptane, (ii) 75% *n*-hep. + 25% p.o., (iii) 50% *n*-hep. + 50% p.o., (iv) 25% *n*-hep. + 75% p.o., (v) pure paraffin oil.

The relaxation time τ_G was determined using the Gopala Krishna method (1957) and the most probable relaxation time τ_{OH} and distribution parameter (a) were evaluated using the Higasi (1966) equations. The details of the determination of the parameters were given by Saxena *et al* (1980). The dielectric dispersion has been further resolved using the method of Higasi *et al* (1971), which gives relaxation times $\tau(1)$ and $\tau(2)$, defined as

$$\tau(1) = \frac{1}{\omega} \cdot \frac{a''}{a' - a_\infty},$$

$$\tau(2) = \frac{1}{\omega} \cdot \frac{a_0 - a'}{a''},$$

where $\tau(2)$ represents the molecular relaxation time and $\tau(1)$ is an explicit function of the molecular τ_1 and intramolecular τ_2 relaxation time as represented by the Cole-Cole relation. The average relaxation time $\tau(0) = (\tau(1) \cdot \tau(2))^{1/2}$. According to Higasi a wide separation in the values of $\tau(1)$ and $\tau(2)$ indicates the existence of more than one relaxation process in the system.

The apparent dipole moment has been calculated using the method of Koga *et al* (1973).

3. Results and discussion

The slopes a_0 , a' , a'' and a_∞ obtained from the linear plots of ϵ_0 , ϵ' , ϵ'' and ϵ_∞ against the weight fractions have been found to be constant and the values for all the compounds investigated have been reported in table 1. The relaxation time parameters, distribution function (a), viscosity (η) of the solution and the dipole moment (μ) have been given in table 2.

The average relaxation times $\tau(0)$, τ_{OH} and τ_G have been found to vary in the

Table 1. Slopes of dielectric constants against weight fractions (range is given in the bracket).

Solvent	n -hep. %	+	p.o. %	a_0	a_∞	a'	a''
Phenol (0.039–0.088)							
	100		00	3.6	0.40	3.0	0.88
	75		25	3.0	0.25	1.7	0.80
	50		50	3.0	0.60	2.0	0.68
	25		75	3.3	0.80	2.4	0.86
	00		100	3.2	0.90	2.2	0.58
<i>o</i> -cresol (0.032–0.084)							
	100		00	3.0	0.38	2.25	0.68
	75		25	3.1	0.96	2.03	0.62
	50		50	3.1	0.54	2.00	0.69
	25		75	3.7	0.73	2.50	0.79
	00		100	3.3	0.73	2.00	0.65
<i>m</i> -cresol (0.033–0.080)							
	100		00	2.9	0.41	1.80	0.80
	75		25	3.4	0.58	1.80	0.88
	50		50	3.2	0.42	2.00	0.75
	25		75	2.8	0.62	1.90	0.55
	00		100	2.8	0.42	1.60	0.60
<i>p</i> -cresol (0.035–0.084)							
	100		00	2.6	0.70	1.60	0.68
	75		25	3.0	0.65	1.50	0.80
	50		50	3.0	0.47	1.70	0.73
	25		75	2.9	0.58	1.80	0.63
	00		100	3.6	0.60	2.00	0.78

order, phenol < *o*-cresol < *m*-cresol < *p*-cresol. This is in accordance with the size and shape of the molecule and agrees well with the studies of Singh and Vij (1975), on substituted benzaldehydes. It may be seen from table 2 that (with increasing η) in lower viscosity region the relaxation time lengthens and approaches a maximum value in neighbourhood of the solvent having concentration 75% *n*-hep. + 25% p.o. On further increasing η , the relaxation time shortens with a minimum occurring at the concentration of 25% *n*-hep. + 75% p.o.. A slight lengthening is observed in the case of pure paraffin oil solvent. This non-linearity of relaxation behaviour with respect to η indicates the possibility of self association of phenol and cresol molecules in the medium.

The group relaxation for non-associative systems, having a common rotating group would be expected to yield almost similar relaxation times in different media (Balogun and Cumper 1973; Srivastava and Crossley 1976b). This varies slightly with viscosity. The range of $\tau(1)$ values is (5.3 – 9.0 ps) for phenol, (5.9 – 9.5 ps) for *o*-cresol, (7.0 – 11.7 ps) for *m*-cresol and (8.4 – 15.3 ps) for *p*-cresol in dilute solutions of the five solvents (cf. table 2). Like other relaxation times, $\tau(1)$ also exhibits a maximum at the concentration 75% *n*-hep. + 25% p.o.

Similar irregular behaviour is also observed in the case of molecular relaxation time $\tau(2)$. The $\tau(1)$ and $\tau(2)$ values are sufficiently different from each other showing

Table 2. Relaxation times (τ), distribution parameter (α) and dipolemoments (μ) of the compounds and viscosity (η) of solutions at 308 K.

Solvent		η mp	Higasi <i>et al.</i>		$\tau(0)$ ps	Higasi		Gopala Krishna	
<i>n</i> -hep. + p.o. %	p.o. %		$\tau(1)$ ps	$\tau(2)$ ps		τ_{OH} ps	α	τ_G ps	μ <i>D</i>
Phenol									
100	0	4.7	5.3	11.1	7.8	5.2	0.17	6.2	1.68
75	25	7.3	9.0	26.4	15.4	14.4	0.33	10.2	1.69
50	50	13.3	7.9	23.9	13.7	11.1	0.33	7.9	1.82
25	75	43.3	7.5	17.0	11.3	10.1	0.20	6.0	1.50
0	100	127.4	7.2	28.0	14.2	11.5	0.40	6.7	1.22
<i>o</i> -cresol									
100	0	4.8	5.9	17.9	10.3	6.1	0.31	6.9	1.73
75	25	6.7	9.5	28.0	16.3	16.4	0.33	11.5	2.00
50	50	16.3	7.7	25.9	14.1	11.5	0.36	8.6	1.56
25	75	44.9	7.2	24.7	13.3	10.2	0.36	6.5	1.70
0	100	234.6	8.3	32.5	16.4	16.8	0.40	7.8	1.62
<i>m</i> -cresol									
100	0	4.9	9.3	22.3	14.4	13.0	0.27	8.3	1.72
75	25	6.9	11.7	29.5	18.6	21.3	0.28	12.6	1.88
50	50	17.3	7.8	26.0	14.2	11.6	0.36	6.3	1.35
25	75	59.9	7.0	26.6	13.6	10.3	0.39	4.9	1.68
0	100	362.0	8.3	32.5	16.4	16.6	0.41	6.3	1.31
<i>p</i> -cresol									
100	0	5.8	12.3	23.9	17.1	17.7	0.21	10.2	1.79
75	25	8.7	15.3	30.5	21.6	34.5	0.21	14.4	1.91
50	50	22.8	9.6	28.9	16.7	17.6	0.33	9.6	1.72
25	75	60.5	8.4	28.4	16.4	14.3	0.37	7.2	1.80
0	100	419.2	9.0	33.3	17.3	20.4	0.39	6.2	1.70

the non-rigidity of solute molecule in the viscous media. Further the higher value of the distribution function (α) also suggests this flexible nature and self association. The amount of aggregation produced in the system is perhaps higher in the low viscosity region (75% *n*-hep. + 25% p.o.), thus the lengthening of the relaxation times occur.

The dipole moments of the phenol and cresol molecules determined by using the method of Koga *et al* (1973) show similar behaviour as exhibited by the average relaxation times of solutes. However, after approaching a maximum in lower viscosity region, μ exhibits an irregular behaviour. The observed variation in μ also suggest the intermolecular H-bonding with maximum aggregation around 75% *n*-hep. + 25% p.o. concentration.

4. Conclusion

It is observed that phenol, *o*-cresol, *m*-cresol and *p*-cresol exhibit varying association due to different amounts of aggregation in various solvents. This association appears to be high in the neighbourhood of solvent of concentration 75% *n*-hep. + 25% p.o.

as seen from the observed large values of α , μ and longer τ values. On further increasing η the relaxation time shortens. This shortening of τ in the higher viscosity region may be attributed to either in-rupturing or weakening of the H-bonds (due to self association).

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