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Macroscopic Viscosity and Dielectric Relaxation Process of Ethyl and Butyl Acetates

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Dielectric constants and losses have been measured at 9.8 GHz microwave frequency for ethyl and butyl acetates in benzene and benzene–paraffin oil mixtures at 18 °C. The data obtained has been analysed in terms of the two relaxation times $\tau_{(1)}$ and $\tau_{(2)}$ using Higasi, Koga, and Nakamura method and their dependence on the viscosity has been examined. Since the observed values of $\tau_{(1)}$ and $\tau_{(2)}$ are significantly different, the systems studied represent two Debye type dispersions. It has been found that the relaxation behaviour giving rise to $\tau_{(1)}$ in both the ester molecules is not effected to any appreciable extent by the increased macroscopic viscosity. The dielectric relaxation time $\tau_{(2)}$ associated with the molecular process lengthens with the increasing macroscopic viscosity of the medium.

Dielectric relaxation process in aliphatic esters (acetates) have been studied by a number of workers[1–5] both in pure liquids and in solutions. The absorption process in these systems have been attributed to the molecular as well as the group rotations. Dependence of the dielectric relaxation time on the viscosity of the medium has been extensively examined by several workers[6–10] and various empirical relations have been proposed. Grubb and Smyth[11] studied some substituted naphthalene, anisole, primary and secondary amines and diamines in paraffin oil and have estimated the relaxation times τ_1 and τ_2 associated with the molecular and group processes. The enthalpies were evaluated for methyl iodide, chlorobenzene, cyanocyclopropane *etc.* by Balogun and Cumper[12] using benzene+liquid paraffin oil as solvents. In study, Crossley and Srivastava[13] reported the value of 'x' $(=\Delta H_\eta/\Delta H_\varepsilon)$ for acetophenone, anisoles, bromobenzene, and *p*-dimethoxybenzene in the mixture of solvents, paraffin oil and heptane, and paraffin oil and hexadecane. Recently in another study[14] using solvent of high viscosity they have resolved the dielectric data of 1-butanol and 1-decanol into two relaxation process (τ_1) and (τ_2). It has been observed that molecular relaxation time changes rapidly with the changing viscosity of the solvent–solute mixture. However, the relaxation time (τ_2) practically remains constant. The effect of the macroscopic viscosity of the solvent on the process which probably arises from the group rotation have been examined only for a few cases with varying high viscosity.

Aliphatic esters have been examined for their dielectric behaviour using various methods.[1–5] The investigations were however confined only to the studies relating to the relaxation mechanism and their structure. It was, therefore, considered worthwhile to examine ethyl acetate and butyl acetate in the solvent mixtures of paraffin oil and benzene which provide a high viscous medium for the dipolar rotations. The dielectric data was resolved into two absorption processes, $\tau_{(1)}$ being an implicit function of τ_1 and τ_2 and weight factor C_1 and $\tau_{(2)}$ associated with the molecular process and the effect of macroscopic viscosity on $\tau_{(1)}$ has been examined. This has been found to be in agreement with the earlier studies of Crossley *et al.*[14] on 1-butanol and 1-decanol.

Experimental

The dielectric constant ε' and dielectric loss ε'' have been measured at x-band at frequency 9.8 GHz by the technique of Robert and von-Hippel[15] as modified by Dakin and Works.[16] The refractive indices of different dilute solutions at infinite frequency was measured by Abbe's refractometer. The dielectric constant at infinite frequency was obtained by squaring the refractive indices of different dilute solutions respectively. The possibility of Poley absorption is ruled out as the microwave frequency used for the measurement is comparatively much low. The static dielectric constant have been measured by the calibrated dipolemeter based on the principle of heterodyne beat method. The measurement of ε' and ε'' are accurate upto ±2% and ±5% respectively.

Average viscosity of the solvent solute mixture was obtained by taking the mean of six values for a group of solutions of various solvents obtained by measuring the fall time of liquid in the capillary of the Ostwald's viscometer.

Chemicals. The chemicals used were of purest quality available, both the ethyl acetate and butyl acetate were obtained from the British Drug House (Ltd.) England. The physical properties of both the esters were checked against the literature values. The solvent benzene were distilled twice before use. The benzene (A. R. grade) was obtained from B. D. H. (England) and medicinal liquid paraffin oil was obtained from Liberty Pharmaceutical (Ltd.) Bombay (India). The mixture of benzene and paraffin oil in the following percentage were used as solvent for the measurements.

1: 100% paraffin oil
2: 10% benzene+90% paraffin oil
3: 20% benzene+80% paraffin oil
4: 30% benzene+70% paraffin oil.

Theory: The slopes a_0, a', a'', and a_∞ have been obtained by plotting the weight fraction *versus* ε_0, ε', ε'', and ε_∞ for both the compounds. The values have been reported in Table 1. The slopes are defined by the set of Eq. 1.

$$\begin{aligned}\varepsilon_0 &= \varepsilon_{10} + a_0 W_2\\ \varepsilon' &= \varepsilon_1' + a' W_2\\ \varepsilon'' &= a'' W_2\\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty W_2.\end{aligned} \tag{1}$$

The subscripts 1 and 2 refer to pure solvent and solute respectively. Similarly ε_∞ refers to the dielectric constant at infinite frequency. ε_0 is the dielectric constant at static field and W_2 is weight fraction of the solute.

The most probable relaxation time τ_{OH} and the distribution

Table 1. The slopes a_0, a', a'', and a_∞ for ethyl and butyl acetate in benzene and paraffin oil (p.o.) mixture at 18 °C

Compound	Concentration	a_0	a'	a''	a_∞
(A) Ethyl acetate	100% p.o.	3.33	2.66	1.05	−0.28
	90% p.o. + 10% benzene	2.86	2.35	0.95	−0.26
	80% p.o. + 20% benzene	2.50	2.12	0.80	−0.256
	70% p.o. + 30% benzene	2.20	1.90	0.70	−0.25
(B) Butyl acetate	100% p.o.	2.96	2.10	1.00	−0.265
	90% p.o. + 10% benzene	2.58	1.80	0.83	−0.25
	80% p.o. + 20% benzene	2.12	1.50	0.70	−0.21
	70% p.o. + 30% benzene	1.74	1.30	0.55	−0.19

Table 2. Distribution parameter 'α', most probable relaxation time τ_{OH} by Higasi method, $\tau_{(1)}$, $\tau_{(2)}$, and $\tau_{(0)}$ obtained by Higasi, Koga, and Nakamura method and dipole moment at 18 °C

Compound	Concentration	α	η poise	τ_{OH} ps	$\tau_{(1)}$ ps	$\tau_{(2)}$ ps	$\tau_{(0)}$ ps	μ(D) expt Debye	μ(D) Lit.
(A) Ethyl acetate	100% p.o.	0.14	0.233	5.7	5.8	10.5	7.8	1.81	1.86
	90% p.o. + 10% benzene	0.12	0.070	5.4	5.7	9.3	7.2	1.76	
	80% p.o. + 20% benzene	0.07	0.038	5.3	5.5	7.8	6.6	1.66	
	70% p.o. + 30% benzene	0.06	0·024	5.1	5.3	7.0	6.1	1.56	
(B) Butyl acetate	100% p.o.	0.25	0.240	7.1	6.9	16.3	10.6	1.98	1.84
	90% p.o. + 10% benzene	0.24	0.090	6.8	6.6	15.5	10.1	1.80	
	80% p.o. + 20% benzene	0.22	0.059	6.6	6.5	14.6	9.7	1.65	
	70% p.o. + 30% benzene	0.20	0.025	6.1	6.1	13.1	8.9	1.45	

parameter 'α' have been calculated from the Eq. 2, given by Higasi *et al.*[17)]

$$\tau_{OH} = \frac{1}{W}\left[\frac{A^2+B^2}{C^2}\right]^{1/2(1-\alpha)}$$
$$1-\alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B}, \tag{2}$$

where

$$A = a''(a_0-a_\infty)$$
$$B = (a_0-a')(a'-a_\infty) - a''^2 \tag{3}$$
$$C = (a'-a_\infty)^2 + a''^2.$$

Having obtained the appreciable value of distribution parameter 'α', the dielectric relaxation mechanism has been further resolved by Higasi, Koga, and Nakamura method[18)] in terms of the two relaxation times $\tau_{(1)}$ and $\tau_{(2)}$ defined by the Eqs. 4 and 5:

$$\tau_{(1)} = \frac{1}{W}\frac{a''}{(a'-a_\infty)}, \tag{4}$$

$$\tau_{(2)} = \frac{1}{W}\frac{(a_0-a')}{a''}. \tag{5}$$

The slopes a_0, a', a'', and a_∞ are defined by the set of Eq. 1. The average probable relaxation time $\tau_{(0)}$ is obtained by the geometrical mean of $\tau_{(1)}$ and $\tau_{(2)}[\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}}]$.

The apparent dipole moment was calculated by Higasi's method[19)] employing Eq. 6.

$$\mu^2 = \frac{27kT}{4\pi N}\frac{M_2}{d_1}\frac{a_0-a_\infty}{(\varepsilon_1'+2)^2}$$
$$= B^2(a_0-a_\infty), \tag{6}$$

where

$$B = \left\{\frac{27kTM_2}{4\pi Nd_1}\right\}^{1/2}\frac{1}{(\varepsilon_1'+2)}$$

M_2 is the molecular weight of the substance and d_1 is the density of the solvent, and other symbols have their usual meaning.

Discussion

(A) Ethyl Acetate. An examination of Table 2 shows that the distribution parameter 'α' for ethyl acetate has a variation (0.14—0.06) when the concentration of paraffin oil varies from 100% to 70% in benzene. The highest value of distribution parameter 'α' is 0.14 in 100% p.o. and the lowest value, 0.06 has been observed in 70% p.o. in benzene. These observations are in agreement with the earlier investigations of Smyth *et al.*[1)] The appreciable value of the distribution parameter 'α', indicates the existence of more than one relaxation process occurring in the system. The most probable relaxation time τ_{OH} evaluated using Higasi method[17)] has been found to vary from 5.1—5.7 ps in the range of concentration changing from 70% p.o. in benzene to 100% p.o. The dielectric

dispersion has been further resolved by Higasi, Koga, and Nakamura method,[18] into two separate processes which gave rise to two relaxation time $\tau_{(1)}$ and $\tau_{(2)}$. $\tau_{(1)}$, which is related to the group process has been found to vary from 5.3—5.8 ps when the concentration varies from 70% p.o. in benzene to 100% p.o. $\tau_{(2)}$, which represent the molecular process has been found to vary from 7.0—10.5 ps in the same concentration range. The average relaxation time $\tau_{(0)}=\sqrt{\tau_{(1)}\tau_{(2)}}$ for the overall process was found to vary from (6.1—7.8 ps). An examination of Table 2 reveals that the relaxation time $\tau_{(1)}$ associated with the group process for all the concentrations remains almost constant, whereas, the other relaxation time $\tau_{(2)}$ related to the molecular process varies appreciably with the concentration of the solvent. These results are in agreement with the previous studies of Srivastava and Crossley[14] on alcohols and of Grubb and Smyth[11] on substituted anisoles, naphthalene, and substituted amines. It has also been observed that $\tau_{(0)}$ the average relaxation time is slightly greater than the most probable relaxation time τ_{OH}. They are consistent with the previous observation of Higasi *et al.*[5] on alkyl acetates.

The dipolemoment of the compound has been calculated in various solvents. It has been observed that the dipolemoment varies from 1.56—1.81 D for the concentration of p.o. varying from 70% p.o. to 100% p.o. These values are not much different from the literature value[20] of dipolemoment (=1.86 D) for ethyl acetate in solution. The value is highest in 100% p.o. and is decreasing with the dilution of paraffin oil with benzene. This is in agreement with the reports on similar data by Srivastava and Crossley[14] for 1-butanol and 1-decanol in paraffin oil and heptane mixture.

(B) Butyl Acetate. The distribution parameter 'α' for butyl actate shows variation (0.20—0.25) in the concentration range of 70% p.o. in benzene to 100% p.o. The 'α' values are found to decrease with the dilution of paraffin oil with benzene, which is in agreement with the previous study by Smyth *et al.*[1] The most probable relaxation time τ_{OH} has been found to vary from 6.1—7.1 ps, while the concentration of paraffin oil and benzene mixture changes from 70% p.o.+30% benzene to 100% p.o. The most probable relaxation time τ_{OH} for butyl acetate is found to be longer than ethyl acetate. This is as expected due to the bigger size of this molecule. On further resolving the absorption by Higasi, Koga, and Nakamura method[18] the two relaxation times obtained were $\tau_{(1)}$ (=6.1—6.9 ps) and $\tau_{(2)}$ (=13.1—16.3 ps) in the concentration range used. The two distinct values for $\tau_{(1)}$ and $\tau_{(2)}$ indicate the existence of two distinct relaxation processes in the system. It has been observed that $\tau_{(1)}$ for butyl acetate is longer than $\tau_{(1)}$ for ethyl acetate for the same concentration range. This is as expected since $\tau_{(1)}$ arises perhaps from the rotation of the heavier group-C_4H_9 around the carbon–carbon bond. Similar results were reported by Grubb and Smyth[11] on α- and β-methoxy- and ethoxy-naphthalenes in the solution of decalin and Nujol. Further it is observed that the relaxation time $\tau_{(1)}$ is practically constant with the varying macroscopic viscosity of the solvent, which is in agreement with the earlier investigations of Srivastava and Crossley[14] on alcohols and Grubb and Smyth[11] on amines, naphthalene, and anisole.

$\tau_{(2)}$ and $\tau_{(0)}$ both are found to be larger for butyl acetate than the values obtained for ethyl acetate in the same concentration range. This follows the usual dependence on the shape and size of molecules in process.

The dipolemoment in the various solvents have been calculated by Higasi method.[19] It is found to vary from (1.45—1.98 D) when the concentration varies from 70% p.o. in benzene to 100% p.o. The value resembles well within the experimental error from the literature value[20] 1.84 D for the butyl acetate in the solution. The highest value for dipolemoment was observed in 100% p.o. which is decreasing with the dilution of paraffin oil with benzene.

A graph has drawn between log $\tau_{(1)}$ and log η_s and log $\tau_{(2)}$ and log η_s (Figs. 1 and 2). It has been observed that the relaxation time $\tau_{(1)}$ is practically constant with the macroscopic viscosity of solvent and solute. A line of greater slope has been observed for $\tau_{(2)}$ showing that molecular relaxation time is varying appreciably with the viscosity for both the ester molecules. It is in agreement with the earlier observations by several workers.[11,14,21]

Conclusion

The microwave absorption studies on ethyl and butyl acetates in high viscous solvents exhibit a flexible behaviour. The two relaxation time $\tau_{(1)}$ and $\tau_{(2)}$ for both the systems have been found to be appreciably distinct. The effect of average macroscopic

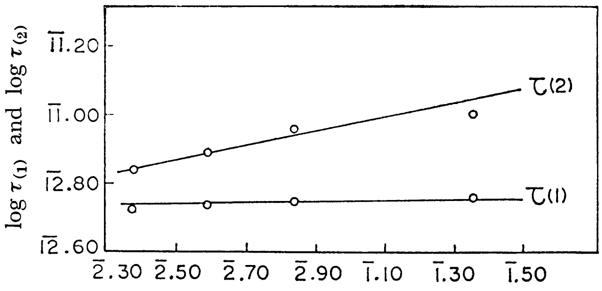

Fig. 1. Plot of log $\tau_{(1)}$ and log $\tau_{(2)}$ *vs.* log η_s (ethyl acetate).

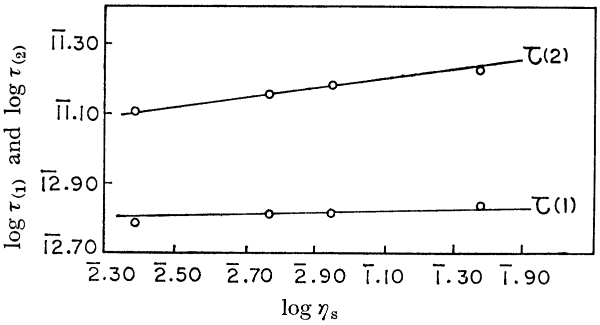

Fig. 2. Plot of log $\tau_{(1)}$ and log $\tau_{(2)}$ *vs.* log $\eta_{(s)}$ (butyl acetate).

viscosity of the medium has been observed for both the molecules. $\tau_{(1)}$ for ethyl acetate varies from (5.3—5.8 ps) while the viscosity changes from (0.024—0.233 poise). $\tau_{(2)}$ for the same system changes from (7.0—10.5 ps). Similarly for butyl acetate, $\tau_{(1)}$ has been found to be slightly longer, in the range 6.1 to 6.9 ps for the viscosity variations from 0.025 to 0.243 poise whereas $\tau_{(2)}$ varies from 13.1 ps to 16.3 ps. This clearly indicates that $\tau_{(1)}$ for both the systems practically remains constant with the macroscopic viscosity of the medium whereas $\tau_{(2)}$ varies in different media according to the size and shape of the molecules. The two straight lines, drawn for the variation of $\tau_{(1)}$ and $\tau_{(2)}$ with viscosity show the similar effect. It can, therefore, be concluded that the viscosity of the medium has hardly any effect so far as the process giving rise to the relaxation time $\tau_{(1)}$ is concerned. This perhaps can be associated with the internal rotation of the group attached to the two species. This is in agreement with the earlier studies on a few other molecular species.[11,14,21]

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