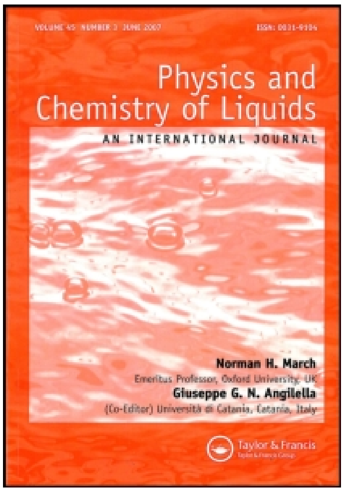

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Dielectric relaxation studies of molecular association: complexing of methyl acrylate and butyl acrylate with phenols in the MW region

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Dielectric relaxation studies of molecular association: complexing of methyl acrylate and butyl acrylate with phenols in the MW region

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Dielectric relaxation measurements on alkyl acrylates (methyl acrylate and butyl acrylate) with phenols (*p*-cresol, *p*-chlorophenol and 2,4-dichlorophenol) have been studied at microwave frequency 9.37 GHz in dilute solution of carbon tetrachloride at 308 K. The relaxation time and activation energy have been determined using the measured dielectric data. The results show a linear dependence of relaxation time on alkyl chain length of acrylic esters and acidity of phenols and also on the nature of the solvent. Comparative study of free energy of activation for the dielectric relaxation and viscous flow suggest the fact that the process of viscous flow involves greater inference by neighbouring than does dielectric relaxation, as the latter takes place by rotation only, whereas the viscous flow involves both the rotational and translational forms of motion. The validity of the single frequency equation of Higasi *et al.* (*Bull. Chem. Soc. Jpn*, **44**, 988 (1971)) for multiple relaxation time $\tau_{(1)}$ is found to be a function of the hydrogen bonding strength of phenolic hydrogen whereas the group rotation relaxation time $\tau_{(2)}$ is a function of the steric interaction of proton donor. The relaxation time is the maximum at 50 : 50 (molar ratio).

Keywords: Acrylic esters; Phenol derivatives; Dielectric relaxation; X-band microwave

1. Introduction

Alkyl acrylates are industrially important chemicals, precursors in the synthesis of polymers and used as adhesives, paints, binders and emulsifiers [1]. Dielectric relaxation investigations, especially in polar liquids dissolved in non-polar solvents have always been of considerable interest to a large number of workers [2–5]. Such studies are very useful in understanding the molecular structure and the molecular forces. Rewar and Bhatnagar [6] have reported the dielectric properties of butyl acrylate, butyl methacrylate and iso-butyl methacrylate in the microwave region at different temperatures. Dielectric parameters for dimethyl formamide–phenol and dimethyl acetamide–phenol were reported by Tucker and Walker [7]. Recently our research

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group [8–13] has investigated the complex formation of acrylic esters with proton donors (alcohols) in non-polar solvents using FTIR spectroscopic method. The study of the H-bonds of the type O–H $\cdots$ O=C occupies a position of considerable importance as it relates to the study of biopolymers. Thus the study and knowledge of dielectric properties of the ternary mixtures of acrylic esters with polar associating liquids in non-polar solvents is expected to provide useful and vital process parameters for efficient design of trans-esterification process of industrial interest. Keeping both the industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between free hydroxyl group of phenol and the carboxyl group of ester using dielectric method. This study is expected to provide better understanding of the nature of molecular orientation process.

2. Experimental

The static dielectric constant were measured by heterodyne beat method at 308 K using a commercial instrument, Dipolemeter DM 01 supplied by Wissenschaijftlich Technische Werkstatter, Germany operated at 220 V. The refractive indices were measured by an Abbe's refractometer. The measurement of dielectric constant at an angular frequency (ε') and dielectric loss (ε''), were carried out in the X-band microwave frequency of 9.37 GHz. The viscosities were measured with the help of Oswald's viscometer. The temperature of all these measurements were maintained at $35 \pm 0.1^\circ$C using a water circulating thermostat. E. Merck variety of methyl acrylate, butyl acrylate and 2,4-dichlorophenol, distilled samples of *p*-cresol and *p*-chlorophenol were used. The physical parameters of all the chemicals used here have been checked against their literature values.

The proton donors (phenols) and the acceptors (alkyl acrylates) under study were separately dissolved at the same molar concentration (0.3 mol L^{-1}) in the solvent carbon tetrachloride. Their dielectric constants were measured separately. Then the two solutions were mixed in different proportions but with the total concentration kept at a fixed value and were subjected to the dielectric constant measurements. As the maximum deviation of dielectric constant for all the systems studied occurs at equimolar ratio of the solutes, it is presumed that the deviation is due to the formation of 1 : 1 complexes alone.

3. Evaluation of dielectric parameters

According to Higasi method [14], the average relaxation time $\tau_{(1)}$ is described by

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

while the overall dielectric relaxation $\tau_{(2)}$ is given by,

$$\tau_{(2)} = \frac{(a_0 - a')a''}{\omega a''} \tag{2}$$
$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}}$$

where $\tau_{(0)}$ may be called the mean relaxation time, ω is the angular frequency, a_0, a', a'' and a_∞ are defined by equation (3)

$$\begin{aligned}\varepsilon_0 &= \varepsilon_{01} + a_0 w_2\\ \varepsilon' &= \varepsilon_1' + a' w_2\\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty w_2\end{aligned} \tag{3}$$

in which subscript 1 refers to the pure solvent and subscript 2 refers to the solute, subscript 0 refers to the static frequency and subscript ∞ refers to the infinite or optical frequency measurements and w_2 is the mass fraction of the solute.

The molar free energies have been calculated using the Eyring's equation,

$$\tau = \left(\frac{h}{kT}\right)\exp\left(\frac{\Delta F_\tau}{RT}\right) \tag{4}$$

$$\eta = \left(\frac{Nh}{V}\right)\exp\left(\frac{\Delta F_\eta}{RT}\right) \tag{5}$$

where, h is the Plank's constant, k the Boltzmann constant, N the Avogadro number and V the molar volume, and ΔF_τ and ΔF_η are the molar free energies for the dielectric relaxation process and the viscous flow process, respectively.

4. Results and discussion

The ternary systems selected were alkyl acrylates (methyl acrylate and butyl acrylate) with proton donors (*p*-cresol, *p*-chlorophenol and 2,4-dichlorophenol) using carbon tetrachloride as solvent. The value of relaxation times $\tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ for all the systems were calculated by Higasi's method and are reported in tables 1 and 2. It is observed that the value of relaxation times $\tau_{(1)}$, $\tau_{(2)}$ and $\tau_{(0)}$ increases with increasing chain length of alkyl acrylates and acidity of phenols [7,15].

The increase in relaxation time may be due to the increase in effective radius of the rotating unit. The observed higher value of butyl acrylate (BA) can be attributed to the larger size of BA molecule in comparison to methyl acrylate (MA) molecules. In these systems, the complex formation is likely to occur between $H^{\delta+}$ of phenols and $O^{\delta-}$ of C=O group of ester. Oxygen atom is sp^3 hybridized and in the ester structure there is a lot of voids available for O–H to penetrate and enter into complexation components. Carbon tetrachloride is a symmetrical and a non-polar molecule. But each chlorine atom in this molecule is highly polarizable due to its three lone pair of electrons and therefore it can function as an electron donor. There is, therefore, a possibility of interaction between the positive hydrogen of hydroxyl group and a chlorine atom of the carbon tetrachloride molecule. The potential hydrogen bonding nature of the carbon tetrachloride molecule may therefore contribute to increasing the relaxation time [16].

It has been found that two opposing effects namely specific interactions between C=O group of ester and –OH group of alcohol and non-specific dispersion interactions, i.e. breaking of intermolecular hydrogen bonds in phenols are possibly operative in these mixtures. The relative size of both ester and phenol molecules determines the

Table 1. Values of relaxation times for various molar ratio of methyl acrylate (MA) with phenol derivatives in carbon tetrachloride.

	Relaxation time (ps) using Higasi's method								
	$\tau_{(1)}$			$\tau_{(2)}$			$\tau_{(0)}$		
Ratio of phenol : MA	*p*-Cresol	*p*-Chloro phenol	2,4-Dichloro phenol	*p*-Cresol	*p*-Chloro phenol	2,4-Dichloro phenol	*p*-Cresol	*p*-Chloro phenol	2,4-Dichloro phenol
1 : 3	7.29	11.36	9.52	8.63	11.11	9.15	7.93	11.23	9.33
1 : 2	9.98	13.16	10.77	10.23	14.12	12.31	10.11	13.63	11.52
1 : 1	15.07	19.89	17.55	15.70	20.11	17.68	15.38	20.01	17.62
2 : 1	12.16	14.33	12.56	13.28	18.36	15.64	12.71	16.22	14.02
3 : 1	10.88	12.11	11.40	11.81	14.41	12.20	11.34	13.21	11.79

Table 2. Values of relaxation times for various molar ratio of butyl acrylate (BA) with phenol derivatives in carbon tetrachloride.

	Relaxation time (ps) using Higasi's method								
	$\tau_{(1)}$			$\tau_{(2)}$			$\tau_{(0)}$		
Ratio of phenol : BA	*p*-Cresol	*p*-Chloro phenol	2,4-Dichloro phenol	*p*-Cresol	*p*-Chloro phenol	2,4-Dichloro phenol	*p*-Cresol	*p*-Chloro phenol	2,4-Dichloro phenol
1 : 3	11.17	13.48	12.78	13.35	20.04	17.41	12.21	16.44	14.92
1 : 2	13.73	24.11	22.47	18.69	27.34	19.26	16.02	25.67	20.80
1 : 1	22.26	32.72	27.58	26.62	31.53	28.95	24.34	32.12	28.26
2 : 1	17.90	26.97	20.96	23.26	27.15	25.47	20.40	27.06	23.11
3 : 1	15.55	22.48	15.30	18.34	25.12	22.24	16.89	23.76	18.45

predominance of a particular type of interaction over the other. Our results show that the relaxation time is larger at 1 : 1 mole ratio of methacrylates with phenols. The relaxation time decreases conspicuously for the other mole ratios but are higher than either of the components. Saxena and Saxena [17] studied the H-bonding in some carbonyl + phenol derivative systems in different compositions. They also observed that the relaxation time of ternary mixtures is always much greater than either of the polar solutes in the inert solvent with excess of phenols the relaxation time of methacrylate + phenol system show a slight increase. This result is in agreement with the earlier investigations of Tucker *et al.* [7]. The results also show that the molecular association between acrylates and phenols is maximum at 50 : 50 (molar ratio) and then decreases at other molar ratio. From this we conclude that the 1 : 1 complex is dominant in acrylate–phenol systems. The relaxation time τ increases with increasing acidity of proton donor in complex systems. The relaxation time of alkyl acrylates (MA and BA) with 2,4-dichlorophenol is less than that of alkyl acrylates with *p*-chlorophenol complexes due to steric hindrance and inductive effect.

At high concentrations of phenol in the mixtures, a large number of alcohol molecules surround the ester molecules. The associative alcohol molecules act as proton donors enabling hydrogen bonding with ester molecules. Thus dipole–dipole interaction occurs in such a way that the effective dipole moment gets increased and linear α-multimers are formed [18]. The dipole–dipole interaction is the interaction of the –OH group of alcohol with C=O of ester.

At low concentration of phenol in the mixtures, there are only a small number of alcohol molecules to enable dipole–dipole interaction through hydrogen bonding with the non-associative ester molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of ester and acidity of proton donor (phenols), indicating that the degree of cooperation for re-orientation of the molecules increases with increasing length and the bulk of cluster increases.

The relaxation time increases with increasing alkyl chain length of ester and acidity of proton donor (phenols), indicating that the degree of cooperation for re-orientation of the molecules increases with increasing length and the bulk of cluster increases. The relaxation time increases with increasing chain length with the fact that the relaxation time is directly related to the size of the molecules [19–21].

The molar free energy of activation for viscous flow ΔF_η and the free energy ΔF_τ are calculated for alkyl acrylate (methyl acrylate and butyl acrylate) with phenols (*p*-cresol, *p*-chlorophenol and 2,4-dichlorophenol) in carbon tetrachloride and given in table 3. It is evident from our data that the ΔF_η is larger than ΔF_τ. This is in agreement with the fact that the process of viscous flow, which involves both the rotational and transnational forms of motion, faced greater interference from neighbours than dielectric relaxation, which takes place by rotation only [22]. Smyth [23] pointed out that the relaxation time of a proton donor increases as the acceptor ability of the solvent environment increases. Similarly for a given proton acceptor, the relaxation time must increase with the proton donor ability of the donor solute. Our results are in accordance with this conclusion.

In the present systems studied, it has been observed that the relaxation time of ternary mixtures (alkyl acrylates with phenols in carbon tetrachloride) is much greater than the binary mixture (phenols with carbon tetrachloride or alkyl acrylates with carbon tetrachloride). This result indicates the formation of hydrogen bond between the

Table 3. The activation energies at 1 : 1 stoichiometric ratios of alkyl acrylate + phenol systems in carbon tetrachloride at 308 K.

	Activation energy	
System	ΔF_τ (kJ mol^{-1})	ΔF_η (kJ mol^{-1})
Methyl acrylate + *p*-cresol	11.92	12.15
Methyl acrylate + *p*-chlorophenol	13.15	13.28
Methyl acrylate + 2,4-dichlorophenol	11.96	12.17
Butyl acrylate + *p*-cresol	12.79	13.01
Butyl acrylate + *p*-chlorophenol	13.28	13.39
Butyl acrylate + 2,4-dichlorophenol	12.93	13.27

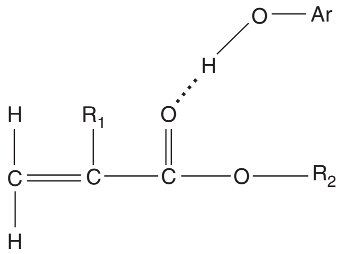
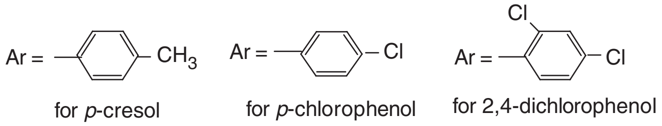


Figure 1. Hydrogen bonding interaction between phenols and alkyl acrylates (MA and BA), where $R_1 = H$, $R_2 = CH_3$ for methyl acrylate (MA) and $R_1 = H$, $R_2 = C_2H_5$ for ethyl acrylate (EA).

hydrogen atom in O–H group of phenol and oxygen atom in C=O group of alkyl acrylates (MA and BA) and is shown in figure 1.



5. Conclusions

The hydrogen bonded complexes of alkyl acrylates (methyl acrylate and ethyl acrylate) and phenols (*p*-cresol, *p*-chlorophenol and 2,4-dichlorophenol) have been studied in dilute solution of carbon tetrachloride using dielectric method. From this study it may be concluded that the alkyl chain length of alkyl acrylates and acidity of phenols plays a significant role in the determination of dielectric properties of the above systems studied.

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