

Dielectric Relaxation Studies of Alkyl Acrylates on Complexation with Phenols Using Time Domain Reflectometry

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Abstract: The dielectric relaxation measurements on binary mixtures of esters (methyl acrylate, ethyl acrylate, and butyl acrylate) with phenol derivatives (*p*-cresol, *p*-chlorophenol, and 2,4-dichlorophenol) were carried out at different concentrations at 303 K using the time domain reflectometry (TDR) over the frequency range from 10 MHz to 20 GHz. The Kirkwood correlation factor and excess inverse relaxation time were determined and discussed to yield information on the molecular interactions of the systems. The relaxation time increased with increasing concentration of phenols and increasing chain length of esters. The excess inverse relaxation time values were negative for all the systems, which indicated the solute-solvent interaction existing between esters and phenols producing a field in such a way that the effective dipole rotation was hindered.

Key Words: Dielectric relaxation; Time domain reflectometry; Phenol derivatives

The dielectric relaxation of solute-solvent mixtures gives information about intermolecular interaction and hydrogen bonding in the system. The study also gives information about formation of monomers and multimers. The acrylates have been an important chemical group with considerable application in industry^[1]. The acrylic esters are unique molecules with unsaturated structures alongside a carbonyl group. The solution chemistry of these compounds can be strongly influenced by the aggregation phenomena, which can play a significant role in the physical properties of these polar molecules^[2]. Syamalamba and Premaswarup^[3] have studied the dielectric properties of methyl, ethyl, and butyl acrylate in the microwave region at different temperature, and compared their result with those on butyrates. Ravi-Dhar *et al.*^[4] also found formation of intermolecular association between mixture of phenol and amine in pure state from dielectric constant, viscosity, density, and refractive index measurements at different temperatures. Shirke *et al.*^[5,6] have reported the dielectric parameters of methyl acetate and ethyl acetate with primary alcohol mixtures at different concentrations and temperatures. Chaudhari *et al.*^[7] studied the dielectric properties of butyl acetate-alcohol mixtures using the time domain technique. There are many studies of the dielectric behaviour of alcohol mixtures with structure breaking and structure making^[8]. The studies of Kirkwood correlation factor provide valuable information regarding the solute-solvent interaction in binary mixtures especially when one of the components has antiparallel orientation of dipoles^[9].

The aim of the present investigation is the use of dielectric relaxation measurements in the microwave region (10 MHz to 20 GHz) to study the molecular interaction of binary mixtures of esters (methyl acrylate, ethyl acrylate, and butyl acrylate) with phenol derivatives (*p*-cresol, *p*-chlorophenol and 2,4-dichlorophenol) at 303 K for different concentrations in the microwave region using time domain reflectometry (TDR).

1 Experimental

1.1 Materials

E. Merck variety of methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), 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.

1.2 Apparatus

The complex permittivity spectra were studied using time domain reflectometry. The Hewlett-Packard HP 54750 sampling oscilloscope with HP 54754 A TDR plug-in module was used. A fast rising step voltage pulse of about 39 ps rise time generated by a tunnel diode was propagated through a flexible coaxial cable. The sample was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell. The physical dimensions of the cell are very important. The impedance of the cell should be matched with that of the coaxial transmission line to which the cell is connected. The impedance of the coaxial line is 50 Ω . The SMA cell has a 3.5 mm outer diameter and a 1.35

mm effective pin length. All measurements were done under open load conditions. The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5 ns was used. The reflected pulses without sample $R_1(t)$ and with sample $R_x(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a PC through a 1.44 MB floppy diskette drive.

A temperature controller system with a water bath and thermostat was used to maintain a constant temperature within accuracy limit of ± 1 °C. The sample cell was surrounded by a heat-insulating container through which the water of constant temperature using a temperature controller system was circulated. The temperature at the cell was monitored using a microprocessor-controlled thermometer.

1.3 Data analysis

The time-dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation^[10,11] as

$$\rho^*(\omega) = (c/d\omega d)[p(\omega)/q(\omega)] \quad (1)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transformations of $(R_1(t) - R_x(t))$ and $(R_1(t) + R_x(t))$, respectively, c is the velocity of light, ω is angular frequency, d is the effective pin length, and $j = \sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method^[12].

The experimental values of ε^* are fitted with the Debye equation^[13]

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + j\omega\tau) \quad (2)$$

with ε_0 , ε_∞ , and τ as fitting parameters. A nonlinear least squares fit method^[14] was used to determine the values of dielectric parameters.

2 Kirkwood model

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter g ^[15]. This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids. For a pure liquid, Kirkwood correlation factor g may be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9kTM} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \quad (3)$$

where μ is dipole moment; ρ is density at temperature T ; M is molecular weight; k is Boltzman constant; N is Avogadro's number; ε_0 is static dielectric constant, and ε_∞ is the dielectric constant at high frequency, often represented by the square of refractive index.

For the mixture of two polar liquids (A) and (B), equation (3) is modified by Kumbharakhane *et al.* with the following assumption^[16,17].

Assuming that for the mixture, g^{eff} is the effective Kirkwood correlation factor in the mixture, the Kirkwood equation for the mixture may be expressed as

$$\frac{4\pi N}{9kT} \left(\frac{\mu_A^2 \rho_A}{M_A} x_A + \frac{\mu_B^2 \rho_B}{M_B} x_B \right) g^{\text{eff}} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \quad (4)$$

where x_A and x_B are the mole fractions of liquids A (phenol) and B (ester), respectively.

3 The excess inverse relaxation time

The information related to the heterogeneous interaction may also be obtained by the value of excess inverse relaxation time^[18]. The excess inverse relaxation time $(1/\tau)^E$ is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A x_A - (1/\tau)_B x_B] \quad (5)$$

The quantitative information regarding the dynamics of solute-solvent interaction obtained from excess inverse relaxation is as follows:

(1) $(1/\tau)^E = 0$; There is no change in the dynamics of liquids A and B interaction.

(2) $(1/\tau)^E < 0$; The liquid A and liquid B interaction produces a field such that the effective dipoles rotate slowly.

(3) $(1/\tau)^E > 0$; The liquid A and liquid B interaction produces a field such that the effective dipoles rotate fastly i.e. the field will co-operate in rotation of dipoles.

4 Results and discussion

The determined values of static dielectric constant (ε_0) and dielectric constant at high frequency (ε_∞) for solutions of different concentrations of phenols are presented in Table 1. The static dielectric constant for the mixtures increases towards the dielectric constant of the respective phenol. Increase of dielectric constant is due to the transition of spherical molecular aggregates into elongated aggregates giving rise to parallel orientation of the dipoles. Similar conclusions were drawn by Shirke *et al.*^[5,6] for alkyl acetate-alcohols systems. It is found that in the phenol-rich region, the dielectric constant for the mixtures increases, whereas when concentration of ester dominates in the mixture, the static permittivity decreases.

From Table 1, it is also noticed that the ε_0 and τ values of mixtures lie between the individual component values, which indicates the solute-solvent interaction between the —OH group of phenol and C=O group of ester^[5].

The dielectric relaxation time shows continuous increase with chain length of esters and acidity of proton donors (phenols) and offers hindrance to the rotation of the molecule. The increase in relaxation time with chain length is to be expected in view of the fact that hydroxyl group reorientation depends to some extent on the length of the alkyl group, and the viscosity of the liquid. The relaxation time increases with increasing alkyl chain length, which indicates that the degree of cooperative for reorientation of the molecules increases with increasing length and the bulk of the cluster increases.

The increase of relaxation time with increasing chain length is in agreement with the fact that the relaxation time is directly related to the size of the molecules^[5,6]. It was also noticed that the ε_0 was gradually decreased by increasing the number of carbon atoms in the alkyl chain of ester and acidity of phenols. This

Table 1 Static permittivity (ϵ_0), dielectric constant at high frequency (ϵ_∞), relaxation time (τ), and effective Kirkwood correlation factor (g^{eff}) of phenol+alkyl acrylate mixtures

Phenol	Volume fraction of phenol (%)	Methyl acrylate				Ethyl acrylate				Butyl acrylate			
		ϵ_0	ϵ_∞	τ/ps	g^{eff}	ϵ_0	ϵ_∞	τ/ps	g^{eff}	ϵ_0	ϵ_∞	τ/ps	g^{eff}
<i>p</i> -cresol	0	6.72	2.45	5.45	0.94	4.52	2.23	6.33	0.89	2.46	2.16	12.32	0.81
	25	5.38	2.52	92.78	1.87	4.29	2.45	112.56	1.63	3.12	2.32	143.87	1.51
	50	7.13	2.68	336.87	2.24	6.78	2.56	387.25	1.92	4.38	2.46	405.33	1.74
	75	8.69	2.81	615.22	2.36	7.51	2.79	678.96	2.22	5.96	2.61	712.15	1.83
	100	11.47	2.93	1221.65	2.58	11.47	2.93	1221.65	2.58	11.47	2.93	1221.65	2.58
<i>p</i> -chlorophenol	0	6.72	2.45	5.45	0.94	4.52	2.23	6.33	0.89	2.46	2.16	12.32	0.81
	25	3.96	2.64	123.21	1.96	2.78	2.53	139.48	1.79	1.13	2.38	178.96	1.67
	50	5.87	2.73	407.15	2.43	4.54	2.69	486.21	2.36	3.86	2.55	523.33	1.93
	75	7.33	2.92	697.33	2.68	5.82	2.71	723.38	2.74	4.38	2.67	801.45	2.23
	100	8.19	3.12	1346.25	2.76	8.19	3.12	1346.25	2.16	8.19	3.12	1346.25	2.76
2,4-dichlorophenol	0	6.72	2.45	5.45	0.94	4.52	2.23	6.33	0.89	2.46	2.16	12.32	0.81
	25	4.33	2.59	89.14	1.22	3.69	2.48	102.69	1.14	2.19	2.33	121.41	0.98
	50	6.52	2.71	298.33	1.38	5.12	2.61	323.42	1.22	4.08	2.48	365.23	1.05
	75	7.08	2.86	493.18	1.56	6.47	2.75	548.85	1.39	5.15	2.63	617.27	1.13
	100	9.36	3.07	769.54	1.69	9.36	3.07	769.54	1.69	9.36	3.07	769.54	1.69

trend could be attributed to decrease in the number of dipoles in the complex, which may lead to a decrease in the molar volume of the rotating molecules^[5,6].

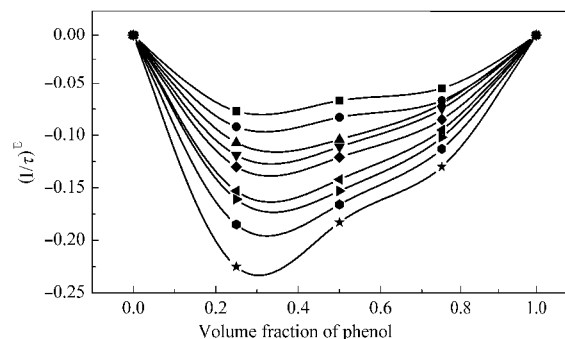
At high concentration of phenol in the mixtures, there are a large number of alcohol molecules surrounding the ester molecules. The associative phenol molecules act as proton donors enabling hydrogen bonding with ester molecules. Thus dipole-dipole interaction occurs in such a way that the effective dipole moment gets increased and linear α -multimers are formed^[9]. The dipole-dipole interaction is the interaction of the —OH group of phenol with C=O of ester. At low concentration of phenol in the mixtures, there are only a small number of phenol molecules to enable dipole-dipole interaction through hydrogen bonding with the non-associative ester molecules. As a result, weak intermolecular interaction occurs.

The calculated values of g^{eff} using Eq.(4) for all the systems at different concentrations are given in Table 1. The effective values of the correlation factor g^{eff} for esters are smaller than its corresponding values in different phenols. The values of g^{eff} for pure liquid esters are less than unity indicating the antiparallel orientation of the electric dipoles, and the g^{eff} values for pure phenols are greater than unity indicating a high degree of coordinated chainlike structures. For the mixtures of phenols with esters, the values of g^{eff} show an increasing trend with the increasing concentration of phenols in all the mixture. This trend suggests reorientation of neighborhood molecules of the constituent polar liquids forming a tendency towards parallel alignment of dipoles. This conclusion is similar to that arrived from the variation of dielectric constant with concentration.

The dielectric relaxation time shows continuous increase as the volume fraction of esters decreases and it increases with acidity of phenol and offer hindrance to the rotation of the

molecule. The relaxation time increases with increasing acidity of proton donors in complex system. The higher value of relaxation time observed in *p*-chlorophenol with esters reveals that the substitution of chlorine in *para* position of phenol induces more proton donating ability and thereby increases the strength of the complexation. In the case of esters with 2,4-dichlorophenol systems, the relaxation values are less than other phenols. This may be accounted for, by (i) the inductive effect of OH and (ii) the steric hindrance of Cl in 2 positions, which inhibits the complex formation.

The variation of $(1/\tau)^E$ for esters (methyl acrylate, ethyl acrylate, and butyl acrylate) with phenols (*p*-cresol, *p*-chlorophenol, and 2,4-dichlorophenol) at different compositions is given in Fig.1. The $(1/\tau)^E$ values are negative for all the system studied. This indicates the formation of multimers through hydrogen bonding with slower rotation and parallel orientation of dipoles. It also

**Fig.1** Excess inverse relaxation time $(1/\tau)^E$ versus volume fraction of phenols for alkyl acrylates in phenols

—■— BA+2,4-dichlorophenol; —●— BA+p-cresol; —▲— BA+p-chlorophenol;
—▼— EA+2,4-dichlorophenol; —◆— EA+p-cresol; —◀— EA+p-chlorophenol;
—▶— MA+2,4-dichlorophenol; —●— MA+p-cresol; —★— MA+p-chlorophenol.

follows from Fig.1 that the BA-phenol systems have lower $(1/\tau)^E$ negative values than that of EA-phenol and MA-phenol systems because of the negative inductive effect of the alkyl group of esters increases in the order from methyl to butyl, and the electron contribution of the butyl group to the C=O group is significantly greater than methyl group. Also the *p*-chlorophenol-ester systems have higher $(1/\tau)^E$ negative values than that of 2,4-dichlorophenol-ester and *p*-cresol-ester systems, revealing that the tendency of complex formation is stronger in *p*-chlorophenol than that of 2,4-dichlorophenol and *p*-cresol. Because of steric hindrance, it is likely that higher acidity of *p*-chlorophenol will have greater probability of complex formation than other phenols. Therefore one would expect that the strongest intermolecular hydrogen bonds would be formed between the C=O group of butyl acrylate and the —OH proton of *p*-chlorophenol and weakest between the C=O group of methyl acrylate and —OH proton of 2,4-dichlorophenol. This is reflected in the dielectric constant, the relaxation time, the Kirkwood correlation factor, and inverse relaxation time values. For the systems of phenols with the esters considered here, the existence of the intermolecular heterointeraction is in the following order: 2,4-dichlorophenol < *p*-cresol < *p*-chlorophenol and methyl acrylate < ethyl acrylate < butyl acrylate.

5 Conclusions

The dielectric constants, the relaxation times, the Kirkwood correlation factors, and the excess inverse relaxation times for alkyl acrylate with phenol mixtures for various concentrations were reported, and the dielectric parameters showed significant change with concentration, alkyl chain length of esters, and acidity of phenols. The negative excess inverse relaxation time values obtained for all the systems indicated that the solute-

solvent interaction hinders the rotation of the dipoles of the system.

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