

Dielectric Relaxation Studies of Alkyl Methacrylate–Phenol Mixtures by Time Domain Reflectometry

Faize Liakath Ali Khan* and Periyasamy Sivagurunathan

Department of Physics, Annamalai University, Annamalai Nagar, Tamilnadu-608 002, India.

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ABSTRACT

Dielectric relaxation studies of alkyl methacrylate (methyl methacrylate, ethyl methacrylate and butyl methacrylate) mixtures with phenol derivatives (p-cresol, p-chlorophenol and 2,4-dichlorophenol) have been carried out using a time domain reflectometry (TDR) technique in the frequency range 10 MHz to 20 GHz at 293 K. Static permittivities (ϵ_0), relative permittivities at high frequency (ϵ_∞) and relaxation times (τ) were found through dielectric measurements for different concentrations of each system. The Kirkwood correlation factor and the excess inverse relaxation time were determined and they yield information on the molecular interactions occurring in the systems. The values of the static permittivity and the relaxation time increase with an increase in the percentage of phenol in the mixtures.

KEYWORDS

Dielectric relaxation, time domain reflectometry, phenol derivatives, alkyl methacrylates.

1. Introduction

The dielectric relaxation of solute–solvent mixtures gives information about intermolecular interaction and hydrogen bonding in the system. The study also gives information about the formation of multimers. The acrylates have been an important chemical group with considerable application in industry.¹ The acrylic esters are unique molecules with unsaturated structures adjacent to a carbonyl group. The solution chemistry of these compounds can be strongly influenced by aggregation phenomena, which can play a significant role in the physical properties of these polar molecules.² Khanna and Sobhandri³ have studied the dielectric properties of methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate in the microwave region at different frequencies and observed that there is an increase in relaxation time and activation energy with an increase in the molecular size of the acrylates. Ravi Dhar *et al.*⁴ have studied the intermolecular association between mixtures of phenols and amines at different temperatures and calculated the dielectric relaxation times. Shirke *et al.*^{5,6} have reported the dielectric parameters of methyl acetate and ethyl acetate mixtures with primary alcohols 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 properties.⁸ Studies of the Kirkwood correlation factor provide valuable information regarding solute–solvent interaction in binary mixtures, especially when one of the components has an antiparallel orientation of dipoles.⁹

The present paper reports dielectric relaxation studies of alkyl methacrylate (methyl methacrylate, MMA; ethyl methacrylate, EMA; and butyl methacrylate, BMA) mixtures with phenol derivatives (p-cresol, p-chlorophenol and 2,4-dichlorophenol) at 293 K for different concentrations in the microwave region (10 MHz to 20 GHz) using time domain reflectometry (TDR).¹⁰

2. Experimental Details

2.1. Materials

Merck samples of methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and 2,4-dichlorophenol, and distilled samples of p-cresol and p-chlorophenol were used. The physical parameters of all the chemicals used here were checked against their literature values.

2.2. Apparatus

The complex permittivity spectra were studied using time domain reflectometry. A Hewlett-Packard HP 54750 sampling oscilloscope with a HP 54754A 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 a 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 was 50 Ω . The SMA cell had 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 at 1024 points in the memory of the oscilloscope.

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

2.3. Data Analysis

The time-dependent data were processed to obtain complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range

* To whom correspondence should be addressed. E-mail: shamisardar@yahoo.com

Table 1 Static permittivity (ϵ_0), relative permittivity at high frequency (ϵ_∞), relaxation time (τ) and effective Kirkwood correlation factor (g^{eff}) for p-cresol + alkyl methacrylate mixtures at 293 K.

Volume % of p-cresol	Methyl methacrylate	Ethyl methacrylate	Butyl methacrylate
ϵ_0			
0	5.38	4.19	3.76
25	6.12	5.36	4.68
50	7.93	7.29	5.39
75	9.18	8.04	6.87
100	11.47	11.47	11.47
ϵ_∞			
0	2.56	2.31	2.23
25	2.61	2.52	2.39
50	2.73	2.64	2.48
75	2.86	2.73	2.65
100	2.93	2.93	2.93
τ/ps			
0	11.73	13.18	15.59
25	97.56	131.87	152.47
50	383.15	402.53	436.63
75	663.58	697.29	748.57
100	1156.65	1156.65	1156.65
g^{eff}			
0	1.08	0.93	0.89
25	1.91	1.69	1.58
50	2.28	1.98	1.79
75	2.41	2.31	1.95
100	2.58	2.58	2.58

Table 2 Static permittivity (ϵ_0), relative permittivity at high frequency (ϵ_∞), relaxation time (τ) and effective Kirkwood correlation factor (g^{eff}) for p-chlorophenol + alkyl methacrylate mixtures at 293 K.

Volume % of p-chlorophenol	Methyl methacrylate	Ethyl methacrylate	Butyl methacrylate
ϵ_0			
0	5.38	4.19	3.76
25	4.23	3.08	2.36
50	6.18	4.76	3.91
75	7.89	5.94	4.74
100	8.19	8.19	8.19
ϵ_∞			
0	2.56	2.31	2.23
25	2.71	2.58	2.41
50	2.85	2.76	2.58
75	3.03	2.84	2.73
100	3.12	3.12	3.12
τ/ps			
0	11.73	13.18	15.59
25	135.64	147.51	183.34
50	438.56	493.63	566.27
75	708.19	783.49	837.33
100	1346.25	1346.25	1346.25
g^{eff}			
0	1.08	0.93	0.89
25	1.73	1.58	1.62
50	2.12	2.25	2.39
75	2.38	2.47	2.51
100	2.76	2.76	2.76

from 10 MHz to 20 GHz using Fourier transformation^{11,12} as

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

where $\rho(\omega)$ and $q(\omega)$ are the Fourier transforms of $(R_1(t) - R_x(t))$ and $d[(R_1(t) + R_x(t))/dt]$, respectively, c is the speed of light, ω is the angular frequency, d is the effective pin length and $i = \sqrt{-1}$.

The complex permittivity spectra $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method.¹³

The experimental values of ϵ^* were fitted with the Debye equation¹⁴

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + i\omega\tau), \quad (2)$$

with ϵ_0 , ϵ_∞ and τ as fitting parameters. A non-linear least squares fit method¹⁵ was used to determine the values of the dielectric parameters.

2.4. The Kirkwood Model

The structural information about the liquids from the dielectric relaxation parameters may be obtained using the Kirkwood correlation parameter g .¹⁶ This factor is also a parameter for obtaining information regarding the orientation of electric dipoles in polar liquids. For a pure liquid the Kirkwood correlation factor g may be obtained by the expression

$$\frac{4\pi N\mu_i^2 \rho_i}{9kT M_i} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)}, \quad (3)$$

where μ is the dipole moment, ρ is the density at temperature T , M is the molar mass, k is Boltzmann's constant, N is Avogadro's constant, ϵ_0 is the static permittivity and ϵ_∞ is the relative permittivity at high frequency, often represented by the square of the refractive index.

For a mixture of two polar liquids, A and B, Equation (3) was

modified by Kumbharkhane *et al.* with the following assumption.^{17,18} 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

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

where X_A and X_B are the volume fractions of liquids A and B respectively in the mixture. The suffixes m, A and B represent mixture, liquid A (phenols) and liquid B (esters), respectively. g^{eff} changes from g_A to g_B as X_B increases from 0 to 1.

2.5. The Excess Inverse Relaxation Time

Information related to the heterogeneous interaction may also be obtained through the value of the excess inverse relaxation time.¹⁹ 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: if $(1/\tau)^E = 0$, there is no change in the dynamics of liquid A and B interaction; if $(1/\tau)^E < 0$, the liquid A and liquid B interaction produces a field such that the effective dipoles rotate slowly; and if $(1/\tau)^E > 0$, the liquid A and liquid B interaction produces a field such that the effective dipoles rotate rapidly, i.e. the field will cooperate in the rotation of the dipoles.

3. Results and Discussion

The determined values of the static permittivity (ϵ_0) and the relative permittivity at high frequency (ϵ_∞) for solutions having different concentrations of phenol are presented in Tables 1–3. The static permittivities of the mixtures increase towards the

Table 3 Static permittivity (ϵ_0), relative permittivity at high frequency (ϵ_∞), relaxation time (τ) and effective Kirkwood correlation factor (g^{eff}) for 2,4-dichlorophenol + alkyl acrylate mixtures at 293 K.

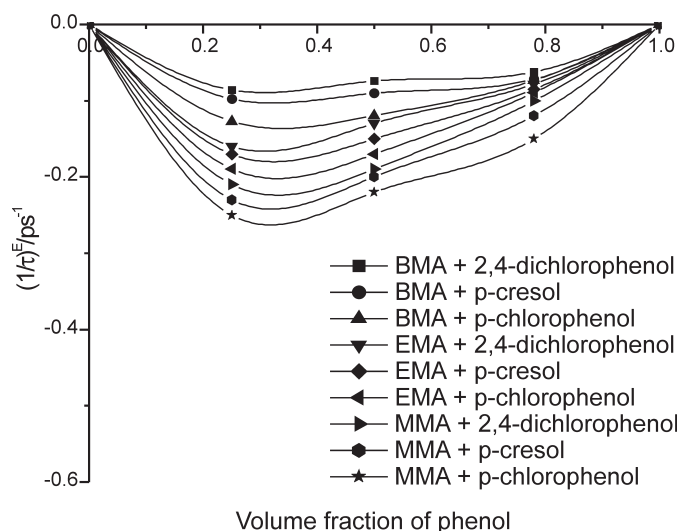
Volume % of 2,4-dichlorophenol	Methyl methacrylate	Ethyl methacrylate	Butyl methacrylate
		ϵ_0	
0	5.38	4.19	3.76
25	4.56	3.85	2.23
50	6.98	5.36	4.38
75	7.52	6.81	5.51
100	9.36	9.36	9.36
		ϵ_∞	
0	2.56	2.31	2.23
25	2.61	2.56	2.48
50	2.79	2.75	2.53
75	2.94	2.89	2.76
100	3.07	3.07	3.07
		τ/ps	
0	11.73	13.18	15.59
25	108.25	124.47	148.96
50	312.54	369.55	387.73
75	565.17	637.28	698.36
100	1089.54	1089.54	1089.54
		g^{eff}	
0	1.08	0.93	0.89
25	1.28	1.18	1.09
50	1.41	1.32	1.17
75	1.63	1.45	1.26
100	1.69	1.69	1.69

relative permittivity of the respective phenol. Increase of relative permittivity 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-alcohol systems. From Tables 1–3 it is also evident that the ϵ_0 and τ values of the mixtures lie between the individual component values, which indicates solute–solvent interaction between the OH group of the phenol and the C=O group of the ester.⁵

The dielectric relaxation time shows a continuous increase with the chain length of the ester and the acidity of the proton donor (phenol), and suggests hindrance to the rotation of the molecules. 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 increase of relaxation time with increasing alkyl chain length indicates that the degree of cooperativity for reorientation of the molecules increases with increasing length and increasing bulk of the cluster. The relaxation time increases with chain length in agreement with the fact that the relaxation time is directly related to the size of the molecule.^{6,7} It is also evident that the ϵ_0 value gradually decreases by increasing the number of carbon atoms in the alkyl chain of the ester and the phenol. This trend could be attributed to the decrease in the number of dipoles in the molar volume of the rotating molecules.^{6,7}

At high concentration of phenol in the mixtures, there is a large number of phenol molecules surrounding the ester molecules. The associating phenol molecules act as proton donors enabling hydrogen bonding to occur with ester molecules. Thus dipole–dipole interaction occurs in such a way that the effective dipole

**Figure 1** Excess inverse relaxation time $(1/\tau)^E$ versus volume fraction of phenol in phenol–alkyl methacrylate mixtures at 293 K.

moment increases and linear α -multimers are formed.²⁰ The dipole–dipole interaction is the interaction of the OH group of the phenol with the C=O group of the ester.

At low concentrations of phenol in the mixtures, there is only a small number of phenol molecules available to enable dipole–dipole interaction through hydrogen bonding with the non-associating ester molecules. As a result, weak intermolecular interaction occurs. The relaxation time increases with increasing alkyl chain length of the ester and acidity of the phenol, indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and increasing bulk of the cluster. The relaxation time increases with increasing acidity of the phenol in the complex system. However, in the alkyl methacrylate–2,4-dichlorophenol systems, the relaxation values are less than those of other phenol complexes, due to steric hindrance and the inductive effect. The acidities of the phenols are in the order 2,4-dichlorophenol < p-cresol < p-chlorophenol.²¹

The values of g^{eff} for pure liquid esters are close to unity, indicating no dipole correlation 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 increasing concentration of phenols in all the mixtures. This trend suggests reorientation of neighbouring molecules of the constituent polar liquids forming a tendency towards parallel alignment of dipoles. This conclusion is similar to that deduced from the variation of relative permittivity with concentration.

The dielectric relaxation times show continuous increase as the volume fraction of alkyl methacrylate decreases, and increases with the acidity of the phenol and increasing hindrance to the rotation of the molecules. The variation of $(1/\tau)^E$ for alkyl methacrylates (methyl methacrylate, ethyl methacrylate and butyl methacrylate) 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 systems studied. This indicates the formation of multimers through hydrogen bonding, with slower rotation and parallel orientation of dipoles. For the systems of phenols with the esters considered here, the strengths of the intermolecular heterointeractions are in the following order: 2,4-dichlorophenol < p-cresol < p-chlorophenol and methyl methacrylate < ethyl methacrylate < butyl methacrylate.

It also follows from Fig. 1 that the BMA-phenol systems have

lower negative $(1/\tau)^E$ values than those of the EMA-phenol and MMA-phenol systems because the negative inductive effect of the alkyl group of the ester increases in the order methyl to butyl, and the electronic contribution of the butyl group to the C=O group is significantly greater than that of the methyl group. Therefore, one would expect that the strongest intermolecular hydrogen bond would be formed between the C=O group of butyl methacrylate and the OH proton of p-chlorophenol and the weakest between the C=O group of methyl methacrylate and the OH proton of 2,4-dichlorophenol. This is reflected in the relative permittivity, relaxation time, Kirkwood correlation factor, and excess inverse relaxation time values.

5. Conclusion

The relative permittivities, relaxation times, Kirkwood correlation factors and excess inverse relaxation times for mixtures of alkyl methacrylates with phenols at various concentrations have been reported. The dielectric parameters show significant changes with concentration, the alkyl chain lengths of the esters and the acidities of the phenols. The negative excess inverse relaxation time values obtained for all the systems indicate that the solute–solvent interaction hinders the rotation of the dipoles of the system.

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