

Dielectric studies of methyl methacrylate and butyl methacrylate with primary alcohols using time domain reflectometry

F Liakath Ali Khan, P Sivagurunathan, S Raja Mohamed Kamil^a & S C Mehrotra^b

Annamalai University, Annamalai Nagar, Tamilnadu 608 002

^aDepartment of Chemistry, Islamiah College, Vaniyambadi 635 752

^bDr B A M University, Aurangabad, Maharashtra 431 004

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Using time domain reflectometry (TDR), dielectric relaxation studies have been carried out for alkyl methacrylates (methyl methacrylate and butyl methacrylate) with primary alcohols (methanol, ethanol, 1-hexanol, 1-nonanol and 1-dodecanol) mixtures over the frequency range 10 MHz-20 GHz at 303K. Static permittivity (ϵ_0), dielectric constant at high frequency (ϵ_∞) and relaxation time (τ) were found through dielectric measurements for different concentration of each system. The Kirkwood correlation factor and the excess inverse relaxation time were determined and discussed to yield information on the molecular structure and dynamics of the mixture. The values of the static permittivity, relaxation time and the Kirkwood correlation factor decrease with increased concentration of alkyl methacrylate in alcohol.

Keywords: Alkyl methacrylate, Alcohols, Dielectric relaxation, Time domain reflectometry

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1 Introduction

Dielectric relaxation spectroscopy has proven powerful tool for an investigation of H-bond rearrangement dynamics and has been widely applied for investigating pure solvents, solvents, solvent-solvent mixtures, supercooled and glass forming liquids, water-organic compound mixtures and electrolyte solutions. Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquids, provide valuable information regarding molecular complex formation in solution. The acrylates have been an important chemical group with considerable application in industry¹. The acrylic esters are unique molecules with unsaturated structures along side a carbonyl group. Alcohols are industrially and scientifically important organics compounds and their physical and chemical properties are largely determined by the -OH group. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding. The strength of the molecular association depends on several factors including the molecular structure, temperature, solvent and other factors. Therefore, 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 molecules². Madhulika Khatri and Gandhi³ have studied the dielectric relaxation

behaviour of n-butyl acrylate, allyl-methacrylate, isobutyl-methacrylate and isobutyl-acrylate in non-polar solvent at different temperatures. Dielectric relaxation studies of aromatic esters in the microwave region for different temperatures are reported by Saxena *et al.*⁴ using the Higasi method. 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.

In the course of the present study, the dielectric parameters for alkyl methacrylates (methyl methacrylate and butyl methacrylate) with primary alcohols (methanol, ethanol, 1-hexanol, 1-nonanol and 1-dodecanol) were investigated experimentally for different concentrations in the microwave region (10 MHz to 20 GHz) at 293 K using time domain reflectometry (TDR). The relaxation behaviour of these mixtures were explained by the Debye model. The excess dielectric properties are reported. The Kirkwood correlation factor is used to understand the molecular orientation in the mixture.

2 Experimental Details

Methyl methacrylate (MMA) and butyl methacrylate (BMA) were purchased from Aldrich with purity > 99% (Spectroscopic grade) and used

without further purification. AR grade alcohols (methanol, ethanol, 1-hexanol, 1-nonanol and 1-dodecanol) were purified by standard procedures⁸.

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 50Ω. 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 $R_I(t)$ and with sample $R_X(t)$ were digitized in 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 accuracy limit of $\pm 1^\circ\text{C}$. 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.

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^{9,10} as;

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

where $\rho(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_I(t)-R_X(t)]$ and $d [(R_I(t)+R_X(t))/dt]$, 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 $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method¹¹.

The experimental values of ϵ^* are fitted with the Debye equation¹²:

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

with ϵ_0 , ϵ_∞ and τ as fitting parameters. A non-linear least squares fit method¹³ was used to determine the values of dielectric parameters.

3 Kirkwood Model

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation¹⁴ parameter g . 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;

$$\frac{4\pi N\mu^2\rho g}{9kTM} = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad \dots(3)$$

where μ is dipole moment, ρ is density at temperature T , M is molecular weight, k is Boltzmann 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), Eq. (3) is modified by Kumbharkhane *et al.*¹⁶ with the following assumption^{15,16}. 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;

$$\frac{4\pi N \mu_A^2 \rho_A V_A}{9kT \epsilon_0 M_A} + \frac{\mu_B^2 \rho_B V_B g^{\text{eff}}}{M_B} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad \dots(4)$$

V_A and V_B are volume fraction of liquids (A) and (B) respectively in the mixture. The suffixes m , A and B represent mixture, liquid A (alcohols) and liquid B (esters) respectively. g^{eff} changes from g_A to g_B as V_B increases from zero to one.

The information related to the heterogeneous interaction may also be obtained by the value of excess inverse relaxation time¹⁷. The excess inverse relaxation time $(1/\tau)^E$ is defined as:

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

where $(1/\tau)^E$ is excess inverse relaxation time.

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 liquid *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 static dielectric constant (ϵ_0) and τ relaxation time (τ) obtained by fitting experimental data with the Debye equation are shown in Table 1. The static dielectric constant for the mixture increases towards the dielectric constant of the respective alcohol. The increase of dielectric constant is due to the transition of spherical molecular aggregates into elongated giving rise to parallel-orientation of the dipoles.

Table 1 — Dielectric data for the binary mixture of methyl methacrylate (MMA) with alcohols (methanol, ethanol, 1-hexanol, nonanol and 1-dodecanol)

Volume of % of MMA	ϵ_{om}	τ (ps)	g^{eff}
MMA+ methanol			
0%	26.24	173.6	2.58
25%	22.57	133.5	2.13
50%	19.74	67.6	1.05
75%	17.78	18.4	0.79
100%	7.89	11.7	0.89
MMA+ ethanol			
0%	23.68	223.6	2.71
25%	20.53	158.3	2.23
50%	17.33	82.7	1.12
75%	14.26	27.5	0.93
100%	7.89	11.7	0.89
MMA+ 1-hexanol			
0%	15.72	847.5	2.88
25%	14.63	223.8	2.65
50%	11.18	176.4	1.83
75%	9.23	62.3	1.52
100%	7.89	11.7	0.89
MMA+ 1-nonanol			
0%	9.09	1013.8	2.23
25%	8.62	526.3	1.98
50%	7.57	382.2	1.75
75%	5.83	97.5	1.58
100%	7.89	11.7	0.89
MMA+ 1-dodecanol			
0%	7.83	1146.3	2.07
25%	6.13	673.5	1.73
50%	5.09	447.8	1.38
75%	4.23	109.5	1.27
100%	7.89	11.7	0.89

Similar conclusions were reported by Shirke *et al.*^{5,6} for alkyl acetate-alcohols systems. This trends to indicate the hetero interaction which may arise due to the formation of hydrogen bonding between the –OH group of alcohol molecules and C=O of ester molecules.

The decrease in dielectric constant of the solution of higher alcohol is mainly due to longer size of molecules. The relaxation time increases in case of higher alcohol due to increase in molecular size. A perusal of Tables 1 and 2 shows that the value of relaxation time increases with increasing chain length of alcohols and alkyl methacrylates and offer hindrance to the rotation of the molecules¹⁸. The increase in relaxation time may be due to the increase in effective radius of the rotating unit. The observed higher value of BMA can be attributed to the larger

Table 2 — Dielectric data for the binary mixture of methyl methacrylate (BMA) with alcohols (methanol, ethanol, 1-hexanol, nonanol and 1-dodecanol)

Volume of % of BMA	ϵ_{om}	τ (ps)	g^{eff}
BMA+ methanol			
0%	26.24	173.6	2.58
25%	24.08	156.3	2.34
50%	21.13	113.7	1.19
75%	18.67	56.2	0.98
100%	9.37	13.5	1.03
BMA+ ethanol			
0%	23.68	223.6	2.71
25%	21.37	177.3	2.46
50%	19.54	121.2	1.28
75%	16.33	79.5	1.13
100%	9.37	13.5	1.03
BMA+ 1-hexanol			
0%	15.72	847.5	2.88
25%	17.89	289.9	2.84
50%	13.26	197.6	2.12
75%	10.68	101.4	1.78
100%	9.37	13.5	1.03
BMA+ 1-nonanol			
0%	9.09	1013.8	2.23
25%	10.58	613.5	2.16
50%	9.16	427.6	1.91
75%	7.75	128.8	1.73
100%	9.37	13.5	1.03
BMA+ 1-dodecanol			
0%	7.83	1146.3	2.07
25%	8.93	736.4	1.92
50%	7.16	512.7	1.66
75%	5.59	155.2	1.45
100%	9.37	13.5	1.03

size of BMA molecule in comparison to MMA molecules. In these systems, the complex formation is likely to occur between $H^{\delta+}$ of alcohols 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 and also provides information regarding the hydrogen bond between interacting components. The dielectric relaxation time shows continuous increase with chain length of esters and alcohol 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.

At high concentration of alcohol in the mixtures, there are a large number of alcohol molecules surrounding 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 formed¹⁹. The dipole-dipole interaction is the interaction of the -OH group of alcohol with C=O of ester.

At low concentration of alcohol 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 alcohol indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases.

The Kirkwood correlation factor, g^{eff} , which provides valuable information about ordering of the molecules in the liquid-state; that is, it quantifies the extent of polarization of the medium is provided in Tables 1 and 2. For the mixtures of alkyl methacrylate (MMA and BMA) with each of the five alcohols considered here, the value of g^{eff} increases from the g of MMA and BMA to that of alcohol. This is an indication of solute-solvent interaction between alkyl methacrylates and alcohols. The value of g for MMA and BMA is close to unity indicating no dipole correlations, whereas higher values of g for alcohols indicate parallel alignment of the electric dipoles. For all the mixtures, at all concentrations, the g^{eff} values are greater than unity, indicating parallel alignment of the electric dipoles. This conclusion is similar to that

arrived from the variation of dielectric constant with concentration of alkyl methacrylates (MMA and BMA). As a result, weak intermolecular interaction occurs.

In pure alcohols, a self-correlation of orientation with strong parallel dipolar alignment exist with g^{eff} values substantially greater than 1 whereas in alkyl methacrylates ($g^{\text{eff}} < 1$) indicating the correlation is more likely due to a combination of both parallel and anti-parallel orientation. On mixing, we find that (g^{eff}) is composition dependent and > 1 for all the system studied. Hence it appears that, in the mixtures, there arises a need to assign each molecular species a cavity of its own specific volume which in turn determines the molar orientation polarizability. For all the mixtures, the g^{eff} values are greater than unity, indicating parallel alignment of the electric dipoles.

The variation of $(1/\tau)^E$ for MMA + alcohols and BMA + alcohols at different composition are given in Figs 1 and 2. The $(1/\tau)^E$ values are negative for all the system studied. The higher negative deviation found in BMA + alcohols than MMA + alcohols systems. This indicates the formation of multimers through

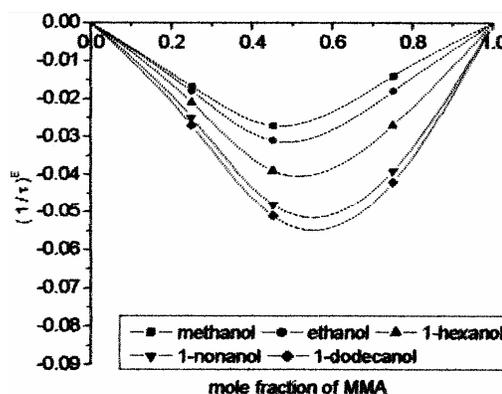


Fig. 1 — Excess inverse relaxation time $(1/\tau)^E$ versus volume fraction of alcohols for methyl methacrylate in alcohols

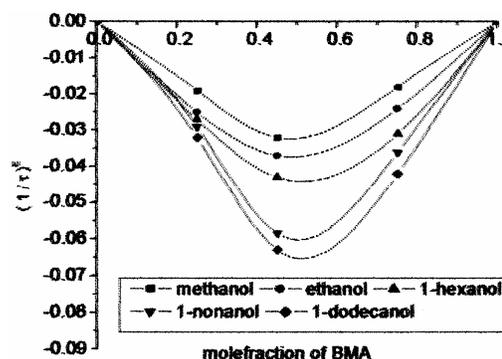


Fig. 2 — Excess inverse relaxation time $(1/\tau)^E$ versus volume fraction of alcohols for butyl methacrylate in alcohols

hydrogen bonding with slower rotation and parallel orientation of dipoles. For the systems of alcohols with the esters considered here, the existence of the intermolecular heterointeraction is in the following order: methanol < ethanol < 1-hexanol < 1-nonanol < 1-dodecanol and methyl methacrylate < butyl methacrylate.

5 Conclusion

Dielectric relaxation parameters, excess inverse relaxation time and Kirkwood correlation factor have been reported for alkyl methacrylate + alcohols mixtures for various concentrations. The investigated values of dielectric parameters show systematic change in dielectric values with increase in concentration of methyl methacrylate and butyl methacrylate in the solution. The negative excess inverse relaxation time values obtained for all the systems indicate the slower rotation of effective dipoles of the system. The relaxation time increases with increase of alkyl chain length of alcohols whereas the reverse trend is observed for static dielectric constant.

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