

# Dielectric Relaxation of Binary Mixtures of Alcohols with Acrylic Esters

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**ABSTRACT:** A dielectric relaxation study on alcohol–acrylic ester binary mixtures has been carried out at different concentrations using time domain reflectometry (TDR). The least-squares fit method has been used to obtain the dielectric parameters (the static dielectric constant  $\epsilon_0$  and the relaxation time  $\tau$ ). By using these parameters, the Bruggeman factor, the Kirkwood correlation factor, and excess inverse relaxation time were determined and discussed to yield information on the molecular structure and dynamics

of the mixture. The  $\epsilon_0$  and  $\tau$  values decreased with an increase in the percent of acrylic ester in alcohol for all the systems. The value of  $t$  increased with an increase in chain length of both the alcohol and acrylic ester, whereas the reverse trend is observed for  $\epsilon_0$ . © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2312–2316, 2008

**Key words:** dielectric relaxation; time domain reflectometry; alcohols; acrylic esters

## INTRODUCTION

Dielectric relaxation studies on binary mixtures are important for understanding the hydrogen bonding and intermolecular interactions in the mixture. A significance of the intermolecular interactions in the dynamics of molecules, as revealed in dielectric relaxation spectroscopy, is one of the most important and still open problems of molecular physics of the liquid state. Acrylic esters are important industrial chemicals and are widely used as precursors in the production of technically important high polymeric and latex systems.<sup>1</sup> Alcohols play an important role in many chemical reactions because of the ability to undergo self-association with manifold internal structures and are in wide use in industry and science as reagents, solvents, and fuels and attract great attention as useful solvents in the green technology.<sup>2</sup>

Dielectric parameters for methyl acetate–alcohol, ethyl acetate–alcohol, butyl acetate–alcohol, pyridine–alcohol, and aniline–alcohol binary systems were reported earlier by Shirke et al.,<sup>3</sup> Chaudhari et al.,<sup>4</sup> Shirke et al.,<sup>5</sup> Chaudhari and Mehrotra,<sup>6</sup> Patil et al.,<sup>7</sup> and Balamurugan et al.<sup>8</sup> All the aforementioned systems showed systematic change in the

dielectric parameters with concentration and chain length of alcohols.

Recently, our research group has investigated the complex formation of alkyl methacrylates with primary alcohols using FTIR spectroscopic<sup>9–16</sup> and frequency domain<sup>17</sup> techniques.

The aim of this article is to report a dielectric study on alcohol–acrylic ester mixtures conducted using time domain reflectometry (TDR) for the frequency range of 10 MHz to 10 GHz. The dielectric parameters, viz. the static dielectric constant  $\epsilon_0$  and relaxation time  $\tau$ , were determined. The Kirkwood correlation factor and excess inverse relaxation time were also obtained in order to obtain structural information about the binary mixtures.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) were purchased from Aldrich with purity >99% and used as received. AR grade alcohols were purified by standard methods.<sup>18</sup> The mixtures of various compositions (0–100%) were prepared by volume before mixing.

### Methods

The complex permittivity spectra were studied using TDR. The Hewlett-Packard HP 54750 sampling

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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 pulse generator was propagated through a coaxial line system of characteristic impedance 50  $\Omega$ . Transmission line system under test was placed at the end of the coaxial line in the standard military application coaxial cell coaxial connector with 3.5 mm outer diameter and 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 1.44-MB floppy diskette drive.

A temperature controller system with a water bath and thermostat has been used to maintain the constant temperature within the accuracy limit of  $\pm 1^\circ\text{C}$ . 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 is checked using the electronic thermometer.

### Data analysis

The time-dependent data were processed to obtain complex reflection coefficient spectra  $\rho^*(\omega)$  over the frequency range from 10 MHz to 10 GHz using Fourier transformation<sup>19,20</sup> as

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

where  $p(\omega)$  and  $q(\omega)$  are Fourier transforms of  $(R_1(t) - R_x(t))$  and  $(R_1(t) + R_x(t))$ , respectively,  $c$  is the velocity of light,  $\omega$  is angular frequency, and  $d$  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.<sup>21</sup>

The experimental values of  $\varepsilon^*$  are fitted with the Debye equation<sup>22</sup>

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

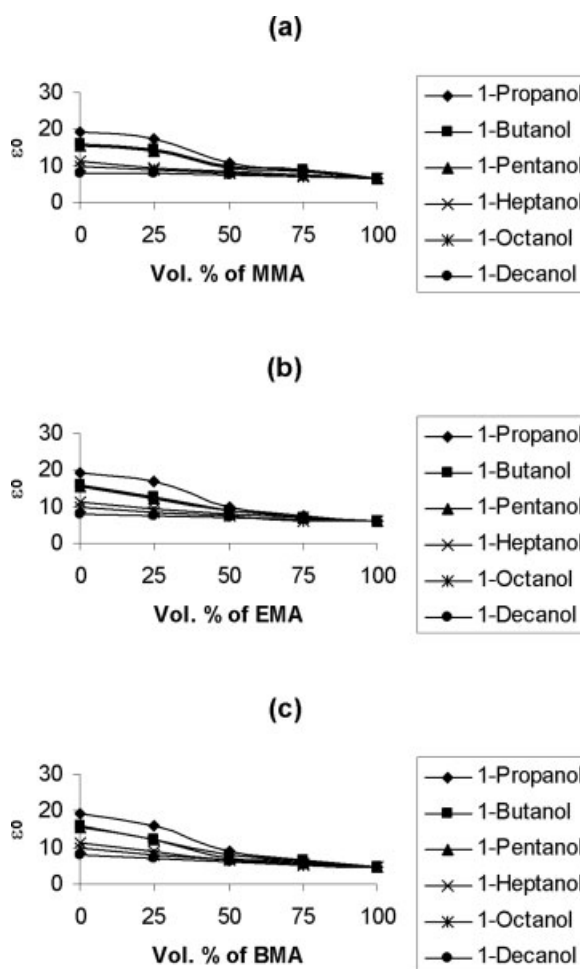
with  $\varepsilon_0$ ,  $\varepsilon_\infty$ , and  $\tau$  as fitting parameters. A nonlinear least-squares fit method<sup>23</sup> was used to determine the values of dielectric parameters.

## RESULTS AND DISCUSSION

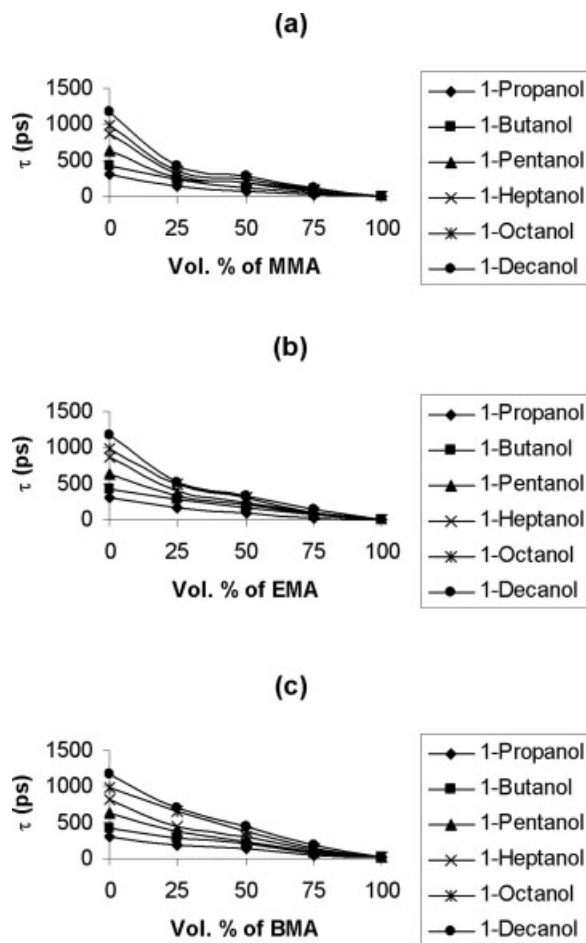
The static dielectric constant ( $\varepsilon_0$ ) and relaxation time ( $\tau$ ) obtained by fitting experimental data to the

Debye equation are plotted in Figures 1 and 2. For all the systems, the static dielectric constant and relaxation time value decrease as the percent of acrylic ester in the alcohol increases. This trend suggests that the intermolecular association takes place between alcohol and acrylic ester in all these systems. Similar conclusions were drawn by Shirke et al.<sup>3,5</sup> for alkyl acetate-alcohol systems.

From Figures 1 and 2, it is clear that the value of static dielectric constant decreases with increasing chain length of both the alcohol and acrylic ester for all the systems. The increase in relaxation time with chain length is to be expected in view of the fact that the 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 cooperativity for reorientation of the molecules increases with increasing length and the bulk of the cluster increases. The relaxation time increases with increasing chain length, in agreement



**Figure 1** Static permittivity versus vol % of (a) MMA for MMA-1-alcohol, (b) EMA for EMA-1-alcohol, and (c) BMA for BMA-1-alcohol systems, respectively.



**Figure 2** Relaxation time versus vol % of (a) MMA for MMA-1-alcohol, (b) EMA for EMA-1-alcohol, and (c) BMA for BMA-1-alcohol systems, respectively.

with the fact that the relaxation time is directly related to the size of the molecules.<sup>24</sup>

According to the Bruggeman mixture formula of static permittivity, the Bruggeman dielectric factor  $F_{BM}$  is given by,<sup>25</sup>

$$F_{BM} = \frac{(\epsilon_{0m} - \epsilon_{01})}{(\epsilon_{02} - \epsilon_{01})} \left( \frac{\epsilon_{02}}{\epsilon_{0m}} \right)^{1/3} = 1 - X_2 \quad (3)$$

where the mole fraction  $X_2$  is used in place of volume fraction. In fact, mole fraction  $X_2$  is a qualitative measure of volume fraction of the solute.  $\epsilon_{0m}$ ,  $\epsilon_{01}$ , and  $\epsilon_{02}$ , respectively, are the values of static permittivity corresponding to mixture, solvent, and solute. This Bruggeman equation assumes that orientation of the solvent molecules does not change in the mixture. This is only true for the nonpolar solvent. When both the solvent and the solute happen to be polar liquids, the Bruggeman equation has to be modified as

$$F_{BM} = 1 - [a - (a - 1)X_2]X_2 \quad (4)$$

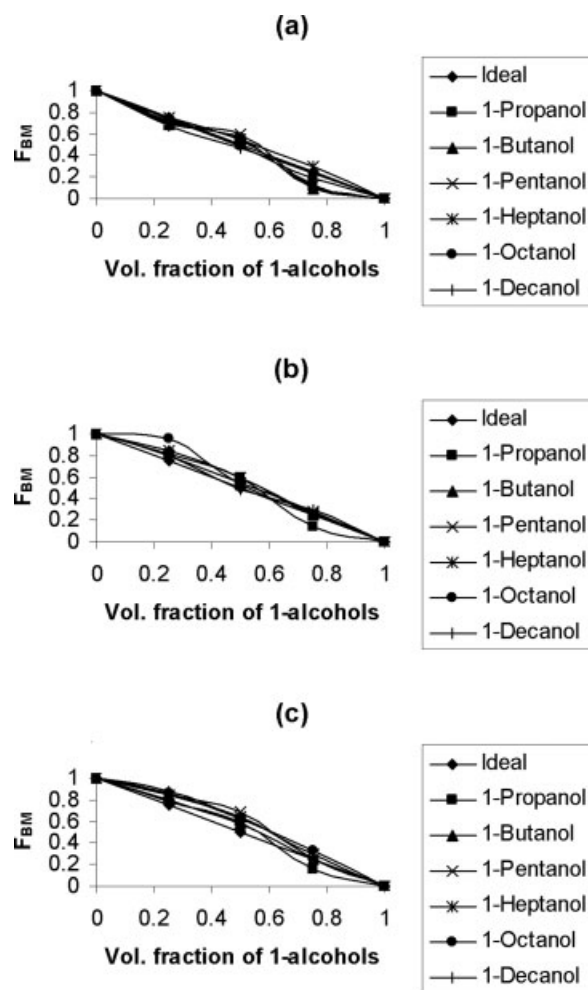
where  $a$  is the interaction parameter.

The Bruggeman plots of volume fraction of alcohol versus  $F_{BM}$  for alcohol-acrylic ester mixtures are given in Figure 3. It can be seen from these figures that  $F_{BM}$  is not a linear function of volume fraction of alcohol. The nonlinearity of the curves indicates heterointeraction, which may be due to hydrogen bonding of the —OH group of alcohol with C=O of the acrylic ester. Similar interpretations were given by Sivagurunathan et al.<sup>24</sup>

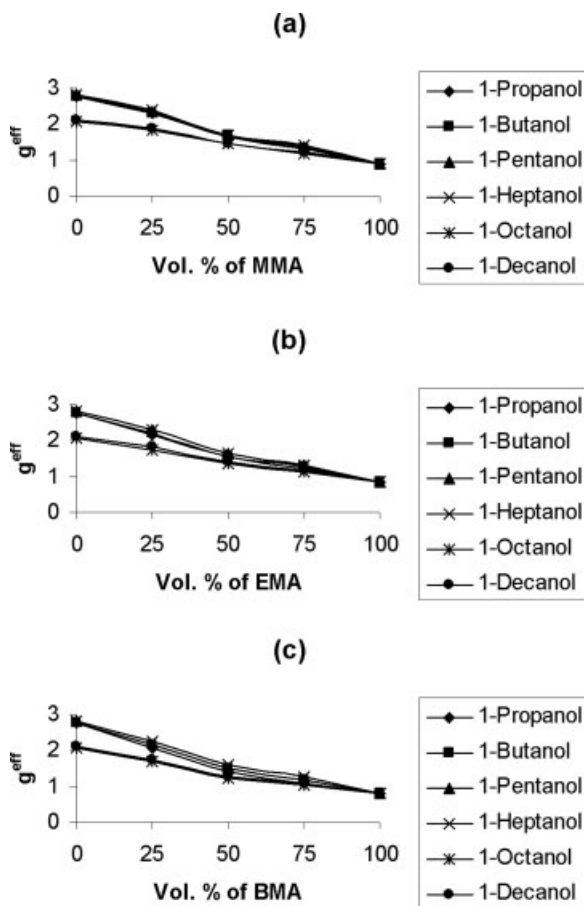
The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter  $g$ .<sup>26</sup> This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids. The  $g$  for the pure liquid may be obtained using the expression

$$\frac{4\pi N\mu^2\rho}{9kT} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (5)$$

where  $\mu$  is the dipole moment,  $\rho$  the density at temperature  $T$ ,  $M$  the molecular weight,  $k$  the Boltzman



**Figure 3** Bruggeman plot for (a) MMA-1-alcohol, (b) EMA-1-alcohol, and (c) BMA-1-alcohol systems, respectively.



**Figure 4** Kirkwood correlation factor versus vol % of (a) MMA for MMA-1-alcohol, (b) EMA for EMA-1-alcohol, and (c) BMA for BMA-1-alcohol systems, respectively.

constant,  $N$  the Avogadro's number,  $\epsilon_0$  the static dielectric constant, and  $\epsilon_\infty$  is the dielectric constant at high frequency.

For the mixture of two polar liquids (1) and (2), Eq. (5) is modified by Kumbharkhane et al. with the following assumption.<sup>27</sup>

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

$$\frac{4\pi N}{9kT} \left( \frac{\mu_1^2 \rho_1}{M_1} X_1 + \frac{\mu_2^2 \rho_2}{M_2} X_2 \right) g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (6)$$

$X_1$  and  $X_2$  are mole fractions of liquids (1) and (2), respectively, in the mixture. The suffixes  $m$ , 1, and 2 represent mixture, liquid 1 (the respective alcohol), and liquid 2 (the respective acrylic ester), respectively.  $g^{\text{eff}}$  changes from  $g_1$  to  $g_2$  as  $X_2$  increases from 0 to 1.

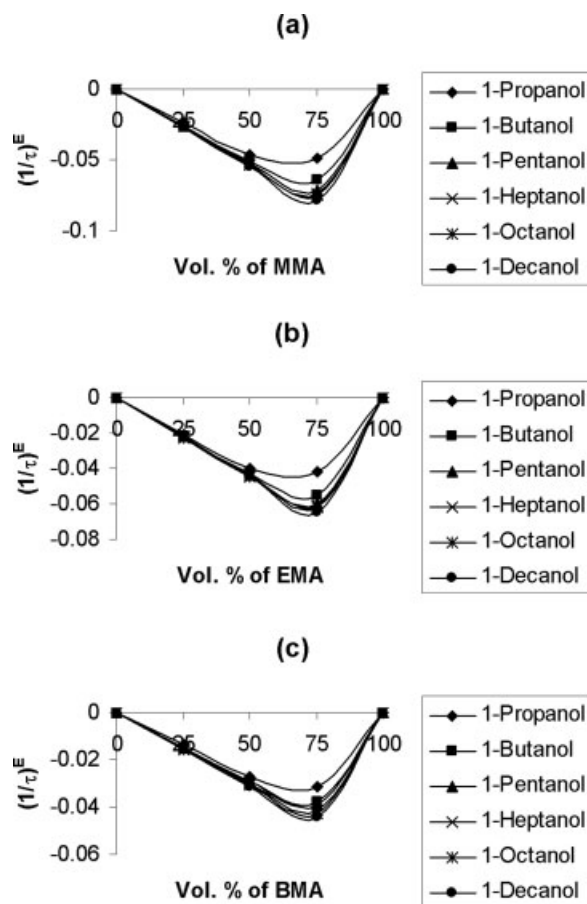
The calculated values of the Kirkwood correlation factor,  $g^{\text{eff}}$ , which provides valuable information

about ordering of the molecules in the liquid-state; that is, it quantifies the extent of polarization of the medium that are plotted in Figure 4. The value of  $g^{\text{eff}}$  increases from the  $g$  of respective acrylic ester to that of respective alcohol. The value of  $g$  for acrylic ester is close to unity for all the temperatures, indicating no dipole correlations, whereas higher values of  $g$  for alcohols indicate parallel alignment of the electric dipoles. The value of  $g^{\text{eff}}$  decreases, for all the systems, as the percent of acrylic ester in the alcohol molecules decreases.

The information related to dynamics of the solute-solvent interaction may be obtained by excess properties<sup>6</sup> related to the relaxation time in the mixture. The excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A x_A + (1/\tau)_B x_B] \quad (7)$$

where  $(1/\tau)^E$  is the excess inverse relaxation time, which represents the average broadening of dielectric spectra. The information regarding the dynamics



**Figure 5** Excess inverse relaxation time versus vol % of (a) MMA for MMA-1-alcohol, (b) EMA for EMA-1-alcohol, and (c) BMA for BMA-1-alcohol systems, respectively.

of solute–solvent interaction from this excess property is as follows:

- (i)  $(1/\tau)^E = 0$ : There is no change in the dynamics of solute–solvent interaction.
- (ii)  $(1/\tau)^E < 0$ : The solute–solvent interaction produces a field such that the effective dipoles rotate slowly.
- (iii)  $(1/\tau)^E > 0$ : The solute–solvent interaction produces a field such that the effective dipoles rotate quickly, i.e., the field cooperates in the rotation of the dipoles.

The variation of  $(1/\tau)^E$  with volume percentage of acrylic ester in alcohols is shown in Figure 5. The value of  $(1/\tau)^E$  is negative for all the concentrations, and all systems indicate the formation of multimer structures, which lead to the slower rotation of the dipoles in the system.

### CONCLUSION

Dielectric relaxation parameters and Kirkwood correlation factor have been reported for alcohol–acrylic ester mixtures for various concentrations. The dielectric constant and relaxation time decrease with an increase in the percent of acrylic ester molecules. The dielectric parameters show a systematic change with concentration and chain length. These data provide information about the interaction of the molecules in the system.

### References

1. Schildknecht, C. E. *Vinyl and Related Polymers*; Wiley: New York, 1977.
2. Savage, P. E. *Chem Rev* 1999, 99, 603.
3. Shirke, R. M.; Chaudhari, A.; More, N. M.; Patil, P. B. *J Chem Eng Data* 2000, 45, 917.
4. Chaudhari, A.; Shirke, R. M.; More, N. M.; Patil, P. B. *J Sol Chem* 2002, 31, 305.
5. Shirke, R. M.; Chaudhari, A.; More, N. M.; Patil, P. B. *J Mol Liq* 2001, 94, 27.
6. Chaudhari, A.; Mehrotra, S. C. *Mol Phys* 2002, 100, 3907.
7. Patil, S. P.; Chaudhari, A. S.; Lokhande, M. P.; Lande, M. K.; Shankarwar, A. G.; Helambe, S. N.; Arbad, B. R.; Mehrotra, S. C. *J Chem Eng Data* 1999, 44, 875.
8. Balamurugan, D.; Kumar, S.; Krishnan, S. *J Mol Liq* 2005, 122, 11.
9. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Indian J Pure Appl Phys* 2005, 43, 905.
10. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Z Phys Chem* 2005, 219, 1635.
11. Dharmalingam, K.; Ramachandran, K.; Sivagurunathan, P. *Z Phys Chem* 2006, 220, 739.
12. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Spectrochim Acta* 2006, 64A, 127.
13. Dharmalingam, K.; Ramachandran, K.; Sivagurunathan, P. *Main Group Chemistry* 2005, 4, 241.
14. Dharmalingam, K.; Ramachandran, K. *Phys Chem Liq* 2006, 44, 77.
15. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Indian J Phys* 2005, 79, 1403.
16. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. *Z Phys Chem* 2005, 219, 1385.
17. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K. and Kalamse, G. M. *Main Group Chemistry* 2005, 4, 227.
18. Vogel, A. I. *Text Book of Practical Organic Chemistry*, 3rd ed.; Longman: London, 1957.
19. Samulon, H. A. *Proc IRE* 1951, 39, 175.
20. Shannon, C. E. *Proc IRE* 1949, 37, 10.
21. Cole, R. H.; Barbarian, J. G.; Mashimo, S.; Chryssikos, G.; Burns, A.; Tombari, E. *J Appl Phys* 1989, 66, 793.
22. Debye, P. *Polar Molecules*; Chemical Catalog: New York, 1929.
23. Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; Mc Graw-Hill: New York, 1969.
24. Sivagurunathan, P.; Dharmalingam, K.; Ramachandran, K.; Prabhakar Undre, B.; Khirade, P. W.; Mehrotra, S. C. *Phil Mag Lett* 2006, 86, 291.
25. Bruggeman, D. A. G. *Ann Phys (Leipzig)* 1935, 5, 636.
26. Kirkwood, J. G. *J Chem Phys* 1939, 7, 911.
27. Kumbharkhane, A. C.; Puranik, S. M.; Mehrotra, S. C. *J Mol Liq* 1992, 51, 261.