Study of solute solvent interaction of nitrobenzene with DGME (diethylene glycol monomethyl ether) through dielectric relaxation study

PRADNYA MAHESHMALKAR¹, ARUNA P. MAHAROLKAR¹, S.B SADDYAD², S.P.KAMBLE, A.L.TIDAR¹, Y S SUDAKE¹, S.S.PATIL¹, P.W. KHIRADE¹* and S.C.MEHROTRA³

¹Microwave Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad - 431 004 (India).
²Miliya College Beed - 431 122 (India).
³Department of Computer Science & IT Dr. Babasaheb Ambedkar Marathwada University, Aurangabad - 431 004 (India).
(Received: August 08, 2009; Accepted: October 15, 2009)

ABSTRACT

Dielectric relaxation measurements for binary mixtures of Diethylene Glycol Monomethyl Ether or 2(2-methoxyethoxy ethanol) with nitrobenzene have been carried out over the entire range of concentration, using Time Domain Reflectometry (TDR) at 288K over the frequency range from 10MHz-20GHz. Bilinear calibration method is used to obtain complex permittivity $\varepsilon^*(\omega)$ from complex reflection coefficient $\rho^*(\varepsilon)$. The complex permittivity, excess permittivity($\varepsilon^E$), excess inverse relaxation time,$(1/\tau)^E$ Bruggeman factor($f_B^*)$, Kirkwood correlation factor($g^{(n)}$) are also calculated to study solute -solvent interactions.

Key words: Time domain Reflectometry; nitrobenzene; 2(2-methoxyethoxy ethanol); Excess parameters; Kirkwood correlation factor; Bruggeman factor.

INTRODUCTION

Dielectric spectroscopy is an important tool to access structural information at molecular level. DGME has wide range of applications. DGME is used in human therapeutics in cosmetics and in adhesives and in oral and sublingual preparations. It is a solubilising agent and an absorption enhancer used in veterinary medicines. These are used as industrial solvents, surfactants, detergentstion Due to great applications in various fields of these liquids, it is ever interesting to investigate the molecular dynamics of these molecules in the solution of nitrobenzene to understand role of hydrogen bonding. The glycol ethers have end (–OH) group so they can enter intermolecular hydrogen bonding. Intermolecular hydrogen bonding plays a vital role in reology and relaxation phenomenon. Sengwa et al.,¹ reported dielectric parameters for monomethyl, monoethyl and monobutyl ether of ethylene glycol with ethyl alcohol using LCR meter. Dutkiewicz et al² reported dielectric constants of nitrobenzene cahydroraphale. Sandeep et al reported dielectric constant of pyridine and nitrobenzene³ Chaudhari et al. reported complex permittivity spectra of ethanol nitrobenzene using TDR⁴. The aim of the present invention to study the solute solvent interaction in DMM-nitrobenzene complex in microwave region (10MHz to 20GHz) with varying concentrations (0% to 100%) using TDR technique at 288K. We also have a particular interest on the presentation of the accurate values
of dielectric constant and relaxation time of the complex from the viewpoint of heterogeneous molecular interaction and the conformation changes originating as a consequence of these interactions. The relaxation behaviors of this complex were explained by the Debye model. The excess inverse relaxation time is reported. The Kirkwood correlation factor is used to understand the molecular orientation in the mixture.

EXPERIMENTAL

Chemicals and sample preparation

DGME of AR grade was obtained from s.d.fine-chem. Pvt. Ltd., India. Nitrobenzene of spectroscopic grade obtained from BDH, India. With 99.9% purity and used without further purification. The solutions were prepared at different volume percentage of DGME in Nitrobenzene in the step of 10% at room temperature. The concentrations were prepared for 5 ml solution at room temperature.

Using these volume percents, the weight fraction is calculated as

$$X_A = \frac{(V_A \times \rho_A)}{(V_A \times \rho_A) + (V_B \times \rho_B)} \quad \ldots(1)$$

Where $V_A$ and $V_B$ are the volume and $\rho_A$ and $\rho_B$ are the density of liquid A and B respectively.

TDR set-up and data acquisition

The Hewlett Packard HP 54750A sampling oscilloscope with HP54754A TDR plug-in module has been used. After observing TDR response for the sample under study, the time window was kept to 5 ns. Also by observing TDR response for the sample under study, the SMA sample cell with 1.35 mm effective pin length has been used. To reduce noise, time dependent response curve was averaged for 64 times and then stored in the memory of the oscilloscope with 1024 points per wave form. First, the reflected pulse from the empty cell is acquired and stored in the memory. The empty cell wave form is used as the reference wave form. Both response wave forms are the reflected wave forms from the sample cell with open termination of transmission line. The data acquisition is carried out for 11 concentrations at 288 K with an accuracy of ±1°C. At each time the response wave-forms without sample and with sample were recorded. The time dependent response wave form without sample is referred as $R_1(t)$ and with sample is referred as $R_x(t)$.

Data analysis

The time dependent data were processed to obtain complex reflection coefficient spectra $\hat{r}^*(\omega)$ over the frequency range from 10 MHz to 10 GHz using Fourier transformation (4-5) as

$$P^*(\omega) = (c/j \omega d)(p(\omega)/q(\omega)) \quad \ldots(2)$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $(R_1(t)-R_x(t))$ and $d(R_1(t)+R_x(t))/dt$, respectively, $c$ is velocity of light, $\omega$ is angular velocity, $d$ is the effective pin length and $j=-1$. The complex permittivity spectra $\varepsilon^* (\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method.

The experimental values of $\varepsilon^*$ are fitted with the Debye equation

$$\varepsilon^* (\omega) = \varepsilon_{\infty} + \varepsilon_0 - \varepsilon_{\infty} / 1 + j \omega \tau \quad \ldots(3)$$

With $\varepsilon^*(\omega)$, $\varepsilon_{\infty}$, and $\tau$ as fitting parameters. A nonlinear least square fit method was used to determine the values of dielectric parameters.

RESULT AND DISCUSSION

In an ideal mixture of polar liquids if the molecules are non-interacting, a linear variation in static dielectric constant and relaxation time with concentration is expected but Figs. 1 & 2 shows non-linear variation in dielectric constant and relaxation time with change in volume fraction of nitrobenzene with DGME. This suggests intermolecular interactions is taking place within these systems. The values of static dielectric constant ($\varepsilon_{\infty}$) and relaxation time ($\tau$) is as shown in Table 1 and are plotted in Fig. 1 and 2 respectively.

The excess permittivity is defined as

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_{\infty})_m - [(\varepsilon_0 - \varepsilon_{\infty})_A X_A + (\varepsilon_0 - \varepsilon_{\infty})_B X_B] \quad \ldots(4)$$
The excess permittivity provides qualitative information about structure formation in the mixture as follows.

$\varepsilon^E = 0$ indicates that the solute and solvent do not interact at all.

$\varepsilon^E < 0$ indicates that the solute and solvent interaction act so as to reduce total effective dipoles. This suggests that solute–solvent mixture may form multimers leading structure to less effective dipoles.

$\varepsilon^E > 0$ indicates that the solute and solvent interact in such a way that the effective dipole moment increases. There is formation of monomers and dimers.

In Fig. 2 as $\varepsilon^E < 0$. The negative values of $\varepsilon^E$ indicate that the solute and solvent interaction act so as to reduce total effective dipoles. This suggests that solute–solvent mixture may form multimers leading structure to less effective dipoles.

![Fig. 1: Variation of mole fraction of NB versus excess dielectric constant at 288K](image1)

![Fig. 2: Variation of estimated excess inverse relaxation time $(1/\tau)^E$ as a function of mole fraction of NB inDGME at 288K](image2)
The excess inverse relaxation time is defined as

\[
\frac{1}{\tau}^E = \frac{1}{\tau} - \left[ \frac{(1/\tau)_A}{X_A} + \frac{(1/\tau)_B}{X_B} \right] \tag{6}
\]

where \(\frac{1}{\tau}^E\) is the excess inverse relaxation time which represents the average broadening of dielectric spectra. This reveals the following solute solvent interaction information as follows.

\(\frac{1}{\tau}^E = 0\): There is no change in the dynamics of the solute solvent interaction.

\(\frac{1}{\tau}^E < 0\): The solvent-solute interaction produces a field such that the effective dipoles rotate slowly.

**Fig. 3:** Kirkwood correlation factor \(g_{eff}\) versus vol% of NB with DMGE at 288K.

**Fig. 4:** Plot of Bruggeman factor \(f_B\) vs. volume fraction of NB at 288K.
(1/|k|) > 0: The solute-solvent interaction produces a field such that the effective dipoles rotate rapidly, i.e. the field will cooperate in rotation of dipoles.

The variation of (1/τ) with mole fraction of NB at 283, K is shown in fig (2). The excess inverse relaxation time values are negative for all temperatures in DGME rich region as the percentage of DGME decreases values increase and studied system indicate fast rotation of the dipoles, due to the solute–solvent interaction which produces a field in such a way that the effective dipole rotation is hindered.

The correlation parameter g is a useful index to the degree of hindered rotation in the liquid. Higher values of g in DGME confirm intermolecular hydrogen bonding. The value of g decreases as the volume of DGME decreases. Higher values of g for DMGE indicate parallel alignment of the electric dipoles. Presence of strong hydrogen bonding (in DGME rich region) the information related to dynamics of the solute-solvent interaction might be obtained by excess properties related to the relaxation time of complex.

The Bruggeman plot shows deviation from ideal line indicates there is strong intermolecular interaction between NB and DGME.

### CONCLUSION

Dielectric relaxation parameters, excess inverse relaxation time and Kirkwood correlation factor have been reported for nitrobenzene-DGME complex for various concentrations and temperatures. These data provide information regarding solute–solvent interaction in liquids. The extent of bonding in the molecules varies with concentration and temperature. The static dielectric constant increases as the concentration of NB increases. In this system the solution properties varies smoothly with solute composition reflecting hetero cooperative interactions.

### REFERENCES

1. J Sengwa, Madhvi .sonu Sankhla, and Shobha Sharma Bull. Korean Chem Soc., 27(5): 718-724.
2. Dutkiewicz, Dutkiewicze Polish Journal of Chemistry 78: 1765-1775 (2004).
3. Sandeep Kumar, D R Sharma, N Thakur, N S Negi, V S Rangra R S S 219(12): 1649-1654 (2005).
4. H.A.Samulon, Proc.IRE 39: 175 (1951).
5. Ajay Chaudhari,Anita Das,Garigipati Raju, Harish Chaudhari, Prakash Khirade, Navinkumar Narayan & Suresh Mehrotra. Proc Natl.Sci Counc ROC (A) 25(4): 205-210 (2001).
6. C.E. Shannon, Proc.IRE 37: 10 (1949).
7. R.H. Cole,IEEE Trans.Instrum.Meas IM-32: 42 (1983).
8. P.Debye, Polar Molecules (Chemical Catalog,New York) (1929).
9. P.R.Bevington, Data Reduction and Error Analysis for the Physical Sciences (McGraw-Hill,New York,1969).
10. R.M.Shirke, A Chaudshari, N.M. More, P.B Patil, J. Mol.Liq. 94: 27 (2001).
11. P.Sivagurunathan, K. Dharmalingam, K.Ramachandran, B.Prabhakar Undre,PW Khirde, S.C.Mehrotra., P.J.Singth, K.S. Sharma, Indian J.Pure Appl.Phys 31: 721
(1993).

12. J. Prakash B. Rai, *Indian J Pure Appl. Phys* 24: 187 (1986).

13. J.G.Kirkwood *J. Chem. Phys.* 7: 911 (1939).

14. S.M. Puranik, A.C. Kumbharakhane, S.C. Mehrotra, *J. Mol. Liq.* 108: 95 (2003).

15. K. Dharmalingam, K. Ramachandran, P. Shivgurunathan, B. Prabhakar Undre, P.W. Khirade, S.C. Mehrotra *Bull. Korean Chem. Soc.* 27(12) 2040-2044 (2006).

16. P.P. Sivagurunathen, K Dharmalingam, K. Ramachandran, B. Prabhakar Undre, P.W. Khirade and S.C. Mehrotra *J of Mol Liquids* 133: 139-145 (2007).

17. P.P. Sivagurunathen, K Dharmalingam, K. Ramachandran, B. Prabhakar Undre, P.W. Khirade and S.C. Mehrotra *Physics B* 387: 203-207 (2007).

18. P.Undre, S.N. Helambe, S.B. Jagdale, P.W. Khirade S.C. Mehrotra. *Praman.* 68(5): 851-861 (2007).

19. B.G. Lone, P.B. Undre, S.S. Patil, P.W. Khirade, S.C. Mehrota *J of Mole. liqu.* 141: 47-53 (2008).