



MICROWAVE DIELECTRIC CHARACTERIZATION OF POLAR PROTIC LIQUIDS USING TIME DOMAIN REFLECTOMETRY

ARUNA P. MAHAROLKAR¹, A. G. MURUGKAR²
AND P. W. KHIRADE*¹

¹*Department of Physics, Dr. Babasaheb Ambedkar Marathwada University,
Aurangabad, (M.S.) -431004, India.*

ABSTRACT

Dielectric measurement on binary mixtures of N-N Dimethylacetamide (DMA) with n-Butanol have been carried out over the entire concentration range (of 0.1 – 1 volume fraction) using Time Domain Reflectometry (TDR) technique at 303.15K temperature at which all measurements have been carried out at the microwave frequency range of 10 MHz to 20 GHz. The static dielectric constant, relaxation time, density, excess static dielectric constant, excess inverse relaxation time, Bruggeman factor, excess molar volume of binary mixtures over the entire concentration range were determined to explore the effect hetero molecular interaction. Excess parameters are fitted to Redlich–Kister equation.

KEYWORDS: Static dielectric constant; relaxation time, Bruggeman factor; excess static dielectric constant.



PROF. P. W. KHIRADE

Department of Physics, Dr. Babasaheb Ambedkar Marathwada University,
Aurangabad, (M.S.) -431004, India.

INTRODUCTION

The dielectric properties and intermolecular interactions of the binary liquid mixtures can be estimated with high accuracy using TDR technique¹⁻⁵. The study of dielectric properties of liquid mixtures and solutions containing polar-polar components are very essential for their application in chemical, textile, leather and nuclear industries. Dielectric parameters are sensitive to the composition of the mixture i.e. molecular arrangement in the solution which results from intermolecular interaction. Dielectric constant depends upon the structure and interactions present in the liquid system as it is fundamentally related to the binding forces between the constituents of the medium and also sensitive to temperature. The study of molecular interactions in the liquid mixtures is of considerable importance in the elucidation of the structural properties of the molecules. The intermolecular interactions affect the structural arrangement including the shape of molecules. Dielectric relaxation studies of polar protic molecules in polar protic solvent using microwave absorption method have been widely used to study the molecular structures including the molecular interactions in liquid mixtures¹⁻³. We have used the Time Domain Reflectometry (TDR) to find the dielectric properties such as static permittivity and relaxation time of binary mixtures of associated liquid i.e. n-butanol with N-N Dimethylacetamide. Butanol is polar liquid and self-associated through hydrogen bonding in the state. n-Butanol is used as a solvent for a wide variety of chemical and textile processes. It is also used as paint thinner. n-Butanol is effective in reducing viscosities of many formulations while simultaneously promoting flow and retarding blush. n-Butanol is also considered as a potential biofuel due to long hydrocarbon chain.

MATERIALS AND METHODS

EXPERIMENTAL

(i) Experimental Section

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used for experimental measurements of dielectric parameters. A fast rising step voltage pulse of about 39 ps rise time generated by a tunnel diode was propagated through a flexible coaxial cable with characteristic impedance of 50 Ω . The sample was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell. The measurements and data analysis is carried out for eleven concentrations at 303.15 K. The experimental detail is same as explained earlier¹. The densities were measured by using Anton Paar DMA 35 densitometer at 303.15K.

(ii) Theory

The information regarding intermolecular interaction between two liquid may be obtained from excess parameters (A^E) of mixtures. It is defined as,

$$A^E = A_m - (X_1A_1 + X_2A_2) \quad (1)$$

where x is mole fraction and suffixes m, 1, 2, A represents mixture, liquid 1 and liquid 2, parameters respectively. The excess parameters were fitted to Redlich-Kister equation.

The Bruggeman factor (f_B) is another important parameter which may be used as an indicator of solute-solvent interactions and is given by,

$$f_B = \left(\frac{\epsilon_m - \epsilon_B}{\epsilon_A - \epsilon_B} \right) \left(\frac{\epsilon_A}{\epsilon_m} \right)^{(1/3)} = 1 - V \quad (2)$$

where V is volume fraction, which is a qualitative measure of volume of the solute in the mixture. The values of static dielectric constant corresponding to mixture, component A and component B are given by ϵ_m , ϵ_A and ϵ_B respectively.

Table 1**Static Dielectric Constant, Relaxation Time, Density of DMA+n-Butanol Binary System**

Volume fraction of DMA	Density (g/cm ³)	Dielectric constant	Relaxation time (Ps)
0	0.8095	17.85	463.
0.1	0.8213	19.55	400.14
0.2	0.8330	21.55	350.11
0.3	0.8448	23.55	299.89
0.4	0.8665	25.53	250.13
0.5	0.8883	27.3	200.12
0.6	0.8965	29.6	150.1
0.7	0.9058	32.2	99.99
0.8	0.9139	34.11	75.03
0.9	0.9210	35.8	50
1	0.9270	37	23.02

The non-linear variation of static dielectric constant, relaxation time, density of DMA+n-Butanol system confirms the formation of strong intermolecular interactions in the mixtures. Increase in static dielectric constant of mixtures with increase in concentration of DMA in n-Butanol confirms the increase in effective

dipole moments. The decrease in the relaxation time is attributed to the decrease in the effective radius of the rotating unit which is due to increase in hydrogen bonding with increase in concentration of DMA. This results in faster rotation of molecules which decreases the relaxation time.

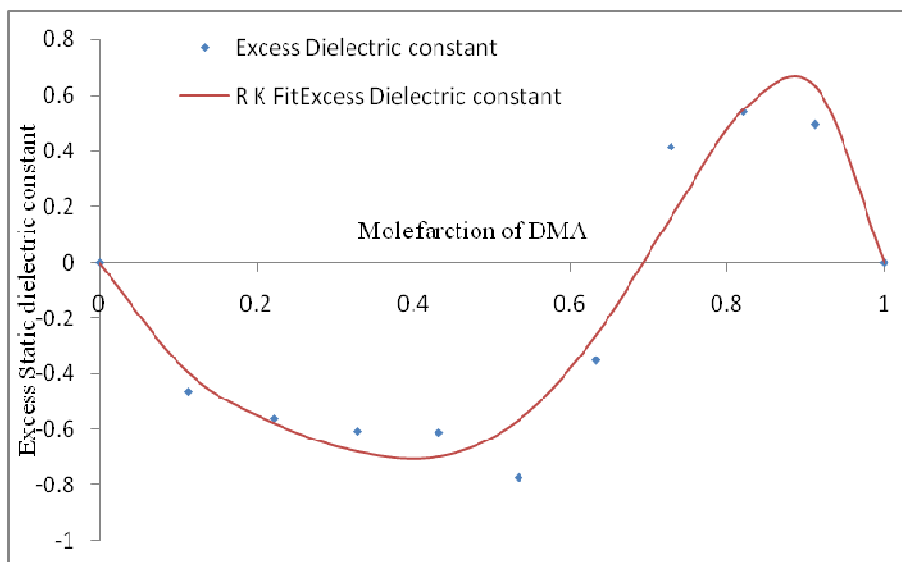


Figure 1
Excess static dielectric constant

The variation of excess static dielectric constant in n-butanol-DMA binary system is shown in figure 1. Excess static dielectric constant provides information about intermolecular

interactions and the molar ratio corresponding to the formation of hydrogen bonded (H-bonded) interactions between the mixture constituents. The negative value (figure 1) of

excess static dielectric constant indicates that the solute and solvent interact in such a manner so as to decrease the effective dipole moment and leads to the formation of multimers. In butanol rich region, dimers of pure butanol combines with dimers of pure DMA and further forms multimers whereas in DMA rich region

positive deviation indicates that as concentration of DMA increases dipoles tends to form dimers structure. The maximum magnitude of ϵ_{ex}^E of DMA+n-Butanol occur at 0.5 mole fraction of n-Butanol. The System shows maximum magnitude corresponding stoichiometric ratio of DMA to butanol is 1:1.

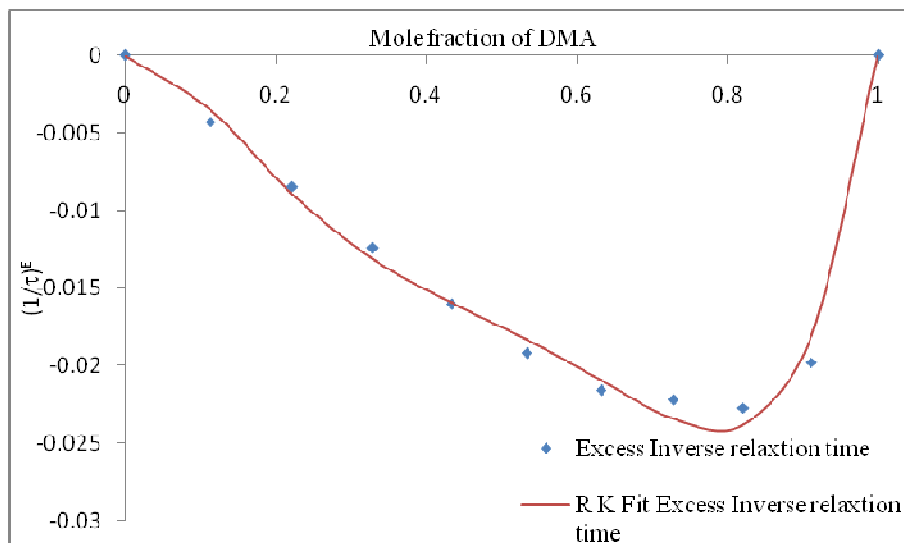


Figure 2
Excess inverse relaxation time of DMA+n-Butanol

The variation of excess inverse relaxation time in n-butanol-DMA binary system is shown in figure 2 respectively. The excess inverse relaxation time represents the average broadening of dielectric spectra. The excess inverse relaxation time renders information about the dynamics of solute-solvent interaction. The negative excess inverse relaxation time also indicates that, addition of n-butanol in DMA has created a hindered field so effective dipole rotate slowly.

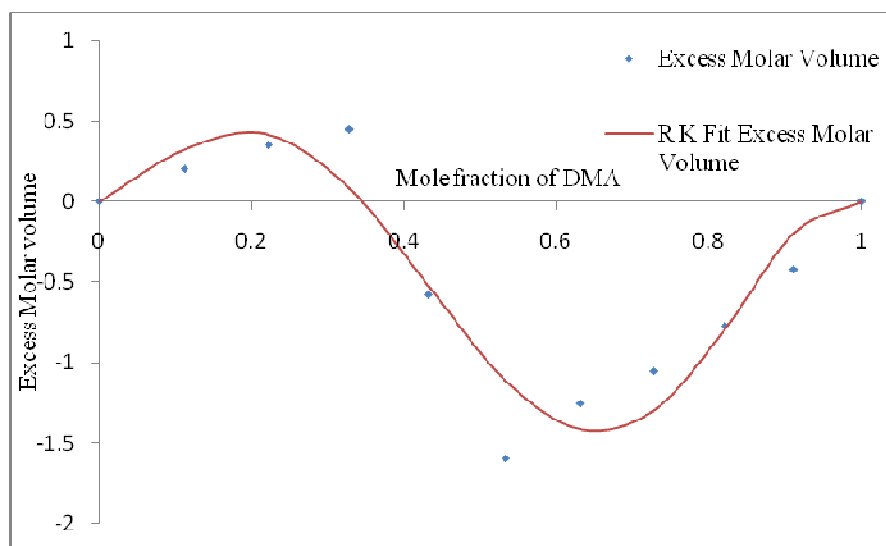


Figure 3
Excess molar volume of DMA+n-Butanol

The negative V^E of n-butanol-DMA system indicates strong interaction via hydrogen bonding between unlike molecules⁷. The negative V^E may be also due to good geometrical fitting of one component to another component⁸. The negative variation of excess molar volume in DMA+n-butanol mixture indicates the structural contribution of constituents arising from proper geometrical fitting in this case i.e. better interstitial

accommodation of solute and solvent in the system. The molecules of DMA cooperates with n-butanol is confirmed from our observation. This cooperation causes the decrease in molar volume. Leading to the formation of tightly packed hydrogen-bonded aggregates (between unlike molecules). Negative value also shows that solute acts as a structure maker. The maximum magnitude of excess molar volume shows the strength of hydrogen bond interaction

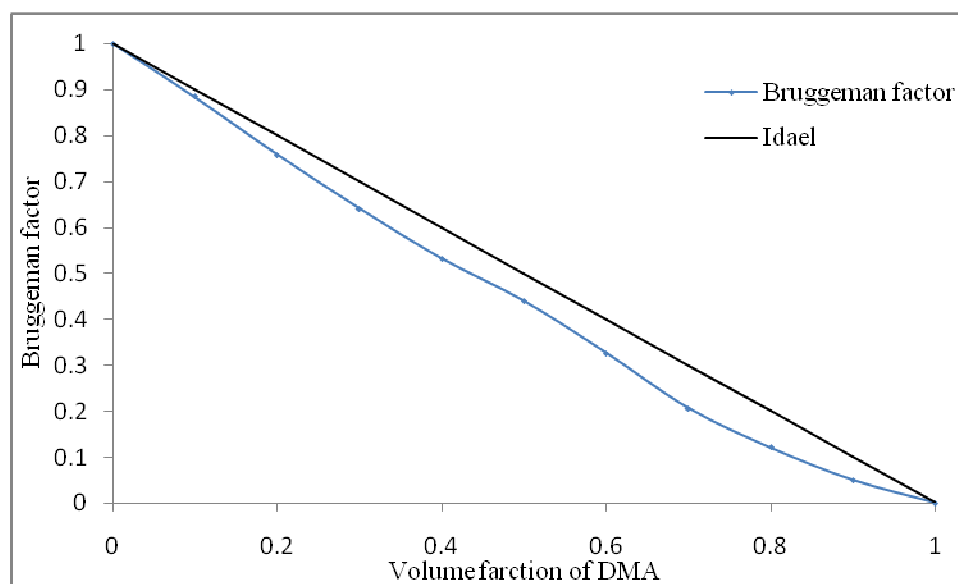


Figure 4
Bruggeman factor of DMA+n-Butanol

Bruggeman plot of DMA-n-Butanol binary system is given in figure 4. The deviation of Bruggeman factor (f_B) leads to formation of intermolecular interaction between mixing components⁶⁻⁸. In this system, it is observed that the value of Bruggeman factor (f_B) deviates (Negative deviation) from ideal line. The nonlinearity of the curve indicates existence of intermolecular interactions in the system

CONCLUSION

The dielectric study at 303.15K of DMA with n-Butanol confirm that there exists strong intermolecular interactions i.e. hydrogen bonding between DMA and n-Butanol. The non linear variation of dielectric constant, relaxation time and density probes the presence of intermolecular interaction within the present system. The deviation of Bruggeman factor also conforms presence strong intermolecular interaction between the systems. Also deviation of excess static dielectric constant and excess inverse relaxation time conforms the presence of strong intermolecular interactions within the system.

REFERENCES

1. P.Sivagurunathan, K. Dharmalingam, K. Ramachandran, P. Undre, P. W. Khirade, S. C. Mehrotra, Lithuanian J. Phys., vol. 46(4), pp. 441, (2006).

2. P. Maharolkar, Y. S. Sudake, S. P. Kamble, A. L. Tidar, A. G. Murugkar, S. S. Patil, P. W. Khirade, S. C. Mehrotra, Int. J. Chem. vol 2(2), pp. 250, (2010).
3. G. M. Dharne, A. P. Maharolkar, P. W. Khirade S. S. Patil, S. C. Mehrotra, Mat. Sci. Res. India, vol. 5(2),91, (2008).
4. Aruna P. Maharolkar , A. G. Murugkar , S. S. Patil P. W. Khirade Asian Journal of Chemistry vol. 25 No. 2, pp. 937-940, (2013)
5. Aruna P Maharolkar, A G Murugkar, S S Patil, P W Khirade International journal of pharma and biosciences vol. 3,(4), pp. 484-444, (2012).
6. Aruna P Maharolkar, Y S Sudake, S P Kamble, A G Murugkar, S S Patil, P W Khirade Asian Journal of Chemistry; (24), 12 5680-5682, (2012).
7. Aruna P Maharolkar, Y. Sudake, S Kamble , A G Murugkar, S S Patil, P W Khirade American Institute of Physics (AIP) Conference Proceeding 1536, 1129-1130, (2013).
8. Aruna P Maharolkar , A G Murugkar, S S Patil, P W Khirade Proceedings of National Conference on Microwave Techniques and Applications. ISBN no.978-93-83587-03-2 page 49-54, 29-30 November (2013)