



Structural Study of a Binary Mixture of Multifunctional Group Molecules Using Time Domain Reflectometry

A.V. Patil^a and V.P. Pawar^b

^aDepartment of Physics, I.C.S. College of Arts, Commerce and Science, Khed-415 709, Ratnagiri

^bDepartment of Physics, Sunderrao Solanke Mahavidyalaya, Majalgaon-431 131, Beed

E-mail: avpatil333@gmail.com

Abstract

The dielectric relaxation study of diethanolamine with triethanolamine binary mixture have been determined over the frequency range of 10 MHz to 20 GHz, at 30°C using time domain reflectometry (TDR) method for 11 concentrations of the system. The present work reveals molecular interaction between same multi-functional groups [-OH and -NH₂] of the alkanolamines (diethanolamine and triethanolamine) using different models such as Debye model, Excess model and Kirkwood model. The dielectric parameters viz. static dielectric constant (ϵ_0) and relaxation time (τ) have been obtained with Debye equation characterized by a single relaxation time without relaxation time distribution by the least squares fit method.

Key words: Structural Properties, Diethanolamine, and Triethanolamine.

1. Introduction

Dielectric study of binary polar liquids provides information regarding solute-solvent interaction. Considerable dielectric relaxation study has been done in aqueous solutions[1-3]. The diethanolamine (DEA) and triethanolamine (TEA) are multifunctional substances that are capable of hydrogen bonding by both donation and acceptance of hydrogen bonds. Their properties, in this respect, have not so far been determined, and it should be of interest to see how one functional group (the two hydroxy and primary secondary functional groups) affects to the behavior of the other (the two hydroxy and tertiary amine functional groups). Diethanolamine (DEA) and triethanolamine (TEA) both are highly polar liquids. Dielectric relaxation of liquid mixture gives information about molecular interactions. Objective of the present work is to report the dielectric relaxation study for DEA-TEA system at various concentrations at 30°C.

Article Info:



2. Experimental Details

DEA (AR grade, Merck Specialties, Pvt. Ltd., Mumbai, India) and TEA (AR grade, Qualigens fine chemicals Pvt. Ltd., Mumbai, India) were used without further purification. The solutions were prepared at 11 different volume percentage of DEA from 0 % to 100 %. Using these volume percent the mole fraction is calculated as

$$x = (v_1 \rho_1 m_1) / [(v_1 \rho_1 m_1) + (v_2 \rho_2 m_2)] \quad (1)$$

where m_i , v_i , and ρ_i represent the molecular weight, volume percent, and density of the i^{th} ($i=1, 2$) liquids, respectively.

The complex permittivity spectra were studied using the time domain reflectometry [4] method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been used.

The relaxation behavior of DEA-TEA system agrees with the Debye model. Therefore the experimental values of $\epsilon^*(\omega)$ were fitted with the Debye equation [5].

A nonlinear Least-Squares fit method [6] was used to determine the values of dielectric parameters.

3. Results and discussions

3.1 Dielectric Properties

The static dielectric constant (ϵ_0), dielectric constant at high frequency (ϵ_∞) and relaxation time (τ) obtained by fitting experimental data with the Debye equation are listed in table (1) for DEA-TEA system.

The values of static dielectric constant randomly increase with increasing the temperatures up to the melting points of DEA and TEA in the system, and then it becomes smoothly decreases with increase in temperatures. This behavior of static dielectric constants of DEA and TEA indicates that the change of phase from semi solid state to liquid state and increase in static dielectric constant may be correlated to disturbance in antiparallel arrangement of dipoles which leads to increase effective dipole moment. The melting point of DEA is 28°C and TEA is 20.5°C. The values of relaxation



time decreases with increase of temperature, but these values suddenly decreases at the melting points.

Table 1 - Temperature dependent dielectric relaxation parameters for DEA-TEA mixture

x_2	T=15°C	T=20°C	T=25°C	T=28°C	T=30°C
ϵ_0					
0.0000	19.07	20.93	22.56	24.69	24.53
0.0743	23.44	25.12	27.20	29.77	27.53
0.1530	25.30	27.68	29.53	31.22	30.04
0.2364	26.80	28.60	30.47	31.53	31.18
0.3251	27.89	29.55	31.22	32.54	31.60
0.4194	28.10	32.05	32.44	33.18	32.74
0.5201	27.33	31.94	31.22	30.92	30.06
0.6277	27.19	31.56	30.64	30.13	29.35
0.7429	26.84	30.77	30.08	29.79	28.93
0.8667	26.12	30.34	29.94	29.02	28.60
1.0000	25.18	29.83	29.26	28.57	28.09
ϵ_∞					
0.0000	2.69	2.78	3.03	2.57	2.46
0.0743	2.84	2.79	3.10	2.59	2.49
0.1530	2.71	2.81	3.13	2.61	2.53
0.2364	2.99	2.81	3.19	2.68	2.55
0.3251	3.12	2.83	3.22	2.70	2.58
0.4194	3.21	2.88	3.27	2.73	2.60
0.5201	3.76	2.91	3.09	2.74	2.63



0.6277	3.04	2.93	3.01	2.81	2.64
0.7429	2.81	2.98	2.98	2.88	2.69
0.8667	2.77	3.13	3.04	2.96	2.71
1.0000	2.61	3.30	3.18	3.02	2.97
$\tau(\text{ps})$					
0.0000	474.21	439.73	414.84	307.48	285.94
0.0743	488.03	441.84	423.10	326.30	298.52
0.1530	496.51	443.98	425.62	332.83	307.03
0.2364	502.47	450.04	428.04	345.31	310.44
0.3251	509.85	452.08	430.16	349.43	316.85
0.4194	513.64	457.24	432.96	353.01	327.24
0.5201	519.33	458.73	435.82	361.60	339.61
0.6277	528.07	460.85	437.44	369.55	358.77
0.7429	531.63	464.52	440.72	384.74	364.64
0.8667	548.70	470.35	441.65	400.33	371.38
1.0000	556.34	472.20	443.13	407.54	383.19

3.2 Excess Dielectric Properties

The information related to liquids 1 and 2 interaction may be obtained by excess properties [7, 8] related to the permittivity and relaxation times in the mixture.

The excess permittivity may provide qualitative information about multimers formation in the mixture as follows:

$\varepsilon^E = 0$ indicates that the unlike molecules of the mixture constituents do not interact at all.

$\varepsilon^E < 0$ indicates that the unlike molecules of the mixture constituents interact in such a way that the total effective dipoles get reduced. These liquids may form multimers leading to the less effective dipoles.



$\epsilon^E > 0$ indicates that the unlike molecules of the mixture constituents interact in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipole aligned in a parallel direction.

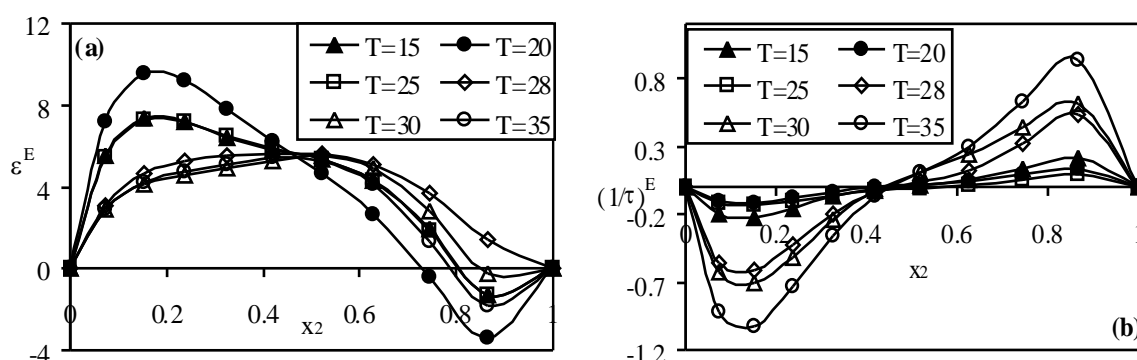


Fig. 1. (a) Excess permittivity (ϵ^E), (b) Excess inverse relaxation time $(1/\tau)^E$ versus mole fraction (x_2) of TEA in DEA at different temperatures.

The excess permittivity values are positive in the DEA rich region and negative in the TEA rich region, except 28°C. Excess inverse relaxation time value has reverse trend for all concentrations and at all temperatures. The positive peak values are different at all temperatures of excess permittivity in DEA rich region. The negative peak in the TEA rich region is at 0.8667 mole fraction of DEA in TEA in the system. The negative peak of excess inverse relaxation times is noted at 0.1530 and the positive peak at 0.8667 mole fraction of DEA in the TEA of the system. The excess permittivity values are positive up to the 80 % of TEA in DEA and then it becomes negative for 15, 25 and 30°C in the system. For 20°C, these values are positive up to the 90 % of TEA in DEA and then it becomes negative. At 28°C, all values are positive. The excess permittivity plots for the system studied show that, with addition of TEA, the values of excess permittivity become positive indicating formation of multimers in the mixture and it is negative in TEA rich region nearly 90 % TEA in the system.

Similarly, the excess inverse relaxation time $(1/\tau)^E$ which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (Which is the inverse of the relaxation time) in the resonant spectroscopy [9, 10].

The information regarding the dynamic of liquid 1 and 2 interactions from the excess inverse relaxation time is as follows:

$(1/\tau)^E = 0$: There is no change in the dynamics of liquid 1 and 2 interaction.



$(1/\tau)^E < 0$: The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate slowly.

$(1/\tau)^E > 0$: The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate quickly i.e. the field will co-operate in rotation of dipoles.

The excess inverse relaxation time values are negative up to the 50 % TEA and then it becomes positive in the system. The negative value of excess inverse relaxation time indicates slower rotation of the dipoles of the system and positive values indicates faster rotation of the dipoles of the system.

3.3 Kirkwood Properties

The Kirkwood correlation factor g [11] is also a parameter for getting information regarding the orientation of electric dipoles in polar liquids. The dipole moments for DEA and TEA in the gas phase are taken as 2.80D and 3.57D [12] respectively.

The structural information about the liquid by dielectric parameters can be obtained using Kirkwood correlation factor. The values of g^{eff} and g_r are tabulated in table (2). The value of g^{eff} is linearly increases up to 50 % TEA in DEA, and then it becomes decreases at 15°C. After all the temperatures (after the melting points) these values are linearly decreases with increase in the % volume of TEA in the system. After 28°C, these values are linearly increases with temperatures in DEA and TEA rich region (i.e. both are in liquid state). These values are greater than one indicating parallel orientation of the electric dipole and less than one indicating anti-parallel orientation of the electric dipole in the system. $g_f < 1$ for all concentrations at 20 to 30°C. The g_f values are close to unity for DEA-TEA system studied, indicating weaker intermolecular interactions between components of the system. The maximum deviation from unity is observed at 15°C, around 20 % of TEA in DEA mixture.

Table 2 - Temperature dependent Kirkwood parameters for DEA-TEA mixture.

ϕ_2	T=15°C	T=20°C	T=25°C	T=28°C	T=30°C
----------	--------	--------	--------	--------	--------



g^{eff}					
1.0	0.8148	0.6783	0.7878	0.9391	0.9590
0.9	1.0304	0.8598	0.9860	1.1874	1.1263
0.8	1.1310	0.9903	1.1001	1.2925	1.2827
0.7	1.2168	1.0641	1.1624	1.3521	1.3852
0.6	1.2847	1.1437	1.2192	1.4477	1.4593
0.5	1.3110	1.2945	1.2982	1.5310	1.5741
0.4	1.2890	1.3396	1.2746	1.4733	1.4958
0.3	1.2986	1.3746	1.2780	1.4868	1.5173
0.2	1.2977	1.3913	1.2823	1.5242	1.5555
0.1	1.2777	1.4260	1.3060	1.5391	1.6004
0.0	1.2456	1.4578	1.3048	1.5723	1.6363
g_r					
1.0	1.0000	1.0000	1.0000	1.0000	1.0000
0.9	0.9823	0.9433	0.9728	0.9727	0.9623
0.8	0.9825	0.9235	0.9684	0.9634	0.9538
0.7	0.9937	0.9100	0.9683	0.9583	0.9538
0.6	1.0112	0.9095	0.9752	0.9698	0.9579
0.5	1.0235	0.9452	0.9977	0.9877	0.9821
0.4	1.0193	0.9529	0.9869	0.9637	0.9500
0.3	1.0279	0.9613	0.9863	0.9631	0.9504
0.2	1.0320	0.9644	0.9866	0.9762	0.9614
0.1	1.0227	0.9806	1.0008	0.9813	0.9805
0.0	1.0000	1.0000	1.0000	1.0000	1.0000



3.4 Conclusion

The Dielectric relaxation properties have been reported for some multifunctional (-OH and -NH₂) compounds binary mixture for various temperatures and concentrations.

- The values of static dielectric constant increase upto their melting points and then it becomes decreases with increasing the temperature in the system.
- The relaxation time of these molecules sudnly drops down at the melting points.
- The excess permittivity may provide qualitative infor-mation about multimers formation in the mixture.
- The information regarding the dynamic of liquid 1 and 2 interactions from the excess inverse relaxation time.
- The Kirkwood correlation factor is also a parameter for getting information regarding the orientation of electric dipoles in polar liquids.
- In semi-solid state, the strong inter-molecular intraction is observed as compaired to liquid state of the system contains same functional groups.

Acknowledgements

Authors are thankful to Rtd. Prof. S.C. Mehrotra, Department of Computer Science & IT, Dr. B. A. M. University, Aurangabad for his valuable guidance.

References

- [1] A.V. Patil, G.N. Shinde, V.P. Pawar, "Dielectric relaxation study of hydrogen bonded structures in ethanolamine with diethanolamine using TDR technique," J. Mol. Liq., 168, 42-46, 2012.
- [2] A.V. Patil and V.P. Pawar, "Microwave dielectric spectra and molecular interaction in a binary mixture of ethanolamine with diethanolamine," J. Mol. Liq., 188, 1-4, 2013.
- [3] A.V. Patil, B.D. Achole, G.N. Shinde and V.P. Pawar, "Study of molecular interaction in binary mixture of dimethylene chloride with dimethylformamide using Bruggeman model," Scholars Research Library, Archives of Applied Science Research, 4(4), 1665-1669, 2012.
- [4] V.P. Pawar, A.V. Patil and S.C. Mehrotra, "Dielectric Relaxation Study of Acetonitrile with 1,2-dichloroethane Using TDR, International conference on dielectric Liquids," IEEE Explore, NTNU, Trondheim, Norway, 1-4, 2011.



- [5] P. Debye, "Polar Molecule; Chemical Catalog," Dover, NY, 1929.
- [6] P.R. Bevington, "Data reduction and error analysis for the physical sciences," McGraw Hill: New York, 1969.
- [7] V.P. Pawar, A.V. Patil, A.R. Patil, S.C. Mehrotra, "Dielectric relaxation study of solute-solvent interaction between dimethylene chloride and dimethylformamide using time domain reflectometry," J. Mol. Liq., 155, 16-19, 2010.
- [8] B.D. Achole, A.V. Patil, V.P. Pawar, S.C. Mehrotra, "Study of interaction through dielectrics: Behavior of -OH group molecules from 10 MHz to 20 GHz," J. Mol. Liq., 159, 152-156, 2011.
- [9] V.P. Pawar and A.V. Patil, "Dielectric relaxation studies on molecular interaction in binary mixture of dimethylene chloride with n-methylformamide," Fluid Phase Equilib., 376, 111-115, 2014.
- [10] V.P. Pawar and A.V. Patil, "Dielectric and thermodynamic properties in a binary mixture of dimethylene with formamide," J. Mol. Liq., 206, 239-243, 2015.
- [11] H. Fröhlich, "Theory of dielectrics", Oxford University press, London, 1949.
- [12] D.R. Lide, "CRC Handbook of Chemistry and Physics", 85th ed, CRC Press: Boca Raton, FL, 2007.