Journal of Advanced Chemical Sciences 2(1) (2016) 198–200

ISSN: 2394-5311

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com/jacs

Dielectric Relaxation Studies of Decanol Complexes with Amines using Time Domain Reflectometry

S. Kumar*, L. Guganathan

Department of Physics, Annamalai University, Annamalainagar – 608 002, Tamilnadu, India.

ARTICLE DETAILS

Article history:
Received 07 December 2015
Accepted 15 December 2015
Available online 18 December 2015

Keywords:
Dielectric Relaxation
Time Domain Reflectometry
Decanol-Amine Mixture
Kirkwood Correlation Factor
Thermodynamic Properties

ABSTRACT

The dielectric relaxation studies for decanol-amine mixtures over the frequency range of 10 MHz – 10 GHz have been carried out using pico-second time domain reflectometry technique. The dielectric quantities like the static dielectric constant (ε_{0m}) and the dielectric constants at infinite frequency ($\varepsilon_{\infty m}$) were obtained. The relaxation time (τ), the effective Kirkwood correlation factor (g_{eff}), the excess dielectric parameter such as excess dielectric permittivity (ε^E) and excess inverse relaxation time $(1/\tau)^E$ were calculated. The thermodynamic properties (ΔF_τ) of the mixtures of decanol with diethyl amine, n-butylamine, triethylamine, aniline and pyridine were evaluated. The Bruggeman factor shows large variation with volume fraction of aromatic amines. The (g_{eff}) is almost unity for amines and > 1 for decanol with diethylamine, triethylamine, aniline and pyridine mixtures, showing a parallel orientation of the dipoles. The studies suggest that these amines effectively break the α-clusters of decanol and form specific complexes without any charge transfer. It is observed that the values of the enthalpy of activation (ΔF_τ) for the dielectric relaxation always greater than the theoretically predicted values for all the mixtures studied.

1. Introduction

Dielectric study provides information about charge distribution in a molecular system. The recently developed Time Domain Reflectometry [1] has proved to be very effective and efficient tool for determination of dielectric constant and loss in the frequency range of 10 MHz – 10 GHz. There is a great interest to study the dielectric relaxation behavior in alcohol system to understand the role of hydrogen bond in liquid alcohol system. This study provides better values of dielectric parameter because of large frequency range covered in a single measurement. The importance of measuring the dielectric constant of liquid lies in the fact that it provides valuable information about ordering of the liquid state. In other words, it quantifies the extent of polarization of the medium. Furthermore, the dielectric relaxation studies enable the determination of the rate of molecular rotation in liquids.

Studies of the dielectric relaxation behavior of alcohol mixtures with structure breaking and structure making are many [2-5]. The formation of a linear hydrogen bonded chain changes according to the amount of shielding of hydroxyl group or to the steric hindrance of the alkyl groups. Addition of electron donating molecule would modify the structured packing and volume of the relaxing systems. The study of Kirkwood correlation factor provides valuable information regarding the solute-solvent interactions in binary mixture especially when one of the components has anti-parallel orientation of dipoles [6]. In this study we report the dielectric behavior of decanol on mixing with electron donating solvents like diethylamine, triethylamine, aniline and pyridine.

2. Experimental Methods

2.1 Materials

Spectro grade decanol from E-merk was used. The amines were treated with KOH refluxed and distilled and collecting at boiling point. The solutions are prepared by volume mixing.

2.2 Apparatus and Data Analysis

The dielectric spectra were obtained by time domain reflectometry (TDR) technique [7, 8]. Tektronix 7854 sampling oscilloscope with 7STDR unit was used. A fast-raising step voltage pulse of 25 ps rise time generated by a tunnel diode was propagated through a coaxial line system. The sample was placed at the end of the coaxial line in a standard military application (SMA) coaxial cell of 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 on 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 pluses without sample Rx (t) were digitized at 1024 points and transferred to a computer through a general purpose interface bus (GPIB) card. The sample cell was surrounded by an insulating container through which the constant temperature water was circulated. The accuracy of the constant temperature bath is within ± 1 °C.

2.3 Data Analysis

The time depended data were processed to obtain complex reflection coefficient spectra over the frequency range of 10 MHz – 10 GHz using the Fourier transformation.

$$\rho^*(\omega) = (C / j\omega d).\,[P(\omega) / q(\omega)] \qquad (1)$$

Where P (ω) and q (ω) are Fourier transformation of [R_1(t) – Rx (t)] and [R_1(t) + Rx (t)], respectively, C is the velocity of light, ω is the angular frequency, d is the effective pin length, and j = $\sqrt{-1}$. Complex permittivity spectra spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by the bilinear calibration method [9-11]. Experimental values of were fitted with Debye equation [12-14].

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + [\,\varepsilon_0 - \varepsilon_{\infty} / 1 + j\omega\tau\,] \qquad (2)$$

With ε_0 and τ as fitting parameter. A non-liner least-square fitting method [15] was used to determine the dielectric parameters.

*Corresponding Author
Email Address: drskumar1962@gmail.com (S. Kumar)

2394-5311 / JACS Directory©2015-2016. All Rights Reserved

3. Dielectric Parameters

The Kirkwood correlation factor (g_{eff}) [16] for a binary mixture can be written as

$$\frac{4\pi N_A}{9KT}\left(\frac{\mu_a^2 X}{V_a}+\frac{\mu_b^2(1-X)}{V_b}\right)g_{eff}=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad (3)$$

Where μ, V, ε_0 and ε_∞ are the dipole moment, molar volume, static dielectric constant and dielectric constant at infinite frequency respectively. The suffixes a, b and m denotes the component a, b and the mixture. X is the concentration of a, the other symbols having usual meaning. The value of g_{eff} will change from g_a to g_b as the concentration of "b" increases from 0% to 100%. g_{eff} is an index of solute-solvent interaction at a given concentration. The structural information on the interacting species is obtained by defining another correlation factor g_f of the mixture.

$$\frac{4\pi N_A}{9kT}\left[\frac{\mu_a^2 g_a X}{V_a}+\frac{\mu_b^2 g_b(1-X)}{V_b}\right]g_f=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad (4)$$

The effective volume of the solute gets modified by solute-solvent interactions and is best illustrated by the non-linear of the Bruggeman's mixture formula [17, 18].

$$f_{BM}=\left[\frac{(\varepsilon_{0m}-\varepsilon_{0a})}{(\varepsilon_{0b}-\varepsilon_{0a})}\right]\left(\frac{\varepsilon_{0b}}{\varepsilon_{0m}}\right)^{\frac{1}{3}}=(1-X) \quad (5)$$

The excess parameter [19] i.e. excess permittivity (ε^E) and excess inverse relaxation time $(1/\tau)^E$ were computed as,

$$\varepsilon^E=(\varepsilon_0-\varepsilon_\infty)_m-[(\varepsilon_0-\varepsilon_\infty)_A X_A+(\varepsilon_0-\varepsilon_\infty)_B X_B] \quad (6)$$

Where 'X' is the mole fraction and subscripts m, A and B represent mixture, component A and component B, respectively and

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

Where $(1/\tau)^E$ represents the average broadening of the dielectric spectra.

4. Result and Discussion

The static dielectric constants, the relaxation time obtained by fitting the experimental data in the Debye equation for the liquid mixtures studied are given in Table 1. The decrease in the dielectric constant of the solution with increasing amine concentrations and the systematic change in the relaxation time of the solution except the pyridine with decanol system can be explained on the basis of molecular interactions [20, 21]. The information related to the solute-solvent interaction is also given by the Bruggman factor. It shows a negative deviation for the mixtures of decanol with aliphatic amines like diethylamine, n-butylamine and triethylamine whereas it shows a positive deviation for the mixtures of the aromatic amines such as aniline and pyridine (Fig. 1). If higher the deviation from linearity then the interaction is also found to be more.

In pure decanol, a self-correlation of orientation with strong parallel dipolar alignment exits with g_a values substantially greater than 1 whereas in amines (g_b <1) the correlation is more likely due to a combination of both parallel and anti-parallel orientation with later one being dominant. On mixing we find that g_{eff} is composition dependent and < 1 for decanol + n–butyl amine systems whereas g_{eff} >1 for decanol + triethylamine system in all the volume fraction. But in the cases of decanol with diethylamine, aniline and pyridine, the obtained g_{eff} values are both less than and greater than 1. 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.

It is also significant to note that g_f is tending to the ideal value of 1 in the mixtures of decanol with aromatic amines and triethylamine but not in the case of decanol with Diethylamine and n–butylamine. g_f = 1 does not imply that there are no hetero molecular interactions but the dynamical equilibrium of the nonrandom orientations of the alcohol species, on mixing with amine yields a value of unity for g_f. This is evidenced by the variation of Buruggman factor. However the hetero molecular interactions must be weaker here. The values of g_f are less than one, in diethylamine and n – butylamine systems indicating that the dipoles are oriented in anti-parallel direction. It should be noted that g_f values are greater than one in the decanol + triethylamine system indicating that the dipoles are oriented in parallel direction. In the case aniline and pyridine then g_f value is tending to the ideal value 1. g_f = 1 does not imply that there is no hetero molecular interaction but the dynamical equilibrium of the alcohol species, on mixing with the amines yields a value of unity for g_f. This is evidenced by the variation of Buruggman factor. However, the hetero molecular interaction must be weaker here.

The studies of excess enthalpy for the mixtures of methyl ethyl ketone with five alcohols by Pikkarainen et al [22] showed large positive values due to the breaking of alcohol-alcohol interactions. The effect of hetero association equilibrium which can give a negative contribution was found to be negligible. This is in support of our view that there may not be any charge transfer taking place between the solute and solvent except for a weak – bonding. Smith et al [23] have studied the dipole moment of the complexes of a number of alcohol-amine system and showed that the excess dipole moment of complexes is never more than 0.3 D and hence the bonding cannot be associated with any charge shift.

Clerbaux et al [24] have calculated the mean square dipole moments of the solute species present in the mixture of n-butanol and aliphatic amines dissolved in cyclohexane. They showed that the average N – O direction of the bond does not coincide with the direction of the free electron pair of the nitrogen atom and there exists a certain proportion of the complex with multiple bonds involving the N – H bond of the oxygen of the alcohol molecules. This support our view that there are more than one specific site of interactions with no significant charge shift and g_f tends to unity. Information regarding the dynamics of the solute-solvent interactions is obtained from the excess properties like the excess dielectric permittivity (ε^E) values and the excess inverse relaxation time $(1/\tau)^E$ values.

The excess permittivity may provide qualitative information about multimer formation in the mixture as follows (i) indicates the solute and solvent do not interact at all (ii) indicates the solute and solvent interaction is in such a way that the effective dipole moment gets reduced. The solute and solvent may form multimers leading to the less effective dipoles (iii) indicates the solute and solvent interact in such a way that the effective dipole moment increases.

Table 1 Dielectric data, Kirkwood correlation factor, excess properties and free energy of activation of decanol with amines

Volume fraction of amine	ε_{0m}	$\varepsilon_{\infty m}$	τ (ps)	F_{BM}	g_{eff}	g_f	ε^E	$(1/\tau)^E$ (ps)	ΔF_τ KJ / mol
Diethylamine									
100%	3.04	2.19	025.02	0	0.81	-	-	-	12.753
70%	4.82	2.27	073.98	0.008	1.10	0.94	1.715	0.013	15.485
50%	5.62	2.34	159.94	0.136	1.01	0.81	0.811	0.012	17.427
30%	5.96	2.43	259.06	0.469	0.84	0.64	0.702	0.007	18.042
0%	5.99	2.54	579.47	1	1.37	-	-	-	20.671
n-butylamine									
100%	3.92	1.99	004.4	0	0.82	-	-	-	8.159
70%	4.67	2.12	033.16	0.149	0.80	0.76	-0.112	-0.129	13.463
50%	5.13	2.20	105.20	0.379	0.78	0.66	0.139	-0.099	16.369
30%	5.64	2.32	254.73	0.602	0.74	0.59	0.246	-0.059	18.600
0%	5.99	2.54	579.47	1	1.37	-	-	-	20.671
Triethylamine									
100%	2.20	1.89	018.36	0	0.91	-	-	-	11.973
70%	3.33	2.16	068.48	0.238	1.35	1.11	-0.176	-0.023	15.290
50%	4.17	2.28	168.28	0.444	1.46	1.14	-0.098	-0.120	17.555
30%	4.82	2.42	341.82	0.611	1.86	1.02	-0.196	-0.013	19.341
0%	5.99	2.54	579.47	1	1.37	-	-	-	20.671
Aniline									
100%	5.57	2.27	015.71	0	0.85	-	-	-	11.581
70%	5.62	2.32	025.83	0.328	0.95	0.99	-0.046	-0.006	12.833
50%	5.71	2.40	057.55	0.611	1.02	0.98	-0.066	-0.027	14.852
30%	5.85	2.49	159.28	0.878	1.12	0.97	0.046	-0.014	17.417
0%	5.89	2.54	579.47	1	1.37	-	-	-	20.671
Pyridine									
100%	11.75	2.27	008.70	0	0.97	-	-	-	10.092
70%	11.62	2.31	029.44	0.641	1.07	1.03	1.726	-0.045	13.263
50%	10.54	2.38	055.08	0.819	1.02	0.92	1.801	-0.061	14.741
30%	9.42	2.46	132.85	0.981	0.96	0.81	1.789	-0.026	16.955
0%	5.99	2.54	579.47	1	1.37	-	-	-	20.671

The variation of $(1/\tau)^E$ for different compositions are given in Table 1. It is almost negative in all the systems showing that the solute – solvent interaction produces a field in such a way that the effective dipole rotation is hindered. $(1/\tau)^E$ is highest for pyridine – decanol mixtures in the case of aromatic amine system, whereas it is higher for n-butylamine – decanol mixtures in the case of aliphatic amine systems.

Generally, the dielectric relaxation time is a function of the effective molar volume of the mixture. the fact that $(1/\tau)^E$ for different proportions of amines is almost the same for the individual systems, shows that the

distribution of relaxation time is more due to the consequences of a statistical distribution molecular masses [25] the thermodynamic parameter (ΔF_{+}) is obtained for all systems [26] and reported.

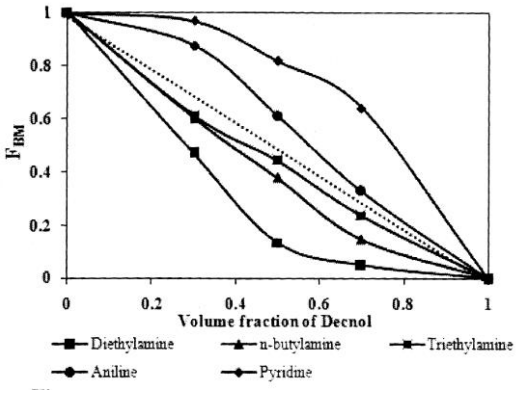

Fig. 1 Bruggeman plot of decanol + amine systems

5. Conclusion

The dielectric relaxation studies for decanol-amine mixtures over the frequency range of 10 MHz – 10 GHz have been carried out using picosecond time domain reflectometry technique. The information related to the solute–solvent interactions is given by Bruggman factor. It shows a negative deviation for the mixtures of decanol with aliphatic amines like diethylamine, n-butylamine and triethylamine where as it shows a positive deviations for the mixtures of decanol with aromatic amines like aniline, pyridine. If higher the deviation from Bruggman line, the interaction is found to be more. If lesser the deviation, then the interactions is less. From our study it is found that pyridine has more interaction in aromatic amines and diethylamine has more interaction in aliphatic amines. The other parameters are discussed on the basis of nature of molecular interactions and multimer formation in the selected mixtures of liquid.

Acknowledgement

The author Dr. S. Kumar is very much thankful to Dr. S.C. Mehrotra, Professor, Department of Physics, Dr. B.A.M University, Aurangabad, Maharastra to carry out this work.

References

[1] S.M. Puranik, A.C. Kumbharhane, S.C. Mehrotra, Dielectric properties of honey-water mixtures between 10 MHz to 10 GHz using Time Domain Technique, J. Microw. Power EM Ener. 26(3) (1991) 196-201.
[2] A.C. Kumbharhane, S.M. Puranik, S.C. Mehrotra, Dielectric properties of 2 propanol water mixture using time domain spectroscopy, J. Pure Appl. Phys. 4(2) (1992) 62-77.
[3] A.C. Kumbharhane, S.M. Puranik, S.C. Mehrotra, Dielectric relaxation study and structural properties of 2 nitroacetophenone ethanol solutions from 10 MHz to 10 GHz, J. Mol. Liq. 51 (1992) 307-319.
[4] S.M. Puranik, A.C. Kumbharhane, S.C. Mehrotra, The dielectric relaxation study of primary alcohol water mixtures using time domain reflectometry technique, Proc. Nat. Acad. Sci., India 63A(II) (1993) 415-421.
[5] S. Kumar, T. Kalaivani, S. Krishnan, Dielectric relaxation study of some binary liquid mixtures using frequency domain technique, Ind. J. Pure Appl. Phys. 41 (2003) 398-401.
[6] M.T. Hosami, R.H. Fatleper, D.K. Deshpande, S.C. Mehrotra, Temperature- and frequency-dependent dielectric studies of *p*-fluorophenylacetonitrile–methanol mixtures using time-domain reflectometry, J. Chem. Soc. Faraday Trans. 91 (1995) 623-626.
[7] S.N. Helambe. M.P. Lokhande, A.C. Kumbharhane, S.C. Mehrotra, S. Doraiswami, Dielctric study of aqueous solution of Acetonitrile, Pramana. 44(5) (1995) 405-410.
[8] R.H. Cole, Time domain reflectometry, Ann. Rev. Phys. Chem. 28(1) (1977) 283-300.
[9] C.E. Shannon, Communication in the presence of noise, Proc. IRE 37 (1949) 10–21.
[10] H.A. Samulon, Spectrum analysis of transient response curves, Proc. IRE 39(2) (1951) 175-186.
[11] R.H. Cole, J.G. Berberian, S. Mashimo, G. Chryssikos, A. Burns, E. Tombari, Time domain reflection methods for dielectric measurements to 10 GHz, J. Appl. Phys. 66(2) (1989) 793-802.
[12] S. Havriliak, S. Negami, A complex plane analysis of α-dispersions in some polymer systems, J. Poly. Sci. C: Poly. Sym. 14(1) (1966) 99-117.
[13] K. Kenneth, S. Cole, R.H. Cole, Dispersion and absorption in dielectrics I. alternating current characteristics, J. Chem. Phys. 9(4) (1941) 341-351.
[14] D.W. Davidson, R.H. Cole, Dielectric relaxation in glycerine, J. Chem. Phys. 18(10) (1950) 1417.
[15] P.R. Bevington, Data reduction and error analysis for the physical science, McGraw Hill, New York, 1969, pp.204-246.
[16] J.G. Kirkwood, The dielectric polarization of polar liquids, J. Chem. Phys. 7(10) (1939) 911-919.
[17] D.A.G. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen, Annal. Der Phys. 416(7) (1935) 636-664.
[18] U. Kaatze, Dielectric properties of aqueous solutions of pyrazine and some of its alkyl derivatives, Z. Phys. Chem. 153 (1987) 141-150.
[19] J.B. Hasted, Aqueous dielectrics, Studies in Chemical Physics, Chapman and Hall, London, 1973.
[20] S. Kumar, T. Ganesh, S. Krishnan, S.C. Mehrotra, Dielectric studies of benzyl alcohol complexes with amines using time domain reflectometery, Bull. Pure Appl. Phys. 20D (2001) 125-132.
[21] S. Kumar, T. Ganesh, S. Krishnan, N.M. More, S.C. Mehrotra, Dielectric studies of cyclohexanol complexes with amines using time domain reflectometry, Microw. Measur. Tech. Applicat. 50s (2003) 51-58
[22] L. Pikkarainen, Excess enthalpies of binary solvent mixtures of 2-butanone with aliphatic alcohols, Thermochim. Acta 114(2) (1987) 239-244.
[23] D. Cleverdon, G.B. Collins, J.W. Smith, Molecular polarisation in ternary systems comprising benzene, pyridine, and an alcohol, J. Chem. Soc. 1 (1956) 4499-4507.
[24] P.T. Clerbaux, P. Duterme, T. Zeegers-Huysken, P. Huyskens, Digest of literature on dielectrics, J. Chim. Phys. 64 (1967) 1326-1330.
[25] M. Pajdowska, L. Sobczyk, Dielectric relaxation in propionic acid-tri-n-butylamine system, Adv. Mol. Relax. Interact. Proces. 22(3) (1982) 159-165.
[26] S. Glasstone, K.J. Ladier, H. Eyring, Theory of rate processes, McGrew Hill, New York, 1941.