

Dielectric Parameters of Aniline, N-Methyl Aniline, N, N-Dimethylaniline with 1, 4 Dioxane Using Time Domain Reflectometry

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ABSTRACT

The dielectric relaxation measurement of Aniline, N-methyl aniline, N, N-dimethylaniline with 1, 4 Dioxane mixtures have been carried out over entire concentrations, at temperatures 25°C using picoseconds time domain reflectometry technique in the frequency range of 10 MHz to 30 GHz. The complex permittivity spectra of Aniline, N-methyl aniline, N, N-dimethylaniline with 1, 4 Dioxane mixtures were fitted using Havriliak-Negami equation. Kirkwood correlation factor for all concentrations have determined using least square fit method. The variations in Kirkwood correlation factor with molecular size is studied.

Keywords: Dielectric Relaxation, time domain reflectometry, Kirkwood correlation factor.

I. INTRODUCTION

The dielectric properties of a substance such as dielectric constant, dielectric loss, relaxation time have provided an insight into the structure of the molecules of the system. In liquids, the molecule has rotational freedom and its dispersion occurs at microwave frequency. Hence studying the dielectric properties at microwave frequency will reveal the dielectric relaxation of polar molecules and its variation with respect to the interaction with the neighbouring polar as well as non polar molecules. Time domain reflectometry gives dielectric relaxation study over a wide frequency range [1-3].

Patil et al. [4] obtained the complex dielectric spectra for alcohols and aniline binary mixtures and reported that ϵ_0 and τ decrease with increasing concentration of aniline in the alcohol. Fattepur et al. [5] measured complex permittivity spectra for aniline-methanol mixture, as function of frequency between 10 MHz to 10 GHz & observed strong interaction between solute-solvent molecules through hydrogen bonding at low methanol concentration. From microwave absorption measurement in dilute solutions, Deogaonkar & coworkers [6] found that aniline and N, N-dimethylaniline form complexes with o-chlorophenol through hydrogen bonding at room temperature. Oswal et al [7] suggested strong cross association due to strong hydrogen bonding between -OH and -NH₂ groups, from the viscosity and excess molar volume studies of liquid mixtures of alcohols with amine.

The present paper consist of , the detail study of dielectric behaviour of aniline-1, 4 dioxane (ANI-DX), N-methylaniline-1, 4 dioxane (NMA- DX) and N, N-dimethylaniline-1, 4 dioxane (NNDA-DX) mixtures in the frequency range of 10 MHz to 30 GHz using Time Domain Reflectometry (TDR) at temperature 25°C. From the dielectric parameters, Kirkwood correlation factor are obtained. On the basis of these parameters, intermolecular interaction and dynamics of molecules at molecular level are discussed.

II. EXPERIMENTAL

Aniline (ANI), N-methyl aniline (NMA) and N, N-dimethylaniline (NNDA) and 1, 4 Dioxane (DX) was obtained commercially (s. d. fine, India) and was used without further purification. The solutions were prepared at different volume fraction of DX in ANI, NMA and NNDA. The dielectric spectra were obtained by the time domain reflectometry (TDR) technique. The Tektronix model no. DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the time domain reflectometry (TDR). A repetitive fast rising voltage pulse with 18ps incident rise time was fed through coaxial line system of impedance 50 ohm. Sampling oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 2ns and digitized in 2000 points.

III. RESULT AND DISCUSSION

The Kirkwood correlation factor 'g' is also parameter containing information regarding orientation of electric dipoles in polar liquids [8]. The value of 'g' for pure liquid is given by expression

$$g\mu^2 \frac{4\pi N\rho}{9kTM} = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (1)$$

where 'μ' dipole moment is in gas phase, 'N' is Avogadro's number, 'M' is molecular weight, 'ρ' is the density of the liquid and 'kT' has usual meaning. We have taken ϵ_∞ value from refractive index ($\epsilon_\infty = n^2$) data at 25°C.

For binary mixture, the static dielectric permittivity needs to be considered as the dipole orientation correlation factor (g^{eff}). The modified form of Eq. (1) is used to study the orientation of the electric dipoles in the binary mixtures as follows [8,9].

$$\frac{4\pi N}{9kT} \left[\frac{\mu_{DX}^2 \rho_{DX} X_{DX}}{M_{DX}} + \frac{\mu_A^2 \rho_A (1 - X_{DX})}{M_A} \right] \times g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (2)$$

where M_{DX} and M_A are molecular weight of DX and ANI, NMA and NNDA respectively. ρ_{DX} and ρ_A are corresponding densities. X_{DX} is volume fraction of DX in ANI, NMA and NNDA. ϵ_{0m} and $\epsilon_{\infty m}$ are the static dielectric constant and dielectric constant at high frequency of the mixtures. To calculate the values of g^{eff} , we have taken $\mu = 1.13, 1.64, 1.66$ and 0.45 D for ANI, NMA, NNDA and DX respectively [10]. The values of g^{eff} for ANI, NMA and NNDA in DX mixtures are given in Table 1. The observed g^{eff} value is greater than unity in ANI-DX mixtures leads to the conclusion that the molecules associate to form multimer. The g^{eff} values of these mixed solvent also have some deviation from ideality, which confirms the net change in dipolar ordering of the mixture constituents due to H-bond complexation.

Table 1. Kirkwood correlation factor (g^{eff}) for ANI, NMA and NNDA with DX mixtures at 25°C.

X_{DX}	NI-DX	NMA-DX	NNDA-DX
	g^{eff}	g^{eff}	g^{eff}
0.0	1.66	0.84	0.63
0.2	1.42	0.72	0.59
0.4	1.31	0.66	0.76
0.6	1.20	0.55	0.86
0.8	1.91	0.58	0.96
1.0	0.69	0.69	0.69

IV. CONCLUSION

From the dielectric relaxation study, it is observed that the Kirkwood correlation factor deviates from the unity, which confirms the net change in dipolar ordering of the mixture constituents due to H-bond complexation.

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VI. REFERENCES

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