Original Research Article

Optical, lower microwave and radio frequency response of binary mixtures of organic liquids - A dielectric approach

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Abstract

Background: Each material displays an unique complex permittivity spectra in the radio/ microwave frequency domain because of their different structures and varying dynamic responses to an external electromagnetic field. These spectra usually include one or more dispersions. A dielectric dispersion is mainly characterized by two parameters, dielectric decrement ($\varepsilon_0 - \varepsilon_\infty$) and relaxation time ($\tau_0$). Complex permittivity of various concentrations 1-Propanol (1-PrOH) and its mixtures with N,N Dimethylformamide (DMF) were obtained in the radio and lower microwave frequency range using Vector network analyzer (VNA). Furthermore to have more insight the dielectric constant (ε') and dielectric loss (ε") of these samples were also determined using standard X-band microwave test bench operated at 9.1 GHz. Optical dielectric constant ($\varepsilon_\infty = n^2$) of these liquids samples were measured using Abbe's refractometer. These data points of different frequencies were fitted into Debye model to evaluate dielectric parameters like, a relaxation time (τ_0), static dielectric constant (ε_0). Excess of static dielectric constant $(\varepsilon_0)^E$ and excess inverse relaxation time $(1/\tau_0)^E$ are determined and fitted with Redlich-Kister polynomial equation to derive the binary coefficients and standard deviations. Kirkwood correlation factor (g) and Bruggeman factor (f_B) were also evaluated for this system. These parameters were used to interpret the molecular interaction between the molecular species of the liquid mixtures.

Key Word: Complex permittivity, Dielectric dispersion, Hydrogen bond, Relaxation time, Vector network analyzer.

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INTRODUCTION

The connection between dielectric permittivity and molecular properties has long been an objective of dielectric studies.[1–3] Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquid system has been extensively studied by many researchers.[4,5] Because, these study provide vital information regarding intermolecular interactions and the consequent structural rearrangement of molecules in solution. Among the associating liquids, alcohols are the center of interest. Because of its outstanding role in basic and applied sciences, hydrogen bonding in liquid systems has been intensively studied for long and it is still subject to a lively scientific debate. Since alcohols are strongly self-associated liquid having a three-dimensional network of hydrogen bond and can be associated with any other group having some degree of polar attractions. Because of this, alcohols present a complex and interesting problem in liquid structure, which has been extensively studied by many researchers.[1-11] 1-Propanol (1-PrOH) is associative polar molecule used principally as a solvent in printing inks, paint, cosmetics, pesticides and insecticides. Among the non-associative liquids, amides have high polarity and strong solvating power; which makes them industrial and technological important solvents. N, N-Dimethylformamide (DMF) has been chosen for the present study because its properties have been the subject

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of considerable interest due to its relationship to peptides and proteins. Therefore, the solution chemistry of these compounds can be strongly influenced by inter and intra molecular H-bonding interactions, which consequently play an important role in determining the physico-chemical properties of these molecules.

Experimental Details: AR grade 1-Propanol (1-PrOH) obtained from Sd-finechem (India). DMF of AR grade was obtained from Merck India. Binary mixtures were prepared at different volume concentration by increasing the concentration of one component and decreasing the concentration other component. The mole fractions of the mixture constituents were determined using standard formula. A Vector Network Analyzer (model- 8714 ES, Agilent made) that operates in the frequency range of 0.3 MHz to 3.0 GHz was used to obtain the dielectric constant (ε') and dielectric loss (ε") of the liquid samples. The method opted to obtain permittivity spectra was of Sridhar *et al.* [8]. Apart from this complex permittivity of each of the liquid samples were measured at single microwave frequency 9.1 GHz using standard microwave test benches and method suggested by Poley [9]. Dielectric constant at optical frequency (ε_∞) taken as square of refractive index (n), which was determined by Abbe's refractometer. Refractive index (n) is accurate to ±0.0001 units. All the measurements were carried out at constant temperature (303 K) and were controlled thermostatically within ±0.5 ^{0}C.

RESULTS AND DISCUSSION

Complex permittivity values obtained in the frequency range 0.03 GHz to 3.0 GHz and at 9.1GHz were plotted on complex plane plots ($\varepsilon'' \rightarrow \varepsilon'$) and fairly smooth Debye type curves passing through the experimental points were obtained. ε_0 and ε_∞were obtained by extrapolating the curves on low frequency and high frequency side respectively. The representative plots showing the variation in real and imaginary parts of the complex permittivity with variation in frequency for the binary mixture of 1-PrOH and DMF is shown in Fig 1. The relaxation time (τ_0) have been determined using Cole-Cole relation.[5]

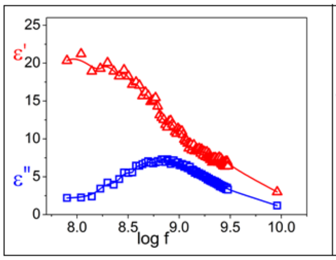

Figure 1

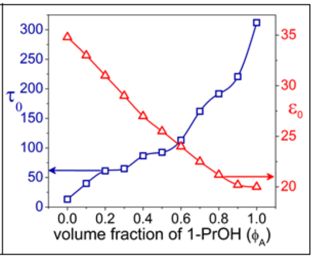

Figure 2

Figure 1: Variation of ε' and ε" against log (f) for 0.9 vol. fraction of 1-PrOH in binary mixture; **Figure 2:** Variation of τ_0 and ε_0 against ϕ_A.

The determined values of values of static dielectric constant (ε_0) and relaxation time (τ_0) for 1-PrOH and DMF at 303 K temperature are 20.0, 312.0 ps and 34.8, 13.2 ps respectively. The larger relaxation time for 1-PrOH is due to the presence of a hydroxyl group in the molecular structures and intra molecular associated clusters formed by (O–H ····O) type of linkage.[6,7] Furthermore the increase in the number of self-associated clusters causes the system to absorb more electromagnetic energy. Due to this, molecules relax very slowly leading to larger relaxation times. The smaller value of relaxation time of DMF suggests its rigid and non-associative nature. Fig. 2 shows the variation of average relaxation time (τ_0) and static dielectric constant (ε_0) against volume fraction of 1-PrOH in the mixture. The plot is non-linear, and this indicates inter/intra molecular interaction between molecular species. As the concentration of 1-PrOH increases, the average relaxation time increases. This indicates the formation of small structures due to breaking of chain like structures of 1-PrOH in the mixtures. Also the systematic increase in the relaxation time indicates that the formation of small structures is concentration dependent. It is noticed that in the volume fraction range of $0 < \Phi_A \leq 0.5$ the change in relaxation time with concentration is very small. This indicates that in this concentration range the molecular structures formed are such that the relaxation time is not affected much by the changes in the environment. While in the volume fraction range of $0.5 \leq \Phi_A \leq 1$ the change in the relaxation time is rapid. This suggests that decreasing concentration of DMF in the mixture leads to an alteration of 1-PrOH relaxation contribution, which indicate hetero interactions of structure breaking character. Further it is clear from (Fig. 2) variation of the static dielectric constant (ε_0) for the mixtures decrease towards the dielectric constant of the 1-PrOH is due to the transition of spherical molecular aggregates into elongated aggregates giving rise to anti-parallel orientation of the dipoles. The deviation of static dielectric constant (ε_0) from linearity is the evidence of formation of H–bonded intermolecular interaction between DMF and 1-PrOH molecules in mixtures. In an ideal mixture of polar liquids if the molecules are interacting, a nonlinear variation in static dielectric constant and relaxation time observed.[6,7] This confirms that the intermolecular association is taking place in the binary mixtures. The excess properties like excess static dielectric constant $(\varepsilon_0)^E$ and excess inverse relaxation time $(1/\tau_0)^E$ have been determined using formula reported elsewhere.[6,7] The binary coefficients and standard deviations of Redlich-Kister polynomial equation for

$(\varepsilon_0)^E$ and $(1/\tau_0)^E$ are ($a = -7.7152$, $b = 1.6178$, $c = -1.4414$, $d = -8.3497$, $\delta = 0.99826$, $r = 0.05519$) and ($a = -0.1096$, $b = 0.08174$, $c = -0.2188$, $d = 0.2651$, $\delta = 0.9946$, $r = 0.0020$) respectively. The excess properties like excess static dielectric constant $(\varepsilon_0)^E$ provide valuable information about the formation of monomers, dimers and multimers in the mixture. From the fig. 3 it is seen that the $(\varepsilon_0)^E$ values are negative for the entire concentration range which indicate that the species of both the molecules interact in such a way that the total effective dipole reduces. This suggests that 1-PrOH-DMF binary mixture may form multimers leading to less effective dipoles. The excess inverse relaxation time $(1/\tau_0)^E$ which gives information regarding the dynamics of solute-solvent interactions and represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant spectroscopy.[11] The excess inverse relaxation time $(1/\tau_0)^E$ values are negative (fig. 3), which indicate the formation of linear structures, which rotate slowly under the influence of an external varying field. This means that addition of 1-PrOH to DMF has created a hindering field such that the effective dipoles rotate slowly.

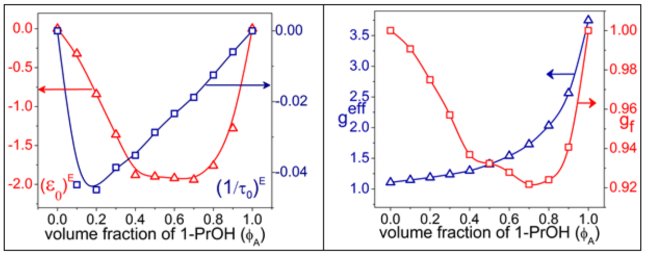

Figure 3 **Figure 4**

Figure 3: Variation of $(\varepsilon_0)^E$ and $(1/\tau_0)^E$ against (Φ_A);**Figure 4:** Variation of g^{eff} and g_f against (Φ_A)

The structural information about the liquids can be obtained using the Kirkwood correlation parameter.[4,6,7,10] This factor is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids. The values of g^{eff}, g_f and f_B are evaluated using the relations described elsewhere.[4,6,7] The effective Kirkwood correlation value g^{eff} for DMF (1.1) is very close to unity confirm the non-associative molecular behavior in pure state. While the g^{eff}value for 1-PrOH (3.74) is higher than unity indicate a high degree of coordinated chainlike structures. It is clear from Fig. 4 that the g^{eff} values for the mixtures vary within the g value of the mixture constituents. However the non-linear behavior of the g^{eff} values of mixtures confirms the significant change in dipolar ordering in the mixtures due to inter molecular H-bond interactions. The values of g^{eff} (Fig. 4) show an increasing trend with the increasing concentration of 1-PrOH, which indicate parallel orientation of electric dipoles in the mixtures. It is observed that the g_f values (Fig. 4) for studied binary mixture have negative deviation from ideality. The extent of departure of g_f from unity represents the degree of interaction. The Magnitude of deviation of g_f values from unity is maximum at 0.70 volume fraction of 1-PrOH. This Suggests that strong molecular interaction is taking place at this concentration. In the 1-PrOH rich concentration in the mixtures, there are a large number of 1-PrOH molecules surrounding the DMF molecules. The associative 1-PrOH molecules act as proton donors enabling hydrogen bonding with the DMF molecules. Bruggeman parameter (f_B) is one of the dielectric parameters, which can give information on the interaction between components in the mixture. The value of Bruggeman fitting parameter $a = 1$ corresponds to the absence of the interaction between the components in the mixture.[6,7] The value of $a < 1$ corresponds to reduction of the effective volume occupied by the component A due to component B. The value of $a > 1$ corresponds to increase in the effective volume of the first component A due component B. In the present study value of *a* found to be 1.38. The value of '*a*' greater than unity indicates that effective volume fraction of 1-PrOH in DMF has decreased indicating the strong heteromolecular interaction between 1-PrOH and DMF molecules.

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