Dielectric dispersion and relaxation of mixtures of 1-propanol and phenol at lower microwave frequencies

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Complex permittivity of 1-propanol, phenol and mixtures of 1-propanol + phenol over wide range of concentration are measured over the frequency range 30MHz to 3.0 GHz using Vector Network Analyzer (VNA). Open ended coaxial probe technique suggested by Wei and Sridhar [Rev Sci Instr, 60 (9) (1989) 304] is used to obtain dielectric constant. The measured values of \( \varepsilon' \) and \( \varepsilon'' \) are fitted to Debye equation to obtain dielectric parameters. Obtained values of relaxation time of liquid mixtures are plotted against the concentration of one of the components of the liquid mixtures. Non-linear variation of relaxation time with concentration has been interpreted in terms of molecular interaction among the molecular species of different kinds in liquid mixtures.

Keywords: Complex permittivity, Relaxation time, Molecular interaction, Vector network analyzer

1 Introduction

Dielectric studies in microwave region provide meaningful information about self association, solute-solute interaction and solute-solvent type of molecular association1-7. Bao et al.8. investigated mixtures of methanol and ethanol and found that they display nearly Debye dispersion. Wang et al.9 measured complex permittivity of alkanediol-water mixtures at microwave frequencies and observed that addition of diol has a strong influence on the dielectric spectrum. Further the characteristic relaxation times of mixtures appear to be mainly governed by the number density of hydrogen bonding groups or molecules. Eid et al.10. studied dielectric behaviour of some monohydric alcohols and their mixtures on dilution with cyclohexane and analyzed their dielectric spectra as sum of up to three type components. Phenols are also strongly associative in liquid state and undergo hydrogen bonding11 with many solvents. Magee and Walker12 investigated phenol in number of non-polar solvents and found that even at the lowest concentration the relaxation time of alcohol is lengthened by intramolecular association due to either solute-solute or due to hydrogen bonding of phenol to the \( \pi \) - electron cloud of solvent or due to both factors. Dielectric relaxations in aliphatic alcohols and their mixtures in dilute solution of benzene at single microwave frequency are found to associate in the concentration range 0.02 to 0.05 weight fraction13. In this paper, dielectric relaxation in 1-propanol, phenol and their mixtures at radio and lower microwave frequency at three different temperatures (30, 40 and 50° C) is studied.

2 Experimental Details

The complex permittivity of 1-propanol, phenol and their mixtures at 30, 40 and 50°C are measured in the frequency range 30MHz to 3GHz by Vector Network Analyzer (Model – 8714ES) supplied by Agilent. A semi rigid coaxial probe of size 0.141 inches with N-type male connector on one end and a flat face, on the other was fabricated. The connector end is mated to VNA, the other end of the coaxial probe was dipped into the liquid. The measurement configuration is shown in Fig. 1. A personal computer was set up to receive pairs of data (real and imaginary part of reflection coefficient (\( \rho \)) for each frequency of measurement) and used for subsequent numerical analysis.

Three calibration terminators described by Wei and Sridhar14 were used and they are an open, a short (liquid mercury) and a standard liquid (acetone). The procedure for experimental data collection is as follows:

With the coax terminated by free space the measurement plane of the VNA was moved to the
coax end using the electrical delay provided. The delay which corresponds to the length of the coax, was adjusted to give a cluster of points near the $\text{Re}(\rho) = 1$, $\text{Im}(\rho) = 0$ point, at the middle of the right hand side of the display. Because of the connector and line mismatches, the cluster is not a point, but can occupy a region. The pair wise $\rho_A$ data were read into the computer.

A short at the coax end was created by raising a small vessel (about-6cc) filled with mercury, until the coax end was well within the liquid. This resulted in a cluster of points around the position $[\text{Re}(\rho) = -1, \text{Im}(\rho) = 0]$, at the middle of the left hand side of the display. The pair wise data $\rho_B$ were again read into the computer.

The mercury cell was removed. At this point, the display was checked to ensure that the data returned to the configuration for an open. A cell with a standard liquid, acetone was now inserted so that the coax end was well immersed in the liquid. The data $\rho_C$ were again read into the computer.

The standard liquid was removed, and the procedure was repeated with the liquid sample, and data $\rho_m$ were collected. The open, short and standard liquid data are used for computerized calibration based on the equivalent circuit given in Fig. 2.

By properly modeling $Z(\omega, \varepsilon^*)$, ($\varepsilon^*$ is the dielectric constant of liquid surrounding the probe end) of the end of the coax, three parameters $\Delta$, $\Delta_{12}$ and $\Delta_{23}$, can be extracted and then the dielectric constant of the sample liquid can be obtained. Complex permittivity $\varepsilon^*$ can be obtained by

$$\varepsilon^* = \frac{Z_{in} - \Delta_{12}}{\Delta + Z_{in} - \Delta_{23}} \ldots (1)$$

AR grade 1-propanol obtained from Sd Finechem (India) was used after drying over CaO and fractional distillation. AR grade phenol supplied by Ranbaxy (India) was used without further purification. Mixtures of 1-propanol and phenol of varying concentrations were prepared just before the measurement. The concentration of the mixture $X$ is defined by the molar fraction of 1-propanol.

3 Results and Discussion

Complex permittivity spectra $\varepsilon^*(\omega)$ were obtained for 1-propanol, phenol and their mixtures at three temperatures. Typical $\varepsilon^*(\omega)$ spectra of 1-propanol and phenol at 40°C is shown in Fig. 3. The experimental values were fitted to the Debye model function given by

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_0}{1 + j \omega \tau} \ldots (2)$$

with $\varepsilon_0$, $\varepsilon_\infty$ and $\tau$ taken as fitting parameters. Where $\varepsilon_0$ and $\varepsilon_\infty$ are the lower frequency and higher frequency limiting values of the permittivity. Obtained values of the fitting dielectric parameters for 1-propanol, phenol and their mixtures are presented in Table 1.

Sato et al. studied 1-propanol-water mixtures using TDR technique for the entire concentration range.
range in the frequency range 100MHz – 25GHz at different temperatures. They found that in case of pure 1-propanol their data can be well described by double Debye model. However, since measurements in this study are upto 3 GHz frequency, single Debye model is used to fit experimental results. At 30°C their values of relaxation time $\tau_1$ for 1-propanol due to main relaxation process is 266 ps and value of static permittivity is 19.96. In this study value of relaxation time for 1-propanol due to main relaxation process is 253.3 ps and static permittivity is 20.33. The small deviations occur in the present results from their results and may be due to two different models used in obtaining dielectric parameters. Further in this study $\varepsilon_\infty$ as a fitting parameter is considered for calculations where as they have taken $\varepsilon_\infty = 3.2$ (at 30°C) as fixed parameter, as Sato et al.$^{16}$ pointed out that estimation of $\varepsilon_\infty$ is critical to high frequency limits of the data. Phenol at 30°C is in the solid crystalline form, so the measurements of pure phenol are carried out at 40 and 50°C. The values of relaxation time and static permittivity for phenol and 1-propanol at different temperatures are also presented in Table 1.

Dielectric relaxation parameters of the mixtures of 1-propanol and phenol were also calculated using the same fitting procedure as was used for the individual components and they are also presented in Table 1. Relaxation time of the phenol-1-propanol mixtures shows non-linear variation with change in concentration of 1-propanol at all three temperatures (Fig. 4). From the figure it can be seen that the relaxation time of mixture decreases as the concentration of 1-propanol in the mixture increases upto 70% (concentration of 1-propanol). Beyond this concentration, the relaxation time of the mixture increases with the increase in concentration of 1-propanol. This behaviour is observed at all the three temperatures. It is well-established fact that alcohols in pure state form long chain multimers via hydrogen bonding. In the mixtures of phenol and 1-propanol, interaction between the molecular species has bond breaking character. At 70% concentration of 1-propanol, value of relaxation time is minimum at all three temperatures. This indicates that at this concentration, smallest molecular structures are formed by intermolecular/intramolecular hydrogen bonding among the molecular species. At 50°C, variation in relaxation time with concentration of 1-propanol is almost uniform with variation in the concentration of 1-propanol in the mixture with

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Fig. 4 — Variation in relaxation time with mole fraction of 1-propanol in mixture of phenol + 1-propanol at 30°C, 40°C and 50°C.
concentration range 40 to 80%. This means that at this temperature and in this concentration range molecular structures are concentration independent where as in all other concentration ranges and temperatures the molecular structures are strongly concentration dependent.

Mashimo and Umehara\(^{17}\) studied the mixtures of primary aliphatic alcohols such as methanol-ethanol, methanol-1-propanol over a wide frequency region from 1MHz to 20GHz by TDR technique and observed that the log \(\tau\) against mole fraction of methanol plots were straight lines in both types of mixtures and they concluded that in these mixtures two different alcohol molecules behave as the same molecules and the same chain like cluster is formed in the mixture as that of pure alcohol. Hydroxyls in these alcohols reorient simultaneously with the applied field. In the present study of mixtures of two hydroxy compounds, one is aliphatic and other is aromatic. These mixtures exhibit more complicated behaviour. In the phenol-1-propanol mixture in the present study (Fig. 5), in 1-propanol rich region, same trend as uniform alcohol mixture is found in the plot of log \(\tau\) against mole fraction of 1-propanol in (0 < \(X\) ≤ 0.7) range. This suggests that chain like clusters are undoubtedly dominant in this region. In the region 0.7 < \(X\) < 1.0 a different kind of cluster appears which may possibly be the cluster of pure phenol molecules.

The excess properties related to permittivity and relaxation time provide valuable information regarding interaction between the polar-polar liquid mixtures. The excess dielectric constant \(\varepsilon_0^E\) of mixtures is calculated using equation

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

where \(X\) is the mole fraction and suffix m, A and B represent mixture, phenol and 1-propanol respectively.

The excess dielectric constant \(\varepsilon_0^E\) of the mixture was plotted against the mole fraction of 1-propanol in the mixtures and is shown in Fig. 6. From the figure it can be seen that \(\varepsilon_0^E\) is positive in phenol rich region (0 ≤ \(X\) ≤ 0.4 & 0 ≤ \(X\) ≤ 0.5 at 50°C and 40°C respectively) and is negative in the concentration range (0.4 ≤ \(X\) ≤ 0.9 & 0.5 ≤ \(X\) ≤ 0.9 at 50 and 40°C, respectively) and again showing a positive value at 90% concentration of 1-propanol at both the temperatures. At the concentrations at which \(\varepsilon_0^E\) is negative indicates that molecules of the mixtures form multimer structures via hydrogen bonding in such a way that the effective dipole moment is reduced, while as at the concentrations at which \(\varepsilon_0^E\) is positive indicates that the molecules of the mixtures form multimer structure via hydrogen bonding in such a way that the effective dipole moments are increased.

The excess inverse relaxation time \((1/\tau)^E\) of the mixtures was calculated using equation

\[
\begin{align*}
\text{Fig. 5 — Plot of log } \tau & \text{ against mole fraction of 1-propanol in mixture of phenol + 1-propanol at 40°C} \\
\text{Fig. 6 — Excess dielectric constant } \varepsilon_0^E & \text{ as a function of mole fraction of 1-propanol in the mixture of phenol + 1-propanol at 40°C and 50°C} \\
\text{Fig. 7 — Excess inverse relaxation time } (1/\tau)^E & \text{ as a function of mole fraction of 1-propanol in the mixture of phenol + 1-propanol at different temperatures}
\end{align*}
\]
\[(1/\tau)^E = (1/\tau)_0 - [(1/\tau)_A X_A + (1/\tau)_B X_B] \quad \ldots \quad (4)\]

and was plotted against the mole fraction of 1-propanol in the mixture. The plot is shown in Fig. 7. From the figure it can be seen that the excess inverse relaxation time is positive in the entire concentration range. This suggests that the solute-solute interaction provides a field such that the effective dipoles rotate faster i.e. the field facilitates rotation of dipoles.

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References