Dielectric properties of benzylamine in 1,2,6-hexanetriol mixture using time domain reflectometry technique

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Received 8 October 2016; Revised 14 November 2016; Accepted 15 November 2016; Published 16 December 2016

The dielectric properties of binary mixtures of benzylamine-1,2,6-hexanetriol mixtures at different volume fractions of 1,2,6-hexanetriol have been measured using Time Domain Reflectometry (TDR) technique in the frequency range of 10 MHz to 30 GHz. Complex permittivity spectra were fitted using Havriliak–Negami equation. By using least square fit method the dielectric parameters such as static dielectric constant (ϵ_0), dielectric constant at high frequency (ϵ_∞), relaxation time τ (ps) and relaxation distribution parameter (β) were extracted from complex permittivity spectra at 25°C. The intramolecular interaction of different molecules has been discussed using the Kirkwood correlation factor, Bruggeman factor. The Kirkwood correlation factor (g_f) and effective Kirkwood correlation factor (g^{eff}) indicate the dipole ordering of the binary mixtures.

Keywords: Dielectric properties; time domain reflectometry; Kirkwood correlation factor; Bruggeman factor.

1. Introduction

In benzylamine [$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$] a benzyl group [$\text{C}_6\text{H}_5\text{CH}_2$] is attached to an amine functional group. This colorless liquid is a common precursor in organic synthesis. In the presence of moisture, benzylamine may weakly corrode some metals. It is used to make pharmaceuticals and other chemicals. Amines have a wide range of chemical, biological, pharmaceutical, industrial and condensed matter physics applications. Since amines and alcohols have the H-bond sites which can enter into intra-and intermolecular hydrogen bonding, it result into different conformations.¹

Dielectric Relaxation Spectroscopy (DRS) technique is a powerful technique to study the intra- and intermolecular interactions in hydrogen bonded liquid system such as alcohols. In alcohol compounds, the hydroxyl ($-\text{OH}$) group is attached to waterlogged hydrogen atom and these hydroxyl groups are classified as monohydric, dihydric, trihydric and polyhydric alcohols. Polyhydric alcohol is the hydrogen bonded liquid, where each molecule has two or more $-\text{OH}$ groups. The O–H bond in alcohol is highly polar. Due to this, hydrogen bonding requires a great agreement of energy in the form of heat to overcome these attractive forces.

In general, polyhydric alcohols exhibit the glass transition at temperature (T_g) relatively higher than those of usual molecular liquids with similar molecular size.² 1,2,

6-hexanetriol is the polyhydric alcohol, which consists of linear back bone chain with OH groups attached to every carbon atoms with aliphatic form. In this network, the reorientational dynamics of OH group is strong in the system. The number of OH groups per molecules is considered to play an important role on their systematic behavior. The OH groups mainly characterizing the liquid are dielectrically active.^{2,3} The dielectric properties of triols have attracted the attention of many researchers.^{2–4} The structural information about 1,2,6-hexanetriol in liquid state has been extensively studied through dielectric relaxation measurements.⁵ The constructive technique of Time Domain Reflectometry (TDR) is used to study the dielectric relaxation parameters of liquids.^{6–9} Significant dielectric relaxation work has been done in our laboratory on diol and 2-butoxyethanol in water mixtures using TDR.^{10,11} Pawar and Patil have studied temperature-dependent dielectric relaxation on molecular interaction in binary mixture of dimethylene chloride with n-methyl formamide using TDR technique.¹² Much research work has been carried out on dielectrics of liquids such as alcohols, bio-polymers, etc.^{13–20}

The key point of these studies were to understand the structure of benzylamine in its pure and alteration of benzylamine in 1,2,6-hexanetriol. The present work deals with time domain dielectric relaxation study of benzylamine in 1,2,6-hexanetriol at 25°C in the frequency range of 10 MHz to

30 GHz. From the measured complex permittivity spectra, static dielectric constant (ϵ_0), dielectric constant at high frequency (ϵ_∞), relaxation time τ (ps) and relaxation distribution parameter (β) were obtained by least square fit method. The Kirkwood correlation factor and Bruggeman factor were determined.

2. Experimental Procedure

2.1. Materials and measurements

The benzylamine (Benzyl) and 1,2,6-hexanetriol (Hex) were obtained commercially from S. D. Fine Chemical Limited, India and was used without further purification. The solutions were prepared very carefully at different volume fractions of benzylamine in 1,2,6-hexanetriol. In order to avoid the uptake of moisture from air (or) evaporation of a nonvolatile solvent tightly packed flasks are used.

The dielectric spectra were obtained by the TDR technique.^{21,22} The Tektronix model no. DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the TDR. Figure 1 shows the experimental setup based on the TDR technique. A repetitive fast rise pulse with 18 ps incident pulse rise time and 20 ps reflected pulse rise time was fed through coaxial line system impedance of 50 ohm. All measurements are carried out in open load condition.

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 5 ns and digitized in 2000 points in the memory of the oscilloscope and transferred to the Computer. The rise time TDR 18 ps corresponds to bandwidth 17.69 GHz (TDR bandwidth $\approx 1/(\pi \times \text{rise time})$).¹¹ The selection of proper time window, sampling rate and bilinear calibration method suggested by Cole *et al.* were useful to measure the accurate complex permittivity at higher frequencies.⁷ The smaller time window causes loss of signal while larger time window includes unwanted reflections. Thus selection of proper time window is important to minimize these effects. Further the

Fig. 1.

Fig. 2. Complex permittivity spectra of benzylamine-1,2,6-hexanetriol mixtures at 25°C.

Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra $\epsilon^*(\omega)$ using nonlinear least squares fit method.^{7,9}

The dielectric permittivity ϵ' and dielectric loss ϵ'' of benzylamine+1,2,6-hexanetriol mixtures at 25°C were measured using TDR technique as shown in Fig. 2. From Fig. 2 it is observed that the real part of complex permittivity spectrum of benzylamine+1,2,6-hexanetriol mixtures is almost independent of frequency below 0.1 GHz. At the relaxation frequency the oscillation of the applied field becomes very fast for the molecules to have time to fully rotate. As a result the real part ϵ' from the complex permittivity will decrease when the relaxation frequency is reached since less of the applied field is canceled by the dipoles as the frequency is increased. In an imaginary part ϵ'' from the complex permittivity spectra the peak value occurs at this frequency since most of the energy is lost at that point. The values of ϵ' decreases with decrease in concentration of 1,2,6-hexanetriol and the peak value of dielectric loss max shifts towards higher frequencies which indicates decrease in relaxation time.

3. Result and Discussion

Recently, dielectric measurements were performed on water + 2-butoxyethanol mixture using TDR technique.¹¹ It is observed that the complex permittivity for water + 2-butoxyethanol mixture is an asymmetric shape i.e., the deviation of the dielectric loss peak occurs for these systems

from the Cole–Davidson function at high frequency.¹¹ It is mathematically proved that asymmetric distribution of relaxation time is associated with the cooperative mechanism of dielectric relaxation.²³ Therefore, for the evaluation of dielectric parameters, the frequency-dependent complex permittivity $[\varepsilon^*(\omega)]$ spectra were fitted in Havriliak–Negami (HN) equation using least squares fit method.²⁴

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta}, \quad (1)$$

where ε_0 is the static permittivity, ε_∞ is the permittivity at high frequency, τ is the relaxation time in picosecond, α and β are the empirical parameters for the distribution of relaxation times with values between 0 and 1. The HN equation includes three relaxation models. The Debye model²⁵ ($\alpha = 0$ and $\beta = 1$) shows the single relaxation whereas the Cole–Cole²⁶ ($0 \leq \alpha \leq 1$ and $\beta = 1$) and Cole–Davidson²⁷ ($\alpha = 0$ and $0 \leq \beta \leq 1$) models suggest the symmetric and asymmetric distribution of relaxation times. The dielectric relaxation parameters (ε_0 , ε_∞ , τ and β) for benzylamine-1,2, 6-hexanetriol mixtures with volume fraction of 1,2,6-hexanetriol at 25°C are listed in Table 1.

Numbers in bracket denotes uncertainties in the last significant digits obtained by the least square fit method. For example, 4.33(2) means 4.33 ± 0.02 and 1470.54(34) means 1470.54 ± 0.34 .

The higher values of relaxation time in the rich region of 1,2,6-hexanetriol suggest that there is cooperative relaxation with larger hindrance. The value of relaxation time for pure 1,2,6-hexanetriol has agreed with the reported value in Ref. 16.

3.1. Kirkwood correlation factor

The Kirkwood correlation factor ‘ g ’ is also parameter containing information regarding orientation of electric dipoles in polar liquids.²⁸ The value of ‘ g ’ for pure liquid is given by expression

$$g\mu^2 \frac{4\pi N\rho}{9kTM} = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}, \quad (2)$$

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 ($\varepsilon_\infty = n^2$) 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. (3) is used to study the orientation of the electric dipoles in the binary mixtures as follows.²⁸

$$\frac{4\pi N}{9kT} \left[\frac{\mu_{\text{HEX}}^2 \rho_{\text{HEX}} V_{\text{HEX}}}{M_{\text{HEX}}} + \frac{\mu_A^2 \rho_A (1 - V_{\text{HEX}})}{M_A} \right] \times g^{\text{eff}} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2}, \quad (3)$$

where M_{HEX} and M_A are molecular weight of 1,2,6-hexanetriol and benzylamine, respectively. ρ_{HEX} and ρ_A are corresponding densities. V_{HEX} is volume fraction of 1,2, 6-hexanetriol in benzylamine. ε_{0m} and $\varepsilon_{\infty m}$ are the static dielectric constant and dielectric constant at high frequency of the mixtures. To calculate the values of g^{eff} , we have taken $\mu = 1.38$ and 2.73 D²⁹ for benzylamine and 1,2,6-hexanetriol, respectively.³⁰ The Kirkwood correlation factor g^{eff} for benzylamine-1,2,6-hexanetriol mixtures at different volume fractions of 1,2,6-hexanetriols are shown in Table 2.

The observed g^{eff} value is greater than unity in benzylamine-1,2,6-hexanetriol mixtures, which suggests that the heterogeneous interaction between the molecules of the constituent polar liquids and in such way that to form multimers with increasing parallel orientation of electric dipoles.

3.2. Bruggeman factor

The static permittivity of two-component mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. The Bruggeman mixture formula has been proposed to understand the dipole interaction in the mixture of two liquids.³¹ This formula state that static permittivity of the mixture $(\varepsilon_0)_m$, benzylamine $(\varepsilon_0)_A$, and 1,2,6-hexanetriol $(\varepsilon_0)_{\text{HEX}}$ can be related to volume fraction of 1,2,6-hexanetriol (V_{HEX}) in the mixture as

$$f_B = \left(\frac{\varepsilon_{0m} - \varepsilon_{0\text{HEX}}}{\varepsilon_{0A} - \varepsilon_{0\text{HEX}}} \right) \left(\frac{\varepsilon_{0A}}{\varepsilon_{0m}} \right)^{1/3} = 1 - V_{\text{HEX}}. \quad (4)$$

Table 1. Dielectric parameters for benzylamine-1,2,6-hexanetriol mixture at 25°C.

V_{HEX}	ε_0	τ (ps)	ε_∞	β
0	4.33(2)	8.62(3)	2.01(2)	1.000
0.1	8.70(2)	65.59(81)	2.24(7)	0.624(3)
0.2	12.83(5)	331.79(54)	2.78(1)	0.723(3)
0.4	15.05(11)	866.55(19)	3.03(1)	0.815(6)
1	19.30(19)	1470.54(34)	2.58(2)	0.884(8)

Table 2. Kirkwood correlation factor g^{eff} for benzylamine-1,2,6-hexanetriol mixtures with volume fraction of 1,2,6-hexanetriol (V_{HEX}) at 25°C.

V_{HEX}	g^{eff}
0.0	1.49(9)
0.1	1.72(10)
0.2	2.51(10)
0.4	3.21(16)
1.0	5.26(11)

Fig. 3. Bruggeman factor (f_B) versus volume fraction of 1,2,6-hexanetriol (V_{HEX}) at 25°C.

The Bruggeman expression predicts a linear relationship between f_B and the volume fraction of 1,2,6-hexanetriol (V_{HEX}) but the experimental values of f_B shows a nonlinear behavior as shown in Fig. 3. To explain the nonlinear relationship Eq. (3) is modified as follows.³¹

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0\text{HEX}}}{\epsilon_{0A} - \epsilon_{0\text{HEX}}} \right) \left(\frac{\epsilon_{0A}}{\epsilon_{0m}} \right)^{1/3}$$

$$= 1 - [a - (a - 1)V_{\text{HEX}}]V_{\text{HEX}},$$

where 'a' is arbitrary parameter, the value of $a = 1$ means the ideal mixture with no interaction between solute and solvent. In Fig. 2 solid line represents the ideal behavior according to Eq. (4). Experimental values represent the deviation from ideal behavior of mixture which shows the solute-solvent molecular interaction between benzylamine-1,2,6-hexanetriol mixtures. The calculated value of 'a' for benzylamine-1,2,6-hexanetriol mixture is determined using least square fit method and it is found to be 3.29 at 25°C.

4. Conclusions

The dielectric relaxation behavior of benzylamine-1,2,6-hexanetriol mixture have been studied using TDR technique in the frequency range 10 MHz to 30 GHz at 25°C. The dielectric constant and relaxation time were determined using HN equation for benzylamine-1,2,6-hexanetriol mixture. The orientation correlations between neighboring molecules due to hydrogen bonding interaction are determined in terms of Kirkwood factors. The modified Bruggeman equation is well fitted with experimental dielectric constant.

Acknowledgments

The Department of Science and Technology, New Delhi is gratefully acknowledged (project No.SR/S2/LOP-25/2007) for laboratory facility. We are thankful to Prof. S.C. Mehrotra, Ramanujan Chair Professor, Department of Computer Science and IT, Dr. B.A.M. University, Aurangabad and Prof. A. C. Kumbharkhane, School of Physical Sciences, S.R. T.M. University, Nanded for the fruitful discussion. We also thank Prof. G. N. Shinde for his helpful suggestions.

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