Microwave Dielectric Relaxation Study of Sorbitol-Dimethyl sulfoxide Binary Mixtures Using Time Domain Reflectometry Technique

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Abstract—Temperature dependent dielectric permittivity of binary mixtures of sorbitol and dimethyl sulphoxided (DMSO) has been measured using the time domain reflectometry (TDR) technique in the frequency range of 10MHz to 30GHz. Measurements were done at different temperatures ranging from 10°C to 25°C for different weight percentage of sorbitol ($0 < W_S \leq 30\%$) in DMSO. It is observed that the dielectric relaxation behaviour of binary mixtures of sorbitol–DMSO can be well described by fitting the dielectric spectra to the Cole-Davidson model. The different dielectric parameters such as static dielectric constant, relaxation time etc. are evaluated using least square fit method. The interactions between sorbitol and DMSO molecules are discussed using the Kirkwood correlation factor and thermodynamic parameter.

Key Words—Dielectric relaxation behaviour of binary mixtures of sorbitol-DMSO, dielectric constant, relaxation time, dielectric spectra, Cole-Davidson model.

INTRODUCTION

In our earlier work we have studied the dielectric relaxation behaviour of some polyhydric sugar alcohols in aqueous solutions [1], [2], [3]. The study of the dielectric relaxation behaviour of solute-solvent binary mixtures provides an important information regarding the intermolecular interactions among the unlike molecules. Literature survey shows that the temperature dependent dielectric behaviour of polyhydric sugar alcohols is extensively studied in its pure form but in binary mixture form it is scarce [4-13]. In this work, temperature dependent dielectric measurements for different weight percent of sorbitol ($\delta$-glucitol) with dimethylsulfoxide (DMSO) have been carried out using time domain technique. Sorbitol is an isomer of D-mannitol. Its molecule is composed of linear backbone chain with OH groups attached to every carbon atom. The number of carbon atoms ($N_C$) and the number of OH groups ($N_{OH}$) are equal in polyhydric sugar alcohol. In case of sorbitol, $N_C = N_{OH} = 6$. DMSO is a highly polar solvent having hydrogen bond acceptor site (-O-) only. DMSO is incorporated into a number of products for healthcare and drug delivery applications due to its ability to act as a carrier for transferring other drugs through the cell membrane [14], [15]. Due to this peculiarity it is interesting to study its structural behaviour with other pharmaceutically useful systems such as sorbitol.

EXPERIMENTAL DETAILS

Materials

The sorbitol was obtained from Sigma-Aldrich Ltd. and the DMSO (99.5%) was obtained from Spectrochem Pvt. Ltd. The solutions were prepared at different weight percentage of sorbitol in DMSO.

Measurements

The Tektronix model no. DSA 8200 Digital Serial Analyzer sampling mainframe along with sampling module 80E08 has been used for the measurements. It generates a 200 KHz repetitive 250 mV voltage pulse with 18 ps incident rise time and 20 ps reflected rise time. This was fed through coaxial line system of impedance 50 ohm. The reflected pulses with sample $R_S(t)$ and without sample $R_X(t)$ from the flat end sampling cell were recorded.

Data Analysis

The detailed data analysis to obtain the complex permittivity spectra have been discussed by Cole et.al. [16] and in our earlier work [17]. The complex dielectric permittivity spectra for various concentrations of sorbitol-DMSO binary mixtures are shown in Fig.1. Generally, the complex permittivity spectra of binary mixtures show the non Debye type behavior. Therefore it is convenient to fit the complex permittivity spectra of binary mixtures of sorbitol with DMSO to Cole-Davidson model given in equation (1) [18]. The dielectric parameter such as static dielectric constant ($\varepsilon_0$), relaxation time ($\tau$), dielectric constant at high frequency ($\varepsilon_\infty$) and distribution parameter ($\beta$) for various concentrations and at temperature ranges from 10°C to 25°C were determined by using least square fit method. The value of $\beta$ is obtained in the range $0<\beta\leq1$ which indicate the Cole-Davidson behavior of sorbitol-DMSO mixtures. The parameters show a systematic change with the concentration.

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

RESULTS AND DISCUSSIONS

Dielectric Parameters

Static dielectric constants of binary mixtures of sorbitol-DMSO against the weight percent of sorbitol are plotted in Fig.2. On increasing the amount of sorbitol in DMSO the values of static dielectric constants increases. As observed from Fig.3 it is clear that, on addition of sorbitol in DMSO, there is rise in relaxation time for sorbitol–DMSO mixtures in non-linear manner. The non linearity in relaxation time is also function of temperature.
and it increases with decrease in temperatures. This may happen due to favourable condition for complex formation between the sorbitol-DMSO molecules at lower temperatures. From 0% to 15% of sorbitol in DMSO the rise in relaxation time is slow. But above this concentration of sorbitol in DMSO, there is a fast rise in relaxation time. It may be attributed as the heteromolecular cooperative nature in sorbitol-DMSO molecules.

**Kirkwood Correlation Factor**

The departure of ‘g’ value from unity is a measure of degree of short range dipole ordering due to hydrogen bond interactions. The information on dipole-dipole orientation correlation in associating polar liquid can be determined from effective Kirkwood correlation factor ($g_{\text{eff}}$) in binary mixtures by modified Kirkwood equation as [19].

$$g_{\text{eff}} = \left( \frac{\varepsilon_{\text{mix}} - \varepsilon_{\text{sat}}}{\varepsilon_{\text{sat}} + 2} \right)$$  \hspace{1cm} (2)

The $g_{\text{eff}}$ values of the binary mixture can be evaluated using the dipole moment of sorbitol as a whole molecule or dipole moment of OH group which may rotate individually. The latter method has been adopted by Nozaki et.al. [12] The values of dipole moments for sorbitol molecule and DMSO used from literature are $\mu_S=3.3D$ and $\mu_D=3.96D$ respectively [12], [13]. The dipole moment of OH group is 1.69D. $\rho_s=1.489$ g/cm$^3$ and $\rho_D=1.010$ g/cm$^3$ [20] are their corresponding densities. In our earlier work, it is observed that in aqueous solutions the $g_{\text{eff}}$ values for sugar alcohols are greater than unity. Again in literature it is found that the $g_{\text{eff}}$ value for pure DMSO is less than unity inferred as antiparallel ordered structure. From Fig. 4, it is found that in either case, sorbitol as whole molecule or OH group of sorbitol molecules, the orientational correlation factor ($g_{\text{eff}}$) value is less than unity. The $g_{\text{eff}}<1$ indicate that the antiparallel orientation correlation of dipoles. The $g_{\text{eff}}$ values for various concentrations and temperature range studied here are shown in Fig. 4. It suggests that, as the amount of sorbitol in DMSO increases, orientation correlation factor also increases. But still upto 30% it is less than unity indicates antiparallel ordering of dipole structure of sorbitol-DMSO molecules.

**Thermodynamic Parameter**

The thermodynamic parameters evaluated using Eyring equation is as follows [21],

$$\tau = (h/kT) \exp (\Delta H/RT) \exp (-\Delta S/R)$$  \hspace{1cm} (3)

where $\Delta S$ is the entropy of activation, $\Delta H$ is the activation energy in KJ/mole. $\tau$ is the relaxation time in ps and $T$ is the temperature in K and $h$ is the Planck’ constant. The values of activation energy (Fig. 5) are obtained by least square fit method. As small amount sorbitol added in DMSO, the corresponding activation energy decreases from pure DMSO to 5% of sorbitol in DMSO. Above this, the activation energy increases linearly showing that it requires more energy for rotation than DMSO. At $W_s = 30\%$ in DMSO the value of $\Delta H$ is approximately three fold than for the pure DMSO. It may be due to the possibility of association between the sorbitol-DMSO molecules through hydrogen bonding.
CONCLUSION

The temperature dependent complex permittivity spectra of sorbitol in DMSO have been studied using time domain reflectometry technique in the frequency range 10MHz to 30GHz. The dielectric parameters show systematic change in their values. The short range dipole interaction is well studied using the Kirkwood correlation factor and thermodynamic parameter. The Kirkwood correlation factor is less than unity shows that sorbitol-DMSO molecules form antiparallel ordering of their dipole moments.

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