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Full Length Article

Dielectric relaxation and thermodynamic study of polyhydric sugar alcohols in DMSO using TDR technique

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ABSTRACT

The measurement of complex permittivity spectra of binary mixtures of sugar alcohols with DMSO were carried out using picosecond time domain technique at the temperatures ranging from 283.15 K to 298.15 K. In order to obtain the dielectric parameters, the measured complex permittivity spectra were fitted to the Cole-Davidson model. These dielectric parameters are further used to evaluate the Kirkwood correlation factor and thermodynamic parameters to discuss hydrogen bond formation.

1. Introduction

Dimethyl Sulphoxide (DMSO) with structural formula $(CH_3)_2SO$ is a highly polar, aprotic solvent. There is no hydrogen bonding between pure DMSO molecules [1]. However, it can act as a hydrogen bond acceptor. Several attempts have been made to reveal the structural information of DMSO-Water mixture through dielectric spectroscopy, molecular dynamics [2–10]. The nonlinear behaviour of these systems suggests the existence of association between the DMSO-water molecules. 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 [1,2]. This property creates an interest to study its structural behaviour with other pharmaceutically useful systems such as polyhydric sugar alcohols.

In polyhydric sugar alcohols, number of OH groups (N_{OH}) and number of carbon atoms (N_C) are equal. A sugar alcohol molecule is composed of linear backbone chain with OH groups attached to every carbon atom. Polyhydric sugar alcohols have large applications in food, confectionary and pharmaceutical industry. These have sweet taste of sugar but fewer amounts of calories as compared to sucrose [11–13]. Sugar alcohols don't develop dental decay. Also, they are useful for diabetic patients because they don't require insulin for their metabolism [11–14].

The literature survey shows that dielectric properties of binary mixtures of DMSO and Water [2–10], 2-Methoxy ethanol [15], 3-Nitrotoluene [16], benzene [17], *N,N*-dimethyl formamide [18], 2-amino ethanol [19], ethylene glycol [20] etc. have been extensively investigated using various theoretical and experimental methods. Also, the dielectric relaxation in sugar alcohols is extensively studied [21–29]. But, the dielectric relaxation study of DMSO–Sugar alcohol binary mixtures is scarce. Macdonald et al. studied the dielectric relaxation of DMSO-water. In this study it is revealed that the interaction between water and DMSO by hydrogen bonding reaches a maximum at a DMSO molar fraction of 0.33 [3]. Recently we have studied the dielectric relaxation in binary mixtures of sugar alcohols Erythritol, D-mannitol and Xylitol with water at various temperatures and concentrations using time domain reflectometry (TDR) technique [30–32]. The Kirkwood correlation factor (g^{eff}) for these mixtures deviates from unity indicates the parallel orientation of dipoles. The activation energy (ΔH) is found minimum at 20% of erythritol in water whereas in mannitol-water it decreases with increasing weight percent of mannitol.

A DMSO molecule contains a highly polar S═O group while a sugar alcohol molecule contains OH groups which are dielectrically active. The electronegative oxygen atom of DMSO favours the formation of hydrogen bond with electropositive hydrogen atom of OH group of sugar alcohol.

In the present study, the sugar alcohols erythritol (N_{OH} = 4), xylitol (N_{OH} = 5) and mannitol (N_{OH} = 6) are used to prepare binary mixtures with DMSO. It is interesting to study the effect of number of hydroxyl groups in a sugar alcohol molecule on the hydrogen bond formation between unlike molecules. The complex permittivity spectra of the binary mixtures at various concentrations and temperatures were obtained in the frequency range of 10 MHz–30 GHZ using TDR technique. The dielectric parameters such as static dielectric permittivity (ε_0), relaxation time (τ) are evaluated and discussed. Molecular

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interaction in the binary mixtures has been discussed using Kirkwood correlation factor (g^{eff}) and thermodynamic parameter (activation energy).

2. Materials and methods

2.1. Chemicals

DMSO (99.5%) was obtained from Spectrochem Pvt. Ltd. The sugar alcohols erythritol (99%), xylitol (99%) were purchased from Alfa Aesar and mannitol (99%) from s. d. Fine Chem. Ltd. All the chemicals were used without further purification.

2.2. Measurements

The dielectric spectra were obtained by the TDR technique. The dielectric relaxation measurements were carried out in the frequency range of 10 MHz–30 GHz using the Tektronix DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 at the temperatures 283.15, 288.15, 293.15 and 298.15 K. A vertically positioned flat end coaxial line was immersed into the sample. The binary mixtures of the sugar alcohols erythritol, xylitol and mannitol with DMSO were prepared by taking different weight percents of the corresponding sugar alcohol in DMSO depending upon the solubility. The weight measurements were done at room temperature using an electronic balance with an accuracy of ± 0.005 g. The mole fractions of the mixture constituents were determined from the weight measurements and used wherever necessary. The temperature of the sample under test was maintained using calibrated temperature controller system within the accuracy of ± 0.1 K. Data analysis to determine complex permittivity spectra $\varepsilon^*(\omega)$ were discussed elsewhere [30–33].

3. Results and discussion

3.1. Complex permittivity spectra

The arcs in the Cole-Cole plot of Sugar Alcohol-DMSO mixtures at 298.15 K (Fig. 1a–c) are not semicircles but skewed at higher frequencies showing the asymmetric distribution of relaxation times in these systems. It is a non Debye type behavior.

The dielectric relaxation parameters of all the binary mixtures studied here are obtained by using the least squares curve fitting procedure on the complex permittivity spectrum of the binary mixtures. The raw data fits well to the Havriliak Negami (HN) [34] and Cole-Davidson (CD) [35] model. The dielectric relaxation time is generally estimated by using the relation $\tau = 1/2\pi f$ where f is the frequency corresponding to the loss peak in the ε'' spectra. The values of the relaxation times obtained by fitting the data to the CD function are matching with the experimental values. Therefore the raw data best fits to the Cole-Davidson model. It was also pointed out for neat DMSO by Lu et al. [3]. The Cole-Davidson function is

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

The shape parameter β describes the asymmetry in the loss peak. The values of β varies such that $0 < \beta \le 1$. The Cole-Davidson relaxation function changes to Debye function when the value of β is 1. Figs. 2–4 shows a) the dielectric permittivity ε', b) dielectric loss ε'' of the complex permittivity spectra of the binary mixtures of erythritol, xylitol and mannitol with DMSO at 298.15 K respectively. The solid lines are the fit lines. The measured values of static permittivity of DMSO are in good agreement with the literature data [18,20]. It can be observed from Figs. 2–4 that on addition of sugar alcohol, the dielectric permittivity increases while the dielectric loss peak shifts considerably towards lower frequency. This may be due to H-bond formation H atom in hydroxyl group of the sugar alcohol molecules and O atom of the S═O group of DMSO molecules. The evaluated values of the static permittivity and relaxation time are reported in Table 1.

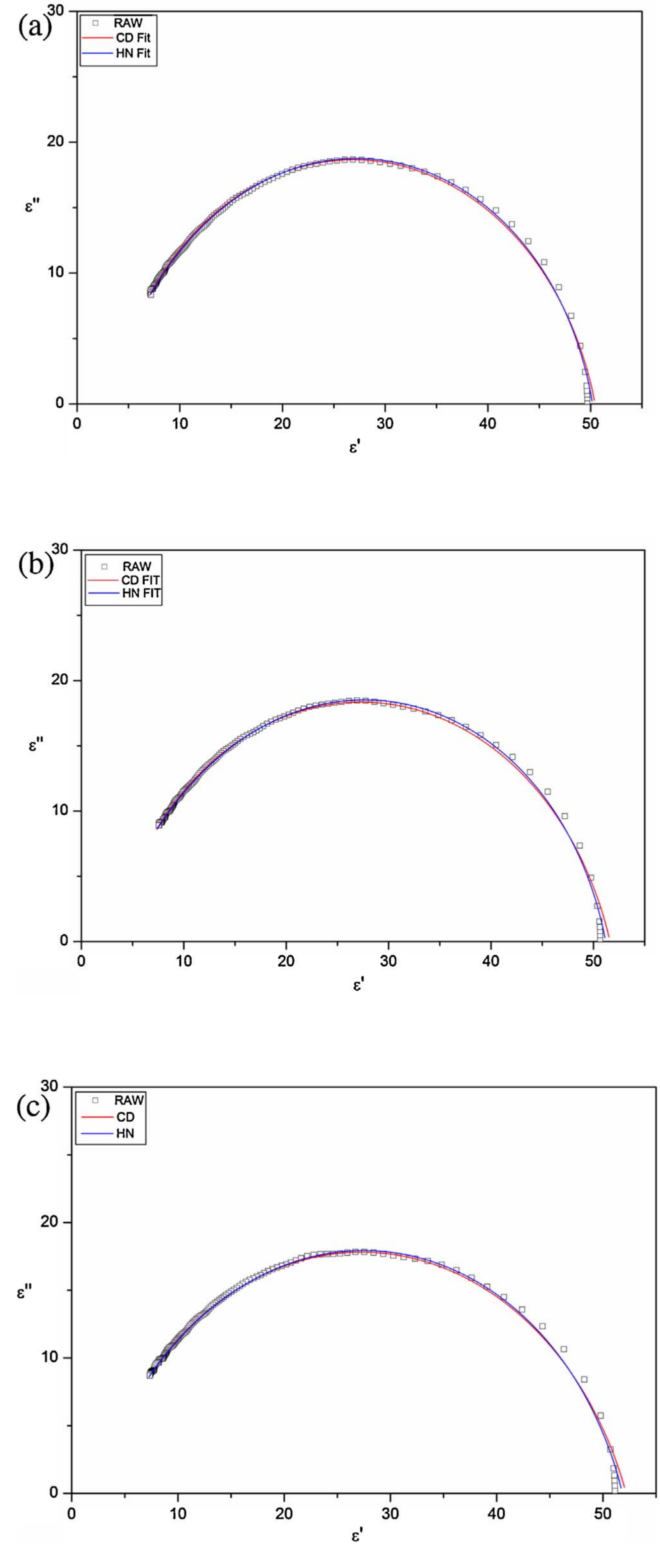

Fig. 1. Cole-Cole plots for the binary mixtures of 15% sugar alcohol in DMSO: a) erythritol – DMSO, b) xylitol – DMSO and c) mannitol – DMSO at 298.15 K.

3.2. Static dielectric permittivity (ε_0)

The static dielectric permittivity $\varepsilon_0 = \lim_{f\to 0} \varepsilon'(f)$ helps us to know the