Relative Dielectric Relaxation Study of Sorbitol and Carbohydrate in Water Mixture using Time Domain Reflectometry

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Abstract: ***The complex permittivity spectra of D-sorbitol and carbohydrates with water mixtures were measured over frequency range 10 MHz to 30 GHz. A temperature dependent complex permittivity spectrum shows the Debye behaviour whereas the relaxation in mixtures can be described by Cole–Davidson function. The dielectric parameters i.e. static Dielectric constant and relaxation time were obtained from the complex permittivity spectra using nonlinear least square fit method. The Kirkwood correlation factor and thermodynamic parameters (Enthalpy and Entropy) have also been determined.***

Keywords: Dielectric relaxation, Kirkwood correlation factor, Time domain reflectometry

1. Introduction

The intermolecular interaction through hydrogen bonds in molecular liquids results in peculiar dynamical properties. The dynamics of hydrogen bonded liquids have been studied by dielectric and other experimental techniques [1-6]. Dielectric relaxation spectroscopy has been used for many years to study the molecular relations in hydrogen bonded liquid system such as Alcohols. Alcohols are compounds in which hydroxyl (—OH) group is attached to saturated hydrogen atom. The hydroxyl group is a functional group of alcohols. Their general formula is R-OH and these are classified as monohydric, dihydric, trihydric and polyhydric alcohols. Polyhydric alcohol is one of the hydrogen bonding liquids, where each molecule has two or more —OH groups. The O—H bond in alcohol is highly polar, because oxygen is highly electronegative. The polarity of O—H bond gives rise to attraction of partially positive hydrogen atoms of other molecules. Due to this, hydrogen bonding requires abundant contract of energy in the form of heat to overcome these attractive forces. In general, polyhydric alcohols show the glass evolution at temperature relatively higher than those of usual molecular liquids with similar molecular size.

D-sorbitol (D-glucitol) is a polyhydric alcohol and a glass forming liquid [1–6]. One of the interesting features of glass forming liquids is the coexistence of many dynamic processes with different characteristic times [6]. Dielectric relaxation spectroscopy has revealed that there are at least four processes commonly recognised at a temperature near glass transition temperature [6,7]. The dielectric relaxation processes originate in the permanent dipole moment in the substance. Dielectric and other relaxations of its supercooled liquid and glassy states have been studied by several groups [6–10]. When sorbitol was mixed with water the dielectric relaxation parameters are changed. The local structures of sorbitol–water are complicated due to molecular clusters and network structures through hydrogen bonds. The sorbitol and its mixtures with water are extensively studied by dielectric spectroscopy technique. Nozaki et al. [11] have reported dielectric properties of sorbitol–water mixtures in the frequency range between 10 Hz and 500 MHz at temperatures from 263 K to 346 K, in the concentration range of 0 V to 0.5 V, where V is the mole fraction of water.

Monosaccharaides are the basic units of carbohydrates. Carbohydrates play a very important role in the living organisms. They are the simplest form of sugar and are water-soluble. Glucose is one of the monosaccharide with molecular formula ($C_6H_{12}O_6$) and is found in all photosynthetic plants, sugar cane, fruits, seeds, flowers, honey etc. In disaccharides, two monosaccharide units are joined together by a glycosidic bond in which anomeric carbon of one unit and –OH is second unit. Sucrose ($C_{12}H_{22}O_{11}$) is a disaccharide and it is obtained from the sugar cane juice and sugar beets. These are important class of biomolecules which are used in cell recognition processes [12–14]. Carbohydrates are significantly smaller than biological macromolecules and larger than the water molecule. Glucose and sucrose are polar, well-soluble in water and they strongly interact with water because of the polar hydroxyl group. Water plays a unique and important role in biology, chemistry and engineering processes. Since biological process take place in aqueous media at relatively low bimolecular concentration. The interactions between bio-molecules and water are often confined to an interfacial region surrounding the biomolecules. It is to be expected that a small amount of water molecules find themselves in a local environment interacting strongly with the bio-molecules.

In this paper, we performed the complex dielectric permittivity measurement for sorbitol & Carbohydrate with water mixtures in the frequency range 10 MHz to 30 GHz using time domain reflectometry technique, which may be expected to produce superior dielectric relaxation parameters in this frequency range because the permittivity spectra are acquired by a single dimension. The activation enthalpy, activation entropy and the Kirkwood correlation factor are also reported.

2. Experimental

2.1 Materials

D-sorbitol was purchased from Molychem Ltd. and used without further purification. Solutions were prepared at different weight fraction of D-sorbitol in deionised water solution.

The monosaccharide (D-glucose) and disaccharides (D-sucrose) 99% purity were purchased from Merk Chemicals Limited. The water used in the preparations of mixtures was obtained by double distillation procedure. The compositions were prepared at different molar concentrations.

2.2 Measurements

The complex permittivity spectra were studied using Time Domain Reflectometry (TDR) method [15, 16]. The basic TDR setup consists of broadband sampling oscilloscope, TDR module and coaxial transmission line. The Tektronix DSA8200 sampling oscilloscope with 30 GHz bandwidth and TDR module 80E08 with step generator unit was used. A 200 mV step pulse with 18 ps incident pulse and 20 ps reflected pulse time and 200 kHz repetition rate passes through coaxial 50 Ω lines. All measurements are carried out in open load condition. Sampling oscilloscope monitors changes in step pulse after reflection from sample. Reflected pulse without sample $R_1(t)$ and with sample $R_X(t)$ were recorded in time window of 5 ns and digitised in 2000 points. Temperature of the sample was controlled electronically within ±1 °C.

3. Data analysis

The step pulses recorded without sample $R_1(t)$ and with sample $R_X(t)$ and are subtracted and added to get

$$p(t) = \left[R_1(t) - R_X(t)\right] \tag{1}$$

$$q(t) = \left[R_1(t) + R_X(t)\right] \tag{2}$$

The complex reflection coefficient $\rho^*(\omega)$ over a frequency range of 10 MHz to 30 GHz were determined as follows.

$$\rho^*(\omega) = \frac{c}{j\omega d}\,\frac{p(\omega)}{q(\omega)} \tag{3}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $p(t)$ and $q(t)$ obtained using summation and Samulon methods [17] respectively, c is the velocity of light, ω is angular frequency and d is effective pin length (~ 0.09 mm). The complex permittivity spectra $\varepsilon^*(\omega)$ was obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying the bilinear calibration method suggested by Cole [15, 16].

4. Result and Discussion

The dielectric relaxation for aqueous D-sorbitol is described by the Havriliak–Negami equation [18].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1 + (j\omega\tau)^{(1-\alpha)}\right]^\beta} \tag{4}$$

where ε_0 is the static permittivity, ε_∞ is the permittivity at high frequency, τ is the relaxation time, α and β are the empirical parameters for the distribution of relaxation times with values between 0 and 1. The Havriliak–Negami equation includes three relaxation models as limiting forms. The Debye model ($\alpha=0$ and $\beta=1$) implies a single relaxation time while the Cole–Cole model ($0\leq\alpha\leq1$ and $\beta=1$) and Cole–Davidson ($\alpha=0$ and $0\leq\beta\leq1$) both suggest a distribution of relaxation times. The magnitudes of α and β indicates the width of the distribution. The aqueous solutions of D-sorbitol could fit Cole–Davidson type dispersion. Therefore, here $\alpha=0$ and $0\leq\beta\leq1$ and experimental values of $\varepsilon^*(\omega)$ were fitted to the Cole–Davidson equation as,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau)^\beta} \tag{5}$$

The value of ε_0, τ & ε_∞ are fitting parameter. A non-linear least squares fit method was used to determine the values of dielectric parameters.

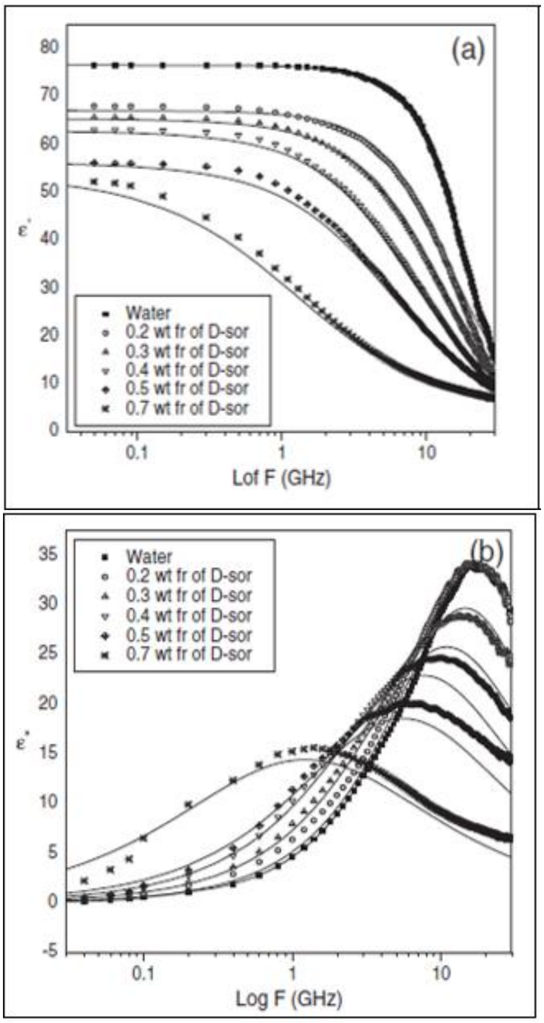

Figure 1: a) Dielectric permittivity whereas b) is the dielectric loss spectra for D – Sorbitol – water mixtures. The solid lines are the theoretical values.

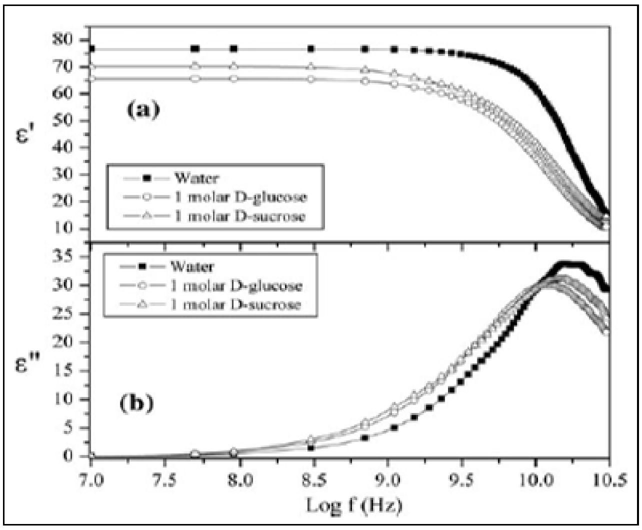

Figure 2: Frequency dependence of the (a) dielectric constant and (b) loss for water and 1 molar concentration of carbohydrates in water

5. Conclusion

The complex permittivity spectra of D-sorbitol & Carbohydrates water mixtures have been studied using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. Temperature dependent complex permittivity, dielectric constant, relaxation time, Kirkwood correlation factor, activation enthalpy and entropy parameters for saccharides in water mixtures has been carried out. The parallel orientation of electric dipoles in molecules has been observed for aqueous solutions of D-glucose and D-sucrose by using dielectric properties.

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