Study of various relaxation processes and breakdown of Stokes-Einstein Debye relation in supercooled D-xylose

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Abstract

Various relaxation procedure in the supercooled state of D-xylose have been investigated using dielectric spectroscopy over a wide frequency (1 mHz – 10 MHz) and temperature range (140-350 K). The main relaxation process (α) that is accountable for the glass transition phenomena, another secondary relaxation process is also visible below glass transition temperature. The attached hydroxymethyl (–CH₂OH) side group to the sugar ring might be responsible for this process. In addition, we have applied Coupling model to find the location of intermolecular relaxation below the glass transition temperature (T_g). The dependence of various dielectric parameters viz. τ_α, τ_β, τ_γ and τ_β cm on temperature have been critically examined. The current experimental result shows that, log_{10} σ_{dc} vs. log_{10} τ_α dependence is nonlinear and hence can be described with the fractional Stokes-Einstein-Debye relation.

Keywords: dielectric spectroscopy, Stokes-Einstein-Debye relation, glass transition phenomena, supercooled D-xylose

1. Introduction

Various important aspects concerning the microscopic origin of relaxation dynamics of glass forming materials are in debate. It is well identified that some secondary relaxations found below the glass transition temperature have an intra-molecular origin which originates from the motion of side groups. In addition, many glass formers show the existence of another secondary relaxation process below the glass transition temperature which reflects the motion of the entire molecule i.e. of intermolecular in nature. This type of secondary processes are commonly referred as Johari-Goldstein (or JG-) [1, 2] relaxation processes which is considered to reflect a universal relaxation mechanism of glass forming materials.

Due to the increasing importance of Johari-Goldstein relaxation (or JG-) in glassy materials, enormous research work has been done to identify the JG-relaxation in glass forming carbohydrates [3-8] as well as plastic crystals [9-12]. Among these glass forming materials, mono-, di-, and polysaccharides have been investigated extensively both in anhydrous form [3, 4, 6-8] as well as in aqueous environment [8, 13, 14]. In carbohydrates, due to the presence of the strong hydrogen bonding...
the dielectric relaxation spectroscopy considered as most versatile technique for understanding the presence of different relaxation processes. Earlier dielectric studies by different groups [3-7] on various carbohydrates (mono-, di-, and polysaccharides) did confirm the existence of JG relaxation. However, the exact location as well as the temperature dependence of relaxation times of this process is still missing in case of aldopentoses except the work of Singh et al. [7] on D-xylose. In order to find the location of JG-relaxation and other dielectric parameters, we measured the dielectric spectra of D-xylose both in the glassy state and supercooled. Here, we compiled and discussed our dielectric results on D-xylose over a wide temperatures range.

2. Experimental

The received anhydrous D-xylose from Sigma Aldrich (purity ≥ 99 %) and used as it is. In order to prepare the sample, the powder form of D-xylose was placed on 30 mm gold plated electrodes. By maintaining the temperature near to its melting temperature, the crystalline powder was heated directly until the sample turns into transparent liquid and efforts were made to prevent thermal degradation. After then another electrode of 20 mm diameter has been put over 30 mm diameter electrode with 0.1 mm Teflon spacers. In order to suppress crystal growth liquid N2 was used. Both real and imaginary part of permittivity in frequency (f) range 1 mHz – 10 MHz was measured by dielectric spectrometer (Novocontrol alpha analyzer). The execution of isothermal frequency scans was done while heating from T = 140 to 280 K having step of 5 K and with steps of 2.5 K for temperature range from T = 280 to 340 K. The stability of sample temperature was better than ± 0.1 K.

3. Results and discussion

D-Xylose is a monosaccharide consisting of five carbon atoms and an aldehyde (-CHO) functional group. Commonly it is known to be wood sugar. Depending on the surrounding conditions, it can adopt different form. The most stable form is dextrorotatory (D-) form which occurs in living things. This form (D-form) has been studied in both glassy and the supercooled state by earlier researchers using differential scanning calorimeter [8] and dielectric spectroscopy [15].

![Figure 1. Frequency dependent of dielectric loss spectra of supercooled D-xylose at various temperatures. Different relaxation processes are highlighted with arrows.](image-url)
They have reported the existence of only one secondary relaxation process in addition to structural relaxation process. Later Kaminski et al. [4] studied both forms of D-arabinose and their equimolar mixture using broadband dielectric spectroscopy, but they also reported only one secondary relaxation process. Probably they could not resolve another secondary relaxation process which is found in between primary and high frequency relaxation processes. In the present work on D-xylose, we examined the data critically and tried to resolve another secondary β relaxation process, that appears on the high frequency side of the primary relaxation process from the excess wing. Depicted in Figure 1 is the frequency dependent of dielectric loss spectra (ε'') of D-xylose at various temperatures. These dielectric loss spectra reveal two clearly resolved relaxation processes viz. primary relaxation (α-process) which give rise to glass transition and a secondary relaxation called γ-process. However, as we move beneath glass transition temperature (Tg), a shoulder can be appeared in the dielectric loss spectra. This emphasis the existence of another secondary relaxation process (in Figure 1) positioned in between the frequency range of primary α- and apparently resolved γ- relaxation processes. The γ-process is more distinct in the glassy region and clearly identified in the proximity of glass transition temperature (Tg). Asymmetry in the glassy state has been observed in case of the γ-relaxation process. We therefore applied the Havriliak-Negami (HN) function [16] defined as:

$$
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon_\alpha}{1 + (i\omega \tau_\alpha)^\alpha} + \frac{\sigma_{dc}}{i\omega \varepsilon_0}
$$

(1)

to the best fit of γ-process. Where $\varepsilon_\infty$, $\Delta \varepsilon_\alpha$, $\tau_\alpha$, $\varepsilon_0$ and $\sigma_{dc}$ are defined as the high frequency dielectric constant, dielectric strength of primary relaxation process (α-process), relaxation time of α-process, vacuum permittivity and dc conductivity respectively. Also, in above equation $\alpha$, $\gamma$ are known as shape parameter determining the broadening along with asymmetry of the loss curve with $0 < \alpha$ and $\alpha \gamma \leq 1$.

**Figure 2.** Frequency dependent of dielectric loss curve of supercooled D-xylose at a fixed temperature 245 K. Solid line represent total fit (HN+CC+HN). Dashed line represents HN-fit of high frequency tail of α-process, dashed dotted line represents CC-fit of resolved β-process and dashed double dotted line represents HN-fit to γ-process.
Here the β-process is well fitted by Cole-Cole function by setting γ = 1 in the above equation in the whole temperature range. The similar behavior of γ-process was also identified recently by Singh et al. [7] for D-lyxose and Kaminski et al. [3-6] for other carbohydrates. One representative example of the fitting procedure used to resolve β-process is depicted in Figure 2 at a temperature 245 K. Clearly the γ-process was well fitted by HN-function (eq. 1) with HN parameters α varies from 0.125 to 0.845 and γ ranges from 0.124 to 1. Similar behavior was also reported by Singh et al. [7] in D-lyxose and other researchers in D-arabinose [3, 13, 15].

Figure 3(a) shows the temperature variation of relaxation times of various relaxation processes present in anhydrous D-xylose in the form of Arrhenius diagram. Clearly the logarithmic relaxation times of α-process (τa) was found to follow Vogel-Fulcher-Tammann (VFT) type temperature dependence [17, 18] as

$$\log_{10}\left[\frac{\tau(T)}{s}\right] = A + \frac{B}{T - T_0}$$

(2)

where T0, A and B denotes the temperature where the dynamics of the system diverges, logarithmic pre-exponential factor and constant respectively. While for both secondary relaxation process (β- & γ-), Arrhenious equation (put T0 = 0 in eq. 2) is used to define the temperature dependence of relaxation times. The best fitting parameters by VFT-equation (2) in the order A, B and T0 for processes α-, β- & γ- are as follows. α-process: -14.99, 888.38 K, 226.22 K; β-process: -20.97, 4977.38 K, 0; γ-process: -14.32, 1793.71 K.

The kinetic freezing temperature of α-process was obtained from VFT-fit imply the dielectric glass transition temperature Tg(α) = 278.6 K. This value is very close to the glass transition temperature obtained from calorimetric measurements by Noel et al. [8] and dielectric Tg found by Gangasharan and Murthy [15].

Let us now focus on the resolved secondary relaxation called β-process, the relaxation time of this process has been obtained by using equation (1) by putting γ = 1 i.e. using Cole-Cole function. However, in this process the uncertainty in the relaxation times is very high. Additionally, we have also calculated the relaxation time of this process using coupling model (CM) which provides reasonable predictions for the activation behavior of JG-type relaxation. As per this model [19], the relaxation time (τβcm) of JG-process can be calculated with the help of the relaxation time of primary relaxation process (τα) for T > Tg on the basis of following relation,

$$\log(\tau_{βcm}) - \log(\tau_α) = (1 - \beta_{KWW})[\log(\tau_c) - \log(\tau_α)]$$

(3)

where $\beta_{KWW}$ is the KWW stretching exponent and $\tau_c$ is the primitive relaxation time close to 2 ps [19]. Interestingly the calculated relaxation times from above equation (3) are close to those obtained from the CC-fittings above glass transition temperature (Tg). The calculated activation energy (below Tg) of this process using equation (2) by setting T0 = 0 is about 4977.38 K or 97.2 ± 5.2 kJ/mol which is closure to the activation energy of secondary process found in one of its isomer D-lyxose [8]. Based on high pressure dielectric measurements, Singh et al. [7] reported that this process is of intermolecular in nature. Also, the activation energy of this process in D-xylose is within the range of 73-98 kJ/mol of JG-process found in other saccharides [5-7]. These results also support that the observed β-process in D-xylose is of intermolecular in nature or JG-relaxation process.

Now focus on the results of another secondary relaxation or γ-process found in D-xylose. This process gives activation energy of about 1793.71 K or 34.3 kJ/mol. Almost similar order of magnitude of the activation energy reported by Gangasharan and Murthy [15] in glassy D-xylose. Other monosaccharides [3, 4] disaccharides as well as polysaccharides [5, 6, 8] also show the same relaxation behavior and approximately same activation energy. Noel et al. [8] suggested that this process may be link to the rotation of hydroxymethyl groups attached to the sugar ring. In case of D-lyxose, Singh et al.
[7] found that γ-process is insensitive to pressure and could be related to the rotation of hydroxymethyl (CH2OH) side group. Since D-xylose, D-arabinose and D-lyxose are isomers and all belong to Aldopentoses family, so it was concluded that the observed γ-relaxation in D-xylose is of intramolecular origin.

It is very well known that primary relaxation time $\tau_\alpha$ (rotational component) and dc conductivity (translational component) are simultaneously measured using dielectric spectroscopy. According to Stokes-Einstein-Debye relation, the dc conductivity ($\sigma_{dc}$) of the liquid varies linearly with inverse of primary relaxation time ($\tau_\alpha$) i.e. the product $\sigma_{dc}(T) \tau_\alpha(T) = \text{constant}$ by varying temperature and pressure. However, the Stokes-Einstein-Debye relationship is violated near the glass transition temperature [20, 21]. Therefore fractional-Stokes-Einstein-Debye equation is used to describe the experimental results:

$$\sigma_{dc}(T) \tau_\alpha(T)^{\zeta} \approx \text{const}$$

Where $\zeta$ is usually known as fractional exponent ($0 < \zeta \leq 1$). In order to verify above relation, a plot of $\sigma_{dc}$ versus $\tau_\alpha$ in log scale for D-xylose is depicted in Figure 3(b). A dotted line having slope -1 is also drawn in the figure. This Figure 3(b) clearly indicates that eq. 4 well describes the experimental results with an exponent value $\zeta = -0.813 \pm 0.02$. The obtained value of $\zeta$ is consistent with commonly reported values ranging from 0.75 to 0.91 [20, 21]. Therefore, we may conclude that for D-xylose, the translational ionic motion is enhanced as compared to the orientational molecular motions at the glass transition temperature ($T_g$) region.

Figure 3. Inverse temperature dependence of relaxation times of supercooled D-xylose for different processes indicated in panel (a). CM prediction (equation 3) of β-process is also shown with symbol star. The solid line along α-process is the best fit to VFT-equation 2, along β- and γ-process are best fits to Arrhenius equation. Panel (b) shows the plot of dc conductivity ($\sigma_{dc}$) with respect to structural relaxation time ($\tau_\alpha$) of supercooled D-xylose. In panel (b), the solid line is fit to equation 4. The dotted line of slope -1 is also shown for comparison.
4. Conclusion

Dielectric spectroscopy has been used to study the relaxation behavior of supercooled D-xylose over a wide range of temperature. We have succeeded to find the location of JG-relaxation process and determined that how temperature depends on relaxation time along with coupling model prediction. The calculated activation energy is about 97.2 ± 5.2 kJ/mol. The other secondary process viz γ-process was also been observed similar to those found by earlier researchers having approximately the same activation energy. In addition, a disruption in the Stokes-Einstein-Debye relation has been observed leading to an enhanced translational ionic motion as compared to orientational molecular motion near the glass transition temperature.

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