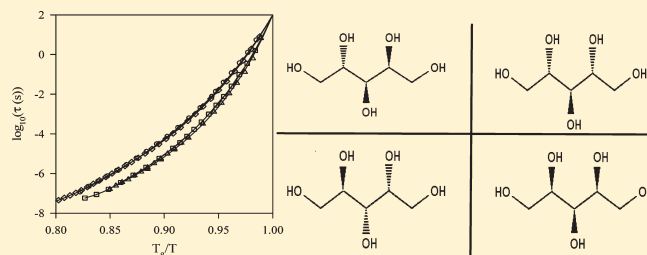


Dielectric Studies of the Mobility in Pentitols

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ABSTRACT: Broad-band dielectric relaxation measurements were performed for the four pentitols isomers, xylitol, adonitol, L-arabitol and D-arabitol. The comparison of the dynamical properties of these compounds shows similarities between the secondary relaxation processes but also important differences for the temperature dependence of the primary process characterized by the steepness index. These differences enable us to distinguish two groups of compounds that correspond to two kinds of molecular conformation. We show that the formation of more or less extended networks of hydrogen bonds, which reflects the more or less non-Arrhenius variation of the primary relaxation, can be related to the differences of conformation of the studied isomers.



I. INTRODUCTION

In the carbohydrate classification, polyhydric alcohols, or polyols, are sugar alcohols of general formula $(C_nH_{n+2}OH_n)$. Polyols constitute a large family of compounds classified according to the number of carbon atoms of the backbone of the molecule and named according to the number of OH groups, $n = 2$ corresponding to a diol, $n = 3$ to a triol, $n = 4$ to a tetritol, $n = 5$ to a pentitol, $n = 6$ to a hexitol, and so on. Some of these molecules have been extensively studied; we can quote in particular ethylene glycol^{1,2} (a diol), glycerol^{3–5} (a triol), *meso*-erytritol⁶ (a tetritol), xylitol^{7,8} (a pentitol), and mannitol and sorbitol^{7–13} which are two hexitols. Used as cryoprotectants, excipients or noncaryogenic sweeteners, these compounds are high value products in the pharmaceutical and agrochemical domains. Their involvements in these different industries are promoted by their capacity to avoid crystallization on cooling. This propensity to undercooling facilitates the obtaining of the amorphous state which, while less stable than the crystalline form, exhibits improved dissolution rate and bioavailability. As a consequence, the control of the stability of the amorphous state with regard to the crystallization is fundamental to optimize the conditions of manufacturing, conservation, or utilization of these compounds. It especially requires the investigation of their molecular mobility, as this latter governs, with the thermodynamic driving force, the structural modifications responsible for the phase transition.

Dynamics in supercooled liquids and glasses are generally described by two kinds of relaxation mechanisms: a slow structural relaxation process, referred as α or primary relaxation, which determines the liquid-glass transition, and faster secondary relaxation processes whose main feature is their persistence into the glassy state, which indicates that this frozen state nevertheless exhibits an important residual molecular mobility. We distinguish for these processes the local motions involving intramolecular degrees of freedom (sometimes referred as γ -relaxation) and the

Johari–Goldstein β -relaxation whose still controversial origin is recognized as being an intrinsic and universal property of the glassy state.¹⁴ Whereas these secondary processes display an Arrhenius behavior below the glass transition temperature, the temperature change of the primary relaxation times is characterized by a wide diversity of behavior with more or less marked deviations from the Arrhenius law. This leads us to introduce the fragility concept, which measures the degree of departure from the Arrhenius dependence and distinguishes two classes of glasses: the “strong” glass formers with a temperature dependence of relaxation times close to the Arrhenius behavior and the “fragile” glass formers exhibiting a markedly non-Arrhenius temperature variation of the relaxation times.¹⁵ In this classification, the polyols play a particular role since, as their molecular weight increases, we switch from a strong behavior (glycerol is one of the strongest organic glass former) to a fragile behavior.¹⁶ Similar changes have also been observed on the amplitude and the activation energy of the JG process. This process, which appears in the dielectric loss spectrum of glycerol through a high frequency flank, gradually evolves into a pronounced peak in the case of xylitol and sorbitol. These observations are related to the formation of an extensive network of intermolecular hydrogen bonds whose character decreases with the increase of the size of the molecule.¹⁷ The building-up of such networks must, however, be favored by specific conformations of the molecules. This influence can be analyzed on subfamilies of polyols (n fixed), which are constituted by compounds with different conformations.

In this paper, we present a broad-band dielectric analysis of the molecular dynamics of the four pentitol isomers in the amorphous state, above and below their respective glass transition

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Table 1. Chemical Structure, Glass Transition, Melting Temperatures, and Heat Capacity Jump at T_g of the Four Pentitols (from Ref 18)

| Name | Synonym | Chemical structure | T_g [K] | ΔC_p (J.g ⁻¹ .K ⁻¹) | T_m [K] |
|------------|---|--------------------|-----------|--|-----------|
| L-Arabitol | L-Arabinitol L-Arabinol L-lyxitol (2S,4S)-pentane-1,2,3,4,5-pentol | | 261 | 1.35 | 372 |
| D-Arabitol | D-Arabinitol D-Arabinol D-lyxitol (2R,4R)-pentane-1,2,3,4,5-pentol | | 261 | 1.35 | 373 |
| Adonitol | Ribitol pentane-1,2,3,4,5-pentol | | 252 | 1.16 | 375 |
| Xylitol | (2R,4S)-pentane-1,2,3,4,5-pentol | | 250 | 1.14 | 367 |

temperature. Except for xylitol, which is one of the four herein investigated compounds and which has a great importance in industry, only a few studies were performed on the other pentitols. The thermal behavior, including heat capacity and glass transition temperature measurements has been reported. These measurements indicated the good ability of these compounds to vitrification.¹⁸ Some features of the molecular mobility by temperature modulated differential calorimetry (TMDSC) and thermally stimulated depolarization currents (TSDC) have also been addressed.^{18,19} Our study focuses on the characterization of the temperature variation of the dielectric α - and JG-relaxation times. After a description of the main properties of the four compounds and of the experimental details relevant for this study, the results related to both processes are presented and discussed by taking into account the molecular conformation of the molecules.

II. MATERIALS AND METHODS

The four isomers of pentitols, of general molecular formula $C_5H_{12}O_5$ and molecular weight $M = 152.15 \text{ g} \cdot \text{mol}^{-1}$, are xylitol, L-arabitol, D-arabitol, and adonitol. They are sometimes found in the literature under other names. The main synonyms are given in Table 1, which also presents their chemical structure and some thermal properties. Their conformation differs according to the following rule: the carbon chain adopts a planar zigzag form when the conformations at alternate carbon centers are different

(L,D-arabitol) and is bent and nonplanar (xylitol and adonitol) when they are the same.²⁰

The crystalline powders of the four pentitols, with over 99% purity, were purchased from Aldrich Chemicals and used as received.

Isothermal dielectric measurements were carried out using a Novocontrol GMBH Alpha dielectric analyzer (10^{-2} to 10^7 Hz). Thermalization was performed by using a nitrogen-gas cryostat controlled by a Novocontrol Quatro cryosystem ensuring a temperature stability better than 0.1 K. The sample was placed between two stainless steel electrodes (diameter 20 mm, gap 0.1 mm was maintained by use of the Teflon spacer). To ensure a complete amorphization, the sample inside the capacitor was heated to ca. 10 K above its melting temperatures and then quenched below the glass temperature. A sample capacitor with vitrified sample was mounted inside the sample holder of the active sample cell.

III. RESULTS AND DISCUSSION

The dielectric relaxation of each compound was measured, at ambient pressure, over the broad frequency range $10^{-2} \leq \nu \leq 10^6$ Hz. Starting at temperatures well below their respective glass transition temperature, the measurements were performed isothermally up to the high temperatures located in the metastable domain of the pentitols, between melting and glass transition temperature. The loss data $\epsilon''(\nu)$ are shown in Figures 1–4 for

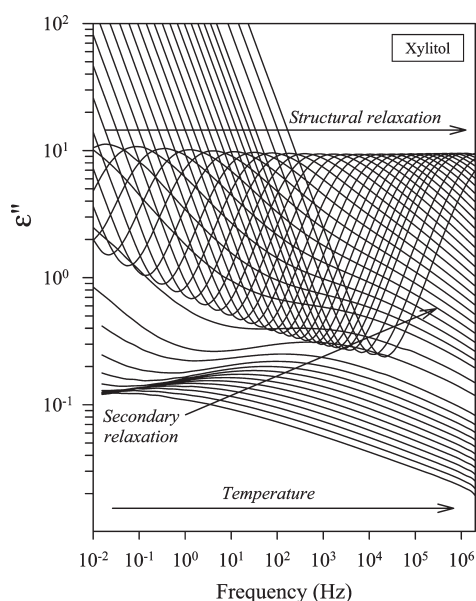


Figure 1. Dielectric loss spectra $\epsilon''(\nu)$ obtained for xylitol. The measurements were performed upon heating from $T = 173$ to 248 K with steps of 5 K, and from 248 to 298 K with steps of 2 K.

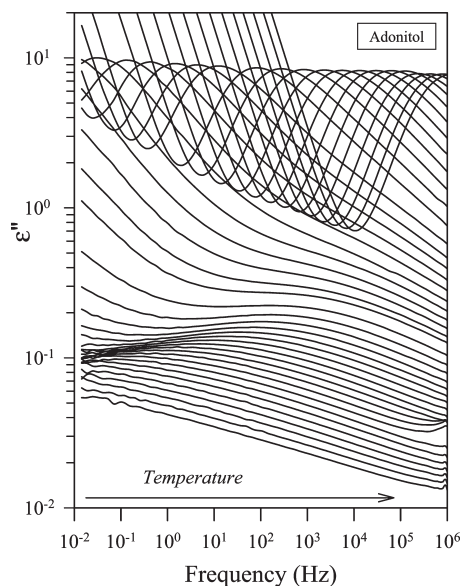


Figure 2. Dielectric loss spectra $\epsilon''(\nu)$ obtained for adonitol. The measurements were performed upon heating from $T = 183$ to 303 K with steps of 3 K.

xylitol, adonitol, L-arabitol, and D-arabitol, respectively. The dielectric spectra of the four compounds exhibit the same main features. At the highest temperatures, one can observe the structural α relaxation and the dc conductivity shifting toward the lower frequencies as the temperature decreases. As a characteristic and well-known feature of supercooled liquids, this α -process exhibits an asymmetrical broadening with respect to the simple Debye behavior. At lower temperatures, an additional contribution to the relaxation pattern enters in the frequency window. This low amplitude contribution, which appears as a high frequency shoulder of the main α loss peak, is the signature

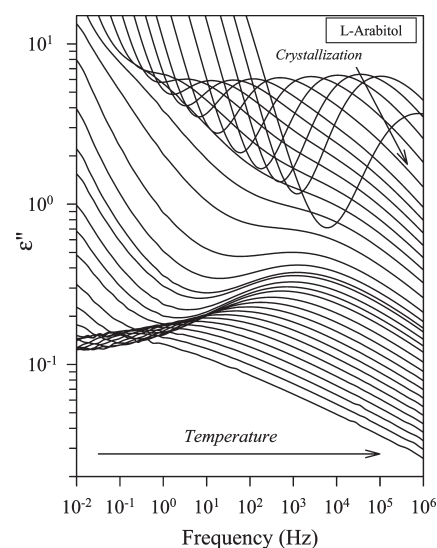


Figure 3. Dielectric loss spectra $\epsilon''(\nu)$ obtained for L-arabitol. The measurements were performed upon heating from $T = 183$ to 285 K with steps of 4 K, and from $T = 285$ to 301 K with steps of 8 K. At $T = 301$ K, an abrupt decreasing of the amplitude is observed, indicating a partial crystallization of the compound.

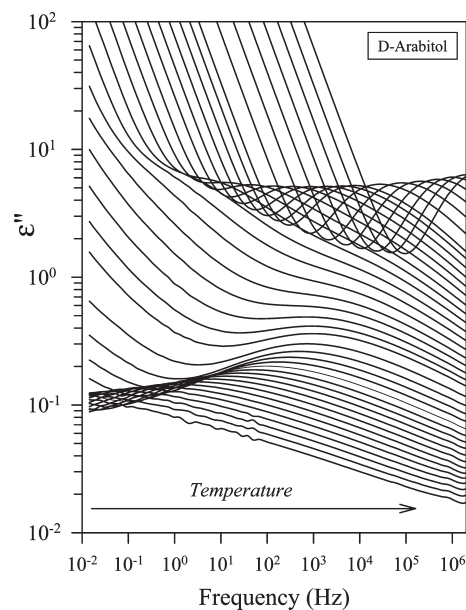


Figure 4. Dielectric loss spectra $\epsilon''(\nu)$ obtained for D-arabitol. The measurements were performed upon heating from $T = 183$ to 253 K with steps of 5 K, from $T = 253$ to 285 K with steps of 2 K and from $T = 285$ to 313 K with steps of 4 K.

of the Johari–Goldstein relaxation mode. Finally, this latter contribution develops into well resolved relaxation peak and remains the only one detectable process below the respective glass transition temperature of the pentitols. For L-arabitol (Figure 3), we can also observe a decreasing of the main loss peak amplitude at the highest temperature ($T = 301$ K). This decrease results from the starting of crystallization of the compound for which the nucleation domain has been localized around $T = 393$ K.¹⁸

To analyze the complex permittivities, we employed a fitting function which consists in the sum of a conductivity term plus the

empirical expressions of Havriliak–Negami (HN) describing the α -process and, of Cole–Cole (CC) describing the β_{JG} process:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_{\text{HN}}}{(1 + (i\omega\tau_{\text{HN}})^{\alpha_{\text{HN}}})^{\beta_{\text{HN}}}} + \frac{\Delta\epsilon_{\text{CC}}}{1 + (i\omega\tau_{\text{CC}})^{\alpha_{\text{CC}}}} - i \frac{\sigma}{\epsilon_0\omega}$$

where $\Delta\epsilon_{\text{HN}}$ and $\Delta\epsilon_{\text{CC}}$ are the dielectric strength and τ_{HN} and τ_{CC} are the relaxation times attributed to the primary and secondary process, respectively. α_{HN} and α_{CC} are the parameters of the distribution width, β_{HN} is a parameter reflecting the asymmetrical shape of the relaxation spectrum of the α -relaxation, ϵ_∞ is the high frequency limit of ϵ^* , and ω is the angular frequency. For all the materials, the temperature dependencies of

the relaxation times of both processes are well described respectively:

- by the Vogel–Fulcher–Temmmann (VFT) relation for the α -relaxation

$$\tau_\alpha = \tau_\infty \exp\left(\frac{B}{T - T_0}\right)$$

where B is a constant having temperature dimension and T_0 is a characteristic temperature corresponding to the divergence of the structural relaxation times.

- in the case of the secondary β -relaxation, by the Arrhenius law corresponding to the limit case where $T_0 = 0$:

$$\tau_\beta = \tau_\infty \exp\left(\frac{E_\beta}{k_B T}\right)$$

where E_β is the activation energy and τ_∞ is the pre-exponential relaxation time for the relaxation process concerned.

The experimental data are displayed, with the results from the refinements, in the Arrhenius plot in Figure 5a, where the solid lines represent the fitting curves. The corresponding parameters are collected in Table 2.

From Figure 5a, we can distinguish two different temperature variations for the α -process with, on one hand, L,D-arabitol and, on the other hand, xylitol and adonitol. These two kinds of evolutions reflect the difference observed on their calorimetric glass transition temperature (Table 1).¹⁸ From the VFT fit, the glass transition temperature, defined as the temperature at which the α -relaxation time is equal to 100s, was estimated for the four compounds and is in good agreement with the calorimetric data. A scaled plot with regard to these T_g values (Figure 5b) clearly shows a difference of curvature in the temperature dependence of τ for the same group of compounds. This difference can be quantified using the steepness index m defined as¹⁵

$$m = \left[\frac{d \log_{10} \langle \tau(T) \rangle}{d(T_g/T)} \right]_{T=T_g}$$

We have obtained important differences between the steepness index values of the four pentitols with $m = 92$ for adonitol, $m = 96$ for xylitol, $m = 122$ for L-arabitol, and $m = 132$ for D-arabitol. Even if these values are much higher than those obtained by temperature modulated DSC,¹⁸ they confirm the classification of pentitols in two pairs according to their steepness index. We can, however, quote an important discrepancy with the results obtained by TSDC,¹⁹ which attribute to the four pentitols identical steepness index values, with $m = 60$.

The molecular dynamics studies in a series of pure polyalcohols (glycerol, threitol, xylitol, and sorbitol) have shown systematic

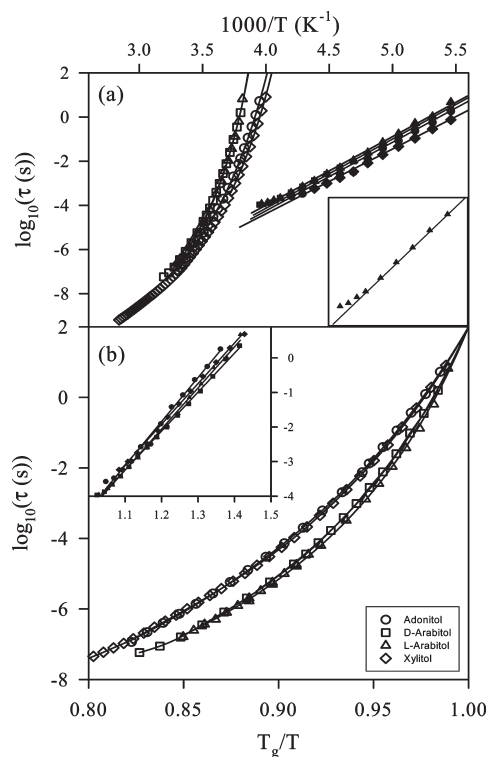


Figure 5. (a) Temperature dependence of the relaxation times τ_α and τ_β of adonitol (circle), D-arabitol (square), L-arabitol (triangle), and xylitol (diamond). The inset shows (for L-arabitol) the departure from the Arrhenius behavior of the secondary relaxation times when T_g is approached. (b) α relaxation times of the four pentitols presented in a T_g -scaled plot clearly show two kinds of behaviors whereas no difference is observed on the β relaxation times as indicated in the inset.

Table 2. Fitting Parameters Obtained from the VFT and the Arrhenius Equations

| | α -process (VFT) | | | | β -process (Arrhenius) | |
|------------|-------------------------------------|-----------------|-------------------|---------------------------------------|-------------------------------------|---|
| | $\log_{10} \tau_\infty \text{ (s)}$ | $B \text{ (K)}$ | $T_0 \text{ (K)}$ | $T_g(\tau = 100\text{s}) \text{ (K)}$ | $\log_{10} \tau_\infty \text{ (s)}$ | $E_\beta \text{ (kJ} \cdot \text{mol}^{-1}\text{)}$ |
| L-arabitol | −12.67 | 1053 | 228 | 259 | −16.8 | 60.8 |
| D-arabitol | −11.98 | 935 | 231 | 259 | −15.9 | 57 |
| adonitol | −14 | 1595 | 206 | 250 | −17.8 | 60.7 |
| xylitol | −13.37 | 1395 | 208 | 247 | −16.1 | 55.6 |

variations of the primary relaxation, which depend on the length of the molecule.¹⁶ Thus, with increasing molecular size, an increase of the fragility has been found. In our case, L- and D-arabitol exhibit particularly high values of the steepness index, comparable to that measured for sorbitol.¹⁸ Therefore, the molecular weight cannot be a unique criterium to describe the fragility of these compounds but should take into account the specific molecular conformation of the different pentitols responsible for different intermolecular arrangements. Indeed, it has been argued that the more or less Arrhenius behavior is related to the network character due to hydrogen bonds, the more Arrhenius-like behavior being characterized by a highly ramified network of molecules.¹⁷ Our observations then suggest the existence of a more extended hydrogen bond network for adonitol and xylitol. As mentioned above, the carbon chain of L,D-arabitol adopts a molecular conformation different from those of adonitol and xylitol, which is bent and nonplanar. This fundamental difference could then favor, for these latter, the involvement of a greater number of hydroxyl groups in the formation of intermolecular links whereas for L,D-arabitol, this number is limited because some of these groups are linked together intramolecularly through the carbon skeleton. Such a difference of local ordering could also be responsible for the increase of the glass transition temperature for L,D-arabitol with regard to xylitol and adonitol. Finally, the β_{HN} and α_{HN} exponents are nearly constant on the analyzed temperature range and are smaller for L, D-arabitol (0.25 and 0.8, respectively) than for xylitol and adonitol (0.35 and 0.9, respectively). This indicates a more marked nonexponential character and a broader distribution of relaxation times for L,D-arabitol, which conforms to the general trend of a strong correlation between fragility and nonexponentiality observed in a majority of supercooled liquids.

The temperature dependence of the secondary relaxation processes, fitted by the Arrhenius equation, is described by the pre-exponential factors and activation energies reported in Table 2. Contrary to the α -relaxations, we do not observe significant differences between the β -processes of the four compounds, which are characterized by mean values of activation energies of $58.5 \text{ kJ} \cdot \text{mol}^{-1}$. When plotted in a T_g -scaled diagram (inset Figure 5b), the secondary relaxation times of the pentitols are superimposable. We do not observe differences on the temperature variation of the broadening parameter α_{CC} on the same kind of plot. As a consequence, the secondary process is not sensitive to the molecular conformation and to the local ordering, the same kind of motion contributes to the dynamical signature in the four compounds. The temperature dependence of the relaxation time of the β -process systematically shows, close to T_g , a slight upward deviation from the Arrhenius-like dependence (see inset in Figure 5a). The corresponding points have been discarded for the calculation of the secondary process activation energy. This deviation also coincide with an abrupt change of the amplitude $\Delta\epsilon_\beta$ of the relaxation whose values, constant at low temperature, rapidly increase from $T_g/T = 1.1$. This change of slope near T_g is generally observed in glass-formers and is similar to the changes observed in thermodynamic quantities, such as enthalpy, entropy and volume.¹⁴

IV. CONCLUSION

In this paper, the four conformers of pentitols xylitol, L-arabitol, D-arabitol, and adonitol have been studied by means of dielectric spectroscopy. Whereas the secondary relaxation

present the same features, the steepness index deduced from the temperature variation of the primary process allows us to separate these compounds in two groups in which the molecules adopt similar molecular conformations. As a consequence, the more or less marked non-Arrhenius character can intuitively be related to the differences of conformation, the bent conformation of xylitol and arabitol then favoring the formation of a more extended hydrogen bond network responsible for a stronger character of the temperature variation of the primary relaxation times.

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