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*The following article appeared in (Bergman, R.; Jansson, H.; Swenson, J. (2010) Slow Debye-type peak observed in the dielectric response of polyalcohols *Journal of Chemical Physics* 132 (4) art no 044504) and may be found at (doi:10.1063/1.3294703).*

Slow Debye-type peak observed in the dielectric response of polyalcohols

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(Received 9 October 2009; accepted 29 December 2009; published online 26 January 2010)

Dielectric relaxation spectroscopy of glass forming liquids normally exhibits a relaxation scenario that seems to be surprisingly general. However, the relaxation dynamics is more complicated for hydrogen bonded liquids. For instance, the dielectric response of monoalcohols is dominated by a mysterious Debye-like process at lower frequencies than the structural α -relaxation that is normally dominating the spectra of glass formers. For polyalcohols this process has been thought to be absent or possibly obscured by a strong contribution from conductivity and polarization effects at low frequencies. We here show that the Debye-like process, although much less prominent, is also present in the response of polyalcohols. It can be observed in the derivative of the real part of the susceptibility or directly in the imaginary part if the conductivity contribution is reduced by covering the upper electrode with a thin Teflon layer. We report on results from broadband dielectric spectroscopy studies of several polyalcohols: glycerol, xylitol, and sorbitol. The findings are discussed in relation to other experimental observations of ultraslow (i.e., slower than the viscosity related α -relaxation) dynamics in glass formers. © 2010 American Institute of Physics.

[doi:10.1063/1.3294703]

I. INTRODUCTION

The most striking experimental feature of structural relaxation of supercooled liquids is the enormous slowing down of the relaxation in a rather narrow temperature range above the glass transition temperature T_g . The main relaxation process, the α -process, exhibits a temperature dependence that is more dramatic than an Arrhenius dependence and can normally be described over a relatively large temperature interval by the Vogel–Fulcher–Tamann (VFT) equation,¹

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right), \quad (1)$$

where τ_0 is the relaxation time extrapolated to infinite temperature, and T_0 is the temperature where the relaxation time τ goes to infinity. The parameter D determines the deviation from Arrhenius temperature dependence. The glass transition temperature T_g corresponds to the temperature where the relaxation time τ of the α -relaxation reaches ≈ 100 s.²

The time evolution of the α -relaxation, $\phi(t)$, is usually well described by the empirical Kolrausch–Williams–Watts (KWW) stretched exponential function,³

$$\phi(t) = A \exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{\text{KWW}}}\right], \quad (2)$$

where τ is a typical relaxation time, $\beta_{\text{KWW}} (\leq 1)$ is the stretching parameter, and A is the amplitude, i.e., the value of $\phi(t)$ at $t=0$. For purely diffusive and Debye processes the relaxation function is exponential ($\beta_{\text{KWW}}=1$), but in the case of α -relaxations in amorphous materials the relaxation pro-

cess is normally considerably stretched and the stretching parameter $\beta_{\text{KWW}} < 1$.

The non-Arrheniusness and nonexponentiality and relations between these and other quantities have turned out to be rather general features of glass formers. Hydrogen bonded glass formers stand out by departing from several of these “universalities.” The departures from universalities are even more pronounced under pressure.⁴ For monoalcohols the dielectric response shows one very striking abnormality, the presence of a strong Debye-like process, which is dominating the frequency spectra, see e.g., Refs. 5 and 6. In fact, the strong so-called Debye-like process was in the past often mistakenly attributed to the α -relaxation. However, lately it has been shown by several studies (e.g., by use of experimental techniques such as differential scanning calorimetry^{7,8} and shear mechanical measurements⁹) that the process is not the α -relaxation and that the true α -relaxation that determines the glass transition temperature is faster and of much lower amplitude than the Debye-like process. Even if it has been clarified without doubt that the Debye-like process is not to be identified with the α -relaxation its origin is still not clear, but several suggestions exist. Clusters, chains, or micelle formations have been put forward as possible structural entities responsible for the Debye-like process.¹⁰ These structures are thought to be formed due to the strong hydrogen bonding between alcohol molecules. If this is the case, one would think, these structures would be possible also for other hydrogen bonded liquids such as e.g., the polyalcohols (though micelle formation seems improbable for molecules with more than one OH-group) and the Debye-like process should be a feature also for these systems. It is probably more likely that chainlike structures are responsible for the process in analogy with the so-called normal mode relaxation in polymers.¹¹ It is also interesting to

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TABLE I. Melting (T_m), boiling (T_b), and glass transition (T_g) temperatures for the here investigated monoalcohol and polyalcohols.

Sample	T_g (K)	T_m (K)	T_b (K)
2-ethyl-1-hexanol	143 ^a	197 ^b	457 ^b
Glycerol	187 ^c	291 ^d	563 ^d
Xylitol	247 ^c	367 ^d	489 ^d
Sorbitol	264 ^c	384 ^d	568 ^d

^aReference 8.^bReference 24.^cReference 25.^dReference 26.

note that, based on recent careful rheological studies, a slow relaxation process due to long-range interactions has been predicted to be present in all polymers and glass-forming liquids.¹² Whether or not this process is related to the dielectric Debye-like process is an open question.

We here report on results from broadband dielectric spectroscopy studies of the polyalcohols: glycerol, xylitol, and sorbitol. We show that the Debye-like process, although much less prominent, is also present in the response of polyalcohols. It can be observed directly in the derivative of the real part of the susceptibility or in the imaginary part if the conductivity contribution is reduced by, for instance, covering the upper electrode with a thin Teflon layer. The results are verified by using the same approach on a monoalcohol, 2-ethyl-1-hexanol, where the Debye-like process is dominating the spectra.

II. EXPERIMENTAL

The samples used in this study, 2-ethyl-1-hexanol ($C_8H_{17}(OH)$), glycerol ($C_3H_5(OH)_3$), xylitol ($C_5H_7(OH)_5$), and sorbitol ($C_6H_8(OH)_6$), were all purchased from Sigma. A compilation of characteristic temperatures (i.e., melting, boiling, and glass transition temperatures) for the samples is given in Table I. The dielectric measurements were performed on a broadband dielectric spectrometer from Novocontrol. The samples were investigated in the frequency range 10^{-2} – 10^7 Hz using an Alfa-S High Resolution Dielectric Analyzer. The samples were placed between two gold plated electrodes and the sample thickness was for all measurements 0.1 mm (determined by silica spacers), and the sample diameter was 20 mm. After preparation each sample was placed in a sample holder and isothermal (± 0.2 K) scans were made at every fifth degree at temperatures given in Table II. Both the real and the imaginary part of the dielectric response, $\epsilon^* = \epsilon'(f) - \epsilon''(f)$, were then analyzed. The

TABLE II. For all measurements isothermal (± 0.2 K) frequency scans were made at every fifth degree in the following temperature intervals.

Sample	Temperature interval (K)
2-ethyl-1-hexanol	120–320
Glycerol	150–350
Xylitol	150–350
Sorbitol	220–400

dielectric loss spectra obtained were fitted to several Havriliak–Negami functions¹³ [Eq. (3)] and a more general fit function¹⁴ [Eq. (4)],

$$\epsilon''(\omega) = \text{Im} \left(\frac{\Delta\epsilon}{(1 + (i\omega\tau)^\alpha)^\beta} \right), \quad (3)$$

$$\epsilon''(\omega) = \frac{\epsilon_p''}{\frac{(1-C)}{a+b} [b(\omega/\omega_p)^{-a} + a(\omega/\omega_p)^b] + C}, \quad (4)$$

where $\omega = 2\pi f$ is the angular frequency. Specific parameters for the equations are in Eq. (3) the relaxation time τ , the dielectric $\Delta\epsilon$, α , and β are shape parameters that determine the symmetric and asymmetric broadening of the relaxation peak, respectively. In Eq. (4) ω_p and ϵ_p'' are the position and the height of the peak. The parameters a and b are shape parameters that describe the slope of the peak at low and high frequency side, respectively, and the C parameter is a parameter that describes the broadening of the relaxation peak without changing the power laws at high and low frequency sides. In the present study we used Eq. (4) with $a = 1$ and $C = 1 - b$, which corresponds to the KWW equation [Eq. (2)] in time domain.

For all samples we measured the dielectric response with and without a Teflon film of 5 μm thickness, placed between the sample and the upper electrode. The Teflon film was used in order to reduce the large contribution of conductivity and electrode polarization to the spectra at low frequencies (since this type of setup has been shown to reduce such effects¹⁵). This method has to be used with caution¹⁶ as this setup is a series circuit of two components, the sample and the insulating Teflon sheet. The resulting permittivity ϵ will therefore be given by $\epsilon = (d_{\text{sample}} + d_{\text{Teflon}}) \epsilon_{\text{sample}} \epsilon_{\text{Teflon}} / d_{\text{sample}} \epsilon_{\text{Teflon}} + d_{\text{Teflon}} \epsilon_{\text{sample}}$, where d is the thickness. In the limit of $d_{\text{Teflon}} \ll d_{\text{sample}}$ we see that $\epsilon \propto \epsilon_{\text{sample}}$ and therefore the Teflon sheet should be as thin as possible. However, in the real experimental situation we found that films of less than 5 μm thickness are very fragile and difficult to handle. We therefore used a Teflon film of thickness 5 μm to cover the upper electrode. Another disadvantage with this method is that the setup can cause the so called Maxwell–Wagner polarization peaks at low frequencies.¹⁷ Any peaks that appear using this setup should therefore be carefully analyzed and preferably the existence should be verified by, for instance, analyzing the real part of the permittivity of the sample (from measurements without Teflon) as done in this work.

One way to separate strongly overlapping broad relaxation peaks is to analyze the negative derivative of the real part of the dielectric susceptibility, $-(\pi/2) \delta\epsilon' / \delta \ln \omega$. This is due to that the peaks are narrower in this representation than in $\epsilon''(\omega)$.¹⁸ An additional advantage with using the real part is that pure conductivity is not contributing to the spectra.¹⁸ This obviously improves the chances to observe low frequency processes that are covered by the conductivity contribution.

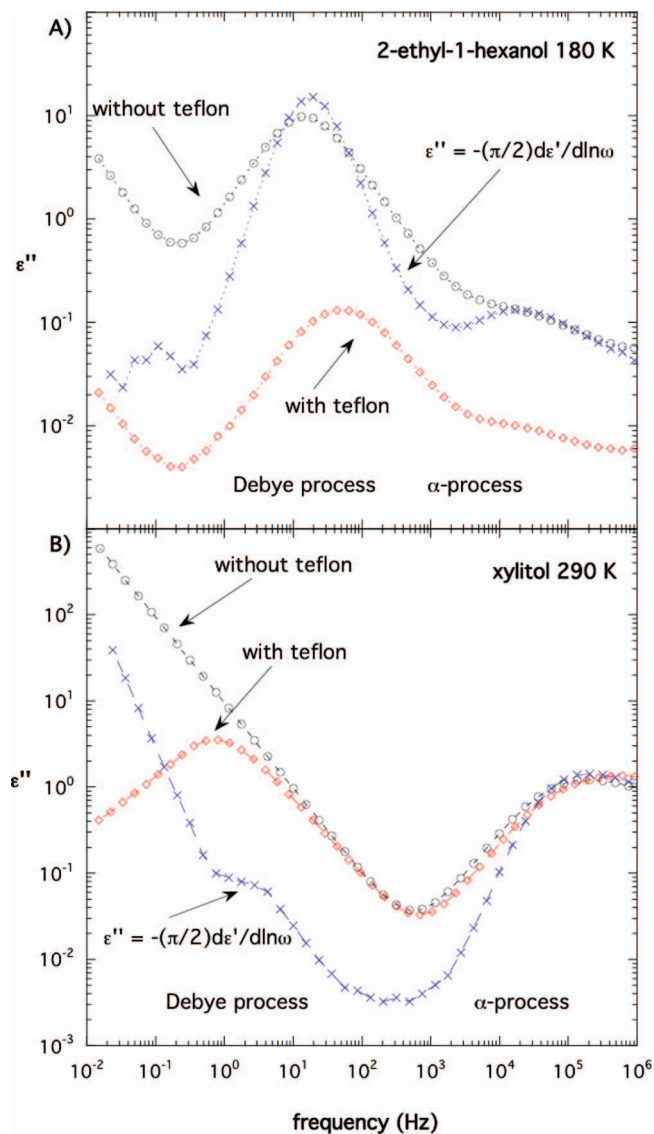


FIG. 1. Dielectric permittivity vs frequency for (a) 2-ethyl-1-hexanol and (b) xylitol at the indicated temperatures. Data measured with [black circles (\circ)] and without [red diamonds (\diamond)] the insulating layer of Teflon are compared to the derivative of the real part of the permittivity [blue crosses (\times)], see text.

III. RESULTS AND DISCUSSION

In Fig. 1(a) we show the dielectric loss spectrum for the 2-ethyl-1-hexanol exhibiting the typical relaxation peak scenario for monoalcohols. The strong main peak is close to Debye and dominates the spectrum. There is also a smaller, and broader, peak at higher frequencies, which is to be identified as the α -relaxation.^{7,9} We also show the spectra obtained at the same temperature using a thin (5 μm) Teflon sheet covering the upper electrode. We see that, apart from a general reduction of the response, contributions from dc conductivity are reduced without significantly affecting the rest of the spectrum. In particular, there is no extra peak(s) created by this experimental setup, at least not in the frequency interval of interest. Note, however, that the Debye-like peak is slightly faster and somewhat broader with the Teflon sheet. It is also seen that the negative derivative of the real part of

the dielectric response produces more narrow peaks and reduces the low frequency contribution due to conductivity.

Feeling confident that the setup with a Teflon film has the desired effect we show in Fig. 1(b) the spectrum of a polyalcohol (xylitol) that do not normally show a clear Debye-type peak. When the Teflon film is used an otherwise, by conductivity and related polarization, hidden peak appears at frequencies lower than the α -relaxation. In order to verify that this is not due to a Maxwell–Wagner polarization we also analyze the real part of the permittivity obtained from experiments without using the Teflon sheet. In Fig. 1(b) the negative derivative of the real part is shown and a clear shoulder is roughly coinciding with the Debye-like process observed in the ϵ'' spectrum. The observed peak is therefore not generated by the experimental configuration but due to a genuine dynamic process of the sample.

The overall relaxation scenario, for some selected temperatures, of the studied polyalcohols when using a Teflon sheet to decrease the conductivity is shown in Fig. 2. It is shown that both the α -relaxation and the Debye-like process are clearly visible in all the studied samples. The spectra were fitted using Eqs. (3) and (4) and relaxation times and shape parameters were extracted. The overall temperature dependences of the relaxation processes for the different samples are shown in Fig. 3. For some of the samples (sorbitol and xylitol) also a secondary so called β -relaxation can be observed. The data for these secondary relaxations corroborate earlier studies that are discussed thoroughly in the literature and will not be discussed further here. Interestingly, we also find indications for a very weak process between the α -relaxation and the β -relaxation for sorbitol from both experimental setups, i.e., measurements with and without the Teflon film. This process has an Arrhenius temperature dependence parallel to the β -process but roughly four decades slower and intercepting the α -relaxation at $T=275$ K and $\tau \approx 40$ ms. This process is outside the scope of this paper but certainly deserves a closer investigation in the future.

For 2-ethyl-1-hexanol it can also be seen in Fig. 3(a) that the relaxation times for the monoalcohol from the measurements using an insulating Teflon sheet are only slightly faster than the data obtained without the sheet. Moreover, the glass transition temperature ($T_g=T(\tau_\alpha \approx 100$ s)) is for all samples in good agreement with values given in the literature (see e.g., Table I). The temperature dependence of the Debye-like process is, for all samples, non-Arrhenius but not as dramatic as that of the α -relaxation, i.e., the D -parameter of Eq. (1) is larger for the Debye-like process. The different temperature dependences of the two processes imply that their relaxation times would intercept at a temperature somewhat below T_g . In fact, perhaps coincidentally but yet rather intriguingly, for glycerol the T_0 values [Eq. (1)] of the Debye-like process and the α -relaxation are the same (≈ 130 K) in agreement with 2-ethyl-1-hexanol where T_0 is ≈ 100 K for both processes. However, for the larger polyalcohols, xylitol and sorbitol, the T_0 values of the two processes do not strictly coincide.

From Fig. 3 we find that the relaxation time τ when T goes to infinity (i.e., τ_0) is slower for the Debye-like process compared to that of the α -relaxation. From the VFT [Eq. (1)]

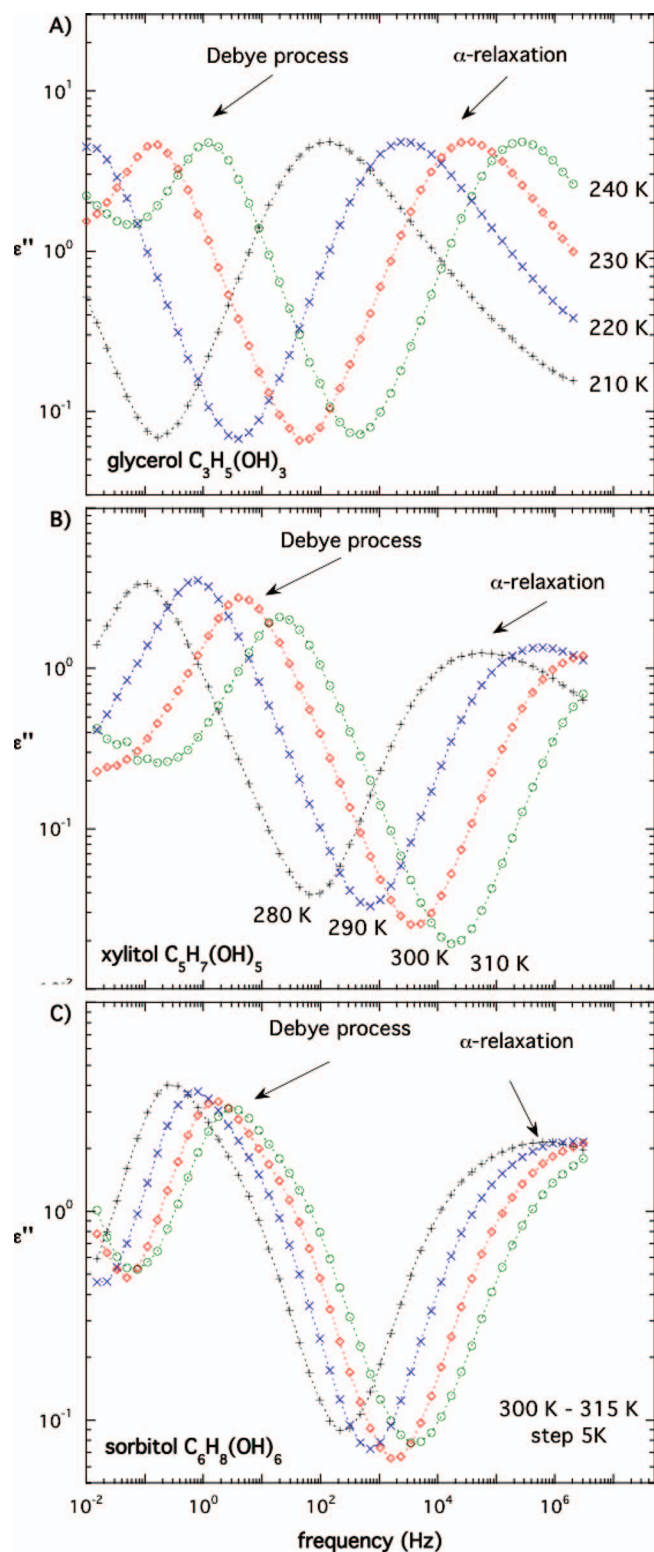


FIG. 2. Temperature evolution of the dielectric permittivity vs frequency for (a) glycerol, (b) xylitol, and (c) sorbitol. For each measurement an insulating layer of Teflon was placed between the sample and one of the electrodes.

curve fitting we found that $\tau_{0\alpha}$ for all samples extrapolates to a value of $\approx 10^{-14}$ – 10^{-15} s, which is the expected value for quasilattice or molecular vibrations that normally is observed for bulk materials. In contrast, we found that $\tau_{0\text{Debye}}$ seems to reach a value around 10^{-11} s, which, in fact, is one characteristic feature⁵ of the Debye-like process in monoalco-

hols. The relatively large value of the $\tau_{0\text{Debye}}$ compared to $\tau_{0\alpha}$ suggests that this process is due to some kind of collective motion of larger structures, rather than due to the fast dynamics of single molecules. Actually, from rheology measurements a similar relaxation process has recently been predicted to be present in all types of glass-forming materials.¹² It was shown that liquid samples of a submillimeter size display a solid behavior far above the glass transition temperature due to long-range interactions, which in turn, could give rise to the here observed large time scale dielectric relaxation of Debye type. A possibility is also that the alcohol molecules are connected to chainlike structures with slow dynamics similar to the so-called normal mode of polymers.¹¹ If such a polymerlike dynamics is responsible for the slow Debye-like process and can be described by the Rouse theory¹⁹ the relaxation time should correspond to a length scale of the chain structures of about 100 nm. However, it should be noted that the normal mode process of polymers is seen dielectrically only when the dipole moments of the monomers line up to reflect the end-to-end vector. Similarly we would then expect that the Debye-like process should follow the same selection rules and therefore be invisible in some systems, even if they have a high dipole moment. This further explains why the Debye-like process is not readily observable in other techniques such as e.g., mechanical spectroscopy.⁹

The shape of the Debye-like peak in the polyalcohols is well described with a Cole–Cole function [Eq. (3) with $\beta = 1$] with only a slight symmetric broadening, partly because of the Teflon film (as discussed above). The shape parameter α was found to be ≈ 0.99 for glycerol, 0.91 for xylitol, and for sorbitol the value increased from ≈ 0.88 to 0.97 with increasing temperature. This could reflect a larger distribution of sizes of the structures responsible for the Debye-like peak in the larger polyalcohols and that for sorbitol this distribution grows with decreasing temperature. This larger distribution may be related to the finding that T_0 for the α -relaxation and the Debye-like process do not coincide for the larger polyalcohols, xylitol and sorbitol. Furthermore, a larger distribution of sizes could also explain the different behaviors seen in Fig. 4, where the relaxation times of the Debye-like process τ_{Debye} is plotted as a function of the relaxation times of the α -relaxation τ_{α} in a double logarithmic plot. In this figure it is obvious that there is a linear relation (indicated by a slope=1 in the plots) between the two processes in 2-ethyl-1-hexanol and glycerol, but that this relation is lost for the two larger polyalcohols, xylitol and sorbitol, where the ratio between τ_{Debye} and τ_{α} decreases with decreasing temperature. Thus, the relaxation processes in glycerol seem to be related to each other in a similar way as previously found for various monoalcohols,^{11,20} where it has been found that the temperature dependence of the Debye-like process is parallel to that of the α -relaxation, and the corresponding viscosity. However, for glycerol the Debye-like process is about 5 orders of magnitude slower than the α -relaxation, whereas for the monoalcohol 2-ethyl-1-hexanol the difference is only about 3 orders of magnitude. The relaxation time (at a given temperature) of a cooperative process is expected to be related to the size of the relaxing unit.

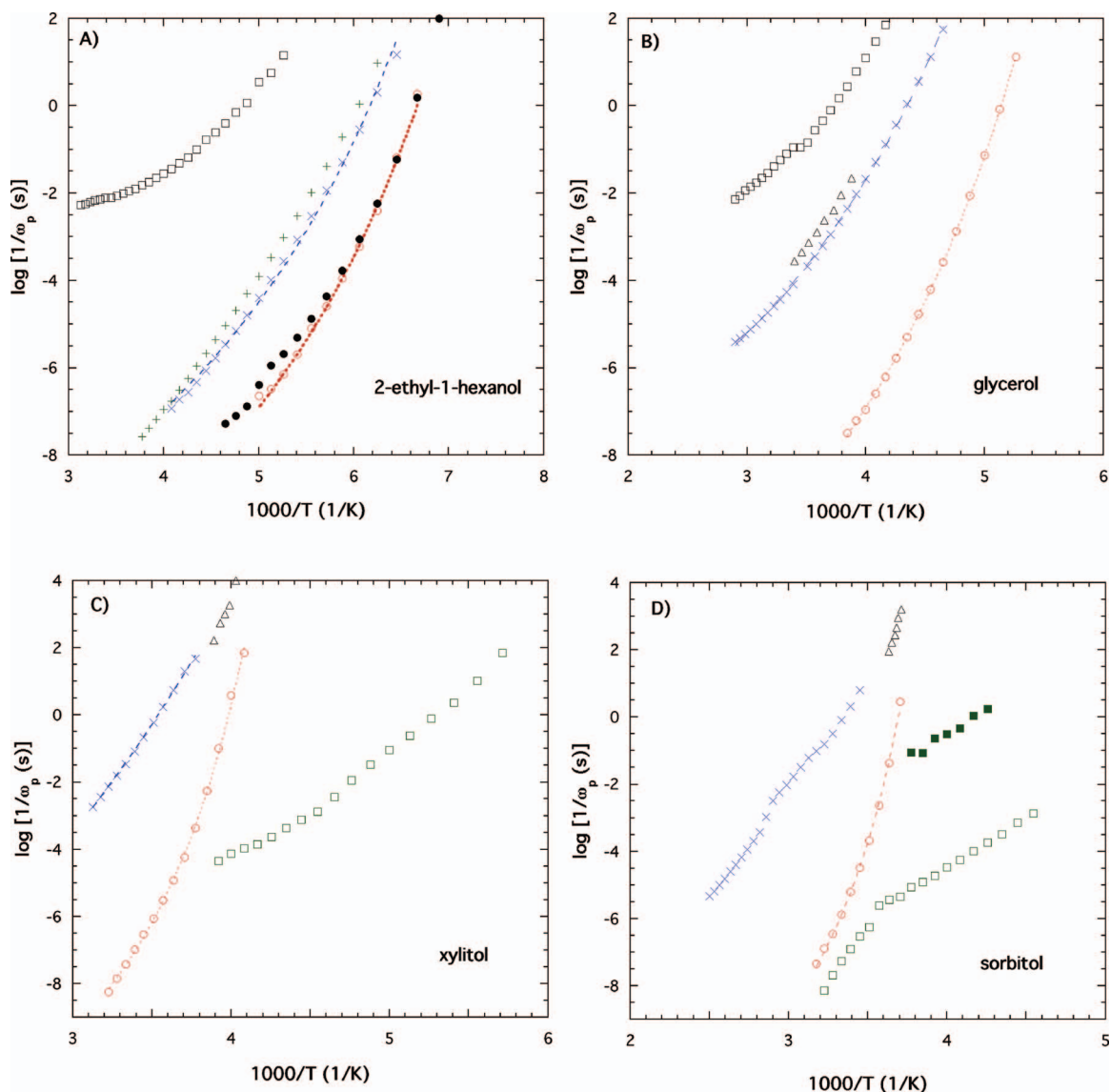


FIG. 3. The obtained relaxation times for the samples (a) 2-ethyl-1-hexanol, (b) glycerol, (c) xylitol, and (d) sorbitol. The α -relaxation is marked with red open circles and the Debye-like process with blue \times . Xylitol and sorbitol have a strong β -relaxation and its relaxation times are here shown with green open squares. For sorbitol we also observed a small process between the α - and the β -relaxation, its relaxation times are marked with green filled squares. The black triangles show literature data of a reported so called “ultraslow process” in the polyalcohols. In (a) the relaxation times obtained without use of the insulating Teflon layer are also shown; the α -relaxation is marked with black filled circles and the Debye-like process with black $+$. The slowest process (black \square) in 2-ethyl-1-hexanol (a) and glycerol (b) is due to Maxwell–Wagner interfacial polarization.

The larger separation between the α -relaxation and the Debye-like process in case of the polyalcohols compared to the general behavior observed in monoalcohols should, therefore, imply that the relaxing units that are responsible for the Debye-like process are of much larger size in polyalcohols than in the monoalcohols. The deviation from a linear dependence for the larger polyalcohols seems to increase with increasing molecular size (more OH-groups) since slope values of about 0.8 and 0.65 were obtained for xylitol and sorbitol, respectively. This implies that the behavior of the Debye-like process is roughly the same for glycerol as for the monoalcohols, but somewhat different in case of xylitol and sorbitol.

It might seem odd that the Debye-like peak has not been observed before in the often studied polyalcohols. In fact, it was recently shown for the same polyalcohols that there in-

deed exists an “ultraslow” process for these materials,²¹ but it is only observable if the conductivity is subtracted. However, these types of subtractions are difficult as one essentially subtracts a huge conductivity contribution to extract a rather small feature in the spectra. The data of Yomigida *et al.*²¹ obtained by time domain dielectric spectroscopy and ours are complementary also regarding the covered frequency windows and their obtained peak relaxation times are compared to our data in Fig. 3. It is seen that we are definitely observing the same process. Our observation thus confirms the observation by Yomigida *et al.*²¹ without resorting to such a difficult subtraction of conductivity from the data. However, in contrast to that study, where it was found that the dielectric strength of the “ultraslow process” decreases with time, we found an almost time independent amplitude of the Debye-like process. This is also observed for the

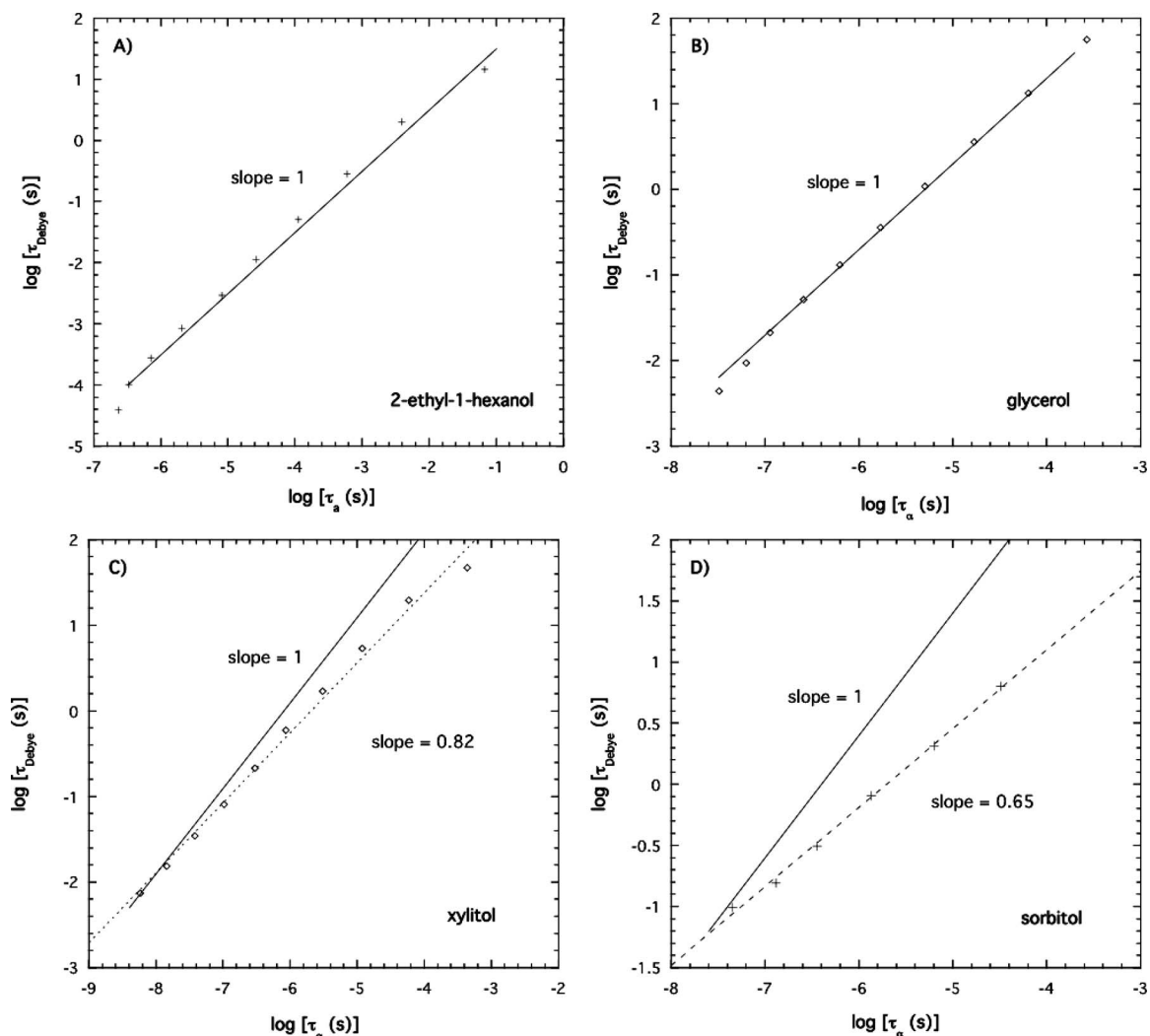


FIG. 4. The relaxation time of the Debye-like process (τ_{Debye}) plotted as a function of the relaxation time for the α -relaxation (τ_{α}). The solid line shows in each plot a slope=1, which corresponds to the case when the two processes are parallel in the measured temperature range. This is the case for 2-ethyl-1-hexanol and glycerol, but not for xylitol and sorbitol.

monoalcohol 2-ethyl-1-hexanol [Figs. 5(a) and 5(b)] and it seems reasonable to attribute the observed peak to the same mechanism responsible for the Debye-like peak in monoalcohols.

Yomogida *et al.* speculate if the observed process could be related to long-range correlations of density fluctuations, the so-called Fischer clusters, a feature so far only observed as an ultraslow relaxation in photon correlation experiments of some glass formers.²² This is an interesting thought and, indeed, the time scale of this process is slower than the α -relaxation with the same order of magnitude as found for the Debye-like process. Furthermore, the Fischer mode was shown²² to be proportional to the α -relaxation in accordance with the here demonstrated behavior for the Debye-like process.

The Fischer clusters are thought to be “fractal aggregations of solid and fluidlike transient associations of molecules.”²² The correlation length of the Fischer clusters is thought to be on the order of 300 nm, i.e., much larger than the nanometer sized cooperatively rearranging regions connected to the α -relaxation. The slow process associated to the Fischer clusters should be a general intermolecular fea-

ture of glass formers regardless of the interactions between molecules. If the Debye-like process is associated to these kinds of dynamic structures it is possible that the Debye-like process is a general feature of glass formers though it might not be detectable in all glass formers as discussed above. A prerequisite for the process to be dielectrically detectable could be that the dipoles are arranged such that they have a component that can be added up along the cluster without canceling themselves out. This is of course very similar to the case for polymers where the normal mode can be observed only in a few cases where this condition is fulfilled.

The comparison to the intramolecular normal mode of polymers could be thought of as somewhat far-fetched since the Debye-like process is clearly intermolecular. However, the Debye-like process, whether or not it is due to Fischer type clusters or other types of long-range interactions,¹² is most likely related to transient intermolecular structures connected via hydrogen bonds (in the case of the present polyalcohols). It is possible that the motion probed is similar in both cases. It is also conceivable that it is a general feature for glass formers, even for nonhydrogen bonded systems, as the presence of dynamical heterogeneities is thought to be

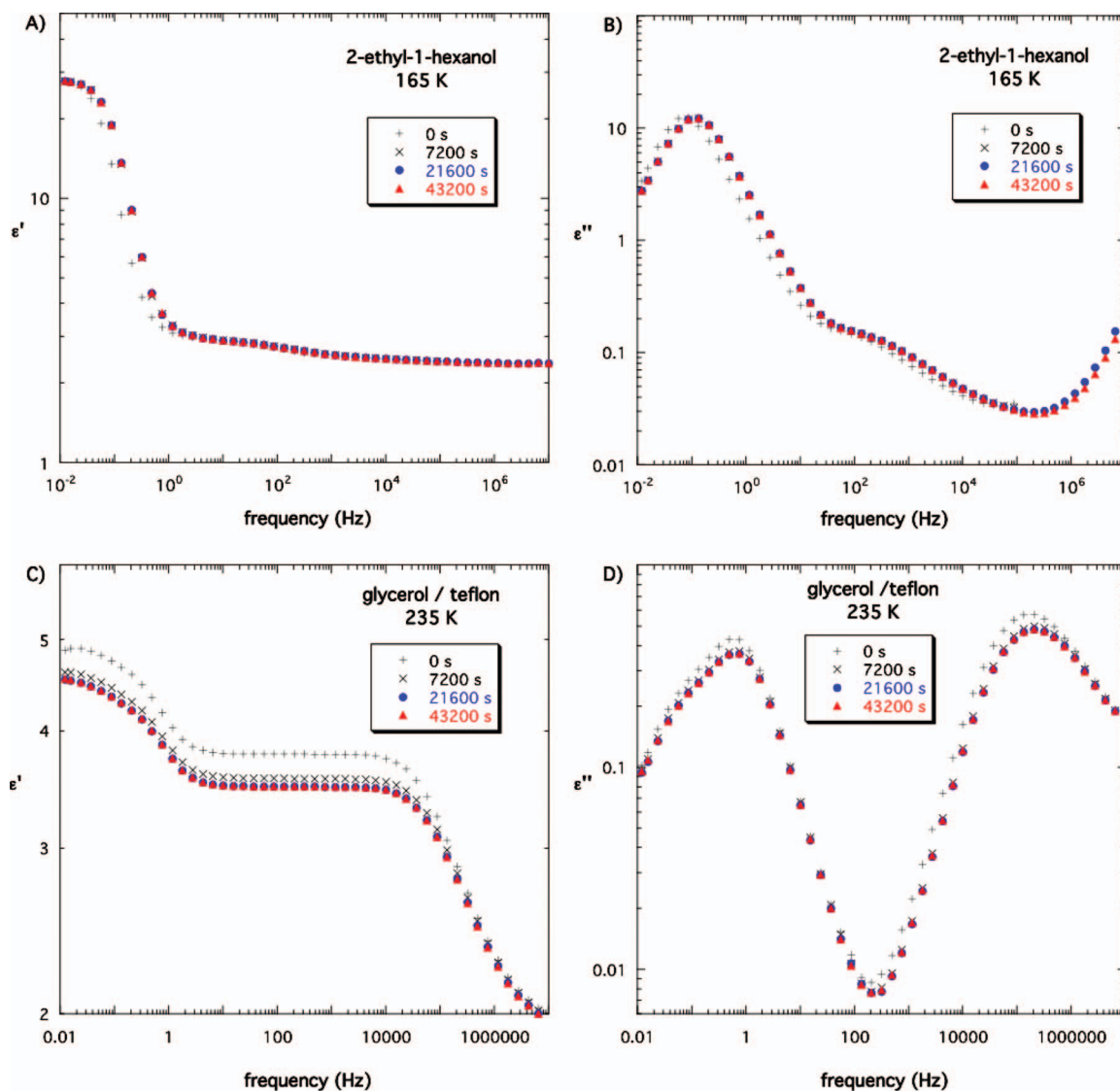


FIG. 5. Time dependences of the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity obtained for 2-ethyl-1-hexanol and glycerol, respectively.

general regardless of the type of intermolecular interactions. The fact that the Debye-like process is clearly strongest in the case of monoalcohols could thus be related more to the fact that the dipoles are favorably placed for probing the motion rather than the character of the intermolecular interaction.

A slow relaxation process has also been observed in glycerol by ^1H NMR relaxometry.²³ It is seen as a low frequency shoulder of the α -relaxation peak, and it is, therefore, not easy to resolve. The slow relaxation appears to be about 2 orders of magnitude slower than the corresponding α -relaxation, and hence, 3 orders of magnitude faster than the here observed Debye-like process. It is thus not clear if the slow relaxation obtained by NMR and the Debye-like process observed by dielectric spectroscopy processes are related. Certainly, more experimental and theoretical studies of dynamics “slower than α -processes” are warranted.

IV. CONCLUSION

We have shown that the Debye-like process dominating the dielectric spectra of monoalcohols can be observed also

in polyalcohols. Normally the process is obscured by the conductivity contribution at low frequencies. The observation thus depends on reducing the conductivity contribution. We achieve this in two different ways: (1) by insulating one electrode with a thin Teflon sheet and (2) by looking at the derivative of the real part of the dielectric permittivity. Both methods give clear evidence for the presence of the Debye-like process in polyalcohols. The process, found at lower frequencies than the α -relaxation process, is much weaker, and for the larger alcohol molecules, also somewhat broader, in the polyalcohols than in the monoalcohols. Our results thus seem to imply that the idea of some buildup of larger hydrogen bonded structures in monoalcohols is also applicable for the polyalcohols, although the effect is much less prominent in the polyalcohols. We speculate about the generality of the process as we believe it is related to transient intermolecular structures, which should be a general feature in glass forming liquids. However, the magnitude of the process in a dielectric relaxation measurement should be related to the dipole moments of the molecules and how they add up when the molecules are connected in larger entities. It may

thus be that the process is not possible to detect at all in many liquids, in particular nonhydrogen bonded ones. Future investigations on nonhydrogen bonded liquids will hopefully clarify this issue.

ACKNOWLEDGMENTS

This work was financially supported by the Swedish Foundation for Strategic Research and the Swedish Energy Agency.

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