



Inelastic light scattering study of hydrogen-bonded glass formers: Glycerol and ethanol

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ABSTRACT

Temperature dependences of the structural relaxation time $\tau_\alpha(T)$ of two hydrogen-bonded glass formers, glycerol and ethanol, were investigated by depolarized light scattering technique. $\tau_\alpha(T)$ of glycerol demonstrates a transition from the Arrhenius law at high temperatures to a non-Arrhenius behavior at $T_A \sim 366$ K. Combination of derivative analysis results for $\tau_\alpha(T)$ from light scattering and dielectric spectroscopies reveals this transition near ~ 200 K in the case of ethanol. The obtained values of T_A are close to the temperatures below which the excess of the Landau-Placzek ratio, associated with the appearance of locally favored structures, was observed earlier.

I. Introduction

Transition of a glass former from a low-viscosity state to a glassy one is accompanied by a tremendous increase in viscosity. Liquid viscosity is related to the structural relaxation (α relaxation) time τ_α . The increase in $\tau_\alpha(T)$ during cooling is accompanied by changes in properties and dynamical response of supercooled liquids. Describing the temperature dependence $\tau_\alpha(T)$ of glass-forming liquids and related phenomena remains to be an important problem in physics and chemistry of glass transition. Usually at high temperatures viscosity or $\tau_\alpha(T)$ is well described by the thermal activation law [1,2].

$$\tau_\alpha(T) = \tau_0 \exp\left(\frac{E}{k_B T}\right), \quad (1)$$

implying the existence of an effective barrier for an elementary act of the α relaxation. This activation barrier can be associated with an effective cage for a relaxing entity. Certainly, in a high-temperature limit this cage should be destroyed [3], and $\tau_\alpha(T)$ should demonstrate stronger temperature dependence towards gas-like values than it is predicted by Eq. (1). Nevertheless, usually Eq. (1) is a good approximation for $\tau_\alpha(T)$ of glass-formers in the low-viscosity state up to the boiling point [4,5], while in some cases a high-temperature super-Arrhenius behavior can be identified near the boiling point (e.g. [6,7]).

A change of the Arrhenius-like behavior of $\tau_\alpha(T)$ to a non-Arrhenius one is commonly observed when a glass-forming liquid is cooled [1]. A super-Arrhenius behavior of $\tau_\alpha(T)$ is observed for liquid viscosity higher than ~ 2 mPa·s [8]. The super-Arrhenius behavior of $\tau_\alpha(T)$ can be

described as an increase in the activation energy $E(T)$ with decreasing temperature. Currently, there is no consensus whether the activation energy diverges at a finite temperature (as it does the Vogel-Fulcher-Tammann (VFT) function [9–11]) or at zero temperature (as it does the double-Arrhenius [12] and some other functions [13–15]), or the apparent super-Arrhenius behavior reflects a transition from the high-temperature Arrhenius law of $\tau_\alpha(T)$ to a low-temperature Arrhenius dependence of $\tau_\alpha(T)$ [16–18]. But there is a general agreement that the transition from the Arrhenius to the super-Arrhenius behavior of $\tau_\alpha(T)$ is caused by a change of the intermolecular cooperativity of the α relaxation [19]. This change can be described in different terms, for example, as an increase in cooperative length [16] or as an appearance of dynamic heterogeneities [20–22], frustration-limited clusters [23,24]. Basically, it assumes an interaction between different neighbor structural units of glass-forming liquids, which can be considered as short-lived locally preferred clusters. Following [25,26] we will call them “locally favored structures” (LFS). It seems that locally favored structures with a local symmetry, which is not consistent with the crystallographic symmetry, suppress crystallization in the case of good glass formers [25]. Indeed, in good glass formers the transition from the Arrhenius to the super-Arrhenius behavior of $\tau_\alpha(T)$ occurs at a temperature T_A , which is higher than the melting temperature [27]. (Formally, the temperature T_A is defined through applying the derivative analysis [6,28].) It is clear that study of glass former behavior in the temperature range, where the transition from the Arrhenius to the super-Arrhenius temperature dependence of $\tau_\alpha(T)$ occurs and where locally favored structures appear, is of great importance.

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Study of a number of glass formers by dielectric spectroscopy [8] reveals that the transition to the super-Arrhenius behavior occurs when the structural relaxation time achieves ~ 60 ps (or α relaxation maximum at ~ 2.5 GHz). This is in good agreement with $\tau_\alpha(T_A) \sim 25 \pm 12$ ps (α relaxation maximum at $\sim 8 \pm 4$ GHz) found for three molecular glass formers by depolarized light scattering technique in [7]. Results of the aforementioned work show that the transition to the super-Arrhenius behavior is quite sharp. The interpretation of the T_A phenomenon as the appearance of locally favored structures is supported by the temperature dependence of the Landau-Placzek ratio (the ratio of the integral intensity of the central Rayleigh peak to the integral intensity of the two Brillouin lines in light scattering) [29,30], where an additional contribution to the elastic line was found at $T < T_A$, and it was associated with the LFS appearance. Also the inhomogeneous broadening of Raman lines at $T < T_A$ in molecular glass formers [31,32] is naturally explained by the LFS hypothesis.

In a simple approach, the appearance of locally favored structures in van der Waals glass formers below a certain temperature implies their absence at higher temperatures. This picture is intuitively acceptable in van der Waals glass formers [24,26,33], since we can imagine that at a sufficiently low density (high temperature) molecules behave independently of each other and at higher density the relaxation has a collective character. This picture fails for network glass formers, since directional chemical bonds are preserved up to the boiling point and molecules/structural units are not isolated. It is not clear whether the language of “locally favored structures” is an effective tool for description of the T_A phenomenon in glass-formers with directional intermolecular bonds. To do a step in solving this problem we present here results of inelastic light scattering study of two hydrogen-bonded glass formers, glycerol and ethanol, in temperature ranges near their T_A 's. Early these liquids were studied by elastic light scattering and an excess of the Landau-Placzek ratio was found below their T_A 's similar to the non-associating liquids [30]. In present work we apply depolarized light scattering technique to find $\tau_\alpha(T)$ dependence of ethanol and glycerol.

Glycerol is a hydrogen-bonded glass former, which was widely studied before by different experimental techniques. $\tau_\alpha(T)$ in the temperature range covering expected T_A was found in some dielectric studies (e.g [34–36].) and by light scattering research [37]. However, as it was noted in [36], determination of T_A values was ambiguous. This ambiguity can be overcome by the derivative analysis [6,28] and is made for the light scattering data of $\tau_\alpha(T)$ of glycerol in the present work. Ethanol in our study serves as a representative of monohydroxy alcohols. Peculiarity of monohydroxy alcohols is the strong contribution of the so-called slow Debye-like relaxation in dielectric spectra, which covers the true α relaxation peak and hinders the analysis of $\tau_\alpha(T)$. $\tau_\alpha(T)$ of liquid ethanol was not studied by light scattering techniques, and this is one of the goals of the present work.

II. EXPERIMENT.

A. Samples.

Glycerol (99.5% purity) and ethanol (99.8% purity, water content $< 0.001\%$) were purchased from Aldrich Chemistry. The both materials were used without further purification. Samples were prepared by sealing each liquid in a glass tube.

B. Experimental method.

The depolarized light scattering experiment was carried out in a backscattering configuration with a 3 + 3-pass Sandercock tandem Fabry-Perot interferometer [38]. Light scattering was excited by a solid-state laser with wavelength 532.1 nm and a power of 200 mW. Several free spectral ranges, from 7 to 300 GHz, were used in the experiment. For more details of the depolarized light scattering experiment, see [7]. Measurements at different temperatures were performed with a home-built oven and a nitrogen flowing cryostat. The glycerol sample was studied in the temperature range from 296 to 454 K, the ethanol sample from 140 to 340 K. In addition, light scattering spectrum of the ethanol sample was measured in the spectral range from 7 to 530 cm^{-1} with a

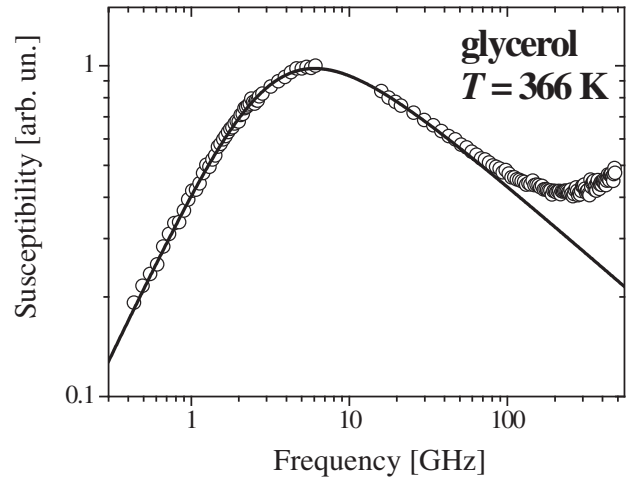


Fig. 1. Susceptibility spectrum of glycerol at $T = 366$ K (circles). The line is the Cole-Davidson fit of the spectrum.

multichannel triple grating Raman spectrometer TriVista 777 in subtractive mode. Combination of the Raman and tandem spectra provided the light scattering spectra of ethanol from 0.4 GHz to 16 THz.

iii. Results

A. Depolarized light scattering spectra of glycerol.

Depolarized light scattering spectra $I(\nu)$ were converted to the susceptibility spectra $\chi''(\nu)$ via the expression.

$$\chi''(\nu) = I(\nu)/[n(\nu) + 1], \quad (2)$$

where $n(\nu) + 1$ is the Bose factor. The spectra of glycerol found in our experiment look similar to the ones in previous works (e.g [39,40].). In the light scattering spectra of glycerol at temperatures above 320 K the α relaxation peak is clearly seen in the spectral range studied. This peak was fitted by the Cole-Davidson (CD) function defined as [41].

$$\chi''(\nu) = \Delta\chi \text{Im}\left(\frac{1}{(1 + i2\pi\nu\tau_{CD})^{\beta_{CD}}}\right), \quad (3)$$

where $\Delta\chi$, τ_{CD} and β_{CD} are fitting parameters, characterizing the amplitude, the weight maximum position and the high-frequency asymptotic power behavior, respectively. An example of the susceptibility spectrum at $T = 366$ K and its fit by the CD function in the range from 0.4 GHz to 40 GHz is shown in Fig. 1. The α relaxation time was found via $\tau_\alpha = \tau_{CD}\beta_{CD}$ [42].

The temperature dependence of $\tau_\alpha(T)$ of glycerol is shown in Fig. 2a. Arrhenius plot used in this figure reveals that $\tau_\alpha(T)$ of glycerol deviates from the thermal activation law, but this deviation is less pronounced than for more fragile glass formers [7]. This is in agreement with the intermediate fragility index of glycerol ($m = 53$ [43,44]). In order to visualize the transition from the Arrhenius to the super-Arrhenius behavior the derivative analysis was applied [6,28]. In this analysis the temperature dependence of the value

$$f_c(T) = (d \log \tau_\alpha / d(1/T))^{-1/2} \quad (4)$$

is considered. $f_c(T)$ for glycerol is shown in Fig. 2b. Temperature independent behavior of $f_c(1/T)$ corresponds to the thermal activation law and a quasi-linear dependence of $f_c(1/T)$ versus $1/T$ to the Vogel-Fulcher-Tammann function [8,45]. Transition between these dependences defines the value of T_A and $T_A = 366$ K is found from Fig. 2b.

B. Depolarized light scattering spectra of ethanol.

Susceptibility spectra of liquid and supercooled ethanol were

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