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## Physics and Chemistry of Liquids

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### Viscous and dielectric properties of $\alpha$ -tocopherol and $\alpha$ -tocopherol acetate

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## Viscous and dielectric properties of $\alpha$ -tocopherol and $\alpha$ -tocopherol acetate

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This article presents the results of the shear viscosity and the dielectric relaxation measurements performed for  $\alpha$ -tocopherol and  $\alpha$ -tocopherol acetate, two principal compounds from the vitamin E group. The temperature dependence of the viscosity and dielectric relaxation time of the compounds can be very well reproduced with the Vogel–Fulcher–Tammann equation. It was found that for both tocopherols, the viscosity and the relaxation time attain their infinite high value (solid-like state) at the temperature of  $\sim 60$  K below the transition to the glass state.

**Keywords:** shear viscosity; dielectric relaxation;  $\alpha$ -tocopherol;  $\alpha$ -tocopherol acetate; Vogel–Fulcher–Tammann equation

### 1. Introduction

Tocopherols and tocotrienols form a family of the compounds termed vitamin E. Natural vitamin E comprises eight different forms ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -) of both tocols, which differ to each other with the number and the place of substitution of the  $-\text{CH}_3$  group. Although all these tocopherols are present in biological materials,  $\alpha$ -tocopherol and  $\alpha$ -tocopherol acetate exhibit the highest biological activity [1–3]. As an *in vivo* antioxidant [4], they protect cells against free radicals and prevent the peroxidation of body fats.  $\alpha$ -Tocopherols are the active compounds used in cosmetic products for hair and skin care, and as effective moisturising agents.

Tocopherols are the subject of numerous physicochemical studies [1]. As they are highly viscous liquids, their ability to flow at different conditions related to the temperature and the flow velocity, is one of fundamental properties of tocopherols. In this article, we present the results of shear viscosity and molecular dynamics studies performed with the use of the dielectric relaxation method for  $\alpha$ -tocopherol and  $\alpha$ -tocopherol acetate in a large range of temperatures.

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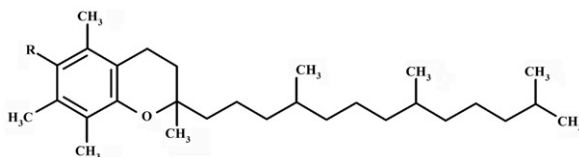


Figure 1. Chemical structure of  $\alpha$ -tocopherol ( $R=OH$ ) and  $\alpha$ -tocopherol acetate ( $R=COOCH_3$ ).

## 2. Experimental

### 2.1. Materials

The compounds studied: D,L- $\alpha$ -tocopherol ( $\alpha$ -T) and D,L- $\alpha$ -tocopherol acetate ( $\alpha$ -TA) were delivered by SERVA and used as supplied. The chemical structure of the compounds is presented in Figure 1.

### 2.2. Measurements

The shear viscosity was measured with a Haake Modular Advanced Rheometer System (MARS) II with a double-cone sensor DC60/1Ti with a small cone angle  $\alpha = 1.004^\circ$ . The cone diameter equals 63.564 mm. The gap size between the cones amounts to  $h = 53 \mu\text{m}$ . The sensor allows one to measure the torque (resulting from the liquid viscous flow) up to  $M_{\text{max}} = 0.2 \text{ Nm}$ , which corresponds, for example, to the limit of the shear rate  $D_{\text{max}} \approx 100 \text{ s}^{-1}$ , which can be used in the case of the viscosity value of  $\sim 10 \text{ Pa s}$ . The tocopherols studied exhibit a Newtonian behavior in the whole share rates used. The viscosity values presented in the article were measured at the shear rate of  $10 \text{ s}^{-1}$ . The temperature was stabilised with the use of a Haake Universal Temperature Controller (UTC) with a Peltier system. Temperature of the samples was stabilised within  $\pm 0.1 \text{ K}$ . The uncertainty of the viscosity determination was 0.1%.

Dielectric properties of tocopherols were measured with a HP 4194A impedance/gain phase analyser in the frequency region of 50 kHz to 100 MHz. The measuring capacitor consisted of three-plane electrodes: one central and two grounded on each side. The electrical heating of high performance, with the use of a Scientific Instruments temperature controller, Model 9700, assured a quite good stabilisation of the temperature (at mK level). Such equipment allows us to determine the permittivity with a relative accuracy: better than 0.5%.

## 3. Results and discussion

The results of the  $\alpha$ -tocopherol viscosity measurements, performed as a function of the temperature, are presented in Figure 2.

The results obtained show that the shear viscosity of the tocopherols studied exhibits exceptionally strong temperature dependence: from  $\sim 30 \text{ Pa s}$  at 278 K to  $\sim 30 \text{ mPa s}$  at 353 K. It seems to be a good occasion to show that in situations where the measured quantity changes in a very large range, an empirical Arrhenius equation:

$$\eta(T) = A \exp\left(\frac{E_A}{RT}\right), \quad (1)$$

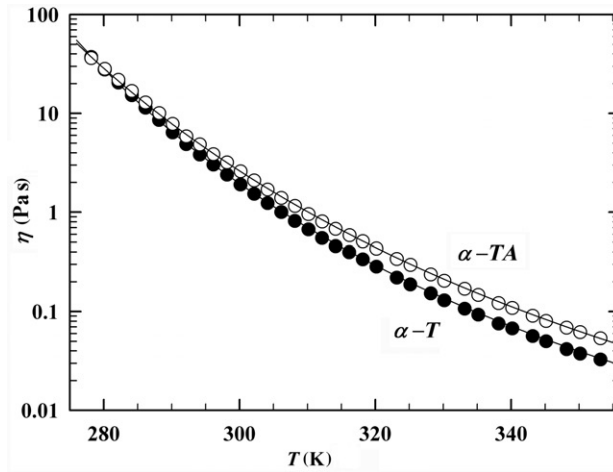


Figure 2. Temperature dependence of the shear viscosity of  $\alpha$ -tocopherol ( $\alpha-T$ ) (●) and  $\alpha$ -tocopherol acetate ( $\alpha-TA$ ) (○). The solid lines represent the best fit of the VFT Equation (2) to the experimental  $\eta(T)$  values (points).

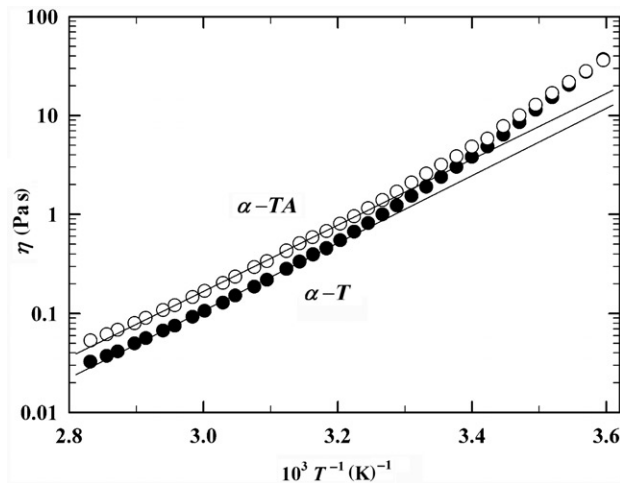


Figure 3.  $\log \eta$  vs  $T^{-1}$  plots for the tocopherols studied. The solid lines represent an Arrhenius behaviour [Equation (1)] for a constant value of the activation energy  $E_A$ .

which predicts the linear dependence of the  $\ln \eta$  on  $T^{-1}$ , can reproduce the experimental dependence in a relatively narrow range of temperature only. In Equation (1),  $E_A$  denotes the activation energy,  $R$  is the gas constant and  $A$  is constant. The data presented in Figure 3 illustrate the limitations of the applicability of an Arrhenius equation in a description of the temperature dependence of the quantity, the value of which changes within three order of magnitude (the problem is discussed in [5,6]).

Like most of the very viscous liquids, the tocopherols studied belong to the group of glass-forming materials [7,8], with the following temperature of the liquid to glass transition:  $T_g^{\alpha-T} \approx 240$  K and  $T_g^{\alpha-TA} = 226$  K. Most of the temperature-dependent quantities concerning the glass-forming materials can be quite well described with an

Table 1. Values of the parameters  $A$ ,  $B$  and  $T_0$  resulting from the best fit of Equation (2) to the viscosity experimental data for  $\alpha$ -tocopherol ( $\alpha - T$ ) and  $\alpha$ -tocopherol acetate ( $\alpha - TA$ ), and the standard deviation  $\sigma$  (Equation (3)).

	$\alpha - T$	$\alpha - TA$
$A$ (Pa s)	3.9 E-06	2.6 E-06
$B$ (K)	1549.4	1872.8
$T_0$ (K)	181.8	164.5
$\sigma$ (Pa s)	0.208	0.249

empirical Vogel–Fulcher–Tammann (VFT) equation [9], which for the viscosity takes the following form:

$$\eta(T) = A \exp \frac{B}{T - T_0}, \quad (2)$$

where  $A$ ,  $B$  and  $T_0$  are the fitting parameters. Unfortunately, there is no exact theoretical interpretation of these parameters [9], but nevertheless, Equation (2) is so frequently used, and the analytical description of the temperature dependence of many physical quantities is so exact, that the theoretical basis of Equation (2) is expected.

The temperature dependence of the shear viscosity of  $\alpha$ -tocopherol and  $\alpha$ -tocopherol acetate presented in Figure 2 can be very well described with the VTF equation (solid lines in the figure). Table 1 contains the values of the fit parameters as well as the values of the standard deviations calculated with the following formula:

$$\sigma = \left( \frac{\sum_i (\eta_{i \text{exp}} - \eta_{i \text{calc}})^2}{n_d - n_p} \right)^{0.5}, \quad (3)$$

where  $n_d$  and  $n_p$  denote the number of the experimental points and the number of the parameters, respectively.

Now, it will be interesting to analyse the temperature behaviour of the dielectric properties of the glass-forming compounds studied here. As both tocopherols under investigation behave dielectrically quite similarly, Figure 4 presents, as an example, the experimental dielectric relaxation data recorded for  $\alpha$ -tocopherol acetate. In the complex plane of imaginary part of permittivity ( $\epsilon''$ ) versus real part ( $\epsilon'$ ) (Cole–Cole plot), the experimental results form a skewed semicircle, which can be analysed with an empirical Davidson–Cole equation [10]:

$$\epsilon^*(\omega, T) = \epsilon'(\omega, T) - i\epsilon''(\omega, T) = \epsilon_\infty(T) + \frac{A(T)}{(1 + i\omega\tau)^\beta}, \quad (4)$$

where  $\omega$  is the angular frequency of the probing electric field,  $A$  is the dielectric strength,  $\tau$  is the relaxation time and  $\epsilon_\infty$  is the high-frequency limits of the real part of the complex permittivity. The fractional exponent  $\beta$  ( $0 < \beta \leq 1$ ) reflects an asymmetric (skew) broadening of the dielectric absorption band, i.e. the deviation from the

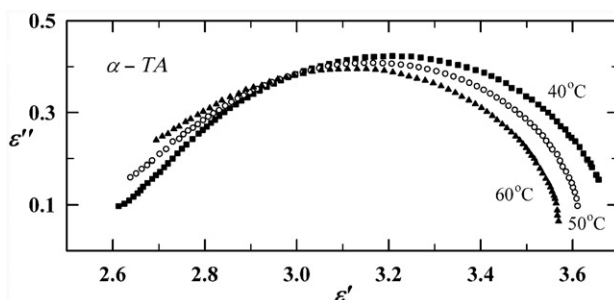


Figure 4. Cole–Cole plots of the dynamic dielectric data for  $\alpha$ -tocopherol acetate ( $\alpha$ -TA) at different temperatures.

Lorentzian shape ( $\beta=1$ , Debye model). As shown in many theoretical papers [11–16], any deviation of the shape of the dielectric absorption band from Debye's is a consequence of the deviation from the exponential decay of the dielectric polarisation, which, as it is well known, corresponds to the random molecular walks in the molecular rotational Brownian motion. Unfortunately, up to now only the anomaly manifesting itself in the experiment as a *symmetrical* broadening (Cole–Cole type of the dielectric relaxation) has its strict molecular interpretation [17–20]. The fractional (anomalous) dynamics can be then described with the continuous-time random walk theory for a power-law distribution of the waiting times between the consecutive jumps of rotation of the molecules. The exponential way of the equilibration of time-depending quantities must be replaced in such cases by a very complex Mittag-Leffler pattern [21].

The values of the parameter  $\beta$ , obtained from the best fit of Equation (4) to the experimental dielectric data, point out a relatively important deviation of the tocopherol molecules' rotational motion from the normal Brownian one. In the case of  $\alpha$ -tocopherol acetate, the fractional exponent has the value of  $\beta \approx 0.6$  and is practically temperature independent, and for  $\alpha$ -tocopherol the exponent shows the temperature dependence from 0.41 at 293 K to  $\sim 0.26$  at 335 K; the effect can be related to the hydrogen bonds between  $\alpha$ -tocopherol molecules.

Figure 5 shows that the temperature dependence of the dielectric relaxation time of both tocopherols studied, obtained from the mentioned about fitting procedure, fulfil the VTF equation perfectly.

As results from Equation (2), at the temperature  $T_0$  the viscosity attains its infinite high value; so, from the flow point of view, the compound studied behaves like a solid. The data presented in Table 1 show that the difference between the glass transition temperature  $T_g$  and the temperature  $T_0$  is equal to  $\sim 60$  K for both studied tocopherols. It means that, after transition to the glass state, tocopherols conserve their capability to flow within a quite large temperature range. The results are compatible with those resulting from the temperature dependence of the dielectric relaxation time. The best fit of Equation (2) to the  $\tau(T)$  experimental dependence shows that the dielectric relaxation time attains its infinite high value at the temperature  $T_0$  equal to 182.8 and 167.0 K for  $\alpha$ -tocopherol and  $\alpha$ -tocopherol acetate, respectively. The values are practically equal to those resulting from the analysis of the viscosity behaviour. As expected, at the temperature  $T_0$ , the transition of tocopherols to the solid-like state

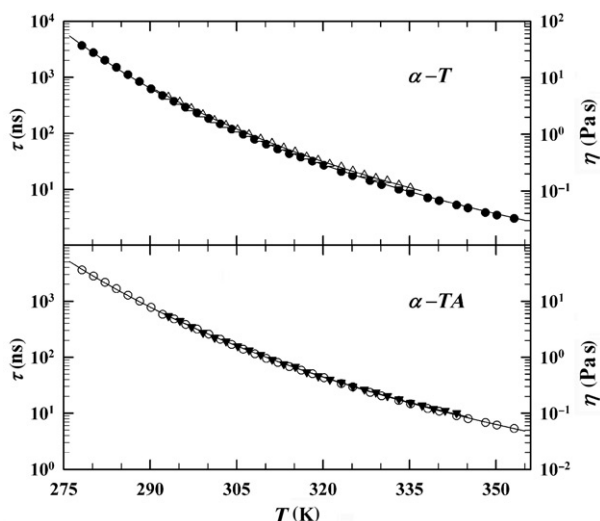


Figure 5. Both the viscosity and the dielectric relaxation time of  $\alpha$ -tocopherol ( $\alpha-T$ ) ( $\Delta$ ) and  $\alpha$ -tocopherol acetate ( $\alpha-TA$ ) ( $\blacktriangledown$ ) fulfil the VFT equation.

manifests itself both in a loss of the flow ability and in a disappearance of the diffusional molecular rotation.

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