

Viscosity of Mixtures of α -Tocopherol Acetate + Mesitylene

Elżbieta Sz wajczak^a, Ryszard Stagracyński^a, Henryk Herba^a, Jolanta Świergiel^b, and Jan Jadżyn^b

^a Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, W. Pola 2, 35-959 Rzeszów, Poland

^b Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

Reprint requests to J. J.; E-mail: jadzyn@ifmpan.poznan.pl

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The paper presents results of the share viscosity measurements performed as a function of temperature and concentration for mixtures of α -tocopherol acetate (vitamine E acetate) and mesitylene, two liquids of essentially different viscosity (four order of magnitude difference at 280 K). The viscosity/temperature dependence for pure α -tocopherol acetate as well as for the mixtures studied can be well described with the Vogel-Fulcher-Tammann equation. The viscosities of the mixtures exhibit a strong negative deviation from the rule of additive dependence on concentration and for increasing temperature the maximum value of the deviation shows an exponential decreasing.

Key words: α -Tocopherol Acetate; Vitamine E; Mesitylene; Share Viscosity; Vogel-Fulcher-Tammann Equation.

1. Introduction

α -tocopherol acetate belongs to a group of compounds of a common name “vitamine E”. The group consists of mono-, di-, and tri-methyl tocots which represent all the eight possible methyl derivatives of the phenol ring conjugated with 6-hydroxychromanol nucleus [1]. Although all these tocopherols are present in biological materials, α -tocopherol and its acetate derivative exhibit the highest biological activity [2, 3]. As an in-vivo antioxidant [4], the tocopherols protect the cells against free radicals and prevent the peroxidation of body fats. Tocopherols are the active compounds used in cosmetic and sun-protection products.

Tocopherols are the subject of numerous physico-chemical studies [1]. As they are highly viscous liquids, their flow ability, which can be quantitatively represented by the shear viscosity, is one of the fundamental physical properties of these compounds. As in practice tocopherols are often used in solutions, the molecular shape of the solvent is expected to play a role in behavior of the mixtures viscosity. In this paper we present the results of the temperature and concentration dependence of the shear viscosity measured for binary mixtures of α -tocopherol acetate dissolved in mesitylene: the solvent composed of the non-polar molecules have the shape close to a spherical.

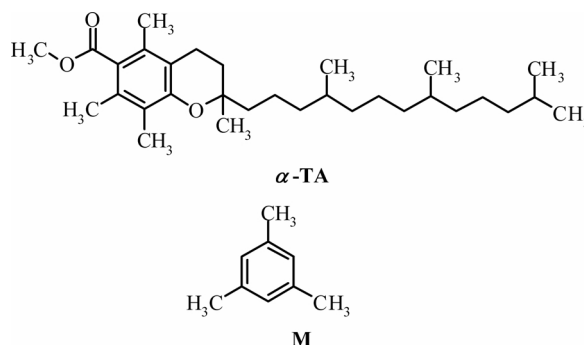


Fig. 1. Chemical structure of α -tocopherol acetate (α -TA) and mesitylene (M).

2. Experimental

The compounds studied are D,L- α -tocopherol acetate, delivered by SERVA (purity $\geq 97\%$), and mesitylene by MERCK (purity $\geq 98\%$). They were used as supplied. The chemical structure of the compounds is presented in Figure 1.

The shear viscosity was measured with a Haake Modular Advanced Rheometer System (MARS) II with a double-cone sensor DC60/1Ti of a small cone angle $\alpha = 1.004^\circ$. The gap size between the cones amounts $h = 53 \mu\text{m}$. The viscosity values were measured at the shear rate (velocity gradient) of 10 s^{-1} .

The liquids studied show a Newtonian behavior up to the shear rates of 200 s^{-1} . The temperature was stabilized with the use of a Haake Universal Temperature Controller (UTC) with a Peltier system. Temperature of the samples was stabilized within $\pm 0.1 \text{ K}$. The uncertainty of the viscosity determination was 0.3%.

3. Results and Discussion

Figure 2 presents the temperature dependence of the shear viscosity measured for the mixtures of α -tocopherol acetate (α -TA) + mesitylene (M). Like of the most highly viscous liquids, tocopherol acetate belongs to the glass-forming materials [5,6]. Numerous temperature-dependent physical properties $X(T)$ of that class of compounds can be quite well described with the empirical Vogel-Fulcher-Tammann (VFT) equation [7–12]:

$$X(T) = A \exp \frac{B}{T - T_0}, \quad (1)$$

where A , B and T_0 are the fit parameters. As shown in Figure 2, (1) (solid lines in the figure) perfectly reproduces the viscosity temperature dependence $\eta(T)$ measured for the solutions of α -tocopherol acetate + mesitylene. Although the fitting parameters in (1) have no explicit physical meaning, the value of the temperature T_0 , at which the viscosity attains its infinite value, can be compared with the temperature T_g of the transition to the glass state. In the

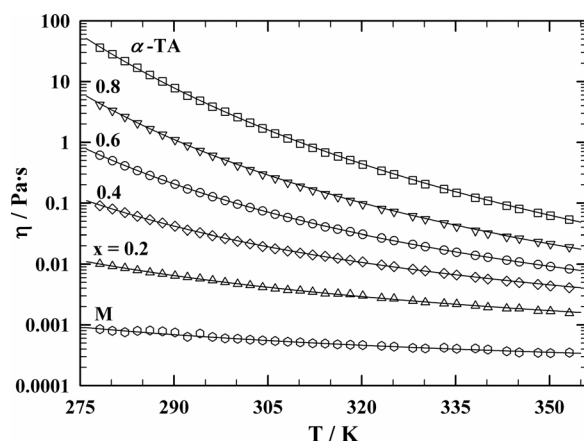


Fig. 2. Temperature dependence of the shear viscosity of mixtures of α -tocopherol acetate (α -TA) and mesitylene (M). x denotes the mole fraction of α -TA. The solid lines represent the best fit of Vogel-Fulcher-Tammann relation (1) to the experimental data (points).

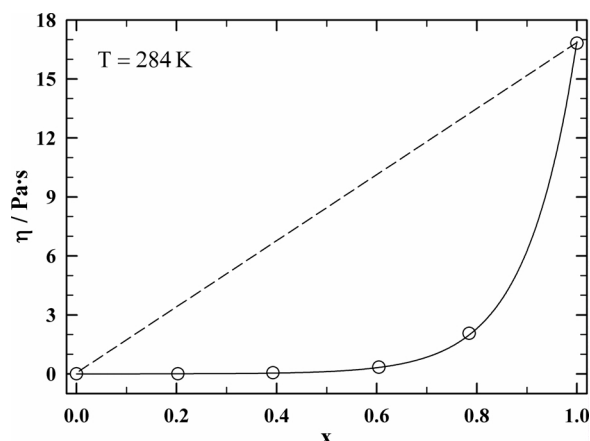


Fig. 3. An example of the experimental results of the viscosity dependence on tocopherol acetate mole fraction (x) in the mixtures with mesitylene, at constant temperature. The dashed line represents the additive viscosity behavior. The results can be well reproduced (solid line) with an exponential dependence (2).

case of pure α -tocopherol acetate $T_g = 226 \text{ K}$ (determined with the DSC method [5]) and $T_0 = 165 \text{ K}$ (from the best fit of (1) to $\eta(T)$). The experimental dependence is presented in Figure 2. This result shows that from the viscosity point of view, α -tocopherol acetate starts to behave as a solid-like material at the temperature of about 60 K below the temperature of the liquid-to-glass phase transition.

In Figure 3 is shown, as an example, the isothermal viscosity dependence on the second parameter used – the tocopherol acetate mole fraction x . As can be seen in the figure, at a constant temperature the viscosity concentration dependence $\eta(x)$ is strongly nonlinear and shows an important deviation

$$\Delta\eta(x) = \eta(x) - [x\eta_{\alpha-TA} + (1-x)\eta_M] \quad (2)$$

from the additive behavior (the dashed line in Fig. 3). In above equation η , $\eta_{\alpha-TA}$ and η_M stand for, respectively, the measured viscosity of a given mixture and the viscosities of its pure constituents. Figure 3 shows that a strong dependence of the mixtures viscosity on the tocopherol mole fraction $\eta(x)$ can be well reproduced (solid line in the figure) with an exponential function

$$\eta(x) = \eta_0 \exp(Dx), \quad (3)$$

where η_0 is the solvent viscosity ($x = 0$) and D is a fit parameter.

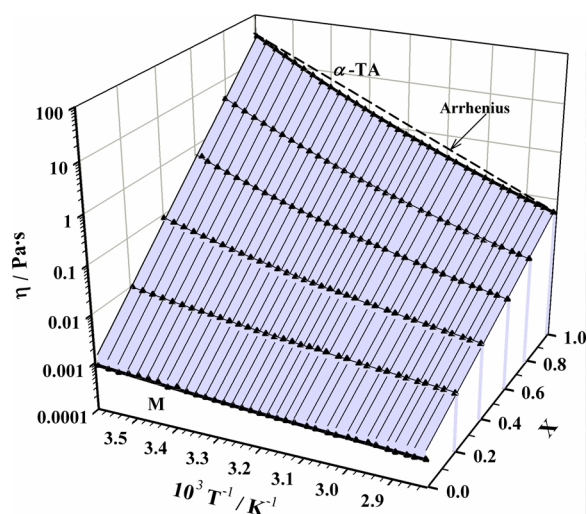


Fig. 4. Temperature and concentration dependences of the shear viscosities measured for mixtures of α -tocopherol acetate and mesitylene. x denotes the mole fraction of α -TA. The points are the experimental viscosity values. The solid lines represent the best fit of the Vogel-Fulcher-Tammann relation (1) to the viscosity dependence on the temperature (at constant x) and fit of (3) to the viscosity dependence on α -TA mole fraction (at constant temperature).

In Figure 4 are gathered the experimental viscosity data (points) obtained for all studied mixtures of α -tocopherol acetate + mesitylene in the whole temperature and concentration ranges used. The solid lines in the figure represent the dependences of $\eta(T)$ for constant tocopherol mole fraction and $\eta(x)$ at the constant temperature, described with (1) and (3), respectively. It is clearly visible, especially for pure α -tocopherol acetate, that the measured $\eta(T)$ dependence does not fulfill a commonly used Arrhenius relation. The data presented in Figure 4 seem to illustrate an important rule: the greater the range of the measured physical quantity, the more based is the conclusion related to the theoretical model which is used for the interpretation of the dependences obtained. A strong temperature dependence of α -tocopherol acetate viscosity, when measured in some narrow (in comparison to the data presented in Fig. 4) temperature range, certainly can be described with an Arrhenius equation but the slope of the dependence (so-called the activation energy) will be different, depending on the temperature range used. On the other hand, the temperature dependence of mesitylene viscosity, measured in the same temperature range as for α -tocopherol acetate, cannot be used for the theoretical model verification. Due to a rather modest viscosity change within the temperature range used, both

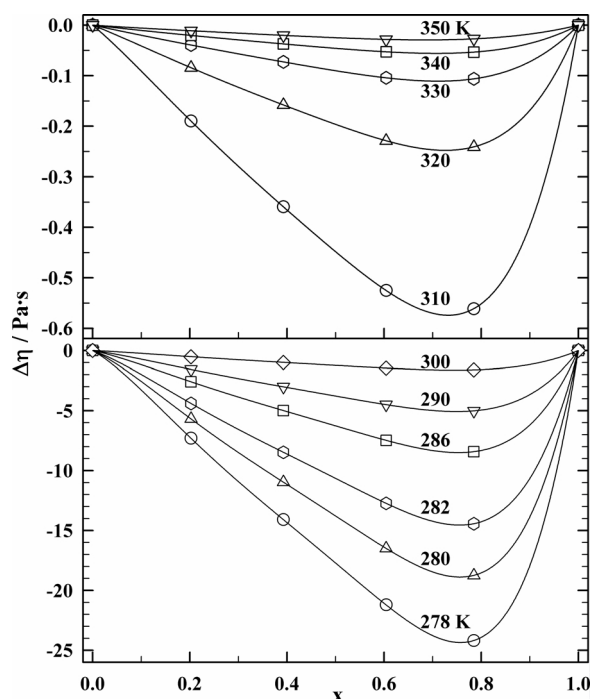


Fig. 5. Viscosity deviation $\Delta\eta$ from the additive behavior in function on α -tocopherol acetate mole fraction x in the mixtures with mesitylene, calculated with (2).

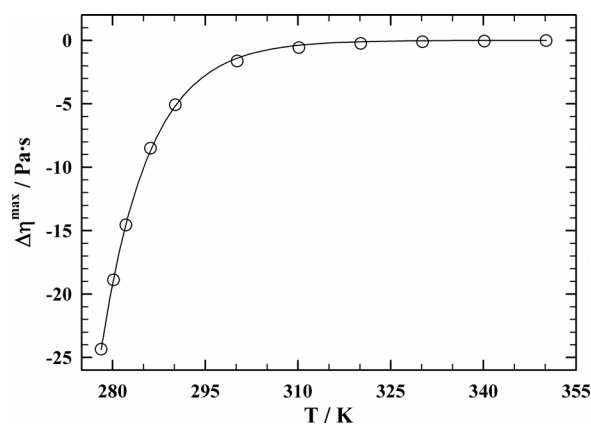


Fig. 6. Value of the maximum of the viscosity deviation from the additive behavior in the mixtures of α -tocopherol acetate + mesitylene decreases with the temperature in an exponential way [$\propto \exp(-CT)$].

the Arrhenius and the Vogel-Fulcher-Tammann relations can fairly well reproduce the experimental $\eta(T)$ dependence for mesitylene.

Figure 5 presents the concentration dependence of the viscosity deviation $\Delta\eta(x)$ from the additive behavior at different temperatures, calculated according

to (2). The dependences show an asymmetry with respect to the equimolar of α -tocopherol acetate and mesitylene concentrations with the position of the maximum ($\Delta\eta^{\max}$) at $x = 0.75$. While the $\Delta\eta^{\max}$ position is practically not dependent on α -tocopherol acetate mole fraction, its value shows a strong temperature dependence and, as depicted in Figure 6 (solid line), the $\Delta\eta^{\max}(T)$ dependence is of the exponential type [$\propto \exp(-CT)$].

The presented results illustrate the viscosity behavior in the binary mixtures composed of the liquids of extremely different viscosities. The main conclusion resulting from the presented studies concerns the viscosity dependence on concentration: the viscosity dependence on the mole fraction of the mixture constituents has an exponential form. Besides, strong negative viscosity deviations from the additive concentration behavior, observed for the mixtures of α -toco-

pherol acetate + mesitylene, can be an important information in analysis of some experimental data related to the practical uses of the mixtures studied or similar ones. It seems to be interesting to mention here that the presented viscosity behavior of α -tocopherol acetate solutions is quite similar to that observed for α -tocopherol solutions [13] what points out the negligible role of the hydrogen bonds $O-H \cdots O$ on the viscosity of such viscous liquids as tocopherols.

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