**Rheological Behavior of Cholesteryl Myristate’s Smectic A and Cholesteric Phases**

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**ABSTRACT**

The compound cholesteryl myristate presents the cholesteric and smectic A mesophases when its temperature is varied. Those mesophases have remarkable structural differences and these differences are related with the rheological behavior of the compound. The cholesteryl myristate’s viscosity was studied as a function of temperature and shear rate for both the mesophases. it is clear that the viscosity decreases with increasing shear rate a typical behavior know as shear-thinning. The viscosity also decreases more strongly to the smectic A mesophase. This is due the better organization of the smectic structure thereby providing greater resistance to movement and consequently increasing the viscosity of the compound when compared to cholesteric phase.

**INTRODUCTION**

At late 20th century a revolution has occurred in displays images technology with the advent of liquid crystal (LCs) displays. The birth of this new technology has enabled the fabrication of small screens that reduce the size of televisions, computers and more. Nowadays the application of compounds that exhibit a LCs phase has grown significantly. There are thermometers and LCs films with polymers for controlling the transmission of light in a window, among other. However the efficacy of these applications is controlled by certain parameters of the material. Some of these parameters are for example the different forms of molecules, the molecular organization and the interaction between the molecules. Another important factor is the viscosity of the material; this factor is described by the rheological behavior of the material.

The deformation of a body under the influence of tensions sets its rheological behavior; this behavior for a liquid is described by its viscosity (η) [1]. The viscosity of a body can influence their applicability in certain technological products which justifies the need for control over this parameter. Newton described the behavior of an ideal liquid; This ideal liquid has no viscosity dependence on shear rate thus its flow curve represented on a graph of shear stress versus shear rate is a straight line with angle of slop α. Through the tangent of this angle it is possible to obtain the viscosity of the sample with only a flow curve [1]. All liquid that regards Newton’s behavior is known as a Newtonian fluid. The liquids that exhibit dependence between viscosity and shear rate are known as a non-Newtonian fluid.

Liquid crystals (LCs) also known as mesophases are intermediate phases presented by some compounds; The LCs phases can be divided into two major groups: thermotropic LCs and lyotropic LCs [2]. Thermotropics LCs has as parameter of phase transition the temperature. Its organic molecules have one common pattern usually involving benzene and derivatives [3]. Thermotropic LCs are very technologically applicable, for example, in the construction of displays [4]. Already the lyotropic LCs are formed from amphiphilic molecules in solvent and has as parameter of phase transition the concentration of the sample [4].

Friedel [5] was the first to propose the classification of LCs according to its different molecular organizations, separating the LCs into three groups: Nematic, Smectic and Cholesteric. The Nematic phase has molecules aligned on average with a preferred direction indicated by a director **n**.

These molecules are generally parallel to each other; as yet analyzing molecules farther away the lack of relationship between the mass centers can be noticed [2]. The Smectic phase has a structure in form of layers spaced in a well-defined distance. The Smectic phases are more ordered than the Nematic phases. The smectic and Nematic phase may occur in the same material, in this case the smectic phase is found at a lower temperature than the Nematic phase. There are several tips of Smectic phases which has different macroscopic textures that can be easily distinguished [2]. The cholesteric phase which occurs mainly in derivatives of cholesterol is a characteristic of LCs that are formed by chiral molecules. These molecules are arranged helically and due to this structure show unique optical properties [3]. The cholesteric phase and nematic phase are not found together in a single liquid crystal, but the cholesteric phase can be found in a LCs which presents smectic phase [2].

The compound cholesteryl myristate is one of the most studied compounds derived from cholesterol [6]; among other derivatives of cholesterol it presents the liquid crystalline phase [7]. The cholesteryl myristate specifically shows the smectic A and cholesteric phases with the variation of its temperature [9]. Temperatures transition of this compound reported in the literature have some variation as described by Sakamoto [8] and Sampaio [9], the temperatures are around 71 ° C for the transition between the crystal phase and smectic one; around 78 ° C for the transition between the smectic and cholesteric phase and finally around 83 º C for the transition phase between the cholesteric and isotropic phases. The molecule of cholesteryl myristate consists of carbon, oxygen and hydrogen atoms and is a relatively large molecule which can exhibit different conformations depending on the conditions applied, as shown by Burks [7].

The search for ever more advanced technologies leads first to the development and improvement of materials. For this development occurs studies are needed on the properties of these materials, thus enabling its possible improvement.

**METODOLHOGY**

The study of the viscosity of cholesterol myristate was performed taking into account the above mentioned parameters, with the main emphasis in dependence of the viscosity in relation to shear rate imposed. The intuited of the study is to relate the dependence of viscosity with the different structures of smectic A and cholesteric phases and compare it with the behavior in the literature.

The experimental values ​​of myristate’s viscosity were obtained in Sampaio’s article [9]. From these digitized values ​​were constructed graphs of viscosity versus shear rate for the smectic A and cholesteric phases. The results of the graphs showed the characteristics of the dependence between viscosity and shear rate. A theoretical survey was undertaken to relate the behavior of myristate’s viscosity and the different structures presented by the compound.

**RESULTS AND DISCUSSIONS**

The viscosity measurements for the Smectic A and Cholesteric phases of the compound (Fig. 1) shows that at low shear rates the effects of molecular orientation have a predominant effect in the viscosity of the sample. For increasing shear rates values from 0 to 10 s-1 there is a drop in the viscosity of the sample. This drop is more pronounced for the smectic A phase.

Fig. 1 – Viscosity versus Shear Rate for the Smectic A and Cholesteric Phase

The rheological behavior of myristate’s cholesteric phase can be well described by a power law model ($η=b\* γ^{c}$ ) as show in figure 2. However this approach is not valid to the smectic A phase (figure 3). That indicates a different behave for the Smectic A phase. The flow aligns the molecules more easily due to lower thermal agitation. The power law can be used in the Smectic A phase after added a term related to the saturated viscosity ($η=b\* γ^{c}+ a)$, shown in fit of the figure 1. This model describes both phases.



Fig. 2 - Logarithm of viscosity versus the logarithm of shear rate for the cholesteric phase.



Fig. 3 - Logarithm of viscosity versus the logarithm of shear rate for the Smectic A phase.

**CONCLUSIONS**

The viscosity of the compound presents a behavior know as shear-thinning [1]. This behavior occurs in compounds that have a large molecule. The molecules of the compounds rearrange themselves according to the direction of flow decreasing the viscosity of the sample.

Even the behavior of the cholesteric and smectic A phases being the same, there are differences of magnitude between the two phases. It’s clear that the decrease of the viscosity with the increase of the shear rate is more abrupt for the Smectic A phase. This is due the higher resistance offer by its structure when compared with the structure of cholesteric phase.

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