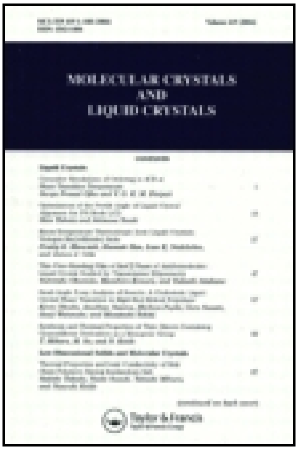

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M. Regina Alcantara [a] & E. G. Fernandes Jr. [a]
[a] Instituto de Química, Universidade de São Paulo, SP, Brasil

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The Effect of Water on the Flow Orientation Process of Lyotropic Liquid Crystals Cholesterized by D(+)-Mannose

M. REGINA ALCANTARA and E. G. FERNANDES JR.

Instituto de Química, Universidade de São Paulo, SP, Brasil

The rheological behavior of cholesteric lyotropic liquid crystals can give information about the chiral forces involved in the formation of the cholesteric arrangement. In the present work, we studied the effect of water availability on the orientation process of a lyotropic liquid crystal system submitted to flow. Different mesophases based on decylammonium chloride were prepared with different amounts of D(+)-mannose added as inductor. It was observed that the flow orientation process on cholesteric lyomesophases is different when occurring in a room atmosphere or a water-saturated atmosphere. For samples sheared in a room atmosphere, the orientation process involves an initial step of destruction of the cholesteric structure caused by shear, leading to the formation of microdomains with different orientations. In a second stage these microdomains orient themselves, forming a new helical structure in the flow direction. When the systems are sheared in a water-saturated atmosphere, the orientation process involves the accommodation of micelles into a new structure seeking the best orientation in the flow direction.

Keywords: liquid crystals, cholesteric liquid crystals, organized systems, rheology, rheological properties

The most common approaches to treating the flow alignment of a liquid crystal include the Ericksen-Leslie Theory [1,2] for nematic director, rigid-rod models dealing with the orientational distribution function of an assembling of uniaxial particles [3,4], and phenomenological theories for the second-rank alignment tensor [5,6]. The stationary rheological techniques may result in complicated responses, mainly because the phase director does

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Address correspondence to Maria Regina Alcantara, Instituto de Química, Universidade de São Paulo, Avenida Professor Lineu Prestes, 748 Cidade Universitária, CEP 05508-900, São Paulo, SP, Brasil. E-mail: mralcant@iq.usp.br

not assume a uniform orientation under small velocity gradients. To avoid this limiting condition, some different rheological techniques have been employed, generally imposing this director orientation throughout the sample by means of strong magnetic fields [7,8].

Over the last few years, rheological properties have been used to understand the spatial arrangement of the units that constitute the system [9–11] and its variations in the phase transition regions [11–16]. Some efforts have been developed to determine the arrangement of the liquid crystal structure by optical microscopy under polarized light together with rheological techniques. These techniques, known as rheo-optical, make it possible to obtain information about the variation of the structural arrangement before, during, and after shear [16–18]. Rheological parameters have also been used to understand the spatial structure of the system's constituent units and the way they change their order near the transition regions [10,12–14,19,20].

The theoretical study of the rheology of cholesteric liquid crystals has provided important information about the positioning and behavior of the helix submitted to flow. Rey [21] proposed that when a cholesteric helix is aligned on a flow direction, an uncoiling process occurs, leading the system to a configuration similar to that obtained for nematic phases.

For lyotropic liquid crystals the flow can be associated with cooperative changes of conformation of flexible layers submitted to frictional forces in the liquid layers [22]. Some results obtained by Penfold et al. [23] showed that under low shear rate lamellae are oriented parallel to the flow-vorticity plane, whereas for high shear rate experiments they are ordered along the orthogonal director, parallel to the flow-shear gradient plane. Results published by our laboratory indicated that systems based on sodium dodecylsulphate, sodium sulphate, and water are pseudoplastic [24] with a complicated transient response, either rheopexic or thixotropic, depending on whether the micelles are cylindrical or discotic, respectively [25,26]. It was possible to verify that the effect of cholesterization on systems composed of cylindrical micelles leads to a decrease of the flow index and to an increase of the consistency index, evidence that the elastic forces originated by the cholesteric arrangement lead to a system more resistant to deformations [24]. The occurrence of edge fractures in nematic systems based on potassium laurate is a clear indication of the existence of strong elastic contributions that should be better evaluated [27]. Results obtained for cholesteric systems, constituted by discotic micelles, showed that the orientation process involves an initial destruction of the cholesteric arrangement, forming microdomains with different orientations followed by the orientation of these microdomains caused either by shear or by the action of elastic forces during the rest time [28].

The present work presents the rheological behavior of nematic and cholesteric lyotropic liquid crystals constituted by discotic micelles of decylammonium chloride (CDA) and submitted to a constant shear rate. The flow orientation process is analyzed as a function of the shear time, the concentration of added hydrophilic inductor, and the concentration of water present in each phase.

EXPERIMENTAL

Two groups of cholesteric phases were prepared by the addition of D(+)-mannose to a nematic system based on decylammonium chloride/H_2O/NH_4Cl. The final phase compositions are presented in Table 1. The samples **CDA1** to **CDA5** have smaller water concentration, i.e., lower water/amphiphile ratio, than the samples **CDA6** to **CDA10**.

The rheograms were obtained using a Brookfield cone-and-plate rheometer, model LV-DVIII, with cone CP-52. The temperature was maintained at 25.0°C within 0.1°C by a Brookfield temperature-controlled bath, model TC-500. Sequences of cyclic rheograms were obtained with speed varying from 0.1 to 100.1 rpm and return to 0.1 rpm with increments of 5 rpm every 30 s in order to follow the orientation process on each system. These experiments were carried out in a water-saturated atmosphere. The water-saturation was obtained using a moistened cotton strip inside the rheometer cup, without direct contact with the sample. An initial rest time

TABLE 1 Compositions for nematic and cholesteric phases (% molar fraction)

Samples	*CDA**	*NH_4Cl*	*H_2O*	*D-(+)-mannose*	*H_2O/CDA (%)*
CDA1	6.80	1.98	91.22	—	13.4
CDA2	6.80	1.98	91.12	0.10	13.4
CDA3	6.79	1.98	91.04	0.20	13.4
CDA4	6.77	1.97	90.76	0.50	13.4
CDA5	6.73	1.96	90.31	1.00	13.4
CDA6	6.05	1.77	92.18	—	15.2
CDA7	6.05	1.77	92.08	0.10	15.2
CDA8	6.04	1.76	92.00	0.20	15.2
CDA9	6.02	1.76	91.71	0.50	15.2
CDA10	5.99	1.75	91.25	1.00	15.2

*Decylammonium chloride.

of 30 min was adopted in order to guarantee the proper stabilization of the atmospheric conditions [25].

In order to verify the orientation process of the systems, sequences of four successive rheograms with different rest times were performed. The cholesterization effect was observed by performing experiments where each mesophase was sheared at a constant shear rate ($100\,s^{-1}$) with measurements taken every 30 s until 500 points were reached. The same experiment was carried out in a room atmosphere and in a water-saturated atmosphere.

The water activity was measured before and after the shear process. For this procedure we used the equipment Aqualab (Decagon Devices, Inc.), with accuracy to within ±0.001, with the same Brookfield temperature-controlled bath for temperature adjustment.

Water activity describes the continuum of energy states of the water in a system. The water in a sample appears to be "bound" by forces to varying degrees. This is a continuum of energy states, rather than static "boundness." Water activity is sometimes defined as "free," "bound," or "available water" in a system. These terms are easier to conceptualize, although they fail to adequately define all aspects of the concept of water activity. Water activity instruments measure the amount of free (sometimes referred to as unbound or active) water present in the sample. A portion of the total water content present in a product is strongly bound to specific sites of the chemicals that comprise the product. These sites may include the hydroxyl groups of polysaccharides, the carbonyl and amino groups of proteins, and other polar sites. Hydrogen bonds, ion-dipole bonds, and other strong chemical bonds hold water. Some water is bound less tightly but is still not available (as a solvent for water-soluble food components). Because water is present in varying degrees of free and bound states, analytical methods that attempt to measure total moisture in a sample do not always agree. Therefore, water activity tells the real story.

In the AquaLab, a sample is equilibrated within the headspace of a sealed chamber containing a mirror, an optical sensor, an internal fan, and an infrared temperature sensor. At equilibrium, the relative humidity of the air in the chamber is the same as the water activity of the sample. A thermoelectric (Peltier) cooler precisely controls the mirror temperature. An optical reflectance sensor detects the exact point at which condensation first appears. A beam of infrared light is directed onto the mirror and reflected back to a photodetector, which detects the change in reflectance when condensation occurs on the mirror. A thermocouple attached to the mirror accurately measures the dew-point temperature. The internal fan is for air circulation, which reduces vapor equilibrium time and controls the

TABLE 2 Water activity (a_w) for different systems at different conditions

Samples	*Before shear (a_w)*	*After shear at room atmosphere (a_w)*	*After shear in water-saturated atmosphere (a_w)*
CDA1	0.944	0.934	0.963
CDA2	0.940	0.936	0.957
CDA3	0.940	0.929	0.953
CDA4	0.931	0.930	0.951
CDA5	0.930	0.923	0.950
CDA6	0.949	0.945	0.963
CDA7	0.950	0.944	0.959
CDA8	0.948	0.944	0.959
CDA9	0.944	0.942	0.957
CDA10	0.940	0.935	0.955

boundary layer conductance of the mirror surface. Additionally, a thermopile sensor (infrared thermometer) measures the sample surface temperature. Both the dew point and sample temperatures are then used to determine the water activity (chilled mirror technology). During a water activity measurement, the AquaLab repeatedly determines the dew-point temperature until vapor equilibrium is reached (chilled mirror technology). Since the measurement is based on temperature determination, calibration is not necessary, but measuring a standard salt solution checks proper functioning of the instrument. An internal, microprocessor-controlled data acquisition system converts these measurements to vapor pressures. The ratio of these values indicates the sample's water activity level. Thanks to this process, accurate a_w measurements are not dependent on precise thermal equilibrium. The water activity data for all systems studied are presented in Table 2.

RESULTS AND DISCUSSIONS

The results obtained for the orientation process of the nematic phase with smaller content of water, i.e., lower water/amphiphile ratio **(CDA1)** are presented in Figure 1. Newtonian behavior can be observed with an increase of the shear stress for successive rheograms. For the systems with D(+)-mannose (**CDA2** to **CDA5**), the first rheogram has a defined pseudoplastic behavior, whereas Newtonian behavior can be seen in the following rheograms. The pseudoplastic behavior seems to be characteristic of a cholesteric system formed by microdomains with different orientations. The shear applied to this system promotes a partial orientation of these microdomains.

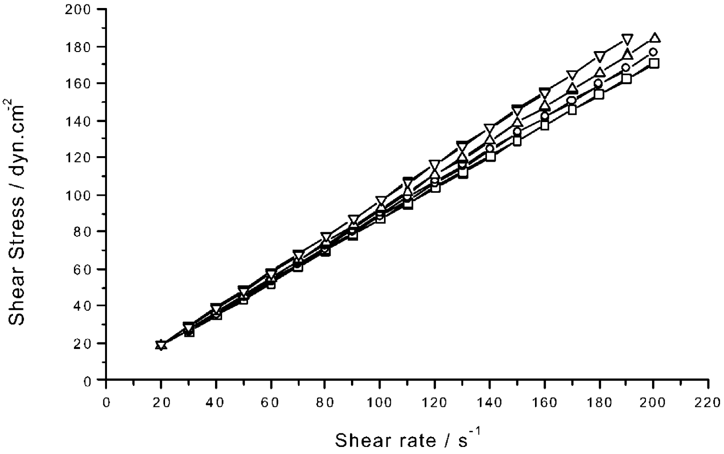

FIGURE 1 Rheograms for the nematic phase (**CDA1**): (□) 1st Sweep; (○) immediately after 1st; (Δ) 10 min after 2nd; (∇) 30 min after 3rd.

During the time of rest the elastic forces, characteristic of these mesophases, help with the orientation, leading to an organization similar to that obtained for the nematic system. As a consequence, the pseudoplastic behavior changes to a Newtonian one.

Successive sweeps without times of rest between them were performed to study the effect of cholesterization on the orientation process. The results obtained showed Newtonian behavior for the nematic phase since the first sweep. All of the cholesteric phases presented pseudoplastic behavior that becomes Newtonian after successive rheograms (Figure 2). In general, it can be said that the shear stress increases during successive sweeps with the decrease of the degree of pseudoplasticity.

The rheograms obtained for these same phases (**CDA1** to **CDA5**) at constant shear rate, after shear in a room atmosphere, present an initial stage with a constant viscosity followed by a decrease of the viscosity until a minimum value is reached (Figure 3). After this period, some systems start to present another increase of viscosity. This result could be explained as an orientation process subdivided into three stages. Apparently, in the first stage the cholesteric structures are moving uniformly as a whole. In the second stage the system undergoes a fragmentation process, probably caused by shear action leading to a decreasing viscosity. In the third stage the fragments rearrange themselves, originating a new superstructure that can be characterized by an increase of the viscosity. This behavior is quite similar to that obtained for the same phases when using cholesterol as inductor [29].

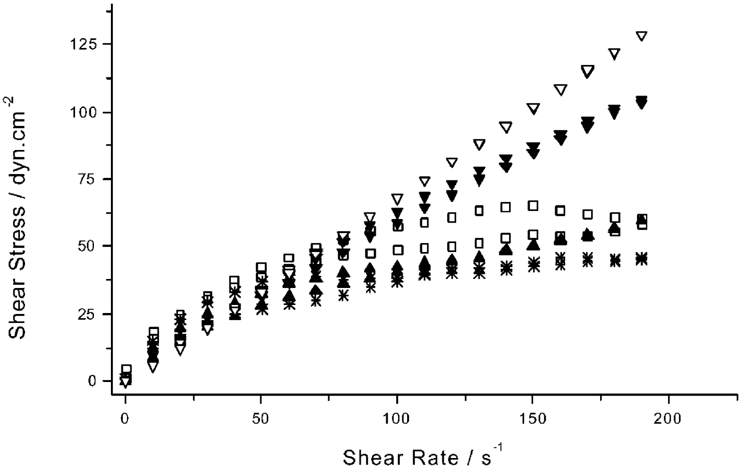

FIGURE 2 Rheograms for the cholesteric phase (**CDA5**) with 1.0% molar of cholesterol: (□) 1st sweep; (▲) 2nd sweep; (∗) 3rd sweep; (▼) 4th sweep; (∇) 5th sweep.

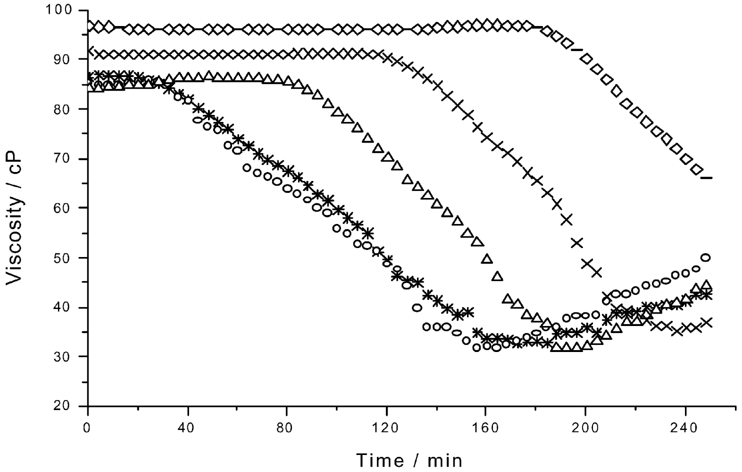

FIGURE 3 Rheograms for phases **CDA1** to **CDA5**. Samples sheared at room-atmosphere: (∗) **CDA1**–nematic; (○) **CDA2**–0.10% of D(+)-mannose; (Δ) **CDA3**–0.20% of D(+)-mannose; (×) **CDA4**–0.50% of D(+)-mannose; (◇) **CDA5**–1.00% of D(+)-mannose.

The results of water activity obtained for the phases with smaller water concentration presented a decrease of the activity with the increase of the D(+)-mannose concentration. This behavior may be due to the presence of −OH group on the sugar structure, responsible for the hydrogen bond between the sugar and the solvent, which will decrease the free water concentration. A decrease of the activity after the shear process could be observed too, indicating a deficiency of water on the system which is worsened by the shear process [30]. For samples sheared in a water-saturated atmosphere an increase of activity can be seen, characterizing the existence of water absorption by the system, possibly to compensate its initial deficiency.

It could also be noticed that the higher the D(+)-mannose concentration, the higher the initial viscosity and the longer the time necessary to reach the minimum value, probably due to the increase of the micelle interactions present in the systems.

The same phases (**CDA1** to **CDA5**), when sheared under a water-saturated atmosphere, present an initial increase of the viscosity followed by its decrease as a function of shear time (Figure 4). The initial increase of viscosity is probably due to a possible accommodation of the micelles during the period of water absorption. After this accommodation period, the system exhibits the behavior expected for an orientation by flow. It can be noticed that this time is shorter the larger the system cholestericity, evidencing the stability of the chiral structure.

The results obtained for the systems with larger concentrations of water, i.e., higher water/amphiphile ratio (**CDA 06** to **CDA 10**), are presented in Figures 5 to 8.

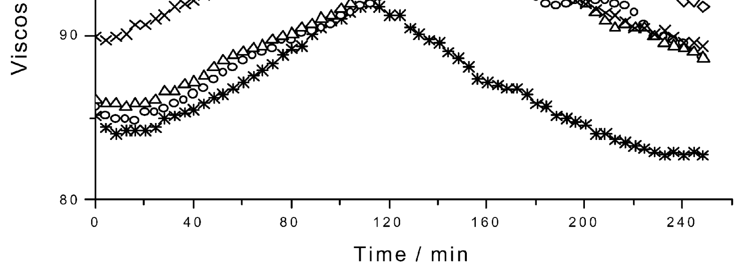

FIGURE 4 Rheograms for phases **CDA1** to **CDA5**. Samples sheared on water-saturated atmosphere: (∗) **CDA1**–nematic; (○) **CDA2**–0.10% of D(+)-mannose; (Δ) **CDA3**–0.20% of D(+)-mannose; (×) **CDA4**–0.50% of D(+)-mannose; (◇) **CDA5**–1.00% of D(+)-mannose.

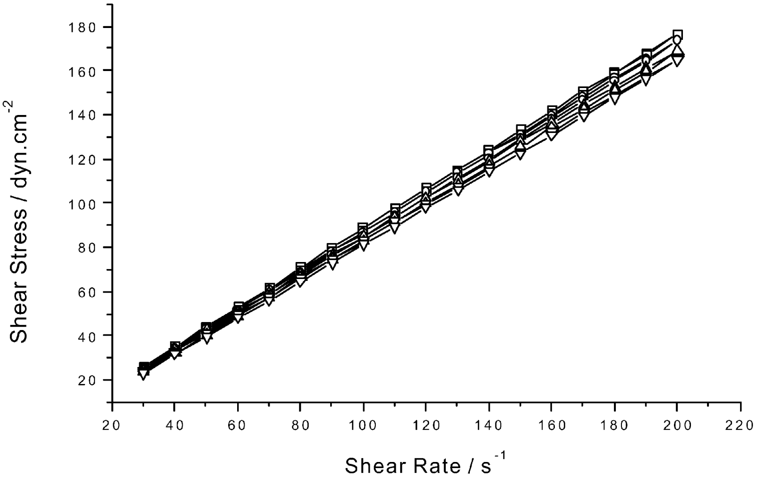

FIGURE 5 Rheograms for the nematic phase (**CDA6**): (□) 1st sweep; (○) immediately after 1st; (Δ) 10 min after 2nd; (∇) 30 min after 3rd.

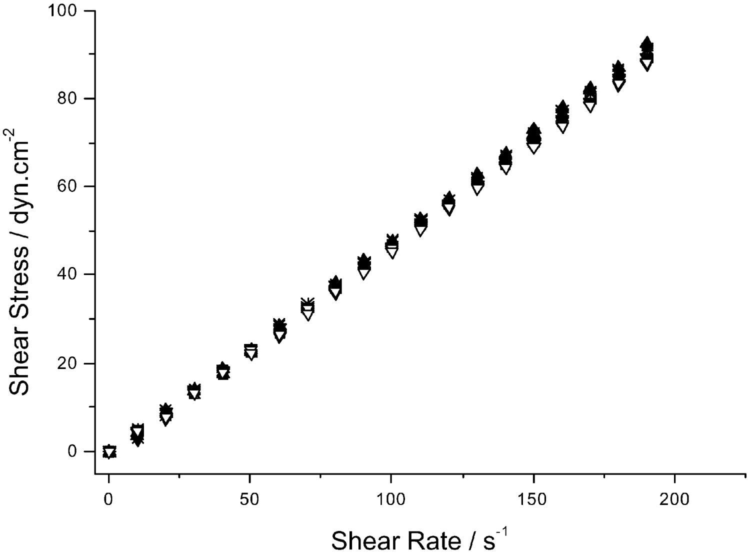

FIGURE 6 Rheograms for the cholesteric phase (**CDA10**) with 1.0% molar of cholesterol: (□) 1st sweep; (▲) 2nd sweep; (∗) 3rd sweep; (▼) 4th sweep; (∇) 5th sweep.

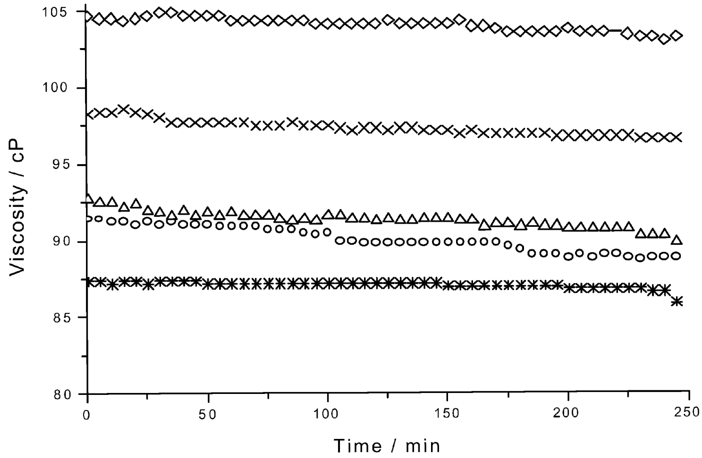

FIGURE 7 Rheograms for phases **CDA6** to **CDA10**. Samples sheared at room atmosphere: (∗) **CDA6**–nematic; (○) **CDA7**–0.10% of D(+)-mannose; (Δ) **CDA8**–0.20% of D(+)-mannose; (×) **CDA9** –0.50% of D(+)-mannose; (◇) **CDA10**–1.00% of D(+)-mannose.

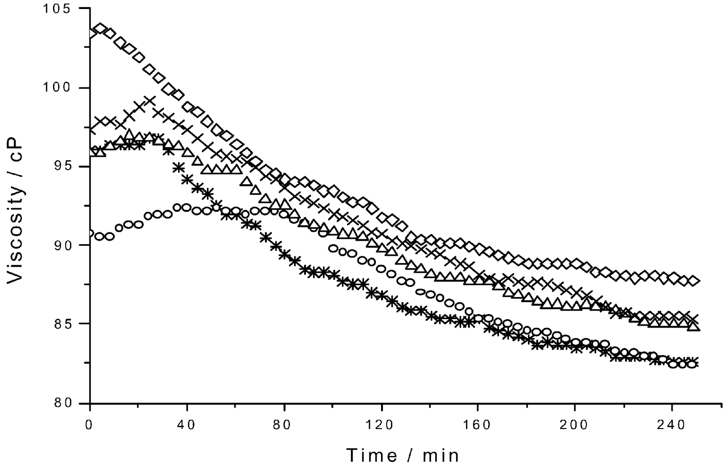

FIGURE 8 Rheograms for phases **CDA6** to **CDA10**. Samples sheared on water-saturated atmosphere: (∗) **CDA6**–nematic; (○) **CDA7**–0.10% of D(+)-mannose; (Δ) **CDA8**–0.20% of D(+)-mannose; (×) **CDA9**–0.50% of D(+)-mannose; (◇) **CDA10**–1.00% of D(+)-mannose.

The orientation process of the nematic phase (**CDA6**) showed a Newtonian behavior with a decrease of the shear stress for successive rheograms (Figure 5). It could be observed that this behavior is the opposite of that obtained for the systems with smaller water content. It could be observed, too, that the addition of D(+)-mannose to this mesophase is not enough to establish pseudoplastic behavior. The rheograms obtained for all cholesteric systems present well-defined Newtonian behavior (Figure 6). Apparently, the high-water content on these systems is helping the orientation of the structure, leading to the complete untwisting of the helix.

When these same phases are sheared in room atmosphere, a viscosity basically constant during all the experiment time can be observed for all phases (Figure 7). Apparently, under these experimental conditions the system behaves as a rigid structure with the micelles moving like a whole. The absence of the fragmentation processes should be noted. Again it could be observed that the viscosity value increases as a function of the inductor concentration, perhaps due to the increase of water-sugar interactions through hydrogen bonds.

The water activity obtained for these phases (Table 2) decreases according to the increase of inductor concentration, and again this decrease is lower than that obtained for the phases with lower water/amphiphile ratio. It could also be observed that the shear process leads to a decrease of the activity, again evidencing the water deficiency of the system.

With the analysis of rheograms and water activity data it is possible to propose that the helical superstructure breakdown is favored by the water deficiency being observed only when the samples are sheared in a room atmosphere. The activity data also indicated water absorption when the phases are sheared in a water-saturated atmosphere. It is interesting to note that the final value of water activity obtained after shear is similar to that observed for the phases with lower water/amphiphile ratio under the same conditions.

Figure 8 presents the rheological data obtained for the same systems (**CDA6** to **CDA10**) after shear in a water-saturated atmosphere. For all systems a behavior similar to that obtained in Figure 4 can be noticed, except for the shorter time necessary to reach the maximum value of viscosity. This behavior can be explained by the higher water availability in the atmosphere, which will cause a decrease in the time necessary for water absorption, leading to a shorter period of accommodation.

CONCLUSIONS

The change from pseudoplastic to Newtonian behavior showed that the initial arrangement of the micelles in the cholesteric systems is different from the final one obtained after shear. It becomes obvious that the chiral force is acting in an opposite direction to the flow alignment.

In general, it can be said that the flow orientation process of cholesteric lyomesophases is different in a room atmosphere from when it occurs in a water-saturated atmosphere. When the samples are sheared in a room atmosphere the orientation process involves three different stages. The first stage can be characterized by the cholesteric structure moving uniformly. In a second step the system undergoes a breakdown of the helical building, originating helix fragments. In the third stage the fragments rearrange themselves into a new superstructure that will be characterized by an increase of the viscosity.

When the systems are sheared in a water-saturated atmosphere, the orientation process involves first the accommodation of the micelles into a new structure seeking the best orientation of the system in the flow direction, followed by the orientation of the micelles in the flow direction.

It can be observed that the flow orientation process is largely influenced by the amount of water present in the system. The results obtained showed that the content of available water determines the existence of fragmentation, rearrangement, and accommodation stages. The water deficiency during the shear process can cause the fragmentation of the structure followed by the structure's rearrangement. On the other hand, the water absorbed from the atmosphere during the same process will promote accommodation of the micelles.

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