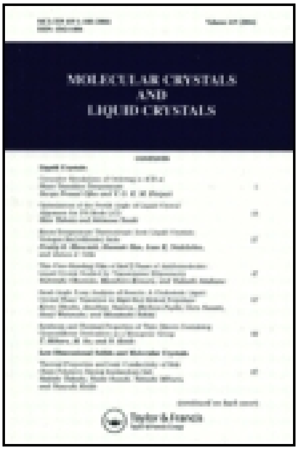

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The Influence of Water on the Orientation Process of Cholesteric Lyotropic Liquid Crystals

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

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THE INFLUENCE OF WATER ON THE ORIENTATION PROCESS OF CHOLESTERIC LYOTROPIC LIQUID CRYSTALS

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. We prepared different mesophases based on decylammonium chloride with different amounts of cholesterol added as an inductor. It was observed that the orientation process should involve an initial step of destruction of a cholesteric structure caused by shear that leads to the formation of microdomains. In a second stage these microdomains will orientate themselves, forming a new helical structure in the direction of the flow. Finally, on the third stage, the accommodation of the micelles on a new structure, seeking the best orientation of the system on the flow direction, could be observed. The obtained results showed that the content of water available would determine the existence of fragmentation, rearrange, and accommodation stages.

Keywords: liquid crystals, cholesteric liquid crystals, organized systems, rheology, rheological properties, non-Newtonian properties

Liquid crystalline systems present highly anisotropic transport properties, usually described by the Ericksen-Leslie Theory [1–3]. According to this theory, the macroscopic viscosity of nematic systems can be described, together with terms accounting for the orientation of the phase director, by six microscopic viscosity coefficients (μ_1 to μ_6) [4]. The stationary rheological techniques may result in complicated responses, mainly because the phase director does not assume a uniform orientation under small velocity gradients. To avoid this limiting condition, some different rheological

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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

techniques have been employed, generally imposing this orientation of the director throughout the sample by means of strong magnetic fields [5].

In the past few years, rheological properties have been used in order to understand the spatial array of the units that constitute the system [6–8] and its variations on the phase transition regions [3,8–13]. 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 [13–15]. Rheological parameters have also been used to understand the spatial structure of the system constituent units and the way they change their order near the transition regions [7,9–11,16,17].

The theoretic study on cholesteric liquid crystals rheology has provided important information about the positioning and behavior of the helix submitted to flow. Rey [18] proposed that when a cholesteric helix is aligned on a flow direction an uncoiling process occurs, leading the system to a configuration similar to the one obtained for nematic phases.

The flow on lyotropic liquid crystal systems can be associated with cooperative changes of conformation of flexible layers submitted to frictional forces in the liquid layers [19]. Some results obtained by Penfold et al. [20] showed that under low shear rate lamellae are oriented parallel to the flow-vorticity plane, whereas for high shear rate experiments they are ordered in the orthogonal director, parallel to the flow-shear gradient plane.

Almost all studies on lyotropic liquid crystal involve lamellar phases [21–23] or micellar “wormlike” systems [24,25], i.e., micelles that simulate living polymeric systems. The few studies developed for cylindrical or discotic lyomesophases were based on sodium decylsulphate [16,17] and potassium laurate [17]. Results published by our laboratory about the rheological behavior of lyotropic liquid crystals indicated that these systems are pseudoplastic [26] with a complicated transient response, either rheopexic or thixotropic, depending on whether the micelles are cylindrical or discotic, respectively [27,28]. It was possible to verify that the cholesterization process on systems composed of cylindrical micelles leads to a decrease of the flow index and to an increase of the consistency index, evidencing that the elastic forces originated by the cholesteric arrangement lead to a system more resistant to deformations [26]. The edge fracture occurrence on nematic systems based on potassium laurate is a clear indication of the existence of strong elastic contributions and should be better evaluated [29].

The present work shows a continuation of a previous study developed for nematic and cholesteric lyotropic liquid crystals, constituted by discotic micelles of decylammonium chloride (DAC) [30]. These systems were characterized by presenting a complex pattern for orientation process involving an initial destruction of the cholesteric arrangement, leading to the formation of microdomains followed by the orientation of these microdomains [30]. This orientation process could be caused either by shear or by a performance of the elastic forces during the rest time [30]. In the present paper we intend to study the rheological behavior of the same systems when submitted to a constant shear rate. The flow orientation process will be analyzed as a function of the shear time, the concentration of hydrophobic inductor added, and the concentration of water present on each phase.

EXPERIMENTAL

Two groups of cholesteric lyomesophases were prepared by the addition of cholesterol to a nematic (N_D) system based on decylammonium chloride/H_2O/NH_4Cl [31]. The final phase compositions are presented in Table 1. The samples **DAC1** to **DAC7** have smaller water concentration, i.e., lower water/amphiphile ratio, than the samples **DAC8** to **DAC12**. All cholesteric systems were characterized using optical properties as Ch_D systems [32].

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 ± 0.1°C by a Brookfield temperature-controlled bath, model TC-500. Each mesophase was sheared on a constant shear rate ($100\,s^{-1}$) with measures taken on each 30 s until 500 points are reached. The same experiment was developed under room-atmosphere ($a_w = 0.424$) and under water-saturated atmosphere. The water saturation was performed using a

TABLE 1 Compositions for Nematic and Cholesteric Phases (% Molar Fraction)

Samples	DAC*	NH_4Cl	H_2O	Cholesterol	H_2O/DAC
DAC1	6.81	1.97	91.22	—	13.4
DAC2	6.81	1.97	91.21	0.01	13.4
DAC3	6.80	1.97	91.20	0.03	13.4
DAC4	6.80	1.97	91.17	0.06	13.4
DAC5	6.80	1.97	91.14	0.09	13.4
DAC6	6.80	1.98	91.07	0.15	13.4
DAC7	6.80	1.98	91.01	0.21	13.4
DAC8	6.06	1.77	92.17	—	15.2
DAC9	6.06	1.77	92.16	0.01	15.2
DAC10	6.06	1.77	92.14	0.03	15.2
DAC11	6.06	1.77	92.11	0.06	15.2
DAC12	6.06	1.77	92.08	0.09	15.2

* Decylammonium chloride.

moistened cotton strip inside the rheometer cup, but without direct contact with the sample. An initial rest time of 30 min was adopted in order to guarantee the proper stabilization of the atmospheric conditions [27].

The water activity was measured before and after the shear process. For this procedure we used the Aqualab (Decagon Devices, Inc.), which has an accuracy of ± 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 easy 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 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; however, measuring a standard salt solution checks

TABLE 2 Water Activity (a_w) for Different Systems on Different Conditions

Samples	Before shear a_w	After Shear at Room Atmosphere a_w	After Shear on Water-Saturated Atmosphere a_w
DAC1	0.942	0.930	0.952
DAC2	0.941	0.932	0.953
DAC3	0.942	0.935	0.952
DAC4	0.941	0.938	0.951
DAC5	0.943	0.936	0.956
DAC6	0.941	0.932	0.951
DAC7	0.939	0.935	0.954
DAC8	0.948	0.943	0.959
DAC9	0.948	0.943	0.960
DAC10	0.948	0.945	0.962
DAC11	0.948	0.942	0.961
DAC12	0.948	0.944	0.962

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

A previous study developed for nematic and cholesteric lyotropic liquid crystals constituted by discotic micelles of decylammonium chloride (DAC) [30] showed a complex pattern for orientation process. Four successive cyclic rheograms were obtained with the speed varying and different times of rest for each sample, with the second immediately after the first, the third 10 min after the second, and the fourth 30 min after the third [30]. The obtained results showed that the cholesteric system acquires an initial pseudoplastic arrangement that turns to a Newtonian as a function of the rest time or the shear time [30]. This orientation process could be explained as composed of an initial destruction of the cholesteric arrangement, leading to the formation of microdomains, followed by the orientation of these microdomains (Figure 1) [30]. It was verified that this behavior was caused either by shear or by a performance of the elastic forces during the rest time [30].

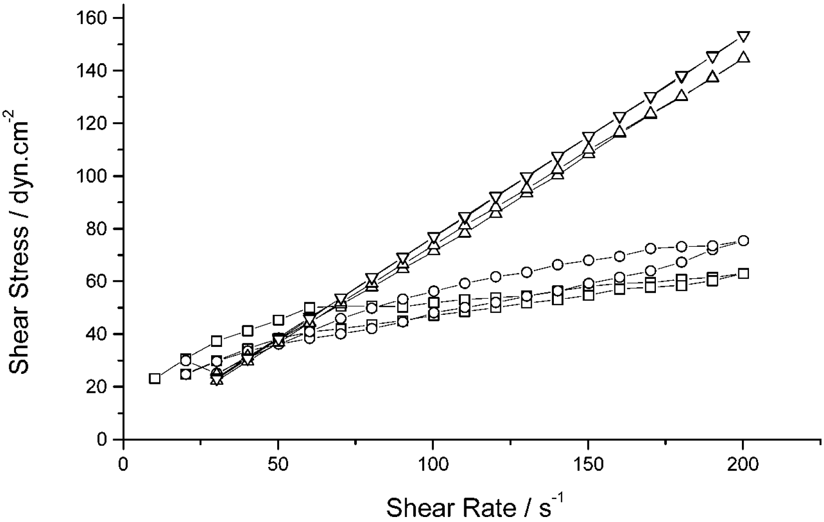

FIGURE 1 Rheograms for the **DAC** cholesteric phase with 0.09% of cholesterol: (□) 1st Sweep; (○) 2nd Sweep (immediately after 1st); (△) 10 min after 2nd; (▽) 30 min after 3rd. (Reprinted from Alcantara and Fernandes [30])

The present work was a continuation of these experiments and presents the study the rheological behavior of the same systems when submitted to a constant shear rate. The flow orientation process was analyzed as function of the shear time, the concentration of hydrophobic inductor added, and the concentration of water present on each phase.

The rheograms obtained under water-saturated atmosphere for lyomesophases with lower water concentration, i.e., lower water/amphiphile ratio (**DAC 01** to **DAC 07**), are presented on Figure 2. For the phases with 0.06% (**DAC4**), 0.09% (**DAC5**), 0.15% (**DAC6**), and 0.21% (**DAC7**) of cholesterol we observed an initial decrease of the viscosity until it reached a minimum viscosity value. On a second stage, we observed an increase of viscosity followed by its stabilization. For the systems with low cholesterol concentration (0.01% (**DAC2**) and 0.03% (**DAC3**)), we observed a slight increase of the viscosity during the first 2 h of shear followed by a slow decrease after this period. In particular this behavior was similar to the behavior observed for the nematic phase (**DAC1**). This result corroborates the previous experiment [30] and again could be explained as a complex orientation process subdivided in 2 stages. In the first stage the cholesteric structure should undergo fragmentation by the shear action, leading to the viscosity decrease. In the second stage the fragments would rearrange

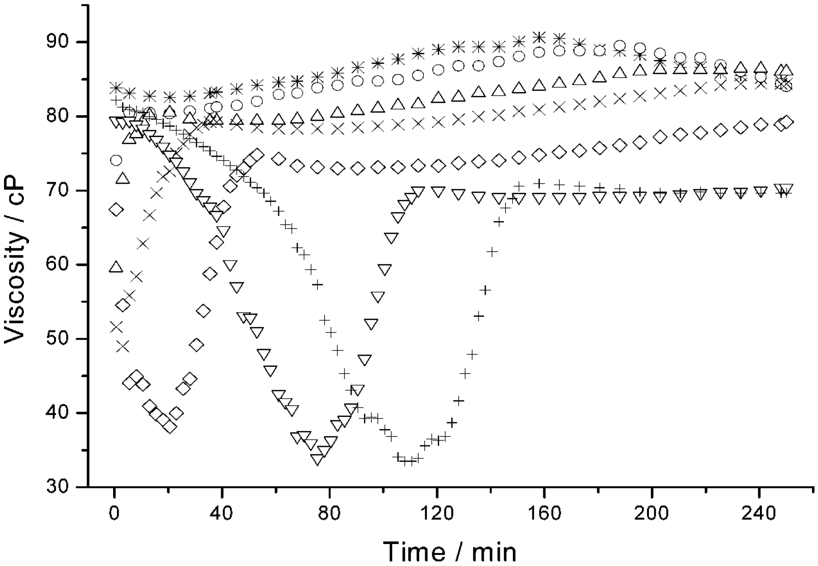

FIGURE 2 Rheograms for phases **DAC1** to **DAC7** (constant shear rate, 100 s^{-1}). Samples sheared on water-saturated atmosphere: (∗) nematic; (○) 0.01% of cholesterol; (△) 0.03% of cholesterol; (×) 0.06% of cholesterol; (◇) 0.09% of cholesterol; (▽) 0.15% of cholesterol; (+) 0.21% of cholesterol.

themselves, originating a new superstructure that could be characterized by the increase of the viscosity.

Since the shear rate is constant during the whole essay, the more cholesteric the system the higher will be the necessary force to break the initial structure, i.e., the higher will be the shear time necessary for the structure fragmentation. The observed increase of the viscosity until a constant value obtained for the phases with smaller cholesterol concentration (**DAC2** and **DAC3**) leads us to think that the structure breakdown should be happen almost instantaneously. For the nematic phase only a slight increase of the viscosity during the shear can be observed, indicating that instead of the breakdown only an accommodation of the micelles, guided by the flow, should happen. These results are similar to the obtained, when the same systems were analyzed as function of the shear rate and the rest time [30].

The data of water activity obtained for the systems with smaller concentration of water (**DAC1** to **DAC7**) are presented in the Table 2. A decrease of the activity after the shear process was observed, indicating the existence of a deficiency of water on phase that is worsened by the shear process [33]. An increase of activity can be seen when the sample was sheared under water-saturated atmosphere, characterizing a water absorption by the system possibly to compensate the initial deficiency [33]. Based on previous work on the same systems [33] it is possible to estimate the change in the water concentration as varying from 0.5 to 1.0% molar. It is important to notice too that, as observed by optical techniques, this change was not enough to lead the systems out of the existence range of the phases N_D or Ch_D that were used from the start.

The complete analysis combining the rheology and water activities results leads us to believe that, when working on water-saturated atmosphere, the rheograms curve profile should be mainly to the system cholestericity instead of the water concentration. The initial cholesteric structure should be stabilized by the increase of the cholestericity, in other words, a higher chiral force will lead to a larger time necessary for the breakdown occurrence. At the same time, the water absorbed from the saturated atmosphere will stabilize the structure fragmentation through its hydration. In a second stage, the fragments will rearrange quickly to originate a new helical structure on a new direction in relation to the flow.

Figure 3 showed the results obtained for the same phases (**DAC1** to **DAC7**) after shear under room atmosphere. For the nematic phase (**DAC1**) and the systems with 0.01% (**DAC2**) and 0.03% (**DAC3**) molar of

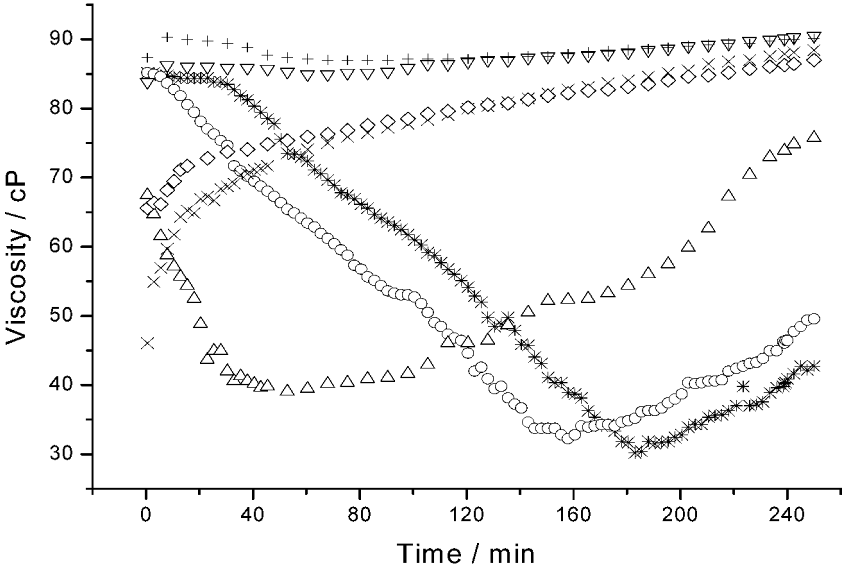

FIGURE 3 Rheograms for phases **DAC1** to **DAC7** (constant shear rate, $100\,s^{-1}$). Samples sheared at room atmosphere: (∗) nematic; (○) 0.01% of cholesterol; (△) 0.03% of cholesterol; (×) 0.06% of cholesterol; (◇) 0.09% of cholesterol; (▽) 0.15% of cholesterol; (+) 0.21% of cholesterol.

cholesterol we observed the viscosity decrease during the initial stage of shear. We also noticed that the higher the cholesterol concentration the lower would be the time necessary to reach the minimum value. An initial increase in the viscosity was observed for the phases with 0.06% (**DAC4**) and 0.09% (**DAC5**) proceeded by a tendency of stabilization of the values. For the phases with 0.15% (**DAC6**) and 0.21% (**DAC7**) of cholesterol we obtained values of viscosity that were basically constant during whole shear process.

These results show an inversion of the pattern when it was compared to those obtained under water-saturated atmosphere. The existence of large valleys that disappear with the increase of the system cholestericity (Figure 3) leads us to think that for highly cholesteric phases the chiral force becomes sufficiently strong to maintain the cholesteric structure stable without fragmentation, or in the case of breakdown occurrence the fragments will rearrange themselves quickly. These results reinforce the idea that the water absorbed by the phase from the atmosphere should act in order to help the orientation process of the fragments originated by the structure breakdown.

The data of water activity for these systems (**DAC8** to **DAC12**) showed a small difference between the values obtained before shear and after shear at room atmosphere. These results corroborate the fact that these phases should not present any water deficiency. On the other hand, on the essays performed under water-saturated atmosphere, the increase of the activity showed that the absorbed amount of water was basically the same as that obtained for phases **DAC1** to **DAC7**. It was also observed that the difference of the activity for the samples after shear and before shear stayed almost constant, indicating that these phases, in spite of having larger water concentration, still would need solvent, probably for a better accommodation of the structure.

The rheograms obtained for the systems with larger concentrations of water, i.e., higher water/amphiphile ratio (**DAC8** to **DAC12**), and sheared under water-saturated atmosphere are presented on Figure 4. It can be observed that an initial increase of the viscosity is probably due to a possible accommodation of the micelles on the lyotropic structure on the flow direction. It was also observed that after this period of accommodation the system exhibits the behavior expected for an orientation by flow, i.e., the viscosity decrease as a shear time function [26]. It can be noticed that this accommodation period is slower the larger the system cholestericity, evidencing the stability of the chiral structure.

The same systems, when sheared at room atmosphere (Figure 5), showed a constant viscosity as a function of the shear time. An absence of the initial increase of the viscosity was obseved, or in other words, the absence of the structure accommodation process. Seemingly, the

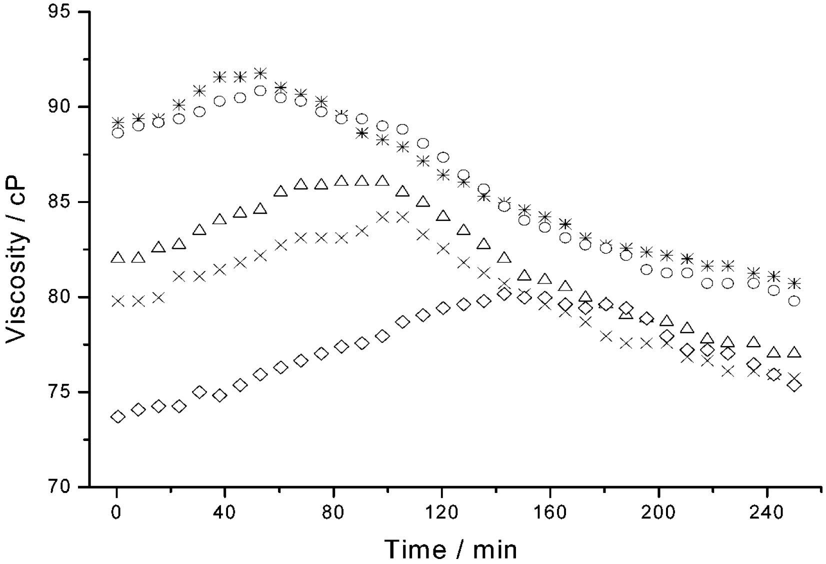

FIGURE 4 Rheograms for phases **DAC8** to **DAC12** (constant shear rate, 100 s^{-1}). Samples sheared on water-saturated atmosphere: (∗) nematic; (○) 0.01% of cholesterol; (△) 0.03% of cholesterol; (×) 0.06% of cholesterol; (◇) 0.09% of cholesterol.

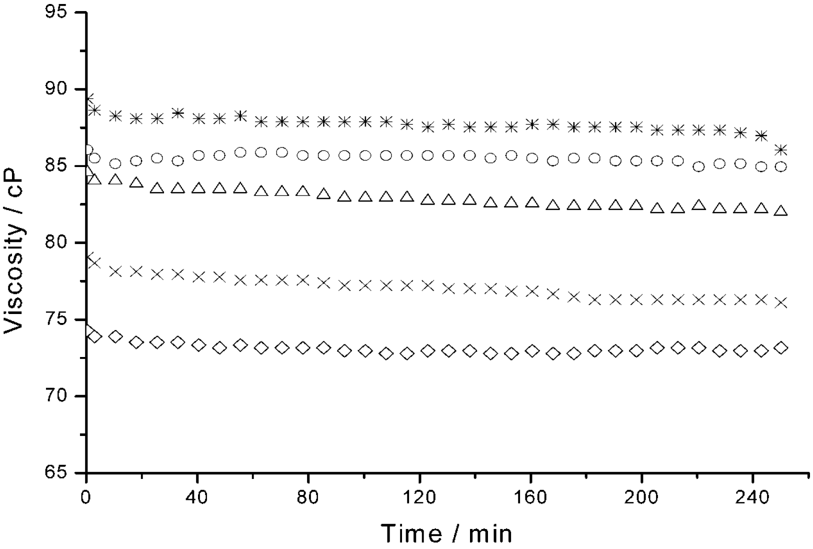

FIGURE 5 Rheograms for phases **DAC8** to **DAC12** (constant shear rate, 100 s^{-1}). Samples sheared at room atmosphere: (∗) nematic; (○) 0.01% of cholesterol; (△) 0.03% of cholesterol; (×) 0.06% of cholesterol; (◇) 0.09% of cholesterol.

concentration of water present on the mesophase composition should be committed with the maintenance of the cholesteric building, resulting in a low amount of water available for the micelles movement on the aqueous bulk.

CONCLUSIONS

In general, the obtained results showed that the flow orientation process on cholesteric lyomesophases should involve three different stages. The first stage should be characterized by the initial breakdown of the helical building originating helix fragments. In a second stage these fragments would rearrange themselves to form a new helical structure in the direction of the flow, and the third stage would involve the accommodation of the micelles on a new structure seeking the best orientation of the system in the flow direction. This behavior is quite similar to that obtained for the same phases when using D-mannose as an inductor [34].

Nevertheless, we also observed that this flow orientation process should be largely influenced by the amount of water present on the system. The obtained results showed that the content of water available could determine the existence of fragmentation, rearrange, and accommodation stages. The water absorbed from the atmosphere during the shear process will help with the hydration of the fragments during the fragmentation stage. On the other hand, the water deficiency during this same stage can cause the suppression of this process. Finally, it can be said that the larger the amount of water present in the system the faster will be the flow orientation process as a whole.

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