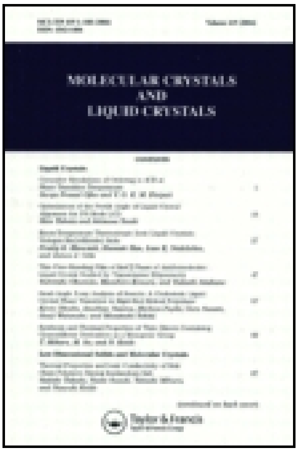

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M. Regina Alcantara [a] [b] , A. F. De Moura [a] & E. G. Fernandes Jr. [a]

[a] Instituto de Química - Universidade de São Paulo, SP, Brasil

[b] Maria Regina Alcantara, Instituto de Química - Universidade de São Paulo, Avenida Professor Lineu Prestes, 748, Cidade Universitária, CEP 05508-900, São Paulo, SP, Brasil Phone: 055 011 818-2054 Fax: 055 011 818-2054 E-mail:

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The Effect of the Cholesteric Structure on the Water Activity of Lyotropic Liquid Crystals

M. REGINA ALCANTARA*, A.F. DE MOURA and E.G. FERNANDES Jr.

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

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The study of the water activity behavior on liquid crystals is reported for lyomesophases based on sodium dodecylsulphate (SLS), decylammonium chloride (CDA) and potassium laurate (LK). Different amounts of chiral solutes (sugars or cholesterol) were added to the nematic matrices in order to form the helical structure characteristic of the cholesteric system. The water activities of all mesophases were measured in order to evaluate how the water availability of lyomesomorphic systems is affected by the formation of the helical structure. It was verified that the helix formation on CDA system leads to a decrease of the intermicellar forces driving to a situation where the water is less tightly bound. Seemingly, after an initial cholesterization, the micelle-solvent interaction increases with the cholesterol concentration. For systems based on SLS the formation of the helical structure leads to a condition where the water molecules are more tightly bound and, after an initial cholesterization, the micelle-solvent interaction does not change with the further addition of inductor. For the LK systems it could be observed that a decrease of the water activity occurs only when hydrophilic inductors are added. LK systems present a rate of loss of water significantly larger than the CDA.

Keywords: water activity; liquid crystals; lyotropic liquid crystals; organized systems; water vapor pressure

INTRODUCTION

For a long time the study of lyotropic liquid crystals was centered on the interaction forces responsible for the existence of an orderly structure and on its cholesterization. In this process, several different mechanisms may be involved depending on the phase type and on the nature of its components (1–4). Usually,

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* Correspondence Address: Maria Regina Alcantara, Instituto de Química – Universidade de São Paulo, Avenida Professor Lineu Prestes, 748, Cidade Universitária – CEP 05508–900, São Paulo – SP – Brasil, Phone Number: 055 011 818–2054, Fax Number: 055 011 815–5579, e-mail: mralcant@quim.iq.usp.br

techniques employed for liquid crystals studies are the nuclear magnetic resonance and the optical microscopy under polarized light, but recently, rheology began to be used for the understanding of basic flow properties (5–6). The rheological behavior of a system evaluates its resistance to flow and to deform, allowing the assessment of a macroscopic mean value of structural and hydrodynamic interactions between its constituent particles.

The understanding of the water properties at the interface of organized systems is a basic pre-requirement for the comprehension of its effects on the reactivity and the balance of chemical reactions. The interfacial water is involved in the solvating processes of all the system constituent species, for example, reagents in the transition state, detergent heads and counterions (7–10). These processes have great effects on the speed of certain reactions involving detergents as reagents, where the polar head or counterion of the surfactant participates covalently in the reaction (7–9). For aqueous micelles, besides the solvating effects on the chemical reactivity, differences between the structure of the interfacial water and that of the bulk contribute to the micellar catalysis, affecting both activation enthalpy and entropy (11,12).

The structure of the interfacial water will be modified with the water availability of the system, usually expressed in terms of its thermodynamic activity ($\mathbf{a}_w$). The water activity may be defined as the ratio between the equilibrium vapor pressure of the system (P) and the vapor pressure of pure water at the same temperature (P_0), that is, $\mathbf{a}_w$=P/P_0. For heterogeneous materials with a high content of water, as they are not necessarily at equilibrium during the adsorption and desorption processes, the a_w value will be inadequate for a direct measure of the water availability. Therefore, many semi-empirical expressions have been proposed for sorption isotherms in the range of water activity from 0.2 to 1.0 (13).

For organized systems, it has been proposed the existence of three states of water: (i) a "structural water", the water that is bound to the surface by hydrogen bonds, (ii) "superficial water", that has its dynamic state disturbed by the presence of the surface and finally (iii) "bulk water", which resembles the free water structurally and energetically. The $a_w$value will be different for these three states if the system has not attained its equilibrium state yet. Thus, the system water activity will be the weighed average of these three states (14).

In the present work we intend to study the water activity behavior as a function of different concentrations of chiral inductors that were added to nematic matrices. We aim to evaluate how the formation of the helical structure affects the water availability on different lyomesomorphic systems.

EXPERIMENTAL

Mesophases were prepared by classic weighing and mixing procedures (10) and were characterized by typical textures observed under polarized light by using a Zeiss Universal microscope. The studied lyomesophases were based on sodium dodecylsulphate (**SLS**), decylammonium chloride (**CDA**) or potassium laurate (**LK**). Different amounts of chiral solutes (sugars or cholesterol) were added to the nematic matrices in order to form the helical structure characteristic of cholesteric systems. The phase compositions are shown in **Table I**. The LK and CDA phases were nematic discotic (**N_D**) and cholesteric discotic (**Ch_D**) types and those of SLS were nematic cylindrical (**N_c**) and cholesteric cylindrical (**Ch_c**) phases.

TABLE I Phase compositions of nematic matrices (% molar fraction)

Systems	*Components*	*% x*
SLS	SLS	3.54
	Na_2SO_4	0.16
	H_2O	96.30
CDA	CDA	6.79
	NH_4Cl	1.98
	H_2O	91.23
LK	LK	3.41
	KCl	2.45
	DeOH*	0.86
	H_2O	93.28

* DeOH = n-decanol

The rheological data were obtained using a Brookfield cone-and-plate rheometer (Brookfield Engineering Laboratories), model LV DV-III, interfaced to a microcomputer through the software Rheowin, version 1.0. The water activity was measured using the equipment Aqualab (Decagon Devices, Inc.), which is accurate to within ± 0.003. Both equipments were thermostatized to within 0.1 °C by a Brookfield temperature controlled bath, model TC-500.

The water activity of the CDA and SLS systems was measured as function of the cholesterol concentration. The **a_w** values were obtained before and after the samples were sheared in the cone-and-plate rheometer for 5 minutes at constant speed (5 rpm). The **a_w** of the LK phases was studied as a function of the addition of hydrophobic (cholesterol) and hydrophilic (sugars) inductors at different concentrations.

Calibration curves of the activity against the water concentration were also obtained. CDA and LK nematic phases were prepared with different water contents, maintaining a fixed proportion between the others components (**Table II**) These calibration curves were used to follow the loss of the system water. In this procedure a sample of each system was placed into an open cup and the a_w measure was taken at regular intervals of time.

TABLE II Phase compositions for calibration procedure (% molar fraction)

	Sample	$\%x_{Det}$	$\%x_{salt}^{*}$	$\%x_{DeOH}$	$\%x_w$
LK	**1**	3.93	2.82	0.99	92.26
	2	3.67	2.64	0.93	92.76
	3	3.42	2.45	0.86	93.27
	4	3.16	2.30	0.80	93.74
	5	2.91	2.09	0.74	94.26
CDA	**1**	7.76	2.26	-	89.98
	2	8.16	2.38	-	89.46
	3	6.06	1.77	-	92.17
	4	6.78	1.99	-	92.13

* KCl for LK systems and NH_4Cl for CDA systems.

RESULTS AND DISCUSSION

The activity values for CDA and SLS phases are presented in the **Table III**. It is noteworthy that the cholesterol concentration is rather small and therefore, all phases of each system have essentially the same water content. The SLS system displays a difference between the a_w values of the nematic and the cholesteric phase and this difference does not seem to be affected as the sample is sheared. An activity decrease implies a decrease of the water chemical potential, i.e., the water has a smaller escape tendency. Seemingly, the formation of the helical structure leads to a situation where the water molecules are more tightly bound. It can also be observed that the a_w does not depend on the added amount of the solute, showing that the micelle-solvent interaction does not change after the initial cholesterization of the system.

On the other hand, the system based on CDA shows a water activity change between the nematic and the cholesteric phases only after the samples be sheared. Apparently, a helical superstructure on these phases is formed only after shearing the samples. The results show that water has a smaller escape tendency in the N_D phase, i.e., the solvent-micelle interaction is stronger in this phase. It can be observed a slight decrease on a_w with the increase of the cholesterol concentration that could be associated to an increase of the micelle-solvent interaction, but the obtained values are close to the error and it's difficult to define exactly its trend. These results could be, probably, associated to a change of the system degree of order caused by the shear that will orient better the nematic system than the cholesteric ones. The increase of this order will raise the interaction forces present and consequently the micelle-solvent interaction, leading to a smaller water activity value.

TABLE III Water activity (a_w) as a function of the cholesterol addition for different systems

Systems	% x_{ind}	a_w *before shear* (± *0.003*)	a_w *after shear* (± *0.003*)
CDA	0.00	0.935	0.919
	0.01	0.937	0.931
	0.03	0.937	0.928
	0.09	0.936	0.925
SLS	0.00	0.989	0.986
	0.05	0.965	0.969
	0.10	0.973	0.978
	0.20	0.974	0.975
	0.25	0.965	0.971
	0.30	0.969	0.975

Rheological data present at **Figure 1** show that the viscosity of the nematic phase is larger than that of the cholesteric ones with a decrease of this values as the inductor concentration increases. It means that the intermicellar interactions between consecutive planes decrease as the cholestericity was increased and the system becomes easier to be sheared. Probably, it should have some competition between the intermicellar and micelle-solvent interactions so, when the intermicellar forces increase, the water becomes less tightly bound.

The different behaviors observed between the SLS and CDA systems must be related mainly to the micelle shape and to their arrangement during the cholesterization process.

The a_w values for LK system with different concentrations of chiral solutes are presented in the **Table IV**. It can be observed an activity decrease as hydrophilic inductors were added, but it was proportional to the water content lowering. This result may be quantified using the water activity coefficient (γ_w), defined as the ratio between the water activity and the water mole fraction of the system. The

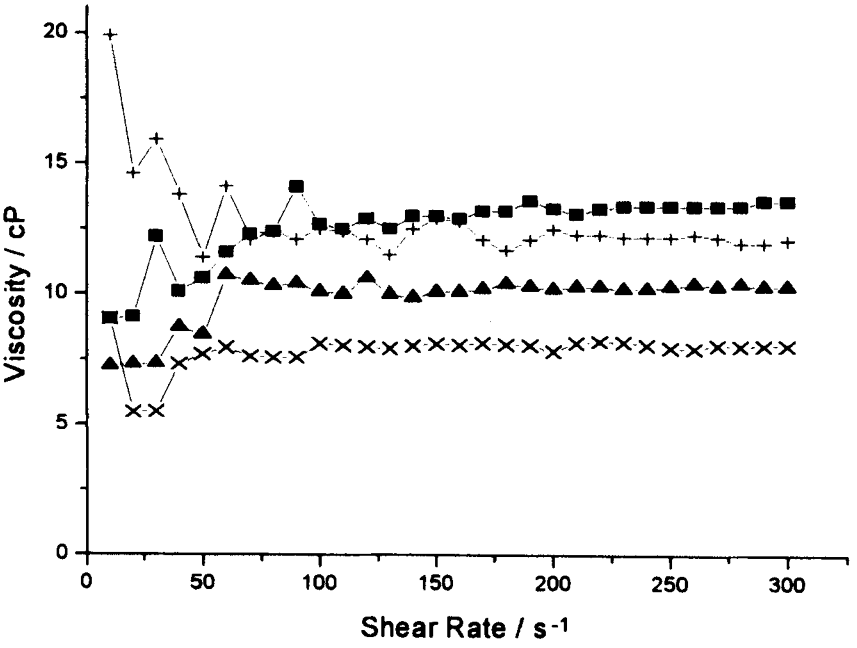

FIGURE 1 Rheograms of **CDA** System (T = 24°C): ■ Nematic; + Cholesteric with 0,01% of inductor; ▲ Cholesteric with 0,03% of inductor; x Cholesteric with 0,09% of inductor

γ_w values do not change significantly, indicating that the micelle-solvent interactions remain unchanged during the cholesterization.

The water activity results, obtained for CDA and LK nematic phases with different water concentrations, are presented in **Table V** and **Figure 2**. One sample of each system was left at room atmosphere and its activity was measured as a function of time. The results are shown on **Figure 3**. The calibration curves may be correlated to yield the rates at which each phase loses its water. The obtained rates were 0.52 mole % hour^{-1} for LK and 0.39 mole % hour^{-1} for CDA systems.

The rate of water loss of LK was also evaluated by differential weighing of another sample. A linear relationship between the molar concentration of water and the time was also obtained, with a rate of loss 0.53 mole % hour^{-1}, in agreement with the value obtained by the activity measurements.

Another LK sample was used to evaluate the change in the system composition when it is placed on contact with an atmosphere saturated with water vapor (the sample stood for five hours in the presence of liquid water in a closed chamber). For this sample the water activity as well its mass did not show any significant change after this period, showing that the water content remained constant.

TABLE IV Water activity for the LK system with different inductors

Inductor	% x_{ind}	a_w (± 0.003)	γ_w
	0.00	0.937	1.00
cholesterol	0.04	0.938	1.01
L(-) sorbose	0.50	0.934	1.01
L(-) sorbose	1.00	0.929	1.01
D(-) frutose	0.50	0.935	1.01
D(-) frutose	1.00	0.929	1.01
D(+) mannose	0.50	0.934	1.01
D(+) mannose	1.00	0.930	1.01
D(+) galactose	0.50	0.930	1.00
D(+) galactose	1.00	0.928	1.00

TABLE V Water activity coefficient (γ_w) as a function of the water molar fraction

Systems	% x_w	γ_w
CDA	89.46	1.02
	89.97	1.03
	91.23*	1.03
	92.17	1.03
LK	92.26	0.996
	92.76	0.999
	93.27*	0.999
	93.74	1.00
	94.26	1.00

Obs: . * samples submitted to the procedure of mass loss.

These last results show that during a typical rheological experiment (about 30 minutes) a sample may lose more than 0.20 mole % of its original water content. To prevent composition changes, the rheological essays with lyomesophases should be carried out in the presence of a humidity saturated atmosphere. This may be accomplished by using humid hydrophilic cotton into the equipment chamber (activity measurements showed that this artifice creates an atmosphere with $\mathbf{a_w} \approx 1$).

Notwithstanding both CDA and LK systems have discotic micelles their water-micelle interactions are unlike. This may be clearly seen if one compares the $\mathbf{a_w}$ values of one phase of each system with essentially the same amount of water. From **Table V**, the γ_w values of the fourth CDA phase and of the first LK phase show that the LK system has a larger micelle-solvent interaction.

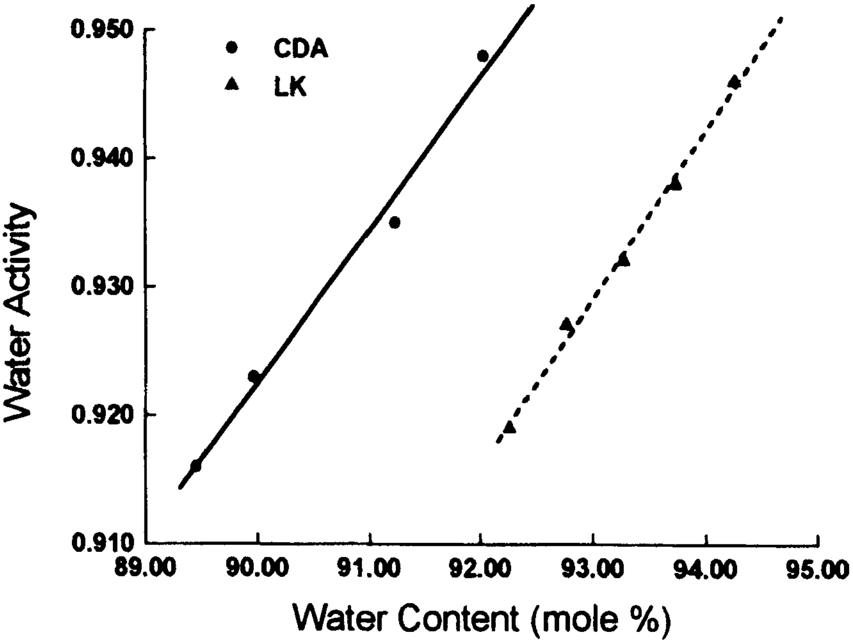

FIGURE 2 Water activity as a function of the water content

It can be concluded that each system has a different behavior in relation to water activity. These differences are due basically to the shape of the micelles and to their arrangement. It should be noted that these systems are formed from different amphiphiles, which interact with the water molecules (by hydrogen bonds) and with the free ions in the solution (by electrostatic attraction) in a different way.

CONCLUSIONS

The results presented show that the system based on SLS has more tightly bound water molecules after the formation of the helical structure. This result is independent of the amount of added solute, showing that after the initial cholesterization of the system the micelle-solvent interaction does not increase with the helical structure formation.

The system based on CDA presented a reduction of the interaction forces between the micelles and the solvent after the formation of the helical structure.

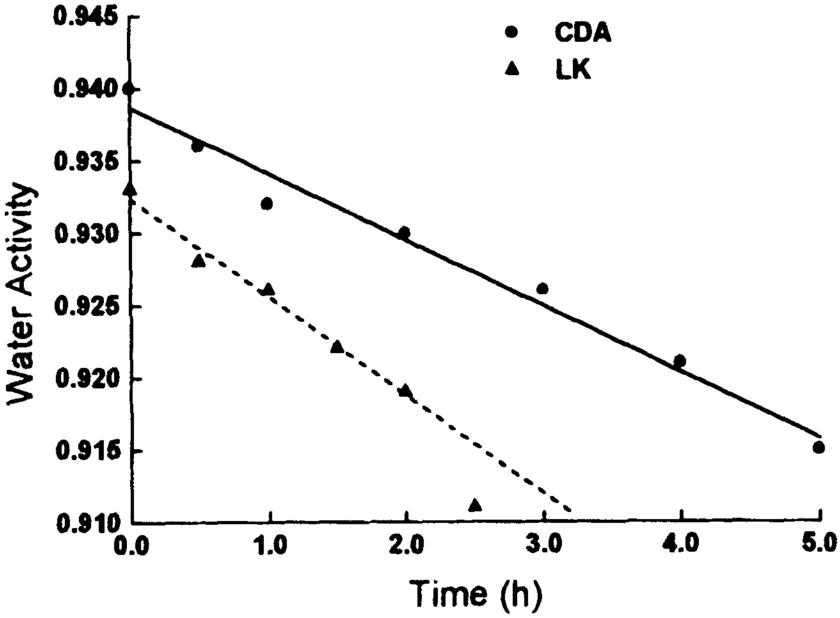

FIGURE 3 Water activity measures as a function of rest time

Rheological data showed that the larger the inductor concentration the smaller are the interactions between micelles in the system.

The system based on LK showed a decrease of the water activity only if hydrophilic inductors were added, possibly because of their high concentration. It was not observed any difference due to the cholesterization itself. It was observed that the LK system presents a rate of loss of water larger than that of the CDA system. However, both systems have high loss rates, making it mandatory to carry out rheological experiments with an adequate control of the humidity.

It can be concluded that each system has a unique behavior in relation to water activity, due, mainly, to differences of micelle geometry and intermicellar arrangement, but also to the fact that they are constituted by different amphiphiles, that interact with the water molecules and with the free ions in the solution in different ways.

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