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Flow activation free energy in cholesteric lyotropic liquid crystals

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The flow activation free energy (ΔG^*) is the minimum energy necessary to induce a flow in a system that is at rest. It can be calculated from the system viscosity using the Andrade–Eyring theory. In the present work the flow activation free energy of cholesteric lyotropic liquid crystals was studied as a function of D-(+)-mannose concentration added to a nematic mesophase. The results obtained showed that all the systems can be characterized as Newtonian, but a smooth time-dependent effect can be observed mainly in systems with a lower chiral inductor concentration. It has also been observed that an increase of cholestericity leads to a decrease of ΔH^* values until a limit is reached at 1 mol % of inductor. From a positive ΔS^* variation it was possible to verify the existence of a locally less organized transient state during the process of micellar diffusion. When the cholesterization process was considered, the increase of the inductor concentration leads to a decrease of ΔS^* and consequently to a system, as a whole, more orderly, possibly as a result of the restriction of movement caused by the presence of chiral interactions.

1. Introduction

Rheology is the study of the deformation and flow of matter, in principle including everything dealing with flow behaviour: aeronautics, hydraulics, fluid dynamics, and even solid mechanics. However, in practice it has usually been restricted to the study of the fundamental relations between force and deformation in materials [1]. The rheological characterization of a system is the determination of its mechanical properties under different deformation and flow conditions [2], being related to the interactions present in the system [3, 4]. In this way rheological parameters may be used to obtain information on the structure of complex systems such as liquid crystals.

Liquid crystalline systems constitute a class of anisotropic liquids with different kinds of structure, which are characterized by flow and order intermediate between those observed for crystalline solids or isotropic liquids [5–8]. The rheological properties of mesophases are affected by their anisotropy, yielding responses with contributions from both flow alignment of the particles and interaction forces of the system [9–11].

In general, rheological properties have been used to obtain information about the spatial rearrangement of units that constitute the systems [12–17] and their variations in the phase transition regions [14–17]. Some results on amphiphile systems discuss the determination of the activation free energy of the viscous flow (ΔG^*), i.e. the minimum energy necessary to induce a flow, and its correlation with the composition and ordering of the system [18–23].

ΔG^* is a system constant that is proportional to the potential energy barrier (ε_0) due to the interaction between the neighbours in the flow direction (figure 1)

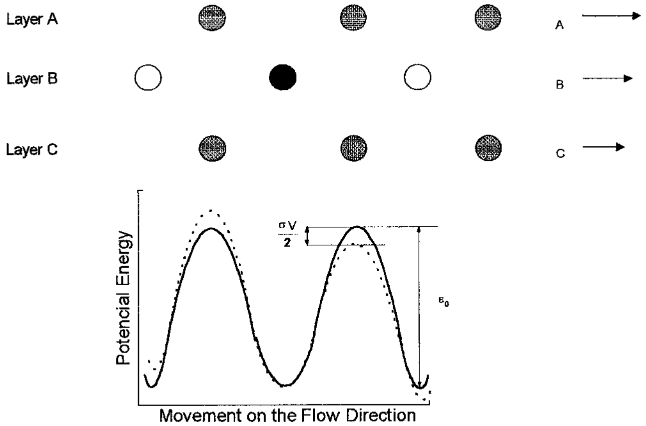

Figure 1. Schematic representation of the potential energy barrier associated with the self-diffusion of a micelle to an empty site of a fcc reticule: — system under rest; ---- system under shear. The dark circle represents a micelle that spreads; grey circles are neighbouring micelles and white circles are spaces in the reticule.

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and can be defined as

$$\Delta G^* = N_A \varepsilon_0 - RT \ln\left(\frac{F^*}{F}\right) \qquad (1)$$

where N_A is the Avogadro number and F^* and F are partition functions, for unit volume, of micelles in the activated state and in initial state, respectively. This energy can be obtained through the viscosity variation with temperature, using the Andrade–Eyring theory that describes viscous flow as a thermically activated diffusion process [24, 25],

$$\eta = \frac{h}{V} \exp\left(\frac{\Delta G^*}{RT}\right) \qquad (2)$$

In equation (2) η is the viscosity, V is the average volume occupied by a micelle, h is Planck's constant, R is the gas constant and T is the absolute temperature. ΔG^* can be replaced by the entropic (ΔS^*) and enthalpic (ΔH^*) components:

$$\eta = \frac{h}{V} \exp\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}\right). \qquad (3)$$

Since the volume of the liquid does not vary greatly with the temperature, it is possible to consider ΔS^* as constant, so

$$\eta = \eta_0 \exp\left(\frac{\Delta H^*}{RT}\right), \quad \text{where} \quad \eta_0 = \frac{h}{V} \exp\left(-\frac{\Delta S^*}{R}\right). \qquad (4)$$

This kind of relationship was suggested empirically by Arrhenius [26] and by de Guzmán [27], and derived theoretically by Andrade [28].

Besides the intermicellar interactions involved, the Andrade–Eyring parameters hold information about the system ordering. They are usually determined from a plot of $\ln(\eta)$ against T^{-1}, in a manner similar to that employed, for obtaining the experimental activation energy in chemical reactions. When working on non-Newtonian systems, viscosity values can be substituted by any other characteristic parameter such as the consistency index (a parameter that reflects how much the system resists permanent change to its shape), in order to obtain an apparent flow activation free energy.

In the present work we determined the entropic and enthalpic components for the activation free energy of viscous flow (ΔG^*) for systems based on potassium laurate, potassium chloride and water. These contributions, well known as the Andrade–Eyring parameters, were used to study the intermicellar interactions involving the cholesterization process and their variation on increasing the concentration of D-(+)-mannose added to the nematic matrix.

2. Experimental

Rheological data were obtained with a Brookfield cone-and-plate rheometer, model LV-DVIII, using a Brookfield thermostatic bath, model TC-500 (Brookfield Engineering Laboratories). The CP52 spindle was employed, which has a cone angle of 3.0° and a radius of 1.2 cm.

The mesophases were analysed at different temperatures varying from 20.0 to 34.0°C, in increments of 2.0°C. Fifteen minute intervals were used between each temperature for thermal equilibration. The temperature for each rheogram was maintained constant to ±0.1°C. All the measurements were made in a water-saturated atmosphere to prevent water loss during the shearing process [10]. For each temperature, a rheogram with ten points was obtained according to the conditions shown in table 1.

The nematic matrix used was a discotic one based on potassium laurate, potassium chloride, *n*-decanol and water. Seventeen samples were prepared, fifteen of them using D-(+)-mannose as chiral inductor. The sample preparation followed classical procedures of weighing and mixing; phase compositions are presented in table 2.

3. Results and discussion

At first sight, all the rheograms obtained can be analysed as Newtonian systems. The viscosities obtained, for all the mesophases at different temperatures, were adjusted to the Andrade–Eyring equation; the obtained results are presented in table 3.

The intermicellar interactions involving the cholesterization process of the liquid crystal systems can be analysed from both the data of flow activation enthalpy (ΔH^*) and its variation with increasing concentration of D-(+)-mannose added to the nematic matrix. These values are presented in figure 2. A smooth fall in ΔH^* as a function of the increase in chiral inductor content can be observed.

Table 1. Experimental design adopted for the rheological determinations.

Temperature /°C	Initial shear rate/s^{-1}	Final shear rate/s^{-1}	Shear rate increment/s^{-1}
20.0	1.2	12	1.2
22.0	1.6	16	1.6
24.0	1.8	18	1.8
26.0	2.2	22	2.2
28.0	2.8	28	2.8
30.0	3.4	34	3.4
32.0	4.2	42	4.2
34.0	5.0	50	5.0

Table 2. Mesophase compositions with chiral inductor D-(+)-mannose (mol %).

Sample	[LK]	[KCl]	[D-(+)-Mannose]	[n-Decanol]	[H_2O]
1	3.42	2.45	—	0.86	93.27
2	3.42	2.48	0.10	0.86	93.14
3	3.38	2.45	0.21	0.85	93.11
4	3.40	2.44	0.30	0.86	93.00
5	3.40	2.44	0.40	0.86	92.90
6	3.40	2.44	0.50	0.86	92.80
7	3.41	2.48	0.60	0.87	92.64
8	3.40	2.47	0.70	0.86	92.57
9	3.39	2.52	0.80	0.86	92.43
10	3.39	2.46	0.90	0.85	92.40
11	3.39	2.45	1.00	0.85	92.31
12	3.39	2.42	1.11	0.85	92.23
13	3.38	2.42	1.20	0.85	92.15
14	3.37	2.41	1.39	0.84	91.99
15	3.36	2.41	1.50	0.85	91.88
16	3.35	2.40	2.00	0.87	91.38
17	3.43	2.47	—	0.84	93.26

Table 3. Flow activation enthalpy and the natural logarithm of the preexponential factor as functions of D-(+)-mannose concentration.

Sample	[D-(+)-Mannose]/mol %	ln(η/cP)	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
1	0.00	−24.9	78.6	90.6
2	0.10	−26.5	83.0	103.9
3	0.21	−23.2	74.8	76.5
4	0.30	−25.5	80.1	95.6
5	0.40	−23.4	75.3	78.1
6	0.50	−23.5	75.3	79.0
7	0.60	−23.4	74.6	78.2
8	0.70	−23.2	74.8	76.5
9	0.80	−22.8	73.8	73.2
10	0.90	−21.9	71.4	65.7
11	1.00	−20.2	67.5	51.5
12	1.11	−21.0	69.5	58.2
13	1.20	−21.2	70.0	60.0
14	1.39	−17.8	61.4	31.6
15	1.50	−18.7	63.1	39.1
16	2.00	−19.7	65.4	47.4

When the data obtained were submitted to statistical analysis it was possible to observe that the error distribution for Newtonian behaviour was not random, evidence that another component may be affecting these results. A closer study of the shear stress values obtained showed the presence of a small viscosity decrease as a function of the shear time.

In order to study this behaviour, a nematic mesophase was submitted to a constant shear rate during a period of 4 hours (figure 3). A damped oscillatory pattern with multiple oscillations was recorded for the shear stress. These features, which confirm the tumbling nature of the system [29], have been measured on other lyotropic systems, including polybenzyl glutamates (PBGs) [29] and hydroxypropylmethylcellulose (HPC) [30, 31]. After shearing for a sufficiently long time with a given shear rate in the tumbling region, a well defined and reproducible polydomain structure is obtained. As predicted theoretically, the director starts to change orientation along the velocity gradient direction, causing director ‘winding up’ and elastic stress changes [32]. As a result, there might be local director rotation but the average orientation over the sample becomes constant. The dampening out of the oscillation is attributed to the breaking up of the monodomain. Since the modelling of the polydomain structure is extremely complex, a semi-empiric approach was adopted where the shear rate was included in the Newtonian model as a polynomial term dependent on time:

$$\sigma = (b_0 + b_1 t + b_2 t^2)\dot{\gamma} \tag{5}$$

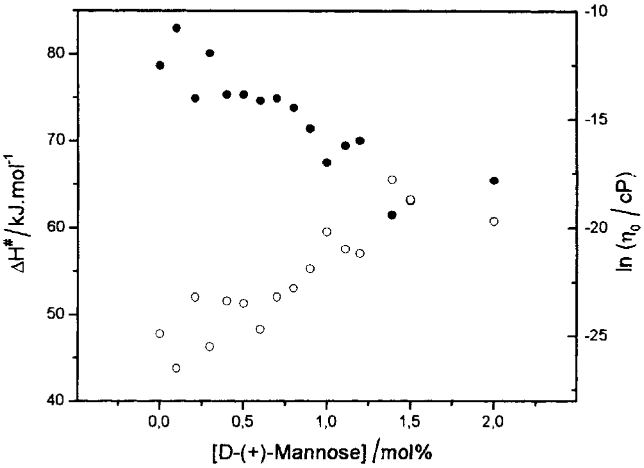

Figure 2. Flow activation enthalpy (●) and natural logarithm of the pre-exponential factor (○) as a function of D-(+)-mannose concentration.

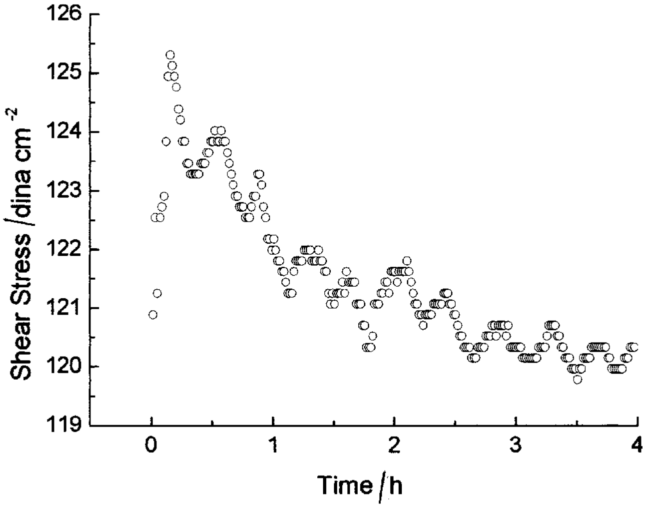

Figure 3. Shear stress for nematic phase (sample 17) obtained at constant shear rate.

where σ is the shear tension and $\dot{\gamma}$ is the shear rate. This model can be considered to describe the curvature observed in the rheograms better since it produces residues which are smaller and approximately random. On this model, only the coefficient b_0 has a defined physical meaning, corresponding to the system viscosity (η). The coefficients b_1 and b_2 varied in a random way and could not be considered as constants of the system.

The new viscosity coefficients ($b_0 \equiv \eta$), determined for each system and at different temperatures, were adjusted again to the Andrade–Eyring equation; the results obtained are presented in table 4 and figure 4. It can be seen that with the increase of the system cholesterization the ΔH^* values decrease until a limiting value that is reached at 1 mol % of inductor. This result is similar to that obtained for the Newtonian model except that in this new approach the tendency to decrease is more visible.

The inclusion of optically active inductors in lyomesomorphic systems generates an additional chiral interaction between micelles that will be responsible for a cooperative effect on the micellar diffusion. Apparently, when one micelle is moved, the others will be progressively dragged by the action of this additional interaction force. Under these conditions, the larger the cholestericity of the system, the smaller the energy necessary for movement and consequently the smaller the resulting ΔH^* values. It can also be observed that the

Table 4. Flow activation enthalpy and the natural logarithm of the preexponential factor as function of D-(+)-mannose concentration with inclusion of temporal function.

Sample	[D-(+)-Mannose]/mol %	ln(η/cP)	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
1	0.00	−23.7	75.3	80.6
2	0.10	−24.8	78.3	89.8
3	0.21	−23.0	73.7	74.8
4	0.30	−24.4	76.9	86.5
5	0.40	−22.3	72.1	69.0
6	0.50	−23.0	73.4	74.8
7	0.60	−23.7	75.2	80.6
8	0.70	−22.4	72.3	69.8
9	0.80	−22.3	71.9	69.0
10	0.90	−21.7	70.2	64.0
11	1.00	−20.9	68.5	57.4
12	1.11	−20.9	68.7	57.4
13	1.20	−20.8	68.5	56.5
14	1.39	−17.8	61.4	31.6
15	1.50	−19.4	64.8	44.9
16	2.00	−19.6	65.2	46.6

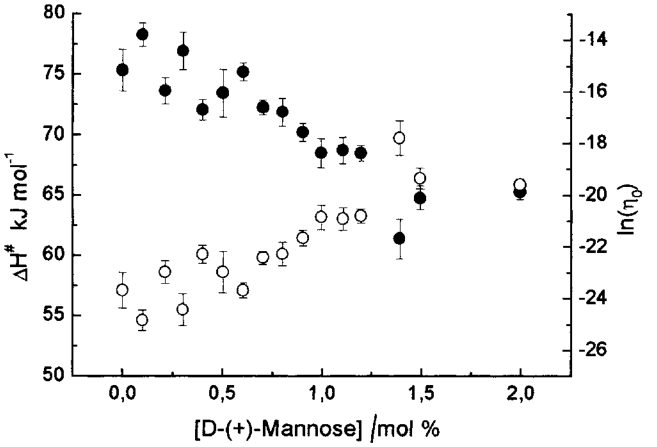

Figure 4. Activation flow enthalpy (●) and natural logarithm of the pre-exponential factor (○) as function of D-(+)-mannose concentration. The error bars are the standard deviations of the linear regression coefficients. Results obtained with inclusion of the temporal function.

values of $\ln(\eta_0)$ increase as a function of the chiral inductor concentration, showing that, the more cholesteric the system, the smaller is its entropy.

According to the Andrade–Eyring model, the pre-exponential factor (η_0) is a function of the volume occupied by the particles that constitute the fluid, as is the flow activation entropy. This volume can be approximated to a cubic box with edge equal to the sum of particle diameter (d) and particle separation (r):

$$\eta = \eta_0 \exp\left(\frac{\Delta H^*}{RT}\right) = \frac{h}{(d+r)^3} \exp\left(-\frac{\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right). \tag{6}$$

Consideration of the micelle packing in lyomesomorphic systems allows us to evaluate the entropic contribution to the pre-exponential factor. In N_D mesophases, the micelle diameter (d) is about 10 nm and the relationship $\delta d^3 \cong 1$ applies, where δ is the numeric density of micelles [13]. Under these conditions it is possible to write:

$$\ln(\eta_0) = \ln\left(\frac{h}{d^3}\right) - \frac{\Delta S^*}{R}, \quad \text{where} \quad \frac{h}{d^3} = \frac{6.63 \times 10^{-34}\ \mathrm{J\ s}}{(10^{-8}\ \mathrm{m})^3}$$

$$\frac{h}{d^3} = 6.63 \times 10^{-10}\ \mathrm{Pa\ s} = 6.63 \times 10^{-7}\ \mathrm{cP},$$

$$\therefore \quad \ln\left(\frac{h}{d^3}\right) \approx -14$$

or

$$\Delta S^* = -R[\ln(\eta_0) + 14].$$

If this relationship and the values of $\ln(\eta_0)$ obtained for the different systems are used (tables 3 and 4; figures 2 and 4), a positive variation of the flow activation entropy (ΔS^*), with values about 6 to 10 times larger than the R constant, is obtained. A tendency for a decrease in these values as a function of the concentration of added inductor can also be observed (figure 5).

According to the Andrade–Eyring theory, ΔS^* is proportional to the degree of order of the activated state in relation to the initial micelle position. A positive variation indicates that, during the micellar diffusion process, the system goes through a transient state that is locally less organized. When we consider the cholesterization process, the increase of the inductor concentration leads to a ΔS^* decrease, and consequently to a system as a whole more orderly, possibly due to the movement restrictions caused by chiral interactions.

It is interesting to note that in both treatments the general behaviour was basically the same. The thixotropic contribution is more pronounced as the cholestericity of the system falls, and the values of ΔH^* and ΔS^* obtained using both methods do not vary much. It can also be observed that when the effect of shear time is taken into account, a small dispersion of the results can be seen.

Finally, the presence of a linear relationship between $\ln(\eta_0)$ and ΔH^* (figure 6) can also be observed, characterizing the existence of a balance between the enthalpy and entropy values ($\Delta S^* \propto -\Delta H^*$). This equilibrium, well known as a compensation effect, tells us that the free energy of flow activation (ΔG^*) does not change significantly during the cholesterization process, meaning that the viscosity also does not change much.

The Andrade–Eyring model is extensively used on rheological characterization of polymers, and the observed

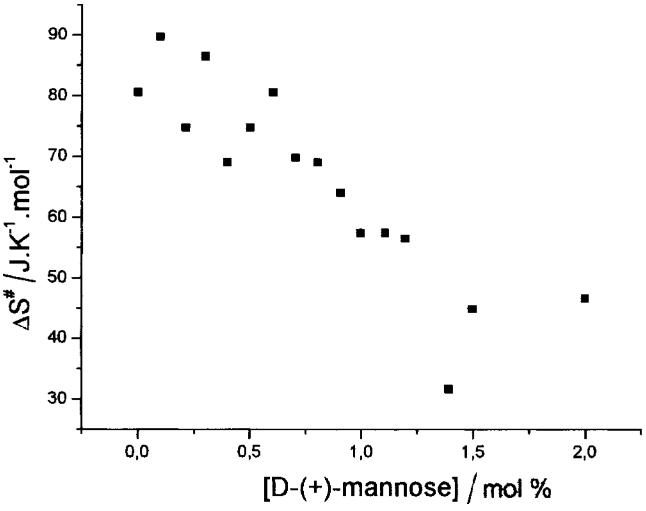

Figure 5. Flow activation entropy as a function of chiral inductor concentration. Results obtained with inclusion of the temporal function.

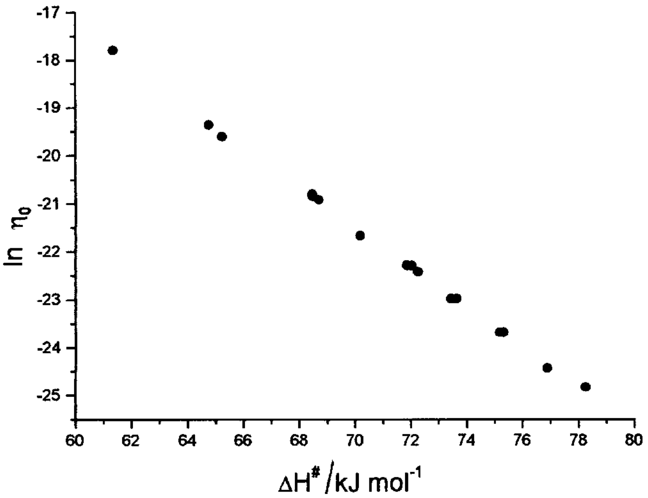

Figure 6. Natural logarithm of the pre-exponential factor as a function of the flow activation enthalpy. Results obtained with inclusion of the temporal function.

ΔH^* values were comparable to those obtained for lyotropic, thermotropic and polymeric liquid crystals. Values of the flow activation energy have been previously obtained for various liquid crystals systems, ranging from 2 J mol^{-1} for lyotropic lamellar [23], and 27 kcal mol^{-1} for lyotropics based on CTAB (cetyltrimetylammonium bromide) [33] to 95 kcal mol^{-1} for polymeric liquid crystals [34]. Thus the results obtained in the present work are quite similar to those obtained for polymeric systems. This is understandable since they are all able to form oriented superstructures.

4. Conclusions

In the present work it has been shown that, although in a first evaluation all the systems could be characterized as Newtonian, a statistical analysis of the results shows the existence of a slight viscosity decrease as a function of the shear time. This feature, characteristic of lyotropic systems, was computed using a semi-empirical approach where the shear rate was included in the Newtonian model as a time-dependent polynomial term. This model can be considered suitable for describing the curvature observed in the rheograms, also in producing smaller and approximately random residues.

In general, the obtained values of ΔH^* decrease with increase in cholestericity up to a limit at 1 mol% of inductor. Seemingly, after the movement of a micelle, the others would be progressively dragged along by action of the chiral interaction. Under these conditions, the larger the system cholestericity, the smaller will be the energy necessary to begin the micelle movement.

The positive ΔS^* variation indicates the existence of a locally transient less organized state during the process of micellar diffusion. On the other hand, the increase of the inductor concentration leads to a decrease of ΔS^* and consequently to a system, as a whole, more orderly.

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References

[1] Macosko, C. W., 1994, *Rheology Principles, Measurements, and Applications* (New York: VCH).

[2] Barnes, H. A., Hutton, J. F., and Walters, K. F. R. S., 1993, *An Introduction to Rheology* (Netherlands: Elsevier).

[3] Leong, Y. K., and Boger, D. V., 1990, *J. Coll. Int. Sci.*, **136,** 249.

[4] Vinogradov, G. V., and Malkin, A. Ya., 1993, *Rheology of Polymers* (Moscow: MIR).

[5] Alcantara, M. R., and Vanin, J. A., 1984, *Mol. Cryst. liq. Cryst.*, **107,** 303.

[6] Alcantara, M. R., and Vanin, J. A., 1984, *Mol. Cryst. liq. Cryst. Lett.*, **102,** 2.

[7] Do Aido, T. M. H., Alcantara, M. R., Felipe Jr., O., Pereira, A. M. G., and Vanin, J. A., 1990, *Mol. Cryst. liq. Cryst.*, **185,** 61.

[8] Do Aido, T. M. H., Alcantara, M. R., Felipe Jr., O., Pereira, A. M. G., and Vanin, J. A., 1991, *Mol. Cryst. liq. Cryst.*, **195,** 45.

[9] Alcantara, M. R., and Vanin, J. A., 1995, *Colloids and Surfaces A*, **97,** 151.

[10] Alcantara, M. R., Dias, L. C. F., and Vanin, J. A., 1996, *An. Assoc. Bras. Quim.*, **45** (2), 47.

[11] Alcantara, M. R., and Dias, L. C. F., 1998, *Colloids and Surfaces A*, **136** (1–2), 155.

[12] Alcantara, M. R., Moura, A. F., and Fernandes Jr., E. G., 1999, *Mol. Cryst. liq. Cryst.*, **333,** 69.

[13] Alcantara, M. R., and Fernandes Jr., E. G., 2001, *Colloids and Surfaces A*, **177,** 75.

[14] Haentzschel, D., Schulte, J., Enders, S., and Quitzsch, K., 1999, *Phys. Chem. chem. Phys.*, **1,** 895.

[15] Montalvo, G., Rodenas, E., and Valiente, M., 1998, *J. Coll. Int. Sci.*, **202,** 232.

[16] Lyou, D. J., and Kim, S. C., 1997, *Polym. J.*, **29,** 279.

[17] Prevysh, V. A., Wang, B. C., Khan, S. A., and Spontak, R. J., 1997, *Colloid Polym. Sci.*, **275,** 284.

[18] Linemann, R., Läuger, J., Schmidt, G., Kratzat, K., and Richtering, W., 1995, *Rheol. Acta.*, **34,** 440.

[19] Walter, L., and Wagner, N., 1994, *J. Rheol.*, **5,** 1525.

[20] Berjano, M., Guerrero, A., Muñoz, J., and Gallegos, C., 1993, *Colloid Polym. Sci.*, **271,** 600.

[21] Soltero, J. F. A., Puig, F. E., and Manero, O., 1996, *Langmuir*, **12,** 2654.

[22] Thurn, H., Löbl, M., and Hoffmann, H., 1985, *J. phys. Chem.*, **89,** 517.

[23] Nèmeth, Z. S., Halàsz, L., Pàlinkàs, J., Bota, A., and Horànyi, T., 1998, *Colloids and Surfaces A*, **145,** 107.

[24] Bird, R. B., and Stuart, W. E., 1960, *Transport Phenomena* (New York: John Wiley).

[25] Glasstone, S., Laider, K. J., and Eyring, H., 1941, *Theory of Rate Processes* (New York: McGraw-Hill).

[26] Arrhenius, S., 1916, *Meddel. Velenskapsakad. Nobelinst*, **3,** 20.

[27] Gusmàn, J. de, 1913, *Anales soc. Españ. Fis. quim.*, **11,** 353.

[28] Andrade, E. N., da C., 1934, *Phil. Mag.*, **17,** 497 and 698.

[29] Burghardt, W. R., 1985, *J. Rheol.*, **35,** 539.

[30] Grizzuti, N., Cavella, S., and Cicarelli, P., 1990, *J. Rheol.*, **34,** 1293.

[31] Metzner, A. B., and Prilutski, G. M., 1986, *J. Rheol.*, **30,** 661.

[32] Burghardt, W. R., and Fuller, G. G., 1990, *J. Rheol.*, **34,** 959.

[33] Candau, S. J., Hirsch, E., Zana, R., and Delsanti, M., 1989, *Langmuir*, **5,** 1225.

[34] Tormes, M., Muñoz, M. E., Peña, J. J., and Santamarìa, A., 1998, *J. polym. Sci. B: polym. Phys.*, **36,** 253.