Eur. Phys. J. B **6**, 511–518 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Flow birefringence and stress optical law of viscoelastic solutions of cationic surfactants and sodium salicylate

C. Humbert and J.P. Decruppe[a]

Laboratoire de Physique des Liquides et Interfaces, Groupe rhéophysique des Colloïdes, Université de Metz 1,
boulevard D.F. Arago, 57078 Metz, France

Received: 18 February 1998 / Revised: 23 June 1998 / Accepted: 22 July 1998

Abstract. The optical and rheological properties of different viscoelastic solutions of surfactant are studied in order to gather experimental data used to calculate the value of the stress optical coefficient C. Three surfactants of the same family (CTAB) have been chosen; they differ by the length of the hydrocarbon chain; it concerns the dodecyltrimethylammonium bromide ($C_{15}H_{34}BrN$ or DoTAB), the myristyltrimethylammonium bromide ($C_{17}H_{38}BrN$ or MyTAB), and the hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$ or CTAB). Different parameters like the temperature of the solution and the salinity of the solvent have been made to vary. Flow birefringence experiments and rheological measurements are performed on these solutions in order to study the dependence of the extinction angle χ, of the birefringence intensity Δn and of the shear stress σ_{yx} with the shear rate $\dot{\gamma}$. These data are used to check the stress optical law which turns out to be valid in a wide range of shear rates. The stress optical coefficient C is then computed: it is found to vary with the salinity of the solvent and the temperature of the solution for a given surfactant. Then, for all solutions of this work the variations of C are related to the variations of the polarizability anisotropy and the persistence length.

PACS. 78.20.Fm Birefringence – 82.70.D Colloids – 83.85.Cg Rheological measurements

1 Introduction

Many surfactants in water, like cetyltrimethylammonium bromide (CTAB), form organized structures called micelles. Various shapes from globular micelles to disk-like, rodlike or wormlike micelles can be found in the solution when the concentration of the surfactant is gradually increased above the critical micellar concentration (CMC) [1–6]. The addition of salt like potassium bromide or sodium salicylate favours the increase of the length of the micelles which can form viscoelastic entanglements [7–12]. Therefore micellar sytems are often compared to polymers molecules [13,14] which behave like Gaussian flexible chains idealized as a sequence of segments free to rotate in any direction around a bond as described in the model of Kuhn and Grün [15]. Segments of micelles between entanglement or branched points are assumed to behave in a similar way [16] in viscoelastic solutions. In such cases the model predicts that the anisotropic part of the refractive index tensor will be proportional to the second moment tensor of the orientation of the end to end vector of the chain [15,17] in the same way as the stress tensor [16]. Since both these tensors are proportional to the same quantity, a linear relation exists between the tensors: $\tilde{n} = C\tilde{\sigma} + A\tilde{I}$. This relation is the stress optical law. This law is valid only for weak form birefringence. $\tilde{I}$ is an isotropic tensor and A a constant. C is the stress optical coefficient which is a very interesting parameter to study since it is related to the microstructure of a given material by the persistence length q or by the difference of polarisability $\Delta\alpha$ for a single Kuhn segment [15,17–22]; this constitutes part of the present study. The relation between the tensors is expressed mathematically through two simple equations relating the optical characteristics, *i.e.*, the extinction angle χ and the birefringence Δn, to the components of the stress tensor.

Solutions of CTAB with NaSal often are highly birefringent even under weak shear condition and this makes them ideal solutions for the study of their rheo-optical properties.

In this paper, we report on the optical and rheological properties of solutions of three surfactants, different by the length of the hydrocarbon chain: dodecyltrimethylammonium bromide ($C_{15}H_{34}BrN$ or DoTAB), myristyltrimethylammonium bromide ($C_{17}H_{38}BrN$ or MyTAB), and hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$ or simply CTAB), dissolved in water with an organic salt: the sodium salicylate (NaSal), at various concentrations and temperatures. The solution is subjected to a simple shear flow in a Couette cell or in cone-plane device.

The birefringence measurements which lead to χ and Δn, and the shear stress σ_{yx} data allow for the computation of the stress-optical coefficient C which in turn

---

[a] e-mail: `decruppe@lpli.sciences.univ-metz.fr`

gives the first normal stress difference N_1. The accurate measurements of normal forces is not always an easy task to do and birefringence measurements thus constitute an indirect and nondisturbing way to reach N_1 when the stress-optical law holds.

In a previous publication we have shown that the stress optical coefficient varies with the concentration in surfactant (CTAB) and salt (KBr) [23]. Here, the coefficient C is found to vary with the salt concentration, the temperature and the length of the hydrocarbon tail. The order of magnitude of C is in agreement with Shikata's value [24].

2 Theoretical section

The stress optical law, first derived by Lodge [18], later extended to overlapping rodlike particles by Doi and Edwards [20] or to solutions of entangled Gaussian chains [15–17], is expressed in terms of two simple equations, in the case of a simple shear flow between parallel plates:

$$\Delta n \sin(2\chi) = 2C\sigma_{yx} \tag{1}$$

$$\Delta n \cos(2\chi) = CN_1. \tag{2}$$

The only non-diagonal term of the stress tensor which is different from zero is σ_{yx}. $N_1 = \sigma_{xx} - \sigma_{yy}$ is the first normal stress difference and is often difficult to measure accurately with a rheometer; it can thus be reached through optical measurements when the law applies.

C is the stress optical coefficient and in the frame of Kuhn and Grün theory [15,17,19,21,22], is given by, for a Gaussian system:

$$C = \frac{2\pi}{45k_BT}\frac{(n^2+2)^2}{n}\Delta\alpha \tag{3}$$

where n is the mean indice of the solution, k_B the Boltzmann's constant, and T the absolute temperature.

$\Delta\alpha$ is the polarizability of a Kuhn segment the length of which is l_k and is expressed as [22,24]

$$\Delta\alpha = \frac{\Delta\alpha^0 l_k}{\lambda} = \frac{2\Delta\alpha^0 q}{\lambda} = \frac{2\Delta\alpha^0\langle\mathbf{r}.\mathbf{r}\rangle}{\lambda L}\,. \tag{4}$$

Shikata *et al.* [24] have proposed a simple model to describe the polarizability anisotropy of the micelles; they consider that the particles consist of a stack of disk-like layers called monomers [25]. In each monomer, the individual cations of surfactant are arranged in a kind of a rosette with the Sal$^-$ ions and the water molecules in the vicinity of the head groups to ensure the cohesion of the structure (see Fig. 1 for the description of a monomer).

λ is the thickness of a monomer, $\Delta\alpha^0 = \alpha_1^0 - \alpha_2^0$, where α_2^0 is the polarisability in the direction of the radius of the monomer and α_1^0 in the direction perpendicular to the radius; q is the persistence length, L the contour length and $\langle\mathbf{r}\cdot\mathbf{r}\rangle^{1/2}$ is the mean quadratic distance of the chain in an unperturbed state.

Different assumptions concerning the mobility of some chemicals groups forming the micelles are also stated: it is assumed that they move fast enough for the corresponding part of the molecule to be considered as optically isotropic. This is supposed to be true for the head formed by the anion Sal$^-$ [24] and the three methyl groups bound to the nitrogen atom and for the last three or four carbon atoms of the tail of the molecule [26]. So the anisotropy of these bonds are supposed to be small enough to be neglected in comparison to the anisotropy of the other –CH$_2$– bond in the tail. Therefore the molecule of surfactant can be compared to a simple paraffin chain; the number n_m of methylene units in a chain is thus respectively 12, 10 and 8 –CH$_2$– bonds in the hydrocarbon tail for $C_{16}H_{33}$, $C_{14}H_{29}$ and $C_{12}H_{25}(CH_3)_3N^+Sal^-$.

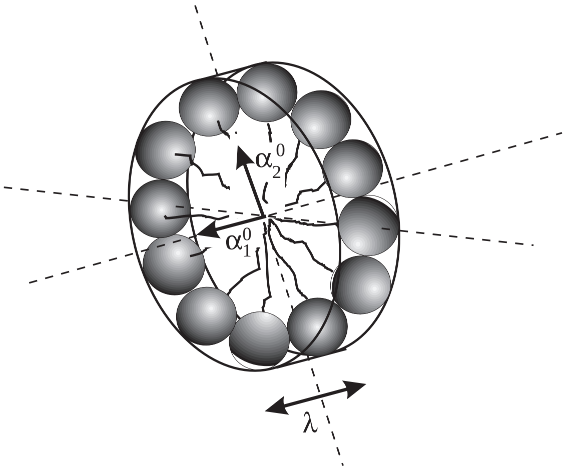


Fig. 1. Schematic representation of a monomer of a worm-like micelle as seen by Shikata *et al.* [24].

We shall at first give an estimate of the polarizabilities b_1 and b_2 of a paraffin chain formed by n_m methylene units; then the principal polarizabilities α_1^0 and α_2^0 of a monomer formed by m of these paraffin chains will be calculated.

The principal polarizabilities of a single –CH$_2$– unit can be quoted in the literature [27]; from the optical point of view it can be considered as an elongated ellipsoid of revolution, the principal polarizabilities of which are $\alpha_\parallel = 19.5 \times 10^{-31}$ m^3 and $\alpha_\perp = 17.95 \times 10^{-31}$ m^3 (the subscript $\parallel$ and $\perp$ refer to a direction parallel and perpendicular to the bond). The average orientation of the chain segment between two carbon atoms is characterized by the order parameter S_m. For the methylene units forming micelles, Seeling [28] found by performing NMR relaxation experiments that $S_m \simeq 0.4$. Thus for a paraffin chain of n_m units, the principal polarizabilities b_1 and b_2 will write

$$b_1 = n_m S_m \alpha_\parallel \text{ and } b_2 = n_m S_m \alpha_\perp. \tag{5}$$

In the Couette device, the light is propagating in the direction of the rotation axis which will be Oz; and the plane xOy is then in parallel to the plane $(\mathbf{v}, \boldsymbol{\nabla} v = \dot{\gamma})$, v is the velocity of the moving cylinder. In the $Oxyz$ coordinates system, the principal polarizabilties are α_1^0 and α_2^0 (α_1^0 is the polarizabilities along the Oy direction). Let $\theta_j = 2\pi j/m$ be the angle between of the average direction of the jth paraffin chain in the monomer with the plane

xOy. Applying the rotation matrix to each chain of the monomer, α_1^0 is simply

$$\alpha_1^0 = mb_2 \tag{6}$$

and we get for α_2^0

$$\alpha_2^0 = b_1 \sum_{j=1}^{m} \cos^2\left(\frac{2j\pi}{m}\right) + b_2 \sum_{j=1}^{m} \sin^2\left(\frac{2j\pi}{m}\right)\cdot \tag{7}$$

The discrete summation could also be replaced by an integral and after averaging over all the possible directions

$$\alpha_2^0 = \frac{m}{2}(b_1 + b_2). \tag{8}$$

The number m of molecules of $C_nH_{2n+1}(CH_3)_3N^+Sal^-$ in a monomer is given by $m \simeq 2\pi r_{micelle}/\lambda$ where λ is also assumed to be the diameter of the head group in a molecule and $r_{micelle}$ the radius of a monomer. We shall write the length l_{tail} of the hydrocarbon chain as: $l_{tail} = r_{micelle} - \lambda$. Tanford [1] has shown that $l_{tail} \simeq 0.75\, l_{max}$ where l_{max} is related to the total number n of carbon atoms in the chain by the relation: $l_{max}(\text{Å}) \simeq 1.5 + 1.265n$. In the frame of these approximations, $r_{micelle}$ will be equal to $0.75 l_{max} + \lambda$ with $\lambda = 0.85$ nm [24]; it turns out that $r_{micelle} = 2.48$ nm for $C_{16}H_{33}(CH_3)_3N^+Sal^-$; this value is in agreement with Shikata's (2.4 nm) for the same micelle but deduced from experimental consideration. The same rule shall be used for $C_{14}H_{29}(CH_3)_3N^+Sal^-$ and $C_{12}H_{25}(CH_3)_3N^+Sal^-$ and $r_{micelle}$ will be 2.29 and 2.10 nm respectively. The number m of molecules in a monomer is then readily computed and turns out to be 18, 16 and 15 for the three surfactants. These values of m shall later be used to compute $\Delta\alpha^0$.

Once the coefficient C has been computed from equation (1), the first normal stress difference N_1 can be obtained from equation (2) as long as the stress optical law remains valid. Finally N_1 computed from the optical measurements of birefringence and from the storage modulus G' should meet in Laun's rule [29]

$$\left(\frac{G'}{\omega^2}\right)_{\omega\to 0} = \left(\frac{N_1}{2\dot\gamma^2}\right)_{\dot\gamma\to 0} = \left(\frac{\Delta n \cos(2\chi)}{2C\dot\gamma^2}\right)_{\dot\gamma\to 0}\cdot \tag{9}$$

The relaxation time can be reached by fitting $\chi(\dot\gamma)$ with [30–32]:

$$\chi(\dot\gamma) = \frac{\pi}{4} - \frac{1}{2}\arctan(\tau\dot\gamma) \tag{10}$$

where χ stands for the extinction angle of the solution which we shall briefly define later. Laun's rule form a very interesting way to check the validity of the optical measurements and of the stress optical coefficient C. In our study, C is found to vary with the temperature T, the salt concentration and the length of the hydrocarbon tail.

3 Experimental section

3.1 Materials

As already quoted, we have used three surfactants which differ by the length of the hydrophobic chain: the dodecyltrimethylammonium bromide ($C_{15}H_{34}BrN$ or DoTAB), the myristyltrimethylammonium bromide ($C_{17}H_{38}BrN$ or MyTAB), and the hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$ or CTAB). All were purchased from Acros Organics and are used without further purification. However special care has been observed for the preparation of the solution of DoTAB which is packaged and kept under dry nitrogen and MyTAB which is very hygroscopic; the different weightings of the powders were performed in a dry inert nitrogen atmosphere.

Water distilled in a quartz vessel is used to prepare the solutions which are kept a few days at 35 °C to reach equilibrium.

3.2 Experimental devices

3.2.1 Rheology

The rheological data presented in this study were all carried out on a Carrimed CSL 100 rheometer working in controlled shear stress mode with a cone-plane device (angle 0.5°; diameter 4 cm). The cone-plane geometry allows for a large scale of shear rate (varying approximatively from 0.01 to 6000 s^{-1}) thus covering the Newtonian and non-Newtonian domain of the micellar solution. Dynamic experiments are performed at different angular frequencies in a range extending from 0.1 to 250 rad/s to obtain the storage modulus $G'(\omega,\gamma)$ which is related to the elastic properties of the medium and the loss modulus $G''(\omega,\gamma)$ proportional to the energy dissipated during the shear flow. In particular for a Maxwell liquid:

$$G'(\omega,\gamma) = \frac{G_0\omega^2\tau^2}{1+\omega^2\tau^2} \tag{11}$$

$$G''(\omega,\gamma) - \eta_s\omega = \frac{G_0\omega\tau}{1+\omega^2\tau^2} \tag{12}$$

η_s is the solvent viscosity, γ the deformation of the medium.

The results of these measurements are mainly used to check our optical results through equation (9) and to appreciate the Maxwellian character of the different solutions. We shall just mentioned the quantitative data obtained with this method: the relaxation time τ and the shear modulus G_0.

3.2.2 Optical measurements

The birefringence intensity and the extinction angle measurements are performed in a conventional Couette cell, the typical dimensions of which are 47 mm and 50 mm for the inner and outer diameters of the cylinders. A laser beam (He-Ne laser) is propagated successively through a polarizer, the solution placed in the gap of the cell and finally through the analyzer (crossed with the polarizer). If one observes light emerging from the analyzer when the solution is subjected to the action of an orientating flow, the liquid is said to show flow birefringence characterized by two quantities: the angle of extinction χ and the retardance Φ. The extinction angle χ which gives the average orientation of the medium, is determined for each value of the shear rate $\dot{\gamma}$ by finding the position of the pair polarizer-analyzer which makes the extinction.

A quarter wave plate is added before the analyzer to measure the retardation Φ according to the method of Senarmont. The birefringence intensity Δn is readily evaluated with the relation

$$\Delta n = \frac{\Phi \lambda_{wave}}{2\pi e} \tag{13}$$

where e is the thickness of the sample and $\lambda_{wave} = 6328$ Å.

We have used cells of different height (30, 50, 73 mm) in order to check the importance of the ends effects; it appears that they are of little importance compared to the birefringence of the micellar solutions which is strong enough for a simple visual observation to give very precise measurements of χ and Φ. Many details of the experimental devices can be found in a previous work [33].

4 Experimental results and discussion

The following three parameters have been made to vary: the concentration C_S of salt when the surfactant is the CTAB, the absolute temperature for a single solution of myristyltrimethylammonium bromide (MyTAB) and the length of the hydrocarbon tail of the surfactant molecule. For each solution, optical and rheological data are gathered as a function of the shear rate $\dot{\gamma}$ to test the validity of the stress optical law and to compute the stress optical coefficient C.

4.1 Constant surfactant concentration C_D (0.1 M) but various concentration of salt C_S

Three solutions of CTAB with different concentrations of NaSal have been prepared ($C_S = 0.03$ M, 0.1 M and 0.23 M). These particular values have been chosen to compare our results with Shikata's and to evaluate the importance of the proportion of salt on the stress optical coefficient.

For each concentration, the extinction angle χ decreases with $\dot{\gamma}$ and the higher the concentration C_S the faster the decrease will be; at the same time, the birefringence of the solution increases and the maximum effect is observed for the solution having the strongest ionic force ($C_S = 0.23$ M).

This behaviour is not surprising since the Coulomb repulsion between the head groups is screened by the addition of counter-ions, the added salt thus favors the formation of long wormlike micelles which are more easily orientated by the flow. Figure 2 shows the variation of $\Delta n \sin 2\chi$ *versus* σ_{yx} (Δn is found to be negative for all the solutions studied in this work and we shall always show the variations of the absolute value of Δn). It can be seen that the stress optical law holds over a wide range of shear stresses thus indicating that the main contribution to the birefringence is the intrinsic birefringence. The slope of each straight line is twice the optical coefficient C which varies from 1.7 to 6.8×10^{-7} Pa^{-1}, the latter which is also the highest corresponds to the equimolar solution. The range of shear stresses investigated with the 0.1/0.03 M solution appears more restricted than the others: this is due to the small value of the viscosity of this solution.

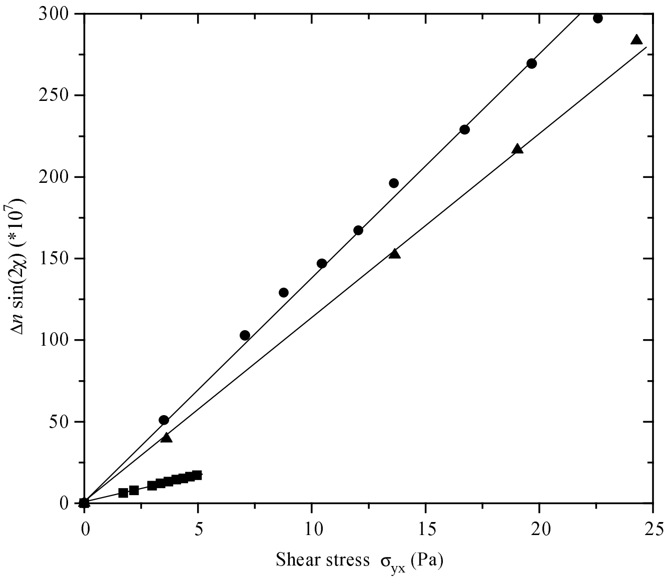


Fig. 2. Stress optical law $\Delta n \sin 2\chi = 2C\sigma_{yx}$ for the first set of experiments $C_D = 0.1$ M; C_s: (■) 0.03 M, (●) 0.1 M, (▲) 0.23 M.

It must be emphasized that the optical characteristics (χ and Δn) still vary when C_S exceeds C_D (at 0.1 M): Δn for example increases very steeply in a range of only a few s^{-1} for the solution having the highest ionic force (0.23 M). This indicates that the length of micelles is still changing in the range 0.1–0.23 M in NaSal. However the maximum of the coefficient C is obtained for the equimolar solution.

The temperature is kept constant (30 °C) and the relative variation of the average index of refraction n is insignificant for the three solutions, the main contribution to the variation of C comes from the variation of the polarizability anisotropy $\Delta\alpha$. Although the Sal$^-$ ion penetrates between the molecules of surfactant, its motion is so fast [24] that we can neglect its contribution to the anisotropy; thus whether the salt is in excess or not, the polarizability anisotropy of a monomer will be the same and we can assume $\Delta\alpha^0$ to be the same for the three solutions. The variation of C is thus mainly due to the variation of the persistence length q the values of which are gathered in Table 1; the fact that q is not a monotonic function of C_S should not be surprising since the surfactant molecules form various structures from elongated micelles to connected networks when the salt concentration is increased [32,34–36].

Table 1 shows the relaxation time τ deduced from the optical (τ_{FB}) and rheological (τ_{Rheo}) experiments. The results are in agreement.

Table 1. Stress optical coefficient, persistence length, relaxation time from flow birefringence (τ_{FB}) and rheological experiments (τ_{Rheo}), and the shear modulus G_0, for different concentrations of the CTAB/NaSal at 30 °C with $\Delta\alpha^0 = 6.69 \times 10^{-30}$ m^3.

	$C \times 10^7$ (Pa^{-1})	q (nm)	τ_{FB} (S)	τ_{Rheo} (S)	G_0 (Pa)
0.1/0.03 M	1.76	31	0.081	–	–
0.1/0.1 M	6.86	120	0.35	0.30	54
0.1/0.23 M	5.74	100	1.23	1.19	55

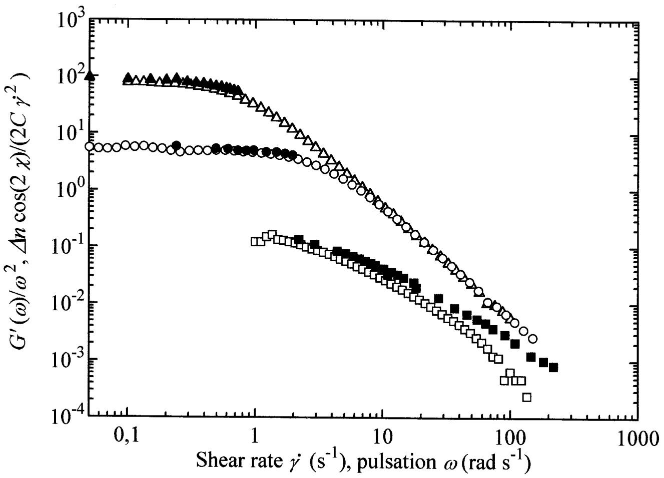


Fig. 3. Laun's relation for the three solutions having the same C_D (0.1 M) but different C_S: (■) 0.03 M, (•) 0.1 M, (▲) 0.23 M. The full symbols represent values computed from the birefringence experiments while the open symbols correspond to the rheological measurements.

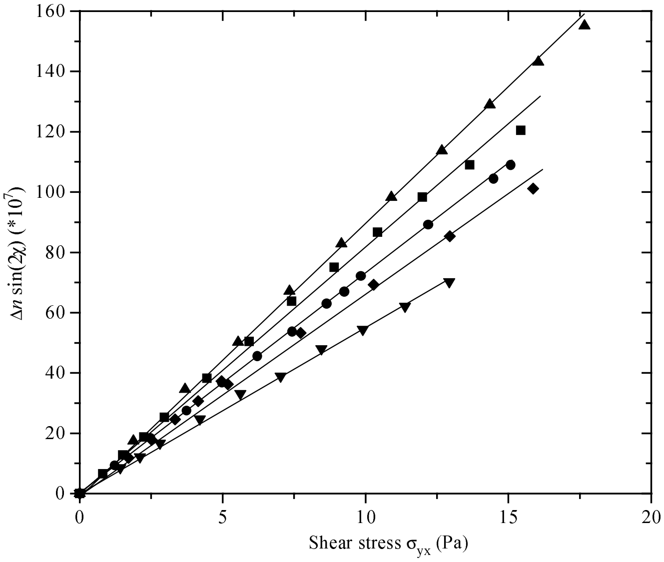


Fig. 4. Stress optical law $\Delta n \sin 2\chi = 2C\sigma_{yx}$ for the solution of the myristyltrimethylammonium bromide. (▲) 20 °C, (■) 25 °C, (•) 30 °C, (♦) 36 °C, (▼) 45 °C.

Figure 3 is the graphic representation of Laun's law for the three solutions of CTAB. The black symbols correspond to the values computed from equation (2) while the open symbols represent G'/ω^2: the agreement is excellent for the two solutions having the highest concentration (0.23 M and 0.1 M) while, in the case of $C_S = 0.03$ M, the two sets of results only meet at low shear rates or pulsation as expected from the theoretical equation.

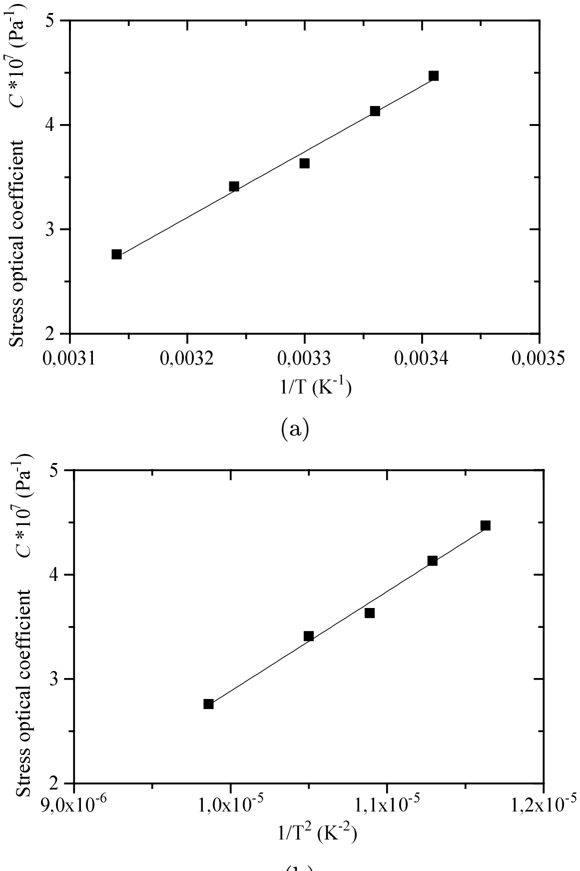
4.2 Single solution of MyTAB/NaSal at different temperatures

A solution of myristyltrimethylammonium bromide and sodium salicylate ($C_D = 0.1$ M and $C_D = 0.23$ M) has been studied at five different temperatures ranging from 20 °C to 45 °C as a function of shear rate $\dot\gamma$. The overall behaviour of the two quantities, extinction angle and birefringence intensity is in agreement with what is usually observed when the temperature is increased. This is consistent with the fact that the average length of the particles diminishes with T and the influence of Brownian motion, which tends to disorganize the particles, is thus strengthened.

It can be seen that the stress optical law holds fairly well over the entire range of shear stresses we have investigated (Fig. 4). The same solutions are subjected to an oscillating shear stress in a cone-plane device to record the behaviour of the storage modulus G' *versus* the angular frequency ω. These values of G' are used to compute the different G'/ω^2 which are then compared to the ratio $\Delta n \cos(2\chi)/2C\dot\gamma^2$ according to Laun's rule (Eq. (9)). Apart from the highest temperature, the agreement is pretty good. The relaxation time τ resulting from the dynamical rheology is then compared with the values computed from the optical measurements with equation (10) at different temperatures and gathered in Table 2 with the different values of C. C varies linearly with the reverse of the temperature according to equation (3). When the different values of C are plotted against $1/T$ (Fig. 5a) the points are well distributed on a single straight line which does not go through the origin; this indicates that the persistence length q is also temperature dependent as already quoted theoretically by Safran [5] who has shown that q is proportional to $1/T$; therefore C should be proportional to $1/T^2$ (see Fig. 5b). Finally we could estimate $\Delta\alpha^0$ which turns out to be equal to 4.96×10^{-30} m^3.

Table 2. Stress optical coefficient, persistence length, relaxation time from flow birefringence (τ_{FB}) and rheological experiments (τ_{Rheo}), and the shear modulus G_0, for the MyTAB/NaSal at different temperatures with $\Delta\alpha^0 = 4.96 \times 10^{-30}$ m^3.

	$C \times 10^7$ (Pa^{-1})	q (nm)	τ_{FB} (S)	τ_{Rheo} (S)	G_0 (Pa)
20 °C	4.47	102	0.10	0.09	61
25 °C	4.13	96	0.040	0.034	60
30 °C	3.63	86	0.015	0.013	58
36 °C	3.41	82	0.005	0.004	56
45 °C	2.76	68	0.0011	–	–



(a)

(b)

Fig. 5. (a) Variation of the stress optical coefficient C with $1/T$. (b) Variation of the stress optical coefficient C with $1/T^2$.

4.3 Single concentration $C_D = 0.1$ M and $C_S = 0.23$ M but three different length of the hydrocarbon tail

In this section, we describe the results obtained with a solution of three surfactants different by the length, l_{tail}, of the hydrocarbon chain. The temperature is the same and kept constant at 30 °C. The birefringence intensity increases with the length of the chain ($\Delta n_{\text{DoTAB}} < \Delta n_{\text{MyTAB}} < \Delta n_{\text{CTAB}}$) and the longer the chain, the faster the extinction angle χ decreases with $\dot{\gamma}$. This behaviour of χ and Δn simply means that the size of the micelles increases with the length of the hydrocarbon chain. Surfactants are molecules where the internal structure ("tail" and "head") play an important role. The forces that govern the assembly of amphiphiles are the consequence of the hydrophobic interaction between the hydrocarbon chains which induces molecular association and the hydrophilic nature of the head groups which impose that they remain in contact with the water. These two forces act principally in the interfacial region: one decreases, the other increases the surface "a" per molecule exposed to the aqueous phase. In this way as "a" decreases, the head-head repulsions are more important because of the electrostatic force and/or the excluded volume action [1–4]. In this study the length of the hydrocarbon chain changes but the dimension of the head is the same. With an increase of l_{tail} the hydrophobic action between the tail and the water are stronger. In other words the amphiphilies with a longer hydrocarbon tail are less soluble in the water, they have less affinity for the water molecules (usually micellar growth is driven by the tendency to reduce the unfavorable effects of the hydrophobic environnement). Since the repulsions between the water and the tail are stronger, the surfactant molecules will rather aggregate in micelles rather than remain dilute in the solution and, for a given concentration in detergent or salt, the larger the radius the bigger the micelles in solution will be. The aggregate situation is more favorable in the energetic sense. Similar results are found by Mukerjee and Mysels who studied the CMC which is found to decrease with the length of the hydrocarbon tail [37].

The computation of the coefficient C which is also found to vary for the three surfactants different by l_{tail} (see Tab. 3 for the different values).

Once C is known, equation (2) leads to the different values of N_1 which are then compared to the computed values resulting from the equation (9) as already done in the previous sections. These results for the CTAB, MyTAB are excellent between the different results (no reliable values of G' for DoTAB could be measured with enough accuracy since the viscosity of the solution was too small). The mean index of refraction of the solution is found to vary only little ($n \simeq 1.34$): the relative variation is only 0.2% between DoTAB and CTAB; thus the main contribution to the variation of C comes from the variation of the polarizability anisotropy $\Delta\alpha$.

Table 3. Stress optical coefficient, difference of polarisability for a disk-shape monomer, persistence length, relaxation time from flow birefringence (τ_{FB}) and rheological experiments (τ_{Rheo}), and the shear modulus G_0, for different surfactants at 30 °C.

	$C \times 10^7$ (Pa^{-1})	$\Delta\alpha^0 \times 10^{30}$ (m^3)	q (nm)	τ_{FB} (s)	τ_{Rheo} (s)	G_0 (Pa)
DoTAB/NaSal	1.88	3.72	59	–	–	–
MyTAB/NaSal	3.63	4.96	86	0.015	0.013	58
CTAB/NaSal	5.74	6.69	100	1.23	1.19	55

5 Conclusion

In this experimental work, we have shown that the stress optical law holds fairly well over a wide range of shear rates in different viscoelastic solutions of surfactant. The optical coefficient C computed from equation (1) allows for the determination of the first normal stress difference N_1. It is also found to depend on the different parameters which have been made vary in this work.

As concerns the first set of solutions (constant surfactant concentration but increasing salinity), C is found to reach a maximum value for the equimolar solution (0.1/0.1 M). This is an indication that the individual surfactant molecules can form micelles of various lengths in solvents of different salinity.

The study of the solution of myristyltrimethylammonium bromide has shown that C depend, linearly, on $1/T$ according to equation (3) with a relative variation of 38% while $\Delta T/T$ is only $\simeq$ 8%. Thus the parameter T cannot explain by itself the variation of C, the persistence length being also temperature dependent. When the temperature T is increased, the micelles become less rigid and the persistence length diminishes in agreement with Safran [5].

Finally, for the three solutions containing molecules of surfactant having different tail lengths, the relative variation of the stress optical coefficient C between CTAB and DoTAB is roughly 67% while $\dfrac{\Delta q}{q} + \dfrac{\Delta(\Delta\alpha^0)}{\Delta\alpha^0} = 85\%$ (for CTAB and MyTAB we have 36% and 41%). The two relative variations are of the same order of magnitude: this show that the theoretical expression for $\Delta\alpha^0$ given by (6,8) with the different assumptions on the polarisability of one amphiphile, the number of surfactants in a monomer, the estimation of tail length and the Gaussian behaviour of the solution are not totally incorrect. With the shear modulus G_0 we can estimate the mesh size $\xi_e = \left(\dfrac{k_BT}{G_0}\right)^{1/3}$ [38]. Indeed our values of G_0, which turn out 50, 60 Pa, give ξ_e close to 40 nm. So persistence length and mesh size are not in agreement ($q > \xi_e$). But with better assumptions on S_m, b_1, b_2, ..., it will be possible to find others (and better) values for the persistence length (moreover we are in the simply case where the monomer is in the xOz plane. In the reality that's not totally true). The rather important values found for the persistence length q compared to ξ_e are not quite fully understood and complementary experiments like quasi-elastic light scattering would be useful in order to confirm this results.

We cannot fully rely on the values of the persistence length deduced from these experiments since the theoretical expression for C has been established in the frame of Kuhn and Grün model for flexible macromolecules and the micelles in the various solutions surely assume different lengths and persistence lengths. The system can be, a dilute solution of long wormlike micelles, an entangled wormlike micellar structure or a multiconnected network for various conditions of surfactant and salt concentrations.

The main result of this experimental work on the stress optical law is that the coefficient C is not a constant but varies significantly with the temperature and depends also greatly on the nature of the surfactant and on the concentration of the added salt for a given surfactant concentration.

References

1. C. Tanford, *The Hydrophobic effect*, 2nd ed. (Whiley, New York, 1980).
2. J.N. Israelachvili, D.J. Mitchell, B.W. Ninham, J. Chem. Soc. Faraday Trans. **2**, 1525 (1976); J.N. Israelachvili, S. Maralja, R.G. Horn, Quart. Rev. Biophys. **13**, 121 (1980); J.N. Israelachvili, *Physics of Amphiphiles: Micelles, Vesicles, and Microemulsions*, edited by V. Degiorgio, M. Corti (North Holland, Amsterdam, 1985).
3. J.N. Israelachvili, *Intermolecular and surface forces* (Academie, New York, 1985).
4. H. Wennerström, B. Lindman, Phys. Rep. **52**, 1 (1979).
5. S.A. Safran, L. Turkevich, F. Pincus, J. Phys. Lett. **45**, L19 (1984).
6. D. Blanckschtein, G.M. Thurston, G.B. Benedek, Phys. Rev. Lett. **54**, 955 (1986); D. Blanckschtein, G.M. Thurston, G.B. Benedek, J. Phys. Chem. **85**, 7268 (1986).
7. F. Kern, P. Lemarechal, S.J. Candau, M.E. Cates, Langmuir **8**, 437 (1992).
8. S.J. Candau, E. Hirsch, R. Zana, M.J. Adam, J. Colloid Interf. Sci. **122**, 430 (1987).
9. H. Hoffmann, H. Rehage, A. Rauscher, *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregats in Solution* (Kluwer Academic Publishers, Amsterdam 1992), pp. 493–510.
10. F. Kern, R. Zana, S.J. Candau, Langmuir **7**, 1344 (1992).
11. H. Rehage, H. Hoffmann, J. Phys. Chem. **92**, 4712 (1988).
12. E.W. Kaler, K.L. Herrington, A.K. Murthy, J.A.N. Zadadzinski, J. Phys. Chem. **96**, 6698 (1992).
13. M.E. Cates, S.J. Candau , J. Phys.-Cond. **2**, 6869 (1990).

14. H. Rehage, H. Hoffmann, Mol. Phys. **74**, 933 (1991).
15. W. Kuhn, F. Grün, Z. Kolloïd **28**, 248 (1942).
16. R.B. Bird, C.F. Curtiss, R.C. Armstrong, O. Hassager, *Dynamics of polymers liquids*, Kinetic theory (A Whiley-Interscience Publication, New York, 1977), Vol. 2.
17. G.G. Fuller, *Optical Rheometry of Complex Fluid* (Oxford University Press, Oxford, 1995).
18. A.S. Lodge, Trans. Faraday Soc. **52**, 120 (1956).
19. L.R.G. Treloar, *The Physics of Rubber Elasticity* (Clarendon Press, Oxford, 1975).
20. M. Doi, S.F. Edward, J. Chem. Soc. Faraday Trans. **2**, 418 (1978).
21. M. Doi, S.F. Edward, *The Theory of Polymer Dynamics* (Oxford, Clarendon, 1986).
22. P.J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience Publishers, New York, 1969).
23. C. Humbert, J.P. Decruppe, Col. Pol. Sci. **276**, 160 (1998).
24. T. Shikata, S.J. Dahman, D.S. Pearson, Langmuir **10**, 3470 (1994).
25. T. Imae, R. Kamiya, S. Ikeda, J. Colloid Interf. Sci. **108**, 215 (1985).
26. O. Söderman, H. Walderhaug, U. Henriksson, P. Stilbs, J. Phys. Chem. **89**, 3693 (1985).
27. D.W. Saunders, Trans. Faraday Soc. **53**, 860 (1957).
28. J. Seeling, W. Niederberger, J. Am. Chem. Soc. **96**, 2069 (1974).
29. H.M. Laun, J. Rheo. **30**, 459 (1986).
30. M. Löbl, H. Thurn, H. Hoffmann, Ber Bunsenges Phy. Chem. **88**, 1102 (1984).
31. H. Thurn, M. Löbl, H. Hoffmann, J. Phys. Chem. **89**, 517 (1985).
32. H. Rehage, H. Hoffmann, J. Phys. Chem. **92**, 4712 (1988).
33. J.P. Decruppe, R. Hocquart, T. Wydro, R. Cressely, J. Phys. II France **50**, 3371 (1989).
34. H. Rehage, H. Hoffmann, Mol. Phys. **74**, 933 (1991).
35. C.A. Bunton, M.J. Minch, J. Hidalgo, L. Sepulveda, J. Am. Chem. Soc. **95**, 3262 (1973).
36. V. Hartmann, R. Cressely, Col. Pol. Sci. (accepted).
37. P. Mukerjee, K.J. Mysels, *CMC of Aqueous Surfactant Systems* (US Dept. of commerce NSDS-NBS 36, 1971).
38. J.D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Whiley, New York, 1980).