

Classification

Physics Abstracts

78.20L — 78.20J — 82.70

## Structure of microemulsions from magnetic and electric birefringence measurements

C. T. Meyer, Y. Poggi

C.N.R.S., Laboratoire d'Electrostatique, 166 X, 38042 Grenoble Cedex, France

and G. Maret

Max Planck Institut für Festkörperforschung, Hoch Feld Magnet Laboratorium, Grenoble, France

*(Reçu le 26 octobre 1981, révisé le 17 janvier 1982, accepté le 19 janvier 1982)*

**Résumé.** — Des expériences de biréfringences magnétique et électrique ont été effectuées sur des microémulsions d'octylbenzène sulfonate de sodium-pentanol-décane-eau (à 0,3 % de NaCl) dans tout le domaine de solution homogène du diagramme pseudo-ternaire. On relie qualitativement la constante de Cotton-Mouton à la structure des microémulsions. On examine les contributions à la biréfringence magnétique de l'effet d'orientation d'objets anisotropes ou d'un film très flexible et de l'effet de déformation de gouttelettes sphériques. On discute l'ordre de grandeur du module élastique de courbure du film de surfactant.

**Abstract.** — Magnetic and electric birefringence experiments have been performed on microemulsions of Na octylbenzene sulfonate (OBS)-pentanol-decane-water (with 0.3 % NaCl), in the homogeneous liquid region of the pseudo-ternary diagram. The Cotton-Mouton constant is related qualitatively to the structure of the microemulsion. It is discussed in terms of magnetic orientation of anisotropic rigid objects or of a very flexible surfactant film, and in terms of magnetic deformation. The order of magnitude of the bending elastic modulus of the surfactant film is discussed.

**1. Introduction.** — Microemulsions are transparent, homogeneous solutions of water, hydrocarbon, surfactant and cosurfactant, the relative amounts of water and oil may be varied in large proportions [1, 2]. Since their discovery by Schulman [3] microemulsions have been extensively studied in particular with regard to their structure. These solutions are generally supposed to contain spherical droplets of water in a continuous oil phase (w/o) [4, 9]. Droplets of oil in water (o/w) have also been observed. The droplets are surrounded by a mixed surfactant-cosurfactant film. For w/o microemulsion some cosurfactant, generally an alcohol, is dissolved in the continuous oil phase. The intermediate structure between the w/o and o/w microemulsions depends on the path chosen in the tridimensional quaternary diagram. A liquid crystalline phase may occur [6, 7]. On a path of dilution, that keeps the droplets identical, it has been shown by conductivity and SANS (small angle neutron scattering) measurements that the w/o to o/w inversion is well-defined and may be described by a percolation

theory [9]. However in the case of a constant surfactant-cosurfactant ratio, self diffusion and conductivity measurements indicate that this inversion is not sharp. Experimental [11, 12] and theoretical arguments [13] are in favour of the existence of a bicontinuous structure in most of the central isotropic region of the pseudo-ternary diagram. Furthermore it is not clear whether or not the individual objects have an anisotropic shape [10]. We have thus undertaken magnetic and electric birefringence measurements, both being sensitive to anisotropy and association.

**2. Experimental methods.** — The system studied here is :

- n-decane,
- water with 0.3 % NaCl,
- sodium p-octylbenzene sulfonate (OBS) as surfactant (synthesized according to [14]),
- 1-pentanol as cosurfactant.

We have used a constant ratio cosurfactant to surfactant of 2.11 in weight or 7 in mole number.

2.1 COTTON-MOUTON EFFECT [15]. — A magnetic field  $H$  induces a small orientation of molecules having an anisotropy  $\Delta\chi$  of the diamagnetic susceptibility. This orientation may be measured by the resulting optical birefringence

$$\Delta n = n_{\parallel} - n_{\perp} = \frac{2\pi}{135} \left( \frac{n_0^2 + 2}{n_0} \right)^2 C \Delta\alpha \frac{\Delta\chi H^2}{kT} \quad (1)$$

$n_{\parallel}$  and  $n_{\perp}$  are the refractive indices for light of wavelength  $\lambda$  polarized parallel and perpendicular to  $H$ ,  $n_0$  its mean value,  $\Delta\alpha$  is the polarizability anisotropy of the molecule and  $C$  the number of molecules per unit volume. Equation (1) results from the birefringence of a completely oriented solution  $\Delta n_{\text{sat}}$  :

$$\Delta n_{\text{sat}} = \frac{2\pi}{9} \left( \frac{n_0^2 + 2}{n_0} \right)^2 C \Delta\alpha \quad (2)$$

and an orientation factor

$$\frac{\Delta n}{\Delta n_{\text{sat}}} = \beta = \frac{\Delta\chi H^2}{15 kT}$$

The Cotton-Mouton constant is defined by

$$\Delta n = C_M H^2 \lambda \quad (3)$$

For objects containing  $N$  molecules, the magnetic and optical anisotropies are respectively  $fN \Delta\chi$  and  $fN \Delta\alpha$ .  $f$  is a parameter giving the fraction of monomers contributing to the anisotropies.  $C$  is to be replaced by  $C/N$ , the concentration of objects. Equation (1) becomes :

$$\Delta n = \frac{2\pi}{135} \left( \frac{n_0^2 + 2}{n_0} \right)^2 C \Delta\alpha \frac{\Delta\chi H^2}{kT} f^2 N \quad (4)$$

The magnetic field may also induce a deformation of isotropic objects containing diamagnetically anisotropic molecules. The resulting birefringence which has been calculated first by Helfrich, is proportional to  $H^2$  [16]. We derive similarly

$$\Delta n = f \Delta n_{\text{sat}} \quad (5)$$

With

$$f \sim \frac{3}{2} \frac{S_2}{r_0} \quad (6)$$

and from [16]

$$S_2 = \frac{1}{12} \frac{r_0^3 \Delta\chi H^2}{AK} \quad (7)$$

$r_0$  is the initial sphere radius and  $\frac{3}{2} S_2$  the difference between the half axes parallel and perpendicular to the field,  $\Delta\chi$  and  $A$  are the diamagnetic susceptibility anisotropy and area per monomer.  $K$  is a curvature elastic modulus of the surfactant film with the dimension of an energy.

The magnetic birefringence measurements have been performed at S.N.C.I.-C.N.R.S.-M.P.I. in Grenoble. The experimental set up which has already been described [17] involves a Bitter coil producing a magnetic field up to 12 T and a birefringence detection system able to measure  $\Delta n$  values of the order of  $10^{-10}$ .

For all samples measured a good linearity between  $\Delta n$  and  $H^2$  has been observed.

The measured Cotton-Mouton constants have been corrected for the contribution of decane and pentanol in proportion of their volume, using our experimental values of  $-1.61 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1}$  and  $-0.97 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1}$  respectively. These corrections, based on the assumption of unorganized decane and pentanol molecules, did not exceed 10%.

The Cotton-Mouton constant has been normalized to OBS concentration  $C$  ( $C$  in mole per liter of solution has been calculated using 1.12 for the density of OBS [12]).

2.2 KERR EFFECT. — The Kerr constant  $B$  is defined by  $\Delta n = B\lambda E^2$ , the optical birefringence induced by an electric field  $E$ . It has been measured with an experimental set-up previously described [18].

Kerr effect measurements could be achieved only in the decane rich region, where the conductivity of the solution was sufficiently low.

3. Results. — Three types of lines in the pseudo-ternary diagram have been explored : constant ratios of water to surfactant (lines DP, DN), of decane to surfactant (lines from W to P, A, B, E, C, F) and constant surfactant concentration (horizontal lines) (Fig. 1).

The results are given as a map of iso- $C_M/C$  lines in the pseudo-ternary diagram (Fig. 2).

Figure 3 gives the plot of  $C_M/C$  versus decane concentration for a constant ratio of 15 water molecules per

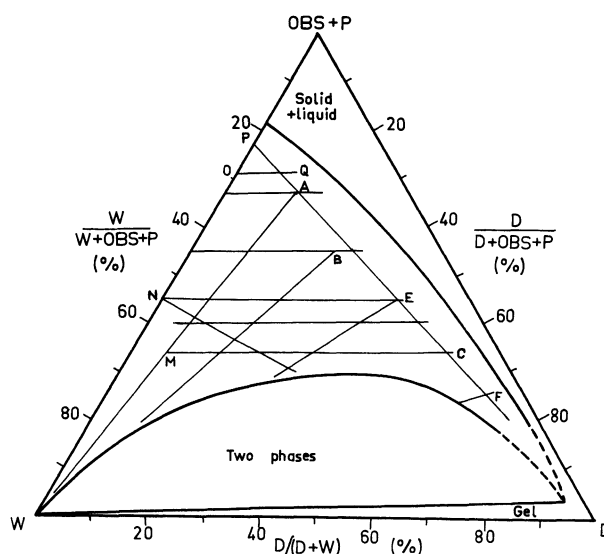


Fig. 1. — Phase diagram of decane (D)-water + 0.3% NaCl (W)-Na octylbenzene sulfonate (OBS)-pentanol (P) at P/OBS = 2.11 by weight (from [11-12]) and lines along which investigations have been made.

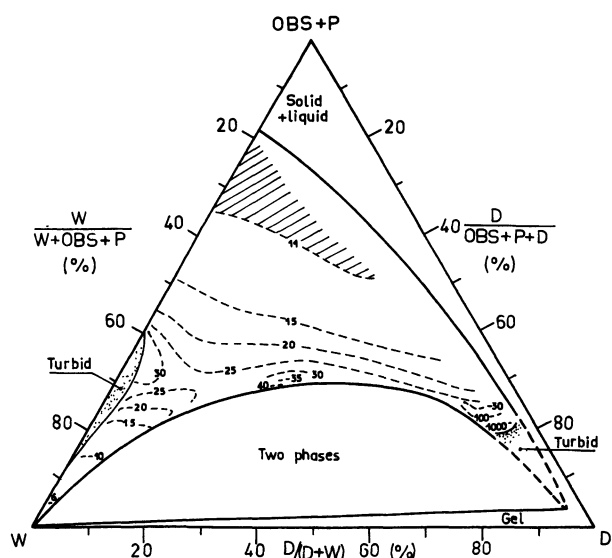


Fig. 2. — Lines of constant value of the Cotton-Mouton constant per OBS,  $C_M/C$ , in the homogeneous liquid region of the phase diagram ( $C_M/C$  values are expressed in  $10^{-6} T^{-2} cm^{-1} (M/l)^{-1}$ ).

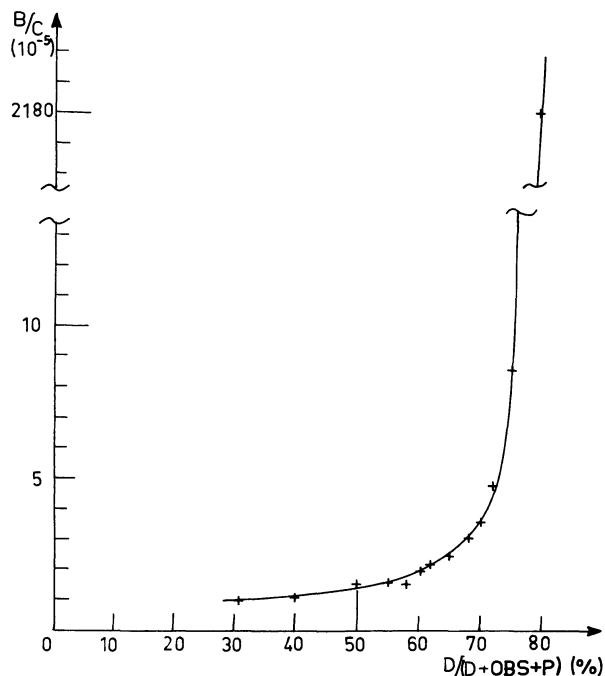


Fig. 4. — Kerr constant per OBS,  $B/C$ , as a function of decane concentration for a water concentration  $W/(W + OBS + P)$  of 23 % (line PD).

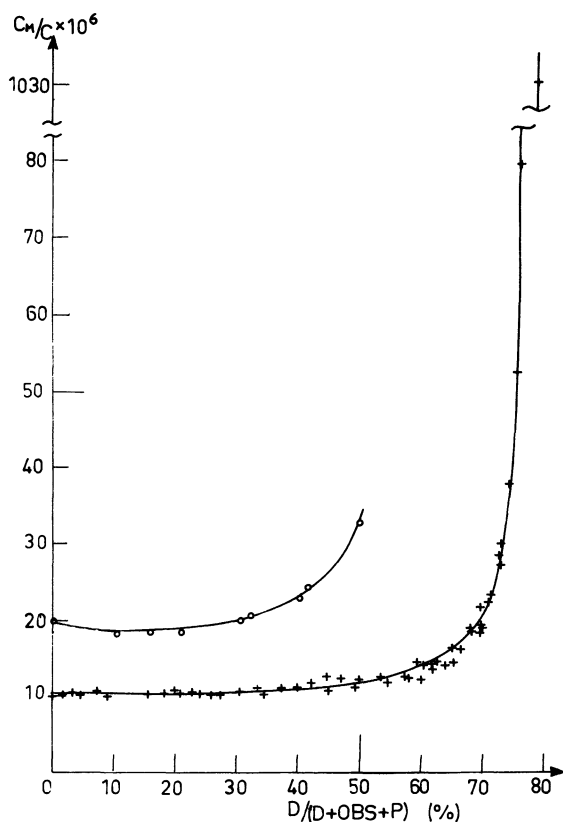


Fig. 3. — Cotton-Mouton constant per OBS,  $C_M/C$ , as a function of decane concentration for water concentration  $W/(W + OBS + P)$  of 23 % (+, line PD) and of 55 % (O, line ND).

OBS (line PD). The  $C_M/C$  value is almost constant when the decane proportion increases up to a decane volume fraction about 60 %. At higher decane contents  $C_M/C$  increases very steeply ( $C_M/C$  diverges as  $(C_0 - C)^{-1}$  with  $C_0 = 0.165 M/l$ ). A similar behaviour has also been observed in Kerr effect (Fig. 4). For volume fractions of decane more than 79 % the solution becomes turbid and highly viscous. This steep increase in  $C_M/C$  and  $B/C$  when approaching the turbid and viscous solution strongly suggests that it is a highly anisotropic and probably liquid crystalline phase, or possibly a mixture containing liquid crystals. Moreover very close to the concentration for which turbidity appears, the solution appears birefringent between cross polarizers even in the absence of any applied field. The presence of liquid crystals had not yet been observed in this region of the diagram for this system.

The plots of  $C_M/C$  versus the water concentration are given in figure 5 for various, constant, decane to surfactant ratios. Without decane (line PW) a similar steep increase of  $C_M/C$  is observed. Between 60 % and 87 % water the solution is highly viscous and turbid. This behaviour again indicates the existence of a very anisotropic ordered phase. For intermediate decane concentration (lines AW and BW) the Cotton-Mouton constant passes through a maximum. For higher decane concentration the  $C_M/C$  variation is monotonous, it increases as the two-phase region is approached (line WE). Furthermore as long as decane concentration increases the steep increase of  $C_M/C$  in the

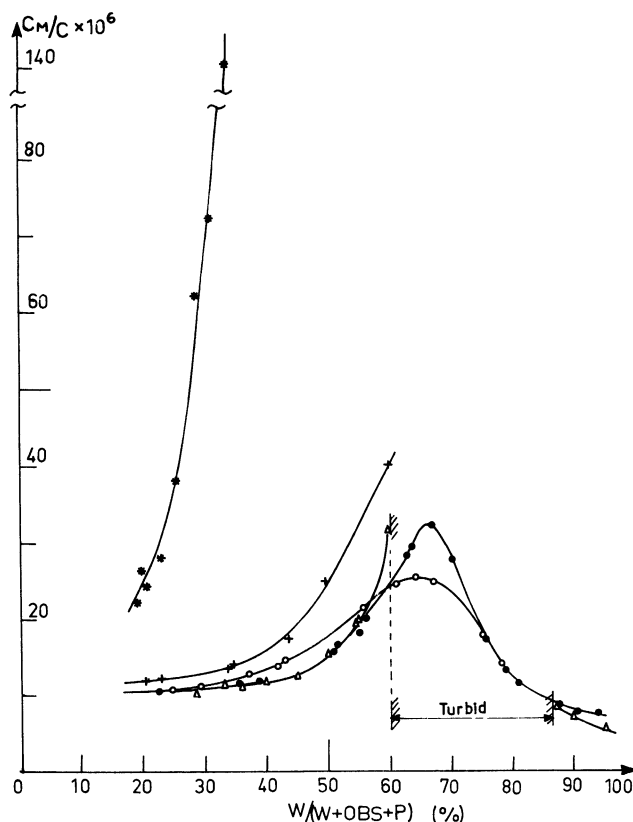


Fig. 5. — Cotton-Mouton constant per OBS,  $C_M/C$ , as a function of water concentration for the following decane concentrations  $D/(D + OBS + P)$  : ( $\Delta$ , 0%, line PW); ( $\bullet$ , 15.8%, line AW); ( $\circ$ , 32.4%, line BW); ( $*$ , 72.8%, line FW).

vicinity of the phase limit is more pronounced (line WF).

Summarizing all these results, one may distinguish four zones (Fig. 2) :

- a zone of very high  $C_M/C$  in the decane rich corner,
- a zone of low  $C_M/C$  in the water rich corner,
- a large central zone with low and slow varying  $C_M/C$ ,
- a transitional zone with higher  $C_M/C$  between the water corner and the central zone.

**4. Discussion.** — These results are discussed at two levels : first the four zones mentioned above may be related qualitatively to the structure of microemulsion. Second the values of the Cotton-Mouton constant are discussed in terms of orientation of anisotropic droplets and deformation of spherical droplets.

1) It has been proposed [4, 6] that the structure of microemulsion may be considered as an extension of the micellar structure observed for the ternary system water-pentanol-OBS. The phase diagram of this ternary system, in the case of water without salt, has been investigated by optical microscopy and X-ray measurements [19]. Following a line of constant pen-

tanol-OBS ratio of 7 in mole number in the direction of increasing water content one crosses an isotropic zone  $L_2$  (reversed micelles) a liquid crystalline phase and an isotropic zone  $L_1$  (direct micelles). On the corresponding line (PW), Cotton-Mouton results can be interpreted in a similar way. The two zones of small and almost constant  $C_M/C$  values can be associated with lightly anisotropic micelles. The intermediate zone, which shows high  $C_M/C$  values, is related to the liquid crystalline phase.

Addition of an hydrocarbon has been shown to lead to a dilution of the reversed micelles of the  $L_2$  phase and to a solubilization of the hydrocarbon in the direct micelles of  $L_1$  zone [4, 6]. Cotton-Mouton results are in agreement with such a description : direct micelles exist in the small zone in the water rich corner. The large central zone can be related to reversed micelles which are surrounded by a continuous phase over the full range from pure pentanol to a diluted pentanol solution in decane. The existence, in this central zone, of a bicontinuous structure as proposed from self-diffusion studies on the same system [11, 12] would also be consistent with our data : Cotton-Mouton measurements do not allow to distinguish between continuous or discontinuous structures. The Cotton-Mouton effect, however, shows that these two regions are separated by a region of higher anisotropy, which is related to the proximity of the liquid crystalline phase for the decane free system. This kind of inversion region had not been observed in self-diffusion and conductivity studies, because these methods are not very sensitive to anisotropy.

The liquid crystalline phase in the decane rich corner can be interpreted in terms of the decrease of pentanol amount in the surfactant film during dilution by decane : for small decane concentrations  $C_M/C$  only weekly depends on the decane content. This suggests that dilution of the external pentanol phase by decane does not modify the size and shape of the objects. On further dilution by decane the anisotropy increases (line PD) : pentanol dissolves progressively in decane and is lacking at the surfactant film ; this implies a transition from a closed almost spherical shape to a more anisotropic, lamellar like structure, because the effect of pentanol is, in general, to reduce micellar surface tension.

2) We estimate first the value of the Cotton-Mouton constant expected for an OBS monomer in a micelle as obtained from known  $\Delta\alpha$  and  $\Delta\chi$  values of individual bonds and molecular groups [20] using equation (1). The contributions of the phenyl ring and of the  $C_8$  chain to  $\Delta\alpha$  and  $\Delta\chi$  are calculated, assuming all trans conformations of the hydrocarbon tail and free rotation of the molecule about its long axis (Table I).

With  $n_0 = 1.33$  and  $\lambda = 0.6328 \times 10^{-4}$  cm we find  $C_M/C = 2.7 \times 10^{-6} T^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$ .

For an isolated OBS monomer, the expected Cotton-Mouton constant should not be very different from

Table I.

	$\Delta\chi$ (erg/T <sup>2</sup> )	$\Delta\alpha$ (cm <sup>3</sup> )
C <sub>8</sub> chain	$-1 \times 10^{-21}$	$3.9 \times 10^{-24}$
Benzene	$+4.5 \times 10^{-21}$	$3 \times 10^{-24}$
OBS	$3.5 \times 10^{-21}$	$6.9 \times 10^{-24}$

that of the octylbenzene which we measured to be  $5.5 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$ . This value is higher than that of OBS in a micelle due to the restricted rotation of this latter about its long axis.

From these values two conclusions may be drawn :

— For other microemulsions [4] in the zone of low water to surfactant ratios, free surfactant molecules, « ion pairs », have been proposed. We find in this zone an almost constant value of  $C_M/C$  of  $10.5 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$  which is about two or four times higher than the monomeric value estimated above. This strongly suggests the existence of higher aggregates : the sole presence of « ion pairs » seems unlikely. This agrees with conclusions from self-diffusion experiments [11].

— Furthermore, throughout the phase diagram, the observed  $C_M/C$  values are higher than both the estimated value for the free OBS molecule and the experimental value for spherical OBS micelles in water ( $C_M/C = 6 \times 10^{-7} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$  [21]). Thus, assuming that the orientation of micelles is exclusively responsible for the magnetic birefringence, it can be concluded that association does not result in spherical objects alone but always in anisotropic objects.

The existence of anisotropic droplets seems more obvious in the vicinity of the two-phase region because of the strong increase of the induced birefringence (line WE or DN and in particular WF in the decane rich corner). Anisotropic droplets are however inconsistent with the conclusions from other studies. When a dilution of a w/o microemulsion was made along the two-phase boundary (this corresponds to a dilution by a mixture alcohol-oil at constant ratio) monodisperse spherical droplets were postulated [8]. In order to elucidate this discrepancy two hypotheses will be examined : the anisotropy may be too weak to be detectable by the other techniques used or there is a contribution to  $C_M/C$  of deformation by the magnetic field.

i) The anisotropy of the droplets containing  $N$  monomers is represented by the effective parameter  $f$  as defined above.  $f$  is calculated using equation (4) [22].  $N$  results from experimental values on microemulsions with 20 water molecules per surfactant [9]. At a line close to the line DP, with  $50 \text{ \AA}^2$  for the area per monomer and a droplet radius  $50 \text{ \AA}$ ,  $N$  is about 630 monomers. With  $C_M/C \simeq 15 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$  (point C) this leads to  $f \simeq 10^{-1}$  and with  $C_M/C \simeq 40$  to  $100 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$  (near the two-phase region) to  $f \simeq 2 \times 10^{-1}$ . Thus, the anisotropy is

small and probably too weak to be seen by methods related to the dimensions of particules such as SANS [9, 10].

ii) We now estimate the magnetic birefringence due to deformation using equations (2, 4, 6, 7). With the numerical values cited above and using  $K = 5 \times 10^{-13} \text{ erg}$  (an order of magnitude observed in liquid crystals) we find  $C_M/C \sim 22 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$ . This is comparable to the experimental values. Thus as long as more reliable values for  $K$  are lacking, it is not possible to exclude a contribution of deformation to  $C_M/C$ . From this experiment, however, a lower limit of the elastic energy  $K$  may be evaluated. Observed  $C_M/C$  values are smaller than  $40$  to  $100 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$ , except in the proximity of liquid crystalline phases. The droplets contain at least 13 water molecules per surfactant so that the droplet radius is at least  $45 \text{ \AA}$ . Therefore  $K$  seems to be higher than  $0.8$  to  $2.1 \times 10^{-13} \text{ erg}$ . These  $K$  values are not very different from  $kT$  and thermal deformations of the micelles must also be taken into account.

The mean thermal deformation of the micelles, as estimated by putting the deformational energy [16] equal  $kT$ , is in the order of  $3 \text{ \AA}$  at  $r_0 = 50 \text{ \AA}$  with  $K = 5 \times 10^{-13} \text{ erg}$  or  $S_2 \sim 10 \text{ \AA}$  for the lowest possible value of  $K$  as given above. In comparison the magnetic deformation does not exceed some  $10^{-4} \text{ \AA}$  in 12 tesla. Hence magnetic deformation is only a small perturbation of thermal shape fluctuations and the thermal deformations themselves are not very large.

Under these circumstances it seems not obvious whether the Helfrich description, as developed for rigid large vesicles without thermal shape fluctuations is appropriate. It is noteworthy, however, that thermal deformations of the order of magnitude mentioned above may probably not result in a magnetic birefringence.

iii) One may also consider the limiting case of strong thermal shape fluctuations i.e. of a very flexible surfactant film. For this case de Gennes has introduced the concept of a persistence area  $\xi^2$  in analogy to the persistence length in semi-flexible polymers [23]. He defines a length  $\xi$  over which the directions of the normals of the surface elements are correlated because of the local stiffness of the film.  $\xi$  is related to the curvature elastic modulus  $K$  by :  $\xi = a \exp(2 \pi K/kT)$ ,  $a$  being a molecular dimension, hence  $a^2 = A$  the surface area per surfactant. The surfactant film may thus be considered as an ensemble of independent plates of surface  $\xi^2$ , each plate containing on the average  $\frac{\xi^2}{A} \sim \exp \frac{4 \pi K}{kT}$  surfactant molecules. This description is valid for flexible micelles ( $\xi \ll r_0$ ) and can also be applied to extended bicontinuous structures.

In analogy to the case of semi-flexible polymers [24] the magnetic field is supposed to orient these plates independently. Thus in this crude approximation the

Cotton-Mouton constant being proportional to the number of correlated molecules, may be given by equation (4) with  $f = 1$  and  $N = \xi^2/A$ . An experimental Cotton-Mouton constant of  $22 \times 10^{-6} \text{ T}^{-2} \text{ cm}^{-1} (\text{M/l})^{-1}$ , characteristic for our microemulsions in the central zone, leads to a value of  $K$  of  $7 \times 10^{-15} \text{ erg}$ , substantially smaller than  $kT$ . Hence, interpreting the magnetic birefringence this way, the surfactant film seems to be very flexible, indeed.

At present we are not able to distinguish between the three descriptions outlined above i.e. orientation of anisotropic rigid droplets, deformation of rigid droplets or orientation of plates representing a flexible surfactant film. Further investigations are necessary. In particular, since  $C_M/C$  varies with  $r_0^2$  in Helfrich's model, whereas it does not depend on the radius in de Gennes's model, magnetic birefringence experiments on well defined micelles at various  $r_0$  should be performed. We also believe that electric field effects, which were not extensively investigated in this work, are an interesting subject for further studies in particular with respect to the question of electric deformation and relaxation times.

**5. Conclusion.** — The Cotton-Mouton constant per OBS,  $C_M/C$ , has been measured in the homogeneous liquid region of the pseudo-ternary diagram. This

region can be divided into four zones, characterized by different values and concentration dependences of  $C_M/C$ : (1) a central zone with reversed micelles, (2) a water rich corner with direct micelles, (3) between these two zones a transitional zone of higher anisotropy, which is, for decane free system, a liquid crystalline phase, (4) in the decane rich corner another liquid crystalline structure has been observed.

Throughout the four zones, the experimental Cotton-Mouton constant is higher than the value expected for a single OBS molecule. This can be explained by the magnetic orientation of anisotropic rigid micelles, or of flexible film segments or by the magnetic deformation of rigid micelles. In the first case the estimated anisotropy of a 50 Å radius droplet is about 10%. The model of highly flexible surfactant film leads to a bending elastic constant  $K$  of the order of  $7 \times 10^{-15} \text{ erg}$ . In the latter case the magnetic deformation turns out to be only about  $10^{-4} \text{ Å}$  in 12 tesla and the bending elastic constant should not be smaller than  $8 \times 10^{-14} \text{ erg}$ .

**Acknowledgments.** — Fruitful discussions with P. G. de Gennes (Collège de France), B. Brun, P. Delord, F. Larche, J. Rouvière (Groupe de Dynamique des Phases Condensées, Montpellier) are gratefully acknowledged.

#### References

- [1] ROSOFF, M., *Prog. Surf. Membr. Sci.* **12** (1978) 405.
- [2] WENNERSTRÖM, H., LINDMAN, B., *Phys. Rep.* **52** (1979) 1.
- [3] HOAR, T. P., SCHULMAN, J. H., *Nature* **152** (1943) 102.
- [4] SJÖBLÖM, E., FRIBERG, S., *J. Colloid Interface Sci.* **67** (1978) 16.
- [5] RANCE, D., FRIBERG, S., *J. Colloid Interface Sci.* **60** (1977) 207.
- [6] FRIBERG, S., BURASCZENSKA, I., *Prog. Colloid Polym. Sci.* **63** (1978) 1.
- [7] SHAH, D. O., HAMLIN, R. M., *Science* **171** (1971) 483.
- [8] GRACIAA, A., LACHAISE, J., MARTINEZ, A., BOURREL, M., CHAMBU, C., *C.R. Hebd. Séan. Acad. Sci.* **B 282** (1976) 547.
- GRACIAA, A., LACHAISE, J., CHABRAT, P., LETAMENDIA, L., ROUCH, J., VAUCAMPS, C., BOURREL, M., CHAMBU, C., *J. Physique Lett.* **38** (1977) L-253.
- [9] DVOLAITZKY, M., GUYOT, M., LAGUES, M., LE PESANT, J. P., OBER, R., SAUTEREY, C., TAUPIN, C., *J. Chem. Phys.* **69** (1978) 3279.
- LAGUES, M., OBER, R., TAUPIN, C., *J. Physique Lett.* **39** (1978) L-487.
- [10] OBER, R., TAUPIN, C., *J. Phys. Chem.* **84** (1980) 2418.
- [11] LINDMAN, B., KAMENKA, N., KATHOPOULIS, T. M., BRUN, B., NILSSON, P. G., *J. Phys. Chem.* **84** (1980) 2485.
- [12] LARCHE, F., ROUVIERE, J., DELORD, P., BRUN, B., DUSSOSSOY, J. L., *J. Physique Lett.* **41** (1980) L-437.
- [13] SCRIVEN, L. E., in « *Micellization, solubilization and microemulsions* », Ed. K. L. Mittal (Plenum Press, New York) 1977, vol. 2, p. 877.
- [14] GRAY, F. W., GERECHT, J. F., KREMS, I. J., *J. Org. Chem.* **20** (1955) 511.
- [15] BEAMS, J. W., *Rev. Mod. Phys.* **4** (1932) 133.
- [16] HELFRICH, W., *Phys. Lett.* **43A** (1973) 409.
- [17] MARET, G., DRANSFELD, K., *Physica* **86-88B** (1977) 1077.
- [18] FILIPPINI, J. C., POGGI, Y., *J. Physique Lett.* **35** (1974) L-99.
- [19] LARCHE, F., *et al.*, Private Communication.
- [20] BOTHNER-BY, A. A., POPLE, J. A., *Ann. Rev. Phys. Chem.* **16** (1965) 43.
- STUART, H. A., *Molekül Struktur* (Springer, Berlin) 1967.
- DENBIGH, K. G., *Trans. Faraday Soc.* **36** (1940) 936.
- [21] PORTE, G., POGGI, Y., *Phys. Rev. Lett.* **41** (1978) 1481.
- [22] Form birefringence is negligible for both orientation and deformation. It has been evaluated according to PETERLIN, A., STUART, H. A., *Z. Phys.* **112** (1939) 129.
- [23] DE GENNES, P. G., Personnal Communication.
- [24] WILSON, R. W., *Biopolymers* **17** (1978) 1811.