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Water in oil microemulsions of the potassium oleate/hexanol/n-dodecane/water system: A magneto-optical investigation

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Abstract: The optical effects induced by a magnetic field up to 0.8 tesla in a potassium oleate/hexanol/n-dodecane/water microemulsion system of the phase diagram monophasic region (w/o type) are investigated at constant alcohol/surfactant and active mixture/oil ratios vs. the increase of the water content. A small variation of the light polarization state with characteristic times of several minutes is observed. An analysis has been done to characterize the phenomenon. No magnetic birefringence is detectable, but a depolarization of the light occurs in crossing the sample. The role of both temperature and magnetic field is investigated. A sample-magnetic field interaction, due to the small but finite conductivity of the microemulsion, cannot be excluded; however, the temperature seems to play the main role and the resulting thermal stabilization of 0.5 °C is not accurate enough to investigate phenomena which are clearly of a hydrodynamic nature.

Key words: Ionic microemulsion, potassium oleate, magneto-optical effects, hydrodynamics, thermal diffusion.

Introduction

Microemulsions are homogeneous transparent dispersions of either water-in-oil or oil-in-water, stabilized by an amphiphilic film. For recent revision of the field, see references [1–3]. The microemulsion studied in our laboratory [4–6] is a potassium oleate/hexanol/n-dodecane/water system exhibiting a large monophasic domain of w/o type in the pseudoternary phase diagram [7] with the constant alcohol/surfactant ratio = 1.6 wt/wt. The investigation regards samples with the constant active mixture/oil ratio = 0.41 wt/wt studied as a function of increasing water concentration up to the one preceeding the occurrence of lyotropic mesophases. In this paper, we report an investigation about the optical effects induced in this microemulsion by a magnetic field up to 0.8 tesla, using a set-up like the one employed for the detection of the Cotton-Mouton effect. Magnetic and electric birefringence studies on different w/o microemulsion systems have been performed by several authors [8–12] with the aim of obtaining structural information; the induced birefringence being interpreted in terms either of deforma-

tion of microemulsion globules or orientation of globule aggregates and/or of parts of the interfacial film. In our case only a small variation of the light polarization state has been observed (with characteristic rise and decay times of the order of several minutes) which cannot be described in terms of the above mentioned magnetic birefringence. The analyses done to characterize the phenomenon and to present evidence for the parameters which play the main role are here reported.

Experimental

Materials

n-dodecane was used as supplied by Merck while the n-hexanol (Merck) was distilled. Water was of Super-Q-Millipore grade filtered through a 0.2 μm Millipore Millistak-GS-filter. Potassium oleate of 99.7 % purity was prepared by reaction of equimolar amounts of oleic acid (Riedel) and KOH (Riedel) in hot ethanol. After evaporation of ethanol, the solution was cooled to promote crystallization. The product was washed twice with acetone and five times with diethyl ether; after filtering it was dried in vacuo. Samples with the ratios hexanol/K-oleate = 1.63 wt/wt and (hexanol plus K-oleate)/n-dodecane = 0.41 wt/wt have been studied by increasing the

water content from above the CMC [7] ($c > 0.10$) to $c = 0.36$ (where c is the weight ratio, water : total).

Method

The typical Cotton-Mouton effect set-up is used for the detection of the magneto-optical effects. Linearly polarized light with its plane of polarization at $\pi/4$ with respect to the direction of the magnetic field enters the cell containing the isotropic microemulsion sample. An analyzer having the optical axis at $\pi/2$ (with respect to the polarizer optical axis) stops the light. In case the magnetic field induces birefringence, the light leaves the sample elliptically polarized and the light intensity (I) measured by the detector is given by [13]:

$$I = I_o \sin^2 (\delta/2) \qquad (1)$$

where I_o is the light intensity incident on the sample and δ is the phase shift between the components, respectively parallel and perpendicular to the magnetic field direction, of the polarized light after leaving the cell. The phase shift depends on the induced birefringence (Δn) according to the relation $\delta = (2\pi/\lambda)\, l\Delta n$ with λ wavelength of the laser beam and l length of the light path within the cell. In the Cotton-Mouton effect [14] Δn is given by $\Delta n = C\lambda H^2$ with H field intensity; C is a constant which depends on the diamagnetic susceptibility and the optical polarizability anisotropies of the orientating object (molecules, molecular aggregates or microemulsion droplets, etc.).

A block diagram of the experimental set-up is shown in Figure 1. The sample is contained into a Hellma glass cell (C) of polarimeter quality and internal dimensions 1 cm^2 × 4 cm, closed by a teflon plug. The sample holder device is thermally controlled by a Haake thermostat (T). The sample temperature is $T = 23\,°C$. Thermal gradients have been measured inside the cell by means of a thermocouple; the vertical gradient is $\sim 0.02\,°C/cm$, the temperature

being higher in the middle of the cell, in correspondence with the optical windows (0.6 cm wide and 1 cm high); the horizontal temperature differences are smaller than 0.01 °C. Furthermore a 0.4 °C temperature increase was directly measured by a platinum probe placed into the cell, during an experimental run with a 1 h field application time. The static magnetic field is produced by a Varian 4005 electromagnet (EM). The field intensity is measured by a Hall probe (Siemens SV 210) previously calibrated by comparison with a gaussmeter (accuracy $\pm$ 2%). Fields up to 0.8 tesla were used, the pole-piece gap being 50 mm; field uniformity within the cell better than 1%. A He-Ne laser beam (NEC, 5 mW polarized) enters: a beam splitter (BS) for continuous recording of the beam intensity by means of the power meter PM2; a total reflecting prism (R), a polarizer (P), the cell (C), an analyzer (A), a light spatial filter (F) (microscope objective of 8 mm focal lenght plus 25 μm pin-hol), a power meter PM1. P and A are high quality 10 mm Glan-Laser prisms (Karl-Lambrecht); to rotate the prism a micrometric device is used (angular accuracy $\simeq 3\ 10^{-4}$ rad). A mechanical apparatus orient the cell with respect to the field and to the laser beam directions. The light spatial filter increases the signal to noise ratio of the transmitted beam [15] leading to a ratio between light intensity at crossed and parallel polarizers equal to 10^{-7} (100 times smaller than without it). The power meter PM1, built in the laboratory using a large area silicon photodiode (Hamamatsu S 875-1010) in photovoltaic mode, is completely controlled by an internal microprocessor; it measures the photodiode electric current (range $10^{-8} \div 10^{-3}$ A, full scale; minimum measurable current is 10^{-11} A) or the light intensity (in watts) directly. The calibration was made by comparison with an EG & G (model 460) power meter. The linearity of the instrument is better than 1% up to 10^{-3} A; absolute accuracy of the current measurements on the lower scale, $\pm$ 3%, and on the other scales, $\pm$ 1%; absolute accuracy on the intensity values, $\pm$ 10%. An analog to digital converter (A/D) sends the electric signals (respectively proportional to the incident and transmitted light intensities) to a HP 9816 S desk computer (MC) for data acquisition and numerical elaboration.
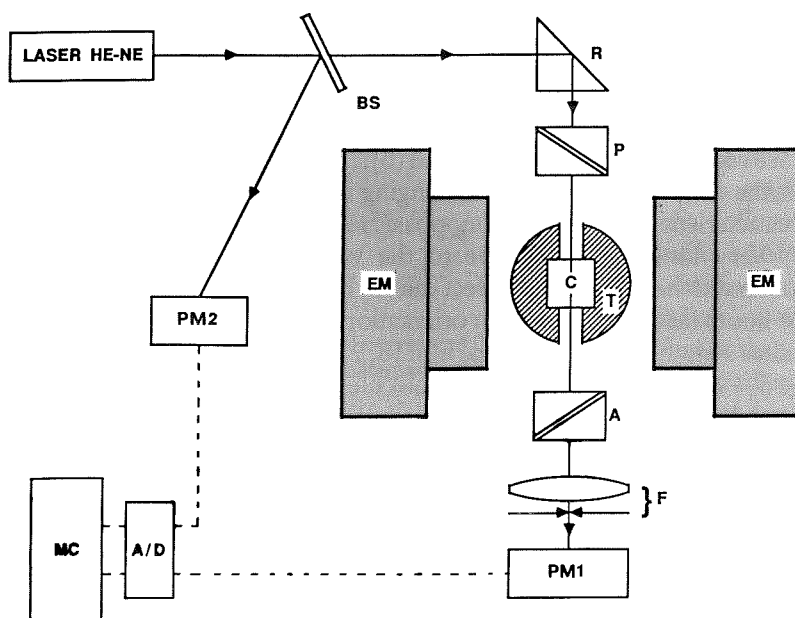

Fig. 1. Block diagram of the experimental set-up for magneto-optical measurements (see text)

An accurate matrix analysis of birefringence measurements is given in Reference [16]. The schematization of the cell as a linear retarder, δ_r being the residual phase shift, is reasonable for polarimeter cells with thin glass windows if a small spot beam enters the cell [16], as it does in our case. Because the residual light intensity measured at crossed polarizers arises from both the apparatus background component and the cell stress-induced birefringence, the light intensity difference (ΔI), due to the sample induced birefringence, for small δ and δ_r, results consequently:

$$\Delta I \simeq I_o\,\delta/2\,(\delta/2 + \delta_r) \qquad (2)$$

at a second order approximation. Because the term linear in δ may be important also for small δ_r values, the residual light must be as small as possible. δ_r, evaluated using Equation (1), is $\sim 10^{-3}$ rad. As the relative sign of δ with respect to δ_r is not known, the value of the birefringence as low as 10^{-7} can be given with an accuracy of 10% and the minimum measurable birefringence is of the order of 10^{-8}. To test the apparatus, the nitrobenzene Cotton-Mouton constant has been measured with the maximum available magnetic field intensity; the correct order of magnitude was obtained. The alignment accuracy introduces an indetermination in the optical path length inside the cell smaller than that specified by the factory (0.01 mm). The stability of the instruments as well as the mechanical stability were tested over time intervals longer than those used during the measurements. The samples were hermetically closed and no change in the light intensity value was recorded in the absence of magnetic field.

Results and discussion

Typical curves of the light intensity transmitted at crossed polarizers (I) vs. time (t) are reported in Figures 2 and 3 (the arrows correspond to the field switching on ($\uparrow$) and off ($\downarrow$)). In Figure 2, the $I(t)$ curves for a single sample $(c = 0.26$ wt/wt) are reported at different magnetic field intensities (0.56 tesla, 0.70 tesla and 0.81 tesla, respectively, for (a), (b) and (c) curves). In Figure 3, $I(t)$ curves for samples at different concentrations belonging to the microemulsion monophasic region of the phase diagram are reported (field intensity 0.81 tesla). For all the curves, the sample temperature was $T = 23\,°C$. The main characteristics of the phenomenon are as follows: (1) Very long response time, (2) no signal saturation observed for any of the tested samples, even for a three hours field application, (3) exponential signal decay after switching off the field (time constant in the range $5 \div 10$ min for all the samples) except in some cases where an oscillatory trend appears superimposed to the curve. In any case, the light intensity with parallel polarizers showed no change because of the applied field over the whole field application time. As no instantaneous variation was observed on the $I(t)$ curves after the application of the field, the birefringence either linked
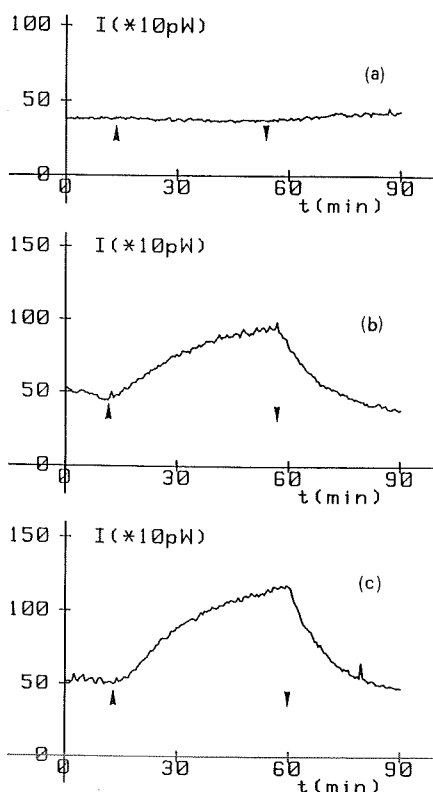

Fig. 2. $I(t)$ plots of a microemulsion sample with $c = 0.26$ wt/wt and $T = 23\,°C$ for different magnetic field intensities: (a) 0.56 tesla; (b) 0.70 tesla; (c) 0.81 telsa. Field switching on and off correspond to arrows up and down, respectively, for all the figures

to distortion or to orientation, induced by the magnetic field, must be lower than 10^{-8}, the limit of resolution of the apparatus.

We will now focus our attention on curves (b) and (c) of Figure 2 and (b), (c) and (d) of Figure 3, obtained for samples belonging to the central part of the phase diagram monophasic region and for which the trend is similar. Due to the very long response times, the observed effect cannot be ascribed either to a deformation or to an orientation of the globules and of parts of the interfacial film [8, 9], as expected, because the system contains molecules with a too low diamagnetic susceptibility anisotropy $(\Delta\chi)$. We recall that field strengths in the range $2 \div 20$ tesla have been used to induce a magnetic birefringence on microemulsions having surfactant molecules with high $\Delta\chi$ value. The first problem is to distinguish between birefringence and light depolarization. In fact, in both cases, we expect an $I(t)$ increase for the given position of the
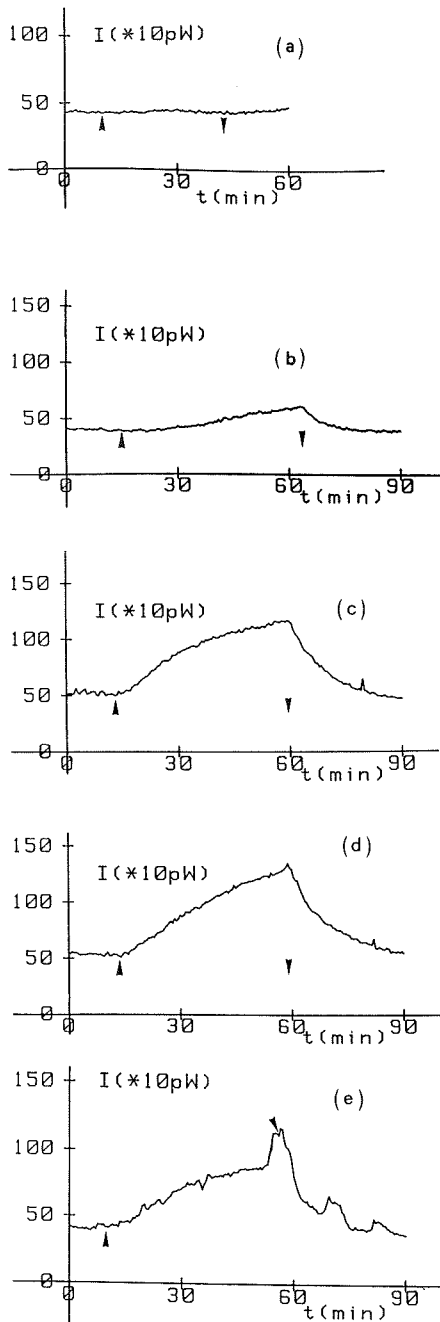
Fig. 3. $I(t)$ plots with a magnetic field intensity of 0.81 tesla at $T =$ 23 °C for microemulsion samples at different concentrations of the phase diagram monophasic region (a) $c = 0.12$; (b) $c = 0.22$; (c) $c = 0.26$; (d) $c = 0.31$ and (e) $c = 0.36$ (proportions given in wt/wt)

polarizers optical axes. Under the hypothesis of bire-fringence, we expect to observe no $I(t)$ variation ($I(t)$ always being the light transmitted at crossed polarizers) when the incoming polarization plane is at $\pi/2$

with respect to the magnetic field direction; on the contrary an $I(t)$ variation similar to that under discussion was indeed detected, indicating that the observed phenomenon is mainly due to a light depolarization in crossing the sample. On the other hand, experimental misleading effects, such as slow drifts in the electronics or the mechanical set-up, as well as modification of the sample during the experiment, have been excluded after very careful controls (see Method).

The fact that the phenomenon is related to a light depolarization excludes the occurrence of any aniso-tropic state induced by the applied field within the sample. The small observed temperature changes inside the sample (see Method) may be responsible in producing motions within the sample which could explain the phenomenon. We recall that in a pure fluid layer of thickness a, convective instabilities develop only when heating is done from below, for a tempera-ture difference (ΔT) such that the Rayleigh number is higher than 1708 [17]. For heptane, with $\Delta T = 0.03$ °C and $a = 1.4$ cm, the Rayleigh number is lower but close to the threshold value (1650). For a microemulsion, in analogy with the behaviour of mixtures, a convective instability may also occur when heating is done from a-bove and with a critical ΔT drastically lower than for a pure fluid [18,19]. For a sample far from a critical point and a phase transition, a 0.5 °C thermal stabilization is usually considered to ensure that the sample is stable; however, thermal diffusion and convective instabilities are likely to occur in this case, due to the measured horizontal and vertical thermal gradients. A thermal diffusion effect (Soret effect) has been experimentally observed, e.g. in macromolecular solutions [20] far from a critical point, with a vertical gradient of a few °C/cm. By measuring the vertical index of refraction gradient over times of the order of 1 h, a very rapid variation was observed due to the thermal expansion of the sample for the step-wise rise temperature gradi-ent, followed by a very slow variation, due to the build-up of the thermally induced concentration gradi-ents; for a thermal diffusion ratio $k_T < 0$, a convective instability was finally observed over very long periods (more than 90 min) which destroyed the concentra-tion gradient. In order to verify whether thermal diffu-sion or convective motion occurs within the sample, we performed an interferometric analysis by means of a point diffraction (Smartt) interferometer (Ealing) [21]. The interferometric pattern has been observed before and during the measurements; no change of the index of refraction was detected over the whole sample window in the limit of resolution of the apparatus

($\sim 10^{-5}$). Therefore no macroscopic motion has been observed, even though we cannot exclude motions over smaller spatial scales, involving very low index of refraction variations for which a more sensitive method should be used.

Returning to Figure 2, the $I(t)$ variation increases as the field intensity increases, at constant thermostat temperature and field application time. However, this fact cannot be completely and certainly ascribed to the effect of the field, as the sample temperature shows small (max. 0.4 °C) but systematic variations with the field intensity. On the other hand, should we exclude the temperature changes effect, the only possibility of a sample-magnetic field interaction could be through the small but finite conductivity of the microemulsion sample [22, 23]. In principle we cannot exclude that, because of the thermal gradients, the ions in the microemulsion interact with the field itself; however, the magnetic field has a damping effect on the motion of a conductive medium, hence, it should have a stabilizing effect. Thus, the existence of a field threshold is probably due to the smaller heating of the electromagnet at lower field intensity.

In Figure 3 $I(t)$ curves for samples at different concentrations are reported for a constant field intensity and identical field application time. The existence of a threshold concentration, below which no effect is detectable, is clearly shown; a low variation of $I(t)$ is displayed at concentration $c = 0.22$ wt/wt (curve b). On the $c = 0.12$ wt/wt concentration (curve a), tests were repeated in different thermal gradient conditions, with no appreciable change in the results.

A peculiar behaviour is displayed by the sample with concentration value (0.36 wt/wt) close to the phase transition towards the liquid crystalline state. The occurrence of oscillations superimposed to the usual trend suggests that some kind of instability develops within the sample; however, we could not detect any macroscopic convection with the Smartt interferometer over periods of several hours. Oscillatory trends have also been observed for lower concentrations during longer periods of measurement.

In conclusion, despite being unable to exclude a sample-magnetic field interaction, the temperature seems to play the main role in the reported experiments and the thermal stabilization of 0.5 °C is not accurate enough to investigate phenomena which are clearly of hydrodynamic nature.

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