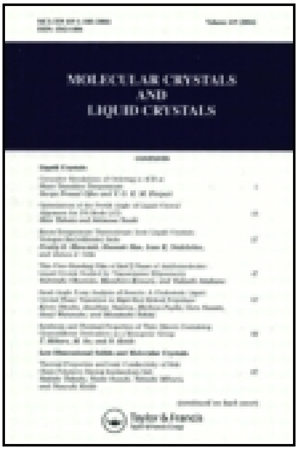

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Experimental Observation of Sessile Water Droplets in Nematic-Water Mixture Cells

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An experimental phenomenon – formation of small (3–5 microns) sessile water droplets attached to the glass plates of the liquid crystal cells with either 96.42 wt % Merck 997–3.58 wt % water mixture or 96.80 wt % Liquid crystal 440–3.20 wt % water mixture after the heating-cooling cycle through the clearing point has been observed. The effect can be enhanced by use of either lecithin dissolved in the liquid crystal, or polyvinyl alcohol (PVA) dissolved in the water. In these cases the number of the sessile water droplets increases and their radius decreases. The sessile water droplets disturb the initial homeotropic orientation of the nematic Merck 997-water mixtures and many cross-like or more complex birefringent patterns are observed. When the orientation of the liquid crystal is planar at both surfaces (Liquid crystal 440-water mixture) one observes the formation of *Schlieren*textures. This effect is explained by phase separation of that part of the water which has been dissolved in the liquid crystalline matrix. The effect of the phase separation of the water is accompanied by increase of the clearing point which can reach that of the pure liquid crystal.

Keywords: nematic-water; mixture; sessile water droplets; phase separation

INTRODUCTION

The experimental and theoretical investigation of the physico-chemical properties of water is of great importance for life, science and technology. Recently one notes an extensive study of the water behavior at various surfaces [1,2]. Water has also been used in some experiments performed with liquid crystals. For instance, Le Roy et al [3] and Candau et al [4] investigated the behavior of nematic droplets dispersed in water or in other isotropic liquids. Proust et al [5] studied in an important paper the behavior of thin nematic layers disposed onto water layer. Blank et

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* Corresponding Author.

al [6] examined the influence of a small amount of water, approximately 1 wt %, on the electro-optical characteristics of nematic cells working in a dynamic scattering mode (DSM). There is a considerable interest in the behavior of inverted and multiplied nematic emulsions. They have been extensively studied both experimentally [7,8] and theoretically [7,9–12]. Inverted nematic emulsion can be prepared when water droplets are dispersed in a nematic host. On the other hand, water droplets suspended in much larger drops of liquid crystal, which are in their turn suspended in water, determine the multiplied nematic emulsions. The interaction of water droplets or other colloidal particles with the nematic host, displaying well-known anisotropic properties, leads to interesting and sometimes surprising effects some of which are observed experimentally [7,8,15] and described theoretically [7–15]. For instance, if single water droplet is introduced into a nematic monodomain with tangential orientation of the director **n** on the bonding surfaces and if one determines a strong tangential anchoring of the nematic on the water surface, the interaction between the water droplet and the nematic host leads to the formation of two surface point defects called *boojums* [7,8,13]. Inversely, if one determines a strong homeotropic anchoring of the nematic on the water surface, the interaction between the water droplet and the nematic host leads to the formation of an accompanying bulk point defect called *hedgehog* [7–12]. Sometimes instead *a hedgehog* one can form a disclination ring which in certain cases can encircle the water droplet at its equator. In this case the disclination ring has been called *Saturn-ring*disclination[9,12–14]. The behavior of the surface and bulk point singularities as well as of the ring disclinations has been extensively studied both theoretically and experimentally [16–39]. These defects are called topological since they are formed under topological constraints. When two or more water droplets are dispersed in the nematic host and the accompanying point singularities are *hedgehogs*, one observes the formation of linear chains of droplets. This arrangement is due to both the long-range dipole-dipole attraction and to the short-range repulsive interaction which prevent contact of the droplets, stabilising them against coalescence [7–10,12]. A pair of water droplet-*hedgehog*forms the well-known dipole [7–12] which is analogous to the −1 surface point-air bubble dipole observed by Meyer [18] and Saupe [20]. When there are *boojums* the water droplets are arranged in another, more complex way, explained in detail by Poulin and Weitz[8]. All the experimental results hitherto reported have been obtained with planar nematics strongly anchored on the glass plates of the cells with either normal or tangential anchoring of the nematic on the water droplets achieved by adding a small amount of various surfactants [7,8].

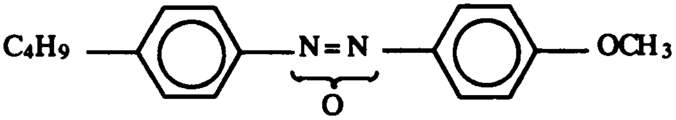
The aim of this paper is to present our experimental observations of the formation of sessile water droplets of diameter ranging between 1.5 and 5 microns which are attached to the glass plates confining the liquid crystal-water mixture. The condensation of the sessile water droplets usually occurs when the liquid crystal-water mixture is heated above the nematic-isotropic phase transition and then cooled back to the nematic phase. The glass plates are not treated and show a hydrophobic behavior. Sometimes they displayed in certain places a hydrophilic character. In these cases we have observed the formation of thin water layer instead of the sessile water droplets. This experimental fact was confirmed by an additional experiment when the glass plates were treated with soap. In this case water wets very well the glass plates and the sessile water droplets were replaced by the formation of a continuous water layer which converted the initial homeotropic orientation of the nematic into a tangential one. In some places however, we have still observed the formation of sessile water droplets evidently attached to hydrophobic places. It is important to note that originally we have observed the formation of sessile water droplets in pure nematic-distilled water mixtures. Since the sessile water droplets formed during the experiment were hardly visible even in a convergent light (see the description of the experimental results) and since we did not know the orientation of the liquid crystal under study on the water droplets, we have decided to use some surfactants which should enhance the observed effect and which can uniquely determine the orientation of the liquid crystal on the water droplets[7,8]. The homeotropic orientation of the liquid crystal on the water droplets was achieved by adding of a small amount of lecithin (approximately 0.1 wt %) dissolved in the liquid crystal. The tangential or planar orientation of the liquid crystal on the water droplets was achieved by 1 wt % polyvinyl alcohol (PVA) dissolved in the previously distilled water. The quantity of the phase separated water is different and critically depends on the time duration of the isotropic phase of the liquid crystal under study and on the value of the temperature which was reached in the nematic phase after the isotropic-nematic phase transition. The manner of the phase separation of the water from the liquid crystalline matrix resulting in the number of water droplets connected evidently with their size depended crucially on the utilisation of additional surfactants [7,8]. It should be pointed out however, that the process of the phase separation of the water initially dissolved in the liquid crystalline matrix was accompanied in all cases by an increase of the clearing temperature of the liquid crystal which can reach that of the pure liquid crystal. The appearance of the water droplets was followed also by disturbance of the initial homeotropic orientation of the nematic which in crossed linear polarizers results in the formation of cross-like domains, or in some cases, of more complex birefringent textures. Evidently, some of the cross-like domains are accompanied by the formation of *boojums*. However, they cannot be simply identified since the water droplets are observed from above (We thank to the Referee of Molecular Crystals & Liquid crystals for this remark [88]). We expose a number of microphotographs which reveal the effect of the phase separation of water, initially dissolved in the liquid crystalline matrix. Finally, we discuss this effect from a simple physicochemical point of view and compare our experimental observations to some experimental results and theoretical considerations of other authors.

MATERIALS, SAMPLE PREPARATION AND METHOD OF STUDY

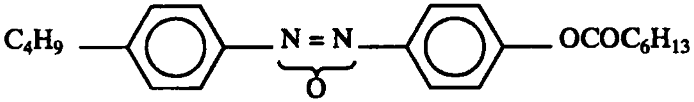
The main experimental investigations are performed with the nematic mixture **Merck** 997 (Licrystal Art 11894 produced in 1976) prepared for a dynamic scattering mode with a negative dielectric anisotropy and the following phase transition temperatures:

$$C < -10°C - N - 78{,}36°C - I \tag{1}$$

Since we did not know the exact chemical composition of the liquid crystal Merck 997, we have also investigated the behavior of a mixture consisting of water and the known liquid crystal 440, produced in Russia[40,41]. This liquid crystal is an isomeric mixture of (2/3) p-n-butyl-p'-methyloxy-azoxybenzene:



and (1/3) p-n-butyl-p'-heptanoyloxy -benzene:



This liquid crystal possesses the following phase transition temperatures:

$$C - (-20°C) - -4°C - N \quad -75°C - I \tag{2}$$

where the possible supercooling temperature is given in the brackets. Some of the material parameters of this mixture, known as a mixture A as well, can be found in the book of Blinov[42], they are:

$\rho = 1.108$ (g/cm^3); $\varepsilon_{\|} = 4.85$; $\varepsilon_{\perp} = 5{,}25$; $\Delta\varepsilon = -0.4$;

$\Delta n = 0.238$; $K_{11} = 8.5 \times 10^{-7}$ dyn; $K_{22} = 7.2\times10^{-7}$ dyn and $K_{33} = 10.3\times10^{-7}$ dyn.

The liquid crystal cells were prepared with soda-lime glass plates of dimensions 15/15/0.5 (in mm) which are not previously treated. The preliminary cleaning of the glass slides was achieved with a distilled water and acetone. We have avoided the use of a chromic acid [43] because it can ruffle the initial smooth surfaces of the glass plates. At first we investigated a mixture 1: 96.42 wt % Merck 997–3.58 wt % distilled water. This mixture was carefully homogenised by vigorously shaking the sample (see also Reference 8). Usually the energy supplied is sufficient to overcome both the interfacial and the elastic energies required to suspend the small water droplets. However, in some cases many water droplets are attached to the glass slides. In addition, some water droplets fused and formed large water regions. The thickness of the empty and filled samples was measured by micrometer with an accuracy of two microns. Since we did not utilise spacers, the capillary forces have determined the thickness of the investigated cells which was around 10 microns. The nematic phase of the liquid crystal Merck 997 was oriented homeotropically on such glass plates. The experiment was performed within a given temperature interval starting at room temperature and ending at temperatures above the nematic-isotropic phase transition. Sometimes we raised the temperature up to 130 °C. To change and control the temperature, the sample was placed on a hot stage (Mettler FP 83) designed with an electronic regulator (made in the Institute of Solid State Physics, Sofia) and a digital thermometer (a Bulgarian product) which shows the temperature with accuracy of 0.01 °C. The observations are performed with polarising microscope MPI 5. We have also investigated a mixture 2: 96.80 wt % Liquid crystal 440–3.20 wt % distilled water. Additionally [44], we have prepared a mixture 3: 95.57 wt % Merck 997–4.33 wt % distilled water-0.1 wt % lecithin (the lecithin was first dissolved in the liquid crystal) and a mixture 4: 96.00 wt % Merck 997–3.96 wt % distilled water-0.04 wt % polyvinyl alcohol (PVA) (1 wt % PVA was dissolved in 99 wt % distilled water)..

EXPERIMENTAL RESULTS

The main feature of the experimental observations, as noted in the Introduction, is the appearance of water sessile droplets attached to the glass plates of the liquid crystal samples as a result of a special change (increase followed by a subsequent decrease) of the temperature around the nematic-isotropic phase transition. Our observations were performed both in parallel or crossed linear polarizers.

First, we started at room temperature. Part of the cell filled with a mixture 1 is shown in Figure 1. Only individual water droplets and large water regions are visible on this microphotograph taken in crossed linear polarizers. In parallel linear polarizers, however, one notes many condensation centers. These centers serve as nucleating centers around which the sessile water droplets are formed. They are clearly visible in Figures 2 and 3 which show the nematic-isotropic phase transition ($T_{N\text{-}I} = 77.02°C$) and the isotropic-nematic phase transition

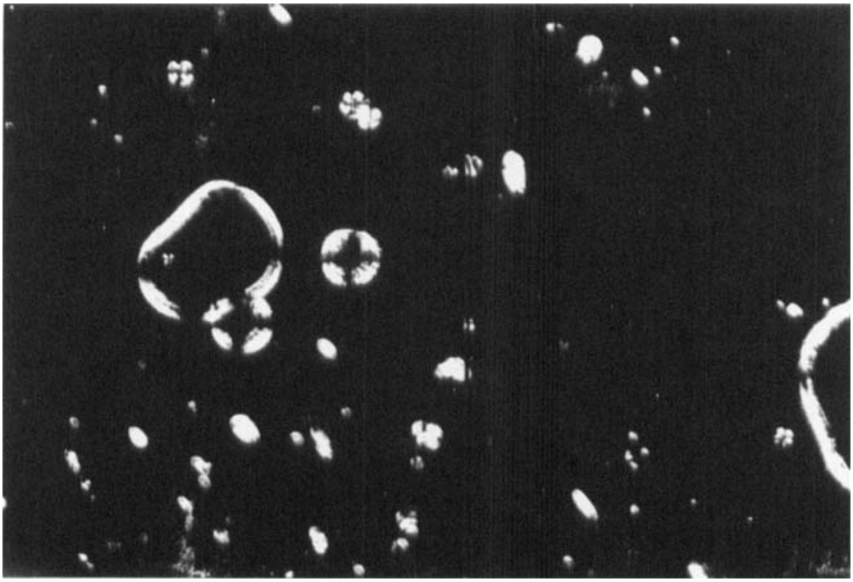


FIGURE 1 A region of a 96.42 wt % 997 Merck – 3.58 wt % water mixture in a cell 1 before the nematic – isotropic phase transition. Crossed linear polarizers, T = 28.31°C. The long side of the photomicrograph corresponds to 800 microns

($T_{I\text{-}N}$ = 77.09 °C), respectively. The nucleating centers are also clearly seen in Figure 4 at a temperature of 75.30 °C. Evidently, they are fixed to the rough points of the glass slides [45,46]. It is necessary to point out that the water droplets situated around large water regions are formed under other circumstances and they not reveal our effect. A further decrease of the temperature manifests the appearance of many sessile water droplets with a diameter between 3 and 5 microns. These water droplets disturb the initial homeotropic orientation of the nematic which results in the appearance of many cross-like domains visible in crossed linear polarizers, as shown in Figure 5 (T=58.5°C). Further decrease of the temperature results in some enhancement of the optical picture. This process is illustrated in Figure 6 (T = 37 °C). A small region of Figure 6 is taken at a bigger magnification. It is shown in Figure 7. The repetition of the heating-cooling cycle through the clearing point leads to an increase of the clearing point of the nematic. The same result can be obtained with the increase of the time duration of the isotropic phase of the liquid crystal. For example, one needs only several minutes to reach the clearing point (T = 78.36 °C) of the pure nematic. The increase of the value of the clearing point unambiguously shows that there is a process of phase separation of that part of the water which has been dissolved in

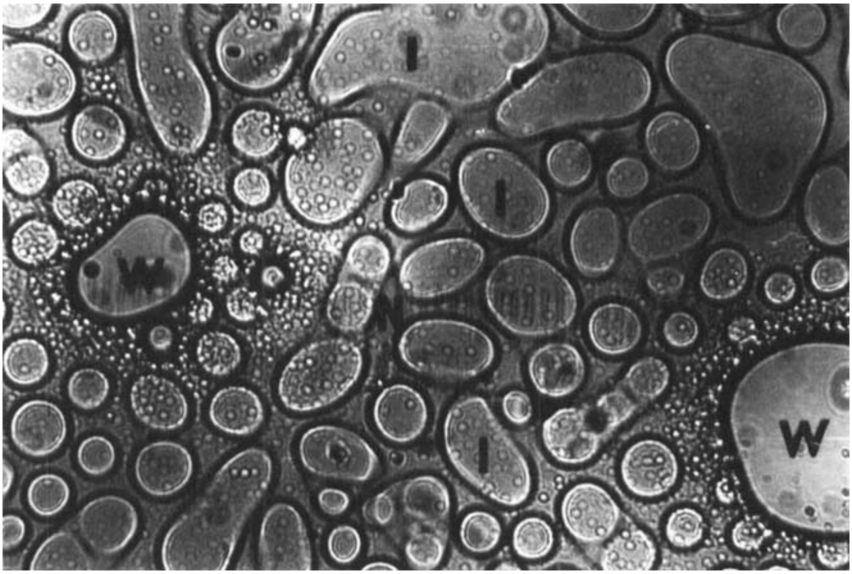


FIGURE 2 The region of the liquid crystal – water mixture shown in Figure 1 in parallel linear polarizers at T = 77.02°C. One observes the nematic – isotropic phase transition and the nucleating centers around which the sessile water droplets grow. Letters W, N and I designate corespondingly water, nematic phase and isotropic phase

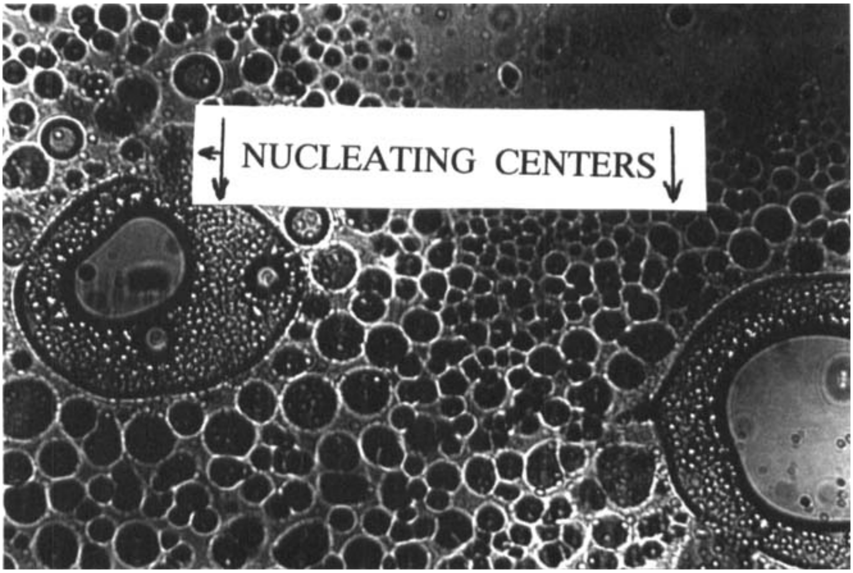


FIGURE 3 The same region at T = 77.09°C

the liquid crystalline matrix. Roy et al[3] and Blank et al [6] have also observed a decrease of the clearing point of the nematics studied in their experiments when water participates as a host [3] or as an additive [6]. Furthermore, the heating of the sample up to 130 °C led to the condensation of a great number of sessile water droplets whose diameters was between 2 and 5 microns. To check the reproducibility of the effect we have prepared a second sample with the same mixture 1 of Merck 997 and distilled water. The aim of these additional observations was to prove the reproducibility of the effect and to show more interesting pictures. In some cases of observations the condenser of the polarising microscope was posed very close to the sample in order to observe the picture in a convergent light and to obtain a highest maximum contrast. At a normal position of the condenser the samples are viewed in a collimated (nearly parallel) light [18]. Due to the different optical indices of water (n = 1.3330 at λ = 5893 Å, T = 20 °C [47]) and the maximal optical indices of the liquid crystal, for instance MBBA: methoxybenzylidene-para-butylaniline ($n_e = 1.769$ at λ=5890 Å, T = 22°C and $n_o = 1.549$ at λ = 5890 Å, T = 22 °C [48]) we have observed the volume relief of the sessile water droplets. It should be noted that this is not possible for an arbitrary three-dimensional liquid crystal picture. It is worthwhile to mention here that water droplets obtained by water vapour condensation on a hydrophobic glass plate [49], or on a methylated quartz surface [50], as well as nitrobenzene droplets obtained by condensation of nitrobenzene on a lyophilised glass surface [51], or the ordered arrays of diethylene glycol droplets on a gold substrate [52] are seen is some cases better than the water droplets observed in our experiment. The reason is that all these droplets have been obtained in better circumstances without the use of a cover slip (compare the sessile water droplets with the nematic droplets observed in Reference 53 obtained in a similar experiment of a phase separation of two nematics). The microphotograph shown in Figure 8 is taken at a temperature of 28 °C in crossed linear polarizers, 24 h after cooling the sample below the temperature of the nematic-isotropic phase transition. The condenser of the microscope is close to the sample. The same picture looks in a different way when the polarizers are parallel. This is shown in Figure 9. The microscope is focused at the upper glass plate of the sample. A select region from Figure 8 with clearly visible sessile water droplets is enlarged photographically 1.5 times and is shown in Figure 10. Another region of Figure 8 is taken at a bigger magnification (about 3 times) and the picture is shown in Figure 11. Here we see a great number of birefringent patterns accompanying the sessile water droplets some of which have a size of 2 microns. Additionally, a region from Figure 11 is enlarged photographically 1.5 times; it is shown in Figure 12. *Boojums* are probably seen in Figures 11 and 12. In addition, another region from the cell 2, viewed in crossed linear polarizers, is shown in Figure 13. One can see in a convergent light many sessile water droplets and accompanying cross-like domains.

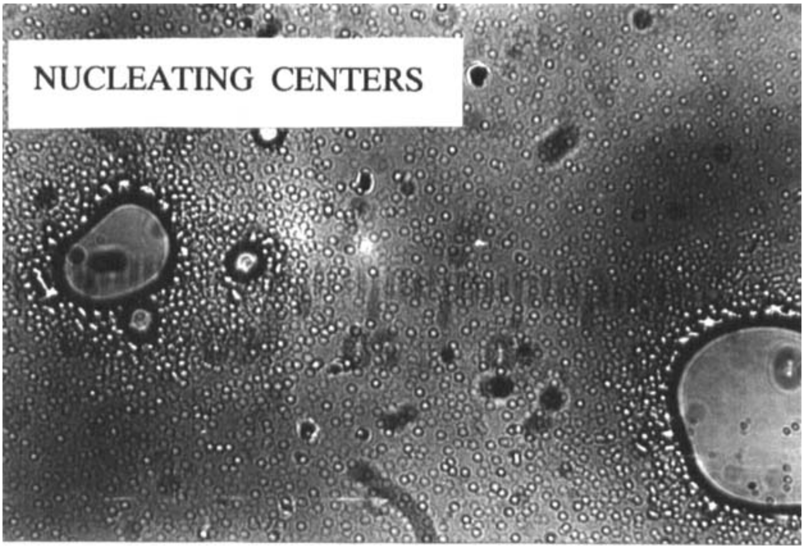


FIGURE 4 The region of the liquid crystal – water mixture shown in Figure 1 viewed in parallel linear polarizers after the isotropic – nematic phase transition at T = 75.30°C. One observes the nucleating centers around which the sessile water droplets grow

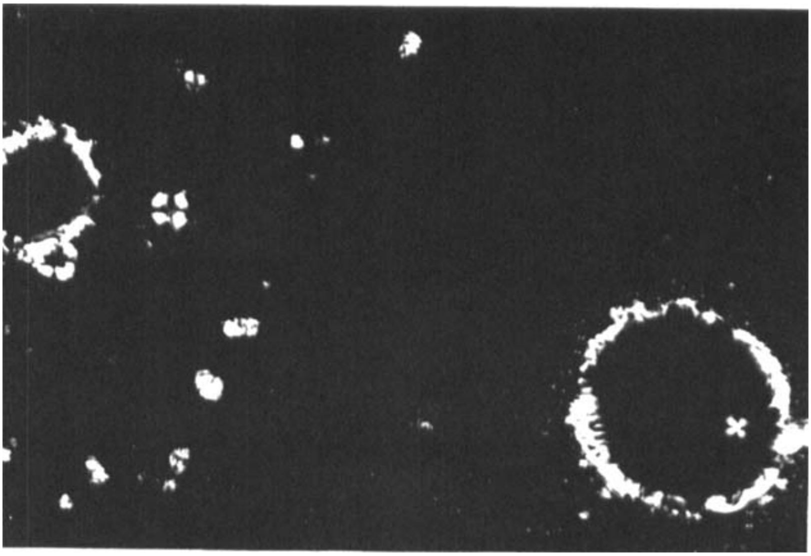


FIGURE 5 The region of the liquid crystal – water mixture shown in Figure 1 (with a slight translation) in crossed linear polarizers after the isotropic – nematic phase transition at T = 58.50°C. One observes the growing of the water droplets revealed by the cross-like domains

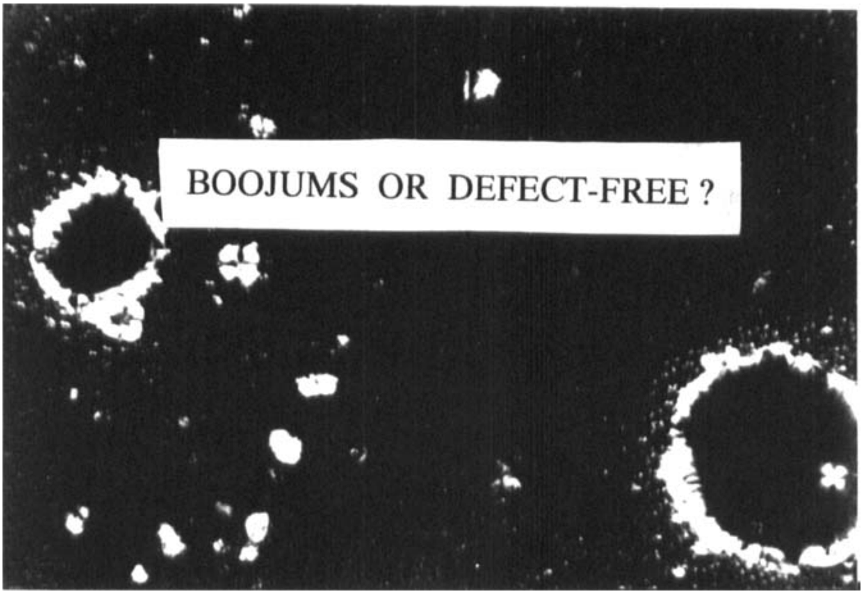


FIGURE 6 The region of the liquid crystal shown in Figure 5 at T = 37°C. One observes that the number of the cross-like domains increases and covers the whole area

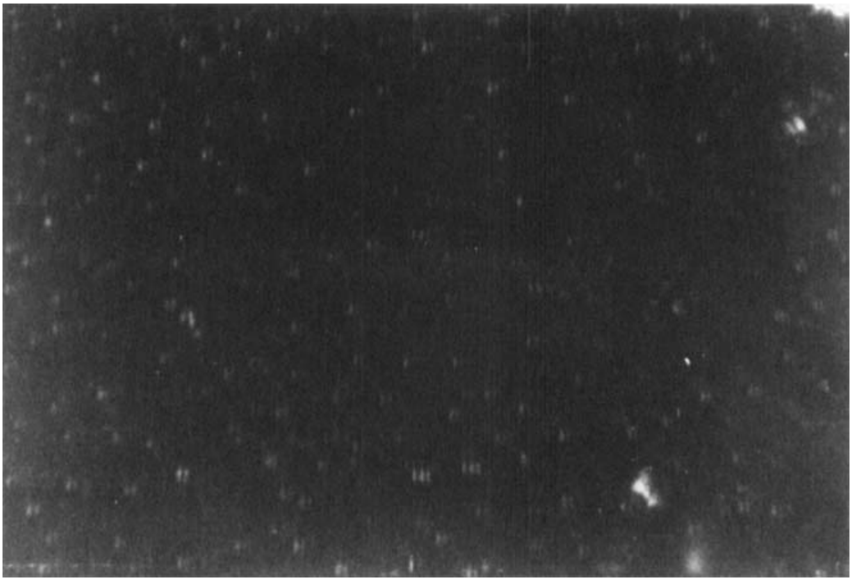


FIGURE 7 A small region of the Figure 6 at a big magnification. The long side of the photomicrograph corresponds to 250 microns. One oserves the cross-like domains

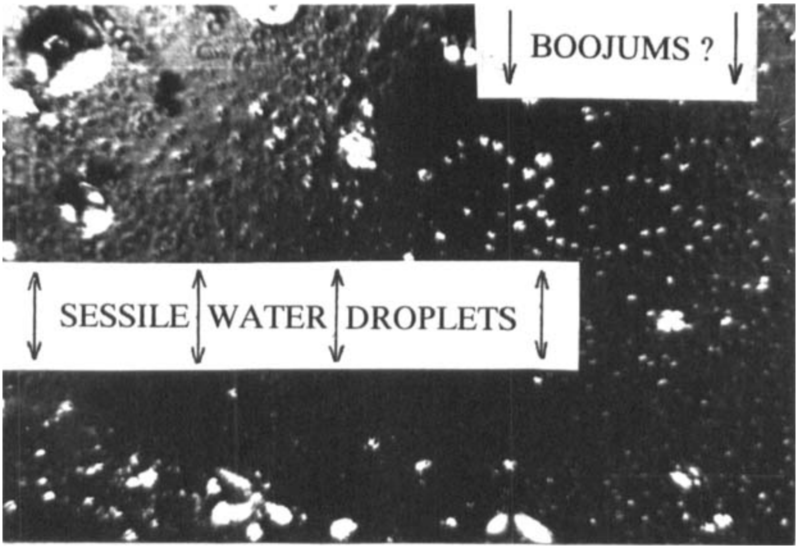


FIGURE 8 A region of a 96.42 wt % 997 Merck – 3.58 wt % water mixture in cell 2 viewed in crossed linear polarizers at T = 28°C, 24 hours after the isotropic-nematic phase transition. The condenser of the microscope is in upper position, close to the sample. One observes sessile water droplets and cross-like domains. Some of these domains probably incorporate in their structure boojums. The long side of the microphotograph corresponds to 1060 microns

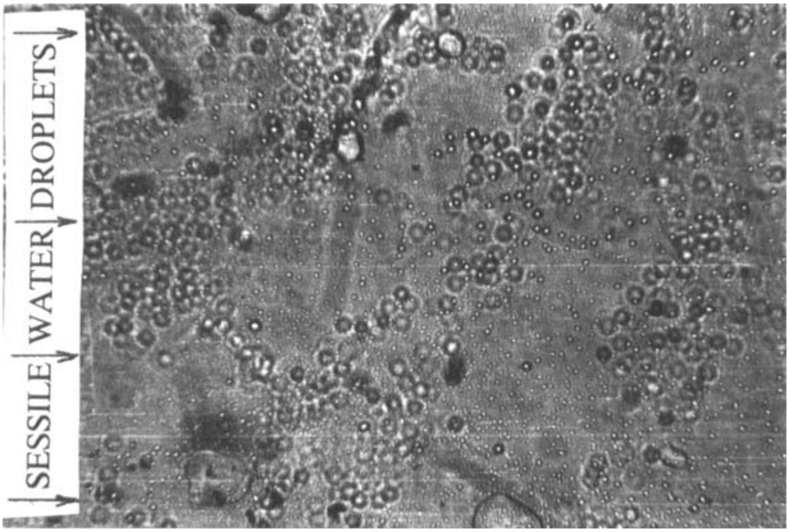


FIGURE 9 The region of the liquid crystal-water mixture shown in Figure 8 viewed in parallel linear polarizers at T = 28°C. One observes many water droplets of various sizes

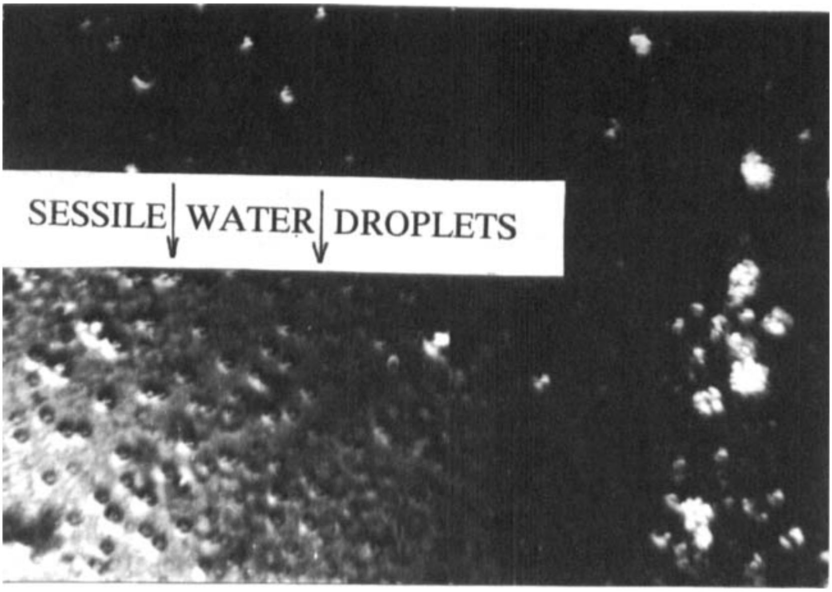


FIGURE 10 A region of Figure 8 enlarged photographically 1.5 times. The long side of the microphotograph coresponds to 707 microns

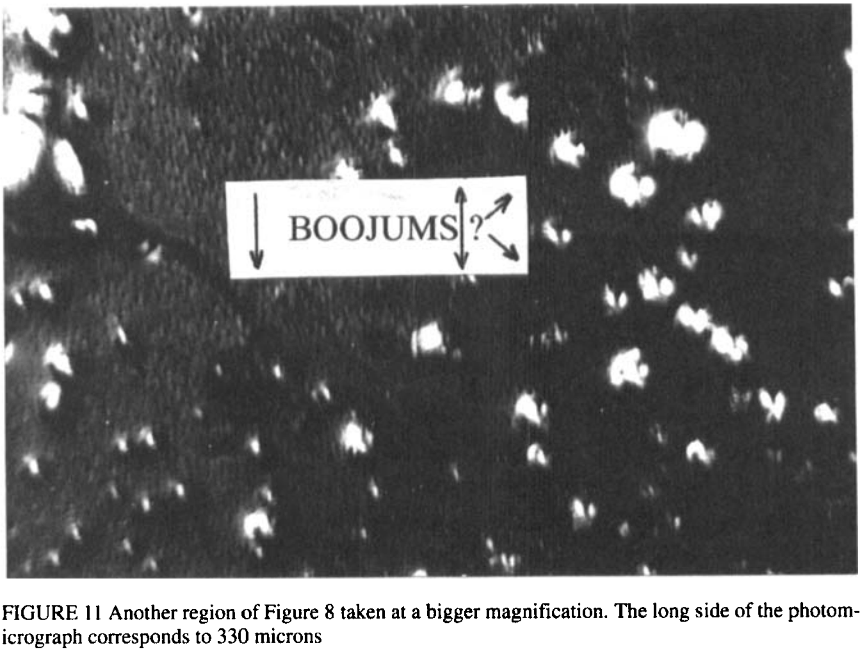


FIGURE 11 Another region of Figure 8 taken at a bigger magnification. The long side of the photomicrograph corresponds to 330 microns

FIGURE 12 A region of Figure 11 enlarged photographically 1.5 times. The long side of the photomicrograph corresponds to 220 microns

We have performed additional experimental observations with the mixture 2 consisting of 96.80 wt %. Liquid crystal 440 – 3.20 wt % distilled water. This liquid crystal orients itself planar on the same glass plates utilised in the cell 1 and the cell 2. When it cools from the isotropic phase down to the nematic phase one observes the formation of *Schlieren* texture which gradually converts into a

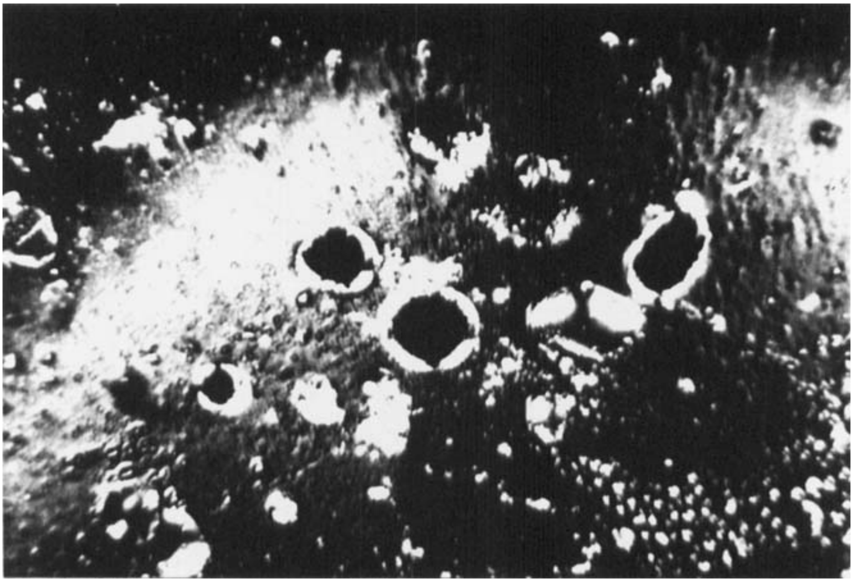


FIGURE 13 Another region in cell 2, viewed in crossed linear polarizers at T = 28°C, 24 h after the isotropic-nematic phase transition. The condenser of the microscope is in upper position, close to the sample. One observes sessile water droplets and cross-like domains. The long side of the microphotograph corresponds to 1060 microns, transition

mosaic texture. During the experimental study of this mixture we have observed the same effect: dissolution of part of the water accompanied by a decrease of the clearing temperature down to 68.5 °C and phase separation of the water from the liquid crystal after the heating-cooling cycle through the clearing point. Due to this phase separation the rise of the clearing temperature was by several degrees (in grad C) and we have observed the formation of a great number of sessile water droplets attached to the glass plates. Instead of cross-like domains however, we have observed a beautiful *Schlieren* texture which remained stable for a long time. The *Schlieren* texture was stable since some of the sessile water droplets have been incorporated in its structure. Furthermore, we have observed that the raising of the temperature above the clearing point enlarges the volume of the free water droplets due to the increase of the pressure, an experimental fact which was observed with the Merck 997-water mixture as well. However, the sessile big and small water droplets attached to the glass plates did not change with the temperature increase. This experimental fact clearly shows that the pressure due to the curvature effects and the ability of wetting can not be overcome by the pressure due to the expansion of the water.

As noted in the Introduction, since the sessile water droplets were hardly visible even in a convergent light, and since we did not know the orientation of the liquid crystal on the water droplets, we have decided to use some surfactants. They, according to the results of other authors[7,8], should enhance the process of the formation of water droplets through their stabilisation and they should also determine the orientation of the nematic on the water surface of the droplets. Consequently, we have used the available lecithin for the achievement of homeotropic orientation and a polyvinyl alcohol (PVA)[7,8] for the achievement of planar orientation of the nematic on the water droplets. The additional experiment [44] was performed with another two cells. The third cell (cell 3) consisted of 95.57 wt % Merck 997–4.33 wt % distilled water-0.1 wt % lecithin mixture. The additional experimental results are shown in Figures 14 to 19 for various regions taken in crossed or parallel linear polarizers. These microphotographs clearly show that the use of lecithin facilitates the formation of both the bulk water droplets and the sessile water droplets which are very clearly seen. Furthermore, the cross-like domains shown in Figure 14 look in a different way (compare for instance with the cross-like domains shown in Figures 6 and 7). In addition, the microphotographs shown in Figures 16and 18 clearly depict that there are hydrophilic regions. In these regions the phase separated water is disposed on the glass plate as a very thin layer which, however, is able to orient the nematic tangentially (see the bright regions in the microphotographs). In order to check this experimental fact additional cell was made [54] with glass plates treated with usual soap. The water wets very well such glass plates. The Merck 997-water-lecithin mixture confined between soap-treated glass plates displays the same effect after the heating-cooling cycle through the clearing point: increase of the clearing temperature and phase separation of the water which, 8°C – 10°C below the isotropic-nematic phase transition, orients tangentially the liquid crystal. Since the glass plates were not treated to determine one preferred direction, large planar not oriented domains of the nematic were observed which were of the size of several hundred microns. The orientation of the liquid crystal on water surfaces will be discussed at length in the next paragraph. On the other hand, the behavior of the 96.00 wt % Merck 997–3.96 wt % distilled water-0.04 wt % PVA mixture (PVA was first dissolved in the distilled water) resembles that of the Merck 997-water-lecithin mixture. In both cases the surfactant (lecithin or PVA) facilitates very much the formation of bulk and sessile water droplets. In both cases the nematic-isotropic and the isotropic-nematic phase transitions are accompanied with the formation of many small sessile water droplets with a diameter between 1.5 and 3 microns. This usually occurs 8°C – 10°C below the isotropic-nematic phase transition. If the liquid crystal-water mixture is held several minutes in the isotropic phase of the liquid crystal, passing to the nematic phase is accompanied with phase separation of the whole water dissolved in the liquid crystal. There is, however, one difference manifested in the birefringent patterns which show the liquid crystal orientation around the sessile water droplets. For the case of PVA they are simple cross-like domains, whereas for the case of lecithin they are in some cases more complicated (see Figure 14). On the other hand, in both cases the sessile water droplets look in a similar way between parallel linear polarizers (see Figure 15). The cross-like domains, accompanying the effect observed with the Merck 997-water-PVA mixture, are visible only at a big magnification of 200–250. Nevertheless they were very clearly visible in crossed linear polarizers at normal position of the condenser. It seems that the PVA facilitates not only the formation of the sessile water droplets but also increases the surface energy of interaction between the nematic and water which evidently determines in this case tangential or planar orientation of the liquid crystal on the water [8].

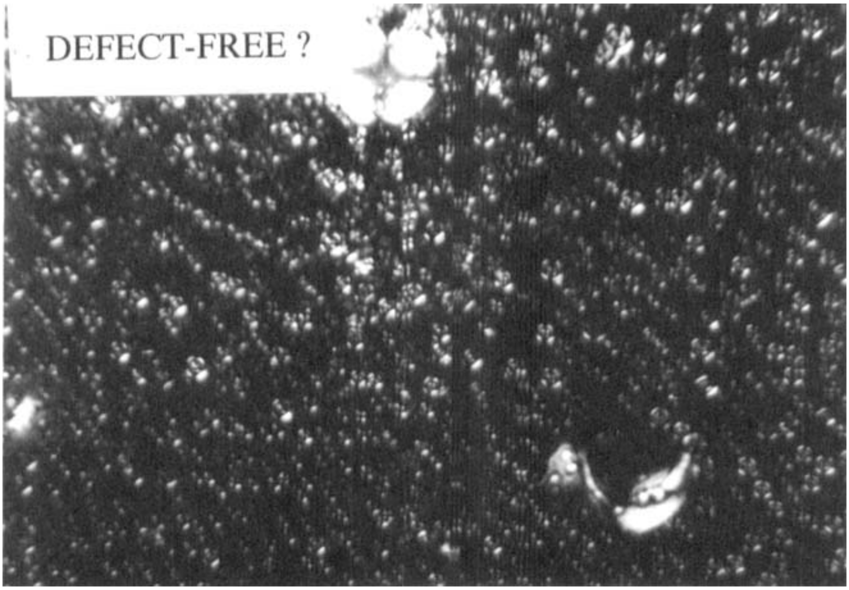


FIGURE 14 A region of a 95.57 wt % Merck 997 – 4.33 wt % distilled water – 0.1 wt % lecithin mixture in cell 3 viewed in crossed linear polarizers at T = 20°C, two hours after the isotropic-nematic phase transitions. One observes cross-like domains and more complex birefringent patterns. The long side of the microphotograph corresponds to 220 microns

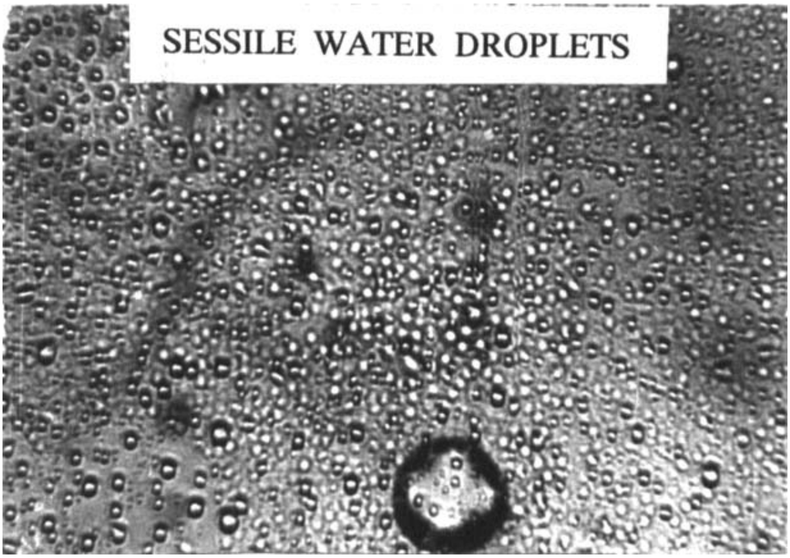


FIGURE 15 The region of the liquid crystal-water-lecithin mixture, shown in Figure 14, viewed in parallel linear polarizers. One observes the sessile water droplets formed at the two glass plates. The microscope is focused at the upper glass plate. The long side of the microphotograph corresponds to 220 microns. The size of the sessile water droplets is in the range of 1.5–3 microns

FIGURE 16 Another region in cell 3 viewed in crossed linear polarizers at T = 20°C, two hours after the isotropic-nematic phase transition. The long side of the photomicrograph corresponds to 410 microns

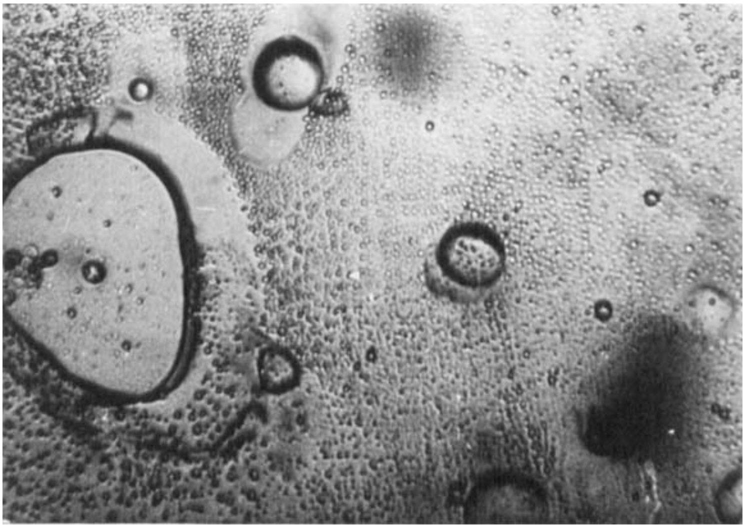


FIGURE 17 The region of the liquid crystal-water-lecithin mixture shown in Figure 16 viewed in parallel linear polarizers at T = 20°C. The long side of the photomicrograph corresponds to 410 microns. The size of the sessile water droplets is in the range of 1.5–3 microns

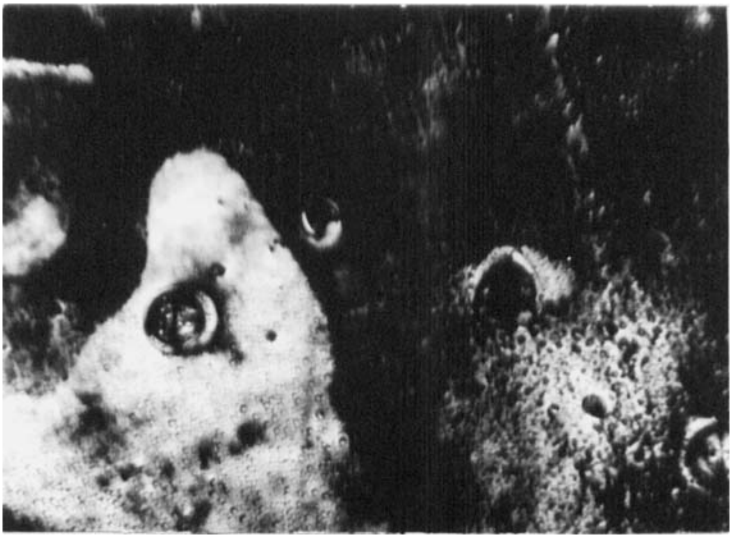


FIGURE 18 A region of the liquid crystal-water-lecithin mixture of cell 3 viewed in crossed linear polarizers at T = 20°C, two hours after the isotropic-nematic phase transition. The bright regions unambigously demonstrate the tangential orientation of the liquid crystal under the influence of the thin water layers formed in some hydrophilic parts of the glass plates. The long side of the microphotograph corresponds to 410 microns

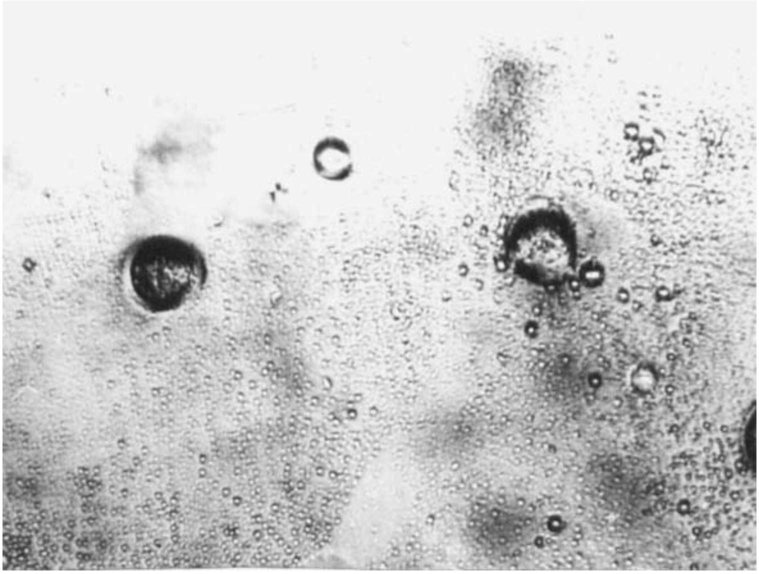


FIGURE 19 The region of the liquid crystal-water-lecithin mixture shown in Figure 18 viewed in parallel linear polarizers at T = 20°C. The size of the sessile water droplets is in the range of 1.5–3 microns. The long side of the microphotograph corresponds to 410 microns

DISCUSSION OF THE EXPERIMENTAL RESULTS

In the papers published for usual and inverted nematic emulsions one investigates either the behavior of nematic droplets dispersed in water or glycerine [3-5] or, inversely, one investigates the behavior of water droplets dispersed in a nematic [7–9]. There are, however, less papers devoted to the study of sessile droplets of water or other liquids[49–53,55–58]. In the best of our knowledge there are no papers studying sessile water droplets in liquid crystal-water mixtures. Our experimental observations clearly show that part of the water (below 1 wt %) can be dissolved in the liquid crystalline matrix. There are a number of papers devoted to the problem of dissolution of nonmesomorphic solutes in the liquid crystal [59–63]. For instance, Schadt [59] and Schadt and Mueler [60] investigated experimentally the influence of solutes on the material constants of the liquid crystal and on the electrooptical properties of twisted nematic displays. The solutes usually decrease the width of the nematic temperature interval and the value of the various physical parameters such as dielectric constant, viscosity, elastic coefficients etc. Similar experimental results have been obtained by Martire et al [61] and Kronberg et al [62]. Indeed, Le Roy et al [3] and Blank et al [6] have noticed the decrease of the nematic temperature interval and the value of the material parameters of the nematic. Normally one accepts that water destroys the chemical stability of the liquid crystals. Contrary to this widely accepted opinion, Kimura et al [64] have discovered the formation of liquid crystal-water-liquid crystal complexes (2:1 complexes) or water-liquid crystal complexes(1:1 complexes). The liquid crystal, the well-known 8CB (4′-octyl-4-cyanobiphenyl), has been studied in the smectic A phase. The quantity of the water has been one water molecule per 90 molecules of the liquid crystal 8CB. On the other hand, Huhnerfuss [65] has determined the hydrophobic and hydrophilic hydration effects by surface potential measurements. According to this author the following groups are hydrophilic: -N=N-, -COOH, -COO- etc. Consequently, on the basis of these important experiments and on the experimental phenomenon observed in our study, we can conclude that part of the water molecules find hydrophilic groups and free space to incorporate themselves into the liquid crystalline matrix [64–66]. The second important experimental fact which has been pointed out by Kimura et al is that the hydrogen bonds between water and the CN group of the liquid crystal 8CB are fairly weak. Consequently, we can accept that the hydrogen bonds between the water molecules and the hydrophilic parts of the molecules of the liquid crystals used in our experiment are also fairly weak and can be destroyed above the clearing point. The phase separated water is condensed on the glass plates. It is clear that we cannot discuss the observed effect in terms of pure water evaporation since the water is placed at unusual circumstances. It is evident, however, that the curvature pressure inside the sessile water droplets, irrespective of their radius, is bigger than the value of the atmospheric pressure [67]. This fact was proved in our experiment by raising the temperature up to 130°C. The shape of the sessile water droplets, irrespective of their radius, did not change and the water inside these droplets is evidently superheated [68]. It seems that the water molecules separated from the liquid crystalline matrix behave as vapour near the glass plates where their concentration is big which leads to the formation of the sessile water droplets [69,70]. We will not discuss in detail how the sessile water droplets are growing on the glass plates, which is a complex phenomenon indeed [71–74].

Further, we will discuss the formation of the sessile water droplets from a simple physicochemical point of view by the Young-Boruvka-Neumann law [75,76]:

$$-\sigma_{\alpha\beta}\cos\theta + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma} + \tau/r = 0 \tag{3}$$

where $\sigma_{\alpha\beta}$, $\sigma_{\alpha\gamma}$ and $\sigma_{\beta\gamma}$ are the surface tension of the following interfaces: liquid crystal – water droplet, liquid crystal – solid and water droplet – solid, respectively, τ is the line tension at the three-phase contact line and r is the radius of the circle, projected on the plane of the glass plates from the inner part. (We adopt the notation used by Widom [77]).

It gives the relation between the physicochemical quantities which determines the wettability of the surface (the value of the angle θ) and the shape of the sessile water droplets (see Figure 20b and Figure 20c). It should be noted that the line tension introduced for the first time in the law of Young by Boruvka and Neumann [76] and studied by many authors [5,50,55–58,78] is of great significance for the formation of sessile water droplets. Proust et al[5] have suggested that the value of the line tension can be important for the nucleation phenomena at the glass slides. Widom[77] has performed exact theoretical calculations for the effect of the line tension on the contact angle θ (see Figure 20) including the free energy of the system. The main result obtained by Widom (see Figure 2 in Reference 77) which can be applied in our experimental observations consists in the existence of a critical radius below which droplets with a positive line tension cannot be spread on the interface, when the dimensionless parameter:

$$\bar{\tau} = \frac{\tau}{\left(\frac{3V}{\pi}\right)\sigma_{\alpha\beta}} \tag{4}$$

is positive and below 1.0. The smallest sessile droplets observed in our experiment are with a radius of 0.75 micrometers. If one knows θ_0 and $\bar{\tau}$ which can be obtained from Figure 2 in Reference 77, it is possible according to the relation (4) to calculate the value of the line tension. Let us discuss the relation between the value of the interfacial tensions for big water droplets according to the Young equation:

$$-\sigma_{\alpha\beta}\cos\theta + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma} = 0 \tag{5}$$

and the liquid crystal orientation. When the critical surface tension of the solid[79] is greater then that the liquid crystal, it adapts planar orientation on the solid; when it is smaller, the liquid crystal orients itself homeotropically [80–83]. We know however, that there are many cases when the orientation of the liquid crystal does not follow this rule. This occurs when the glass plates are treated by various surfactants and the interactions between them and the liquid crystals include not only dispersive forces but also polar, hydrogen, Van der Waals etc. forces. In order to check this rule we have performed a simple experiment as follows : big droplets (in the range of several millimetres) of the pure liquid crystal Merck 997, water or the Merck 997 – water mixture (Merck 997 was in the nematic phase) were posed on one of the glass plates used in our experiment.. The careful examination of these sessile drops with a naked eye shows that water wets the glass plates slightly better than the mixture Merck 997-water and secondly, that the mixture Merck 997-water wets the glass plate slightly better than the pure nematic Merck 997. Although these differences are minor they show that

$$\sigma_{\alpha\gamma} > \sigma_{\beta\gamma} \tag{6}$$

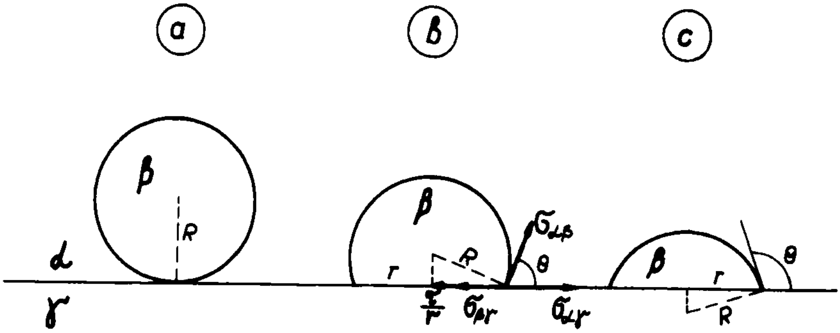


FIGURE 20 Droplet of water immersed in a liquid crystal resting on a nondeformable substrate: a/ the droplet is attached to the substrate b/ the droplet has a form of a truncate sphere (partial drying) c/ the droplet has the form of a spherical cap (partial wetting). The balance of the surface forces is illustrated in Figure 11b according to References 56 and 57

in accordance with our experimental results. On the other hand, this inequality is confirmed by data from the literature as well. For example, according to Cognard[83] σ_β of the water is around 22 dyn/cm whereas σ_α for the liquid crystals of azoxy types is larger than 30 dyn/cm[84]. Some old experiments made by one of us (H. Hinov) investigating DC voltage controlled pulsations of a homeotropic nematic layer with a free slipping water-nematic boundary[85] clearly showed that water or glycerine wet better the glass plates and remove the liquid crystal which is close to the glass slides. In addition, Proust et al[5] have demonstrated in their experiment that the liquid crystal wets completely the water which does not contradict to our experimental results. However it should be pointed out that the tendency of various liquid crystals to orient themselves planar depends crucially on the thickness of the water layer and the density of the package.

In the end of this section we shall discuss the possibility for the appearance of some surface defects in our experiment. The optical birefringence patterns observed by us were usually either cross-like domains (see Figures 6,7,8 and part of Figure 14) or more complex domains (see the other part of Figure 14). In order to clarify whether surface defects are incorporated in these birefringent structures, one should know the orientation of the director **n** of the nematic on the sessile water droplets. On the other hand, the strength of the deformations around the sessile water droplets should be determined by the strength of the surface anchoring of the nematic on the water surface. According to Kuksenock et al [14] relatively strong surface anchoring (approximately 10^{-2} erg/cm^2) can be defined for droplets with a radius of 5–6 microns. Since the sessile water droplets observed in our experiment had a radius between 0.75 microns and 2.5 microns, we can accept that the surface anchoring of the nematic on the water droplet sur-

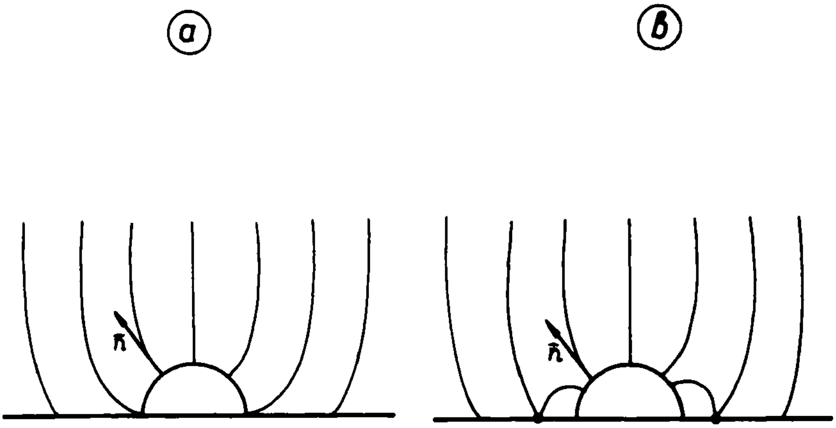


FIGURE 21 Schematic representation of the water droplets and the distortion of the liquid crystal revealed by the cross-like domains and more complex birefringent patterns: a/ there are no surface defects b/ there is *a Saturn-ring* configuration

face should determine the strength of the liquid crystal deformations. If one accepts strong homeotropic anchoring of the nematic on the surface of the sessile water droplets, two possible deformations can arise. They are shown schematically in Figure 21. Inversely, if one accepts strong tangential anchoring of the nematic on the surface of the sessile water droplets, another two possible deformations can occur. They are shown schematically in Figure 22. It is seen that various deformations are possible: defect free or *Saturn-ring* shown in Figure 21, one or two *boojums*, shown respectively in Figure 22. However, these four examples evidently do not exhaust all the possible deformations of the liquid crystal[86]. One accepts usually that polar liquids such as water or glycerine orient most of the liquid crystals tangentially [5,22,23,27,34,35,83,87]. It is important to mention that water orients tangentially nematics with a longitudinal dipole moment (for instance, 5CB [5]) as well as nematics with a transversal dipole moment (for instance, MBBA [22,23]). The second important feature is that the orientation of the liquid crystal in the plane of the water is degenerate[5,22,23] i.e. the liquid crystal can be oriented in all possible directions in the plane of the water. It is interesting to note that the polar (or zenithal) surface energy of interaction between the nematic and water has been measured by Proust et al [5]. The obtained value of 5.10^{-3} erg/cm ^{2} is relatively weak. It is evident that addition of a small amount of PVA considerably increases the surface energy of interaction between the liquid crystal and the water. This was proved in our experiment: cross-like domains were observed even in the case of smallest sessile water droplets. It is very difficult to identify, however, the surface defects or *boojums* among the cross-like domains. This can be done definitely only in the case when the droplet is seen from side [8,88]. Evidently, some of the cross-like domains accompanying the formation of sessile water droplets for the case of Merck 997-water or Merck 997-water-PVA are defect free (see Figure 21a). Although there are many papers devoted to observations or simulation of birefringent patterns either around droplets or sessile droplets or in the droplets themselves[3,4,16,18,22–29,31,33,36–38,89–94], the birefringent patterns observed in Merck 997-water-lecithin mixture (see the brighter patterns in Figure 14) could not be identified..

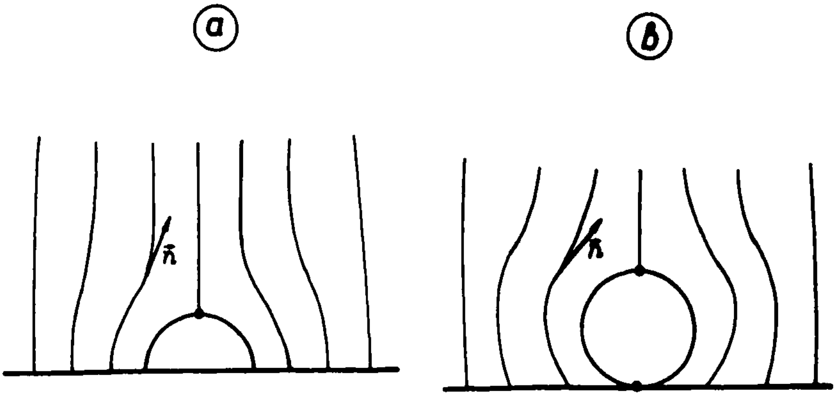


FIGURE 22 Schematic representation of the water droplets and the distortion of the liquid crystal revealed by the cross-like domains: a/ there is one surface defect – *boojum*. b/ there are two surface defects – *boojums*

Finally, it should be mentioned that nematic spherolites have been separated from a nematic-Canada balsam mixture or a nematic-immersion oil mixture by Rosenbaum and Stein [95] after cooling or after a few cycles of heating-cooling the mixtures. We have observed, inversely, the phase separation of water, initially dissolved in the liquid crystalline matrix after heating-cooling cycle of the nematic-water mixtures. This phase separation occurs 8°C to 10°C below the clearing point when additional surfactants were used. For the case of pure nematic-distilled water mixtures this temperature interval increases considerably. The quantity of the phase separated water depends on the time duration of the isotropic phase of the liquid crystal. However, several minutes are sufficient for the phase separation of all the water dissolved in the liquid crystalline matrix. The use of surfactants such as lecithin or PVA enhanced very much the effect. The phase separated water condensed on the two glass plates forming the cells under study was in the form of small sessile water droplets with a diameter between 1,5 – 3 microns for the case of added surfactants or 3 – 5 microns for the case without surfactants. Another proof for the attachment of the water droplets to the glass slides is the experimental fact that they do not show the director field of the liquid crystal as has been demonstrated in the nice experiment of Cladis, Kleman and Pieranski [96]. According to some authors [64] the hydrogen bonds are important for the incorporation of water in the liquid crystalline matrix. Further experiments are needed, however, to clarify which chemical bonds of the liquid crystalline matrix are important for the incorporation of the water in every specific case. The phase separation of water is always accompanied by a distinct increase of the clearing point which reaches that of the pure liquid crystal.

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