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RHEOLOGICAL INVESTIGATION OF MESOMORPHIC LAYERS FORMED AT THE LIQUID/LIQUID INTERFACE

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Résumé. — Les propriétés rhéologiques de phases lamellaires liquides cristallines furent mesurées pendant leur formation spontanée à l'interface liquide/liquide. On a trouvé que l'épaisseur de la couche liquide cristalline augmente en fonction de la racine carrée du temps. Les modules de déformation interfaciale réelles et imaginaires augmentent en fonction de l'épaisseur de couche croissante, tandis que ces modules sont en accord avec les modules de masse correspondants obtenus à l'aide de mesures de masse rhéologiques effectuées dans la phase liquide cristalline équilibre. Les propriétés rhéologiques des systèmes recherchés, octanoate de potasse-eau-décanol et Triton X 100-eau-décanol ne sont pas influencées par des effets directionnels ou superficiels.

Abstract. — The rheological properties of lamellar liquid crystalline phases were measured during their spontaneous formation at the liquid/liquid interface. The liquid crystalline layer thickness was found to increase with the square root of time. The real and imaginary interfacial shear moduli increase with increasing layer thickness, while these moduli are in agreement with the corresponding bulk moduli obtained from bulk rheological measurements of the equilibrium liquid crystalline phase. The rheological properties of the systems investigated, potassium octanoate-water-decanol and Triton X 100-water-decanol, were not found to be influenced by directional or superficial effects.

1. **Introduction.** — This paper discusses the appearance of a third phase formed spontaneously at the interface between two isotropic liquids. Dependent on the composition of the two liquid phases of certain systems, a mesomorphic, or liquid crystalline, phase is formed at the interface [1, 2]. This third phase has properties quite different from those of the two liquids from which it is formed, and may for instance, exhibit anisotropy. In a number of cases, density differences or interfacial tensions between the phases are lowered [3], so that such a third phase may have a stabilizing effect on emulsions [1, 3].

In two model systems, of which the ternary phase diagrams are known from the literature [4, 5], the rheological properties of a spontaneously formed liquid crystalline phase have been measured as a function of time. Since these data can be compared with the results of rheological measurements of bulk liquid crystalline material if the layer thickness of the third phase is also known as a function of time, such a comparison should provide information on the superficial or directional effects occurring during the spontaneous growth of the liquid crystalline layer at the interface. We first determined the thickness and the position — relative to the original liquid/liquid interface — of the liquid crystalline phase as a function of time. The formation of such a layer is

explained by means of the diffusion path in the ternary phase diagram. The rate of formation can be described by a process of molecular diffusion.

After a discussion of these results, the rheological data collected during the formation of the liquid crystalline phase, are compared with the results of equilibrium rheological measurements.

2. **Spontaneous formation of a liquid crystalline layer.** — We investigated the formation of liquid crystalline (LC) layers at the interface of the systems Triton X 100-water-decanol and potassium octanoate-water-decanol. When two isotropic solutions L_1 and L_2 (Fig. 1) are brought into contact, the overall composition of this non-equilibrium two-phase system is the same as that of the liquid crystalline D phase if the correct amounts of L_1 and L_2 are used. This D phase is the equilibrium state at 20 °C for the total system.

To obtain the equilibrium position in the phase diagram at the end of all diffusion processes, the total composition of the system is calculated from the original non-equilibrium system. When this system consists of two phases at the moment of contact, each of them can also be represented by a point in the phase diagram. During the diffusion processes, the compositions of non-equilibrium phases change from those

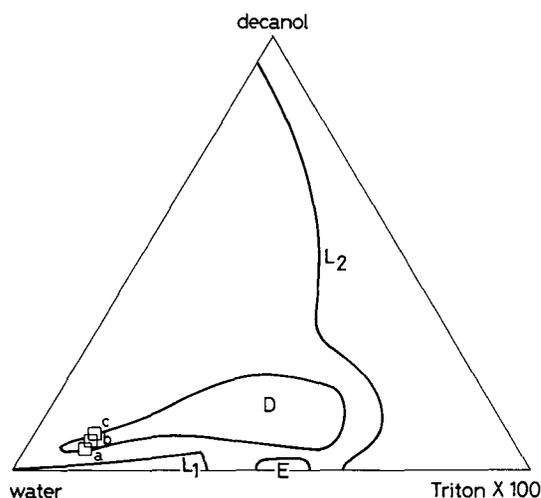


FIG. 1. — Ternary phase diagram of water-Triton X 100-decanol at 20 °C (Ref. [6]). L_1 : aqueous solution; L_2 : decanolic solution; D: lamellar phase; E: hexagonal phase; \square : 83.4% H_2O + 4.0% decanol + 12.6% Triton X 100; \square : 82.1% H_2O + 5.1% decanol + 12.8% Triton X 100; \square : 80.8% H_2O + 6.2% decanol + 13.0% Triton X 100.

of the two initial phases into the equilibrium state [6]. All these compositions together can be represented by one line in the equilibrium phase diagram, which is called the diffusion path [7, 8]. When this diffusion path crosses the LC area in the phase diagram, an interfacial LC layer is formed spontaneously.

The thickness of this interfacial LC layer as a function of time can be described by a simple diffusion process, assuming that:

- diffusion in the LC layer is the rate-determining step for its formation,
- diffusion only takes place perpendicularly to the interfaces,
- diffusion coefficients are constant over the LC layer,
- activity of each component changes linearly over the LC layer.

It then follows (unpublished results) that the layer thickness (h) is a linear function of the square root of time

$$h = k \sqrt{t} \quad (1)$$

where t = time, k = constant; k can be expressed as a function of LC composition, diffusion coefficients of the three components and activity gradients in the LC phase.

When the total volume of the system remains constant, the h_I and h_{II} values are controlled by the volume flux of components of L_1 and L_2 resp. into the liquid crystalline layer. When the average composition of this layer is independent of time it follows that the ratio between these volume fluxes must also be constant, i.e.:

$$\frac{h_I}{h_{II}} = \text{constant} \quad (2)$$

where:

h_I = distance between the interface at $t = 0$ and the interface between LC and L_1 at $t > 0$,

h_{II} = distance between the interface at $t = 0$ and the interface between LC and L_2 at $t > 0$.

This allows us to compare the composition of the LC layer at the interface with the position of the LC area in the equilibrium ternary phase diagram. For instance, the water content of the LC phase according to figure 1 and figure 3 can be compared in this way.

3. Experimental. — The following chemicals have been used: H_2O , double distilled; Decanol-1, purity > 99% (Fluka A.G.); Triton X 100, supplied by Lamens and Indemans, 's-Hertogenbosch, The Netherlands; Potassium octanoate, prepared from KOH and octanoic acid (Merck Darmstadt). Triton X 100 is a polydisperse preparation of p-(1, 1, 3, 3 tetramethylbutyl) phenoxy polyoxyethylene glycol containing an average of 9.5 oxyethylene units per molecule [9].

In our experiments, we used the following two liquid phases for the non-equilibrium state:

- water, saturated with decanol, + 12.5% (w/w) Triton X 100,
- decanol + 12.5% (w/w) Triton X 100.

For the experiments with the other ternary system, which has a similar phase diagram [1] we used several potassium octanoate concentrations.

The diffusion experiments were performed in tubes (30 cm) placed in vertical position. Two liquid phases were carefully brought into contact. The interfacial area was about 0.5 cm^2 and the layer thickness was measured for 1-2 weeks.

The compositions of the phases measured at equilibrium are given in figure 1. The rheological experiments were carried out using a Weissenberg rheogoniometer for the bulk (equilibrium) measurements of shear stress and phase angle (ϕ_b) (for simple shear, two concentric cylinders were used). The outer cylinder was given an oscillatory motion while the stress and phase angle were measured at the inner cylinder. The interfacial shear (non-equilibrium) measurements were carried out using two concentric rings placed in the interface (Fig. 2). The outer ring was given an oscillatory motion and the stress and phase angle (ϕ_s) were measured at the inner ring.

4. Results and discussion. — **4.1 DIFFUSION EXPERIMENTS.** — Figure 3 shows that the positions of the interfaces move linearly with the square root of time. Consequently the ratio between the slopes of the lines, describing the displacement of the interface with time, is a constant (eq. (2)). For the ternary system water-Triton X 100-decanol, there is an agreement between phase diagram and diffusion experiment. After contact between the two solutions, stated under 3, a LC phase (D) is formed spontaneously (Fig. 3).

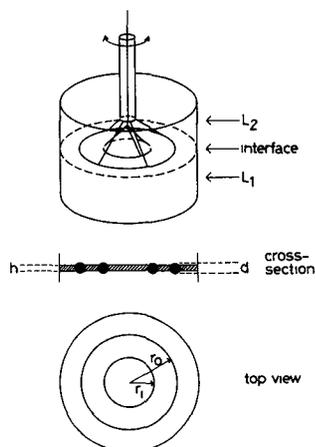


FIG. 2. — Schematic representation of interfacial shear viscosimeter. h = LC layer thickness; $d = 2.0 \times 10^{-3}$ m; $r_1 = 3.10 \times 10^{-2}$ m; $r_0 = 6.05 \times 10^{-2}$ m.

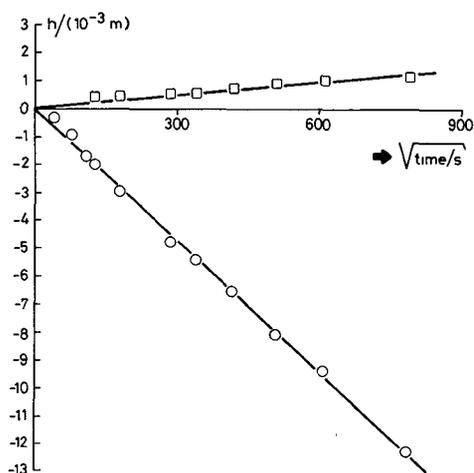


FIG. 3. — Thickness and position of interfacial LC layer between decanol + 12.5 % (w/w) Triton X 100 and water + 12.5 % (w/w) Triton X 100 as a function of the square root of time. □ interface between decanol and LC (Fig. 1); ○ interface between LC and water phase (Fig. 1).

According to the phase diagram, the water content of the LC layer is 92-89 % (Fig. 1). From the ratio between the slopes of the lines in figure 3 a value of 91 % is found.

For the ternary system water-potassium octanoate-decanol similar agreement was found between phase diagram and diffusion experiment for a number of compositions.

This confirms the predicted constant ratio between h_I and h_{II} (eq. (2)).

4.2 RHEOLOGICAL EXPERIMENTS. — To compare the surface rheological properties of the liquid crystalline layer formed at the interface with the bulk properties of this phase, the storage and loss moduli were calculated for both types of experiment from the data obtained for stress and phase angle; G' and G''

respectively for the bulk measurements and μ' and μ'' for the interfacial non-equilibrium state. The rheological properties of the LC phase depend on the composition. The average values of G' and G'' are calculated over the range of compositions expected to occur at the interface according to the phase diagram. We assumed that the diffusion path in the LC area in the phase diagram is a straight line. These compositions are given in figure 1 (a, b, c) for the system water-Triton X 100-decanol. The average values of G' and G'' are then found for the same maximum deformation ($\gamma = 0.04$) and frequencies ($\omega = 0.38$ rad s $^{-1}$ and $\omega = 0.082$ rad s $^{-1}$) as used in our non-equilibrium interfacial measurements. For the water-Triton X 100-decanol system the values of G' and G'' proved to be identical at both frequencies. For the water-potassium octanoate-decanol system the values of G' and G'' of the lamellar LC phase increase slightly with increasing frequency.

From the interfacial rheological measurements performed at a certain thickness of the LC layer, the interfacial moduli have been calculated. This means that the results are interpreted in such a way that the forces are acting in the plane of the interface. In bulk experiments the tangential stress forces are measured over a thickness h . Bulk and interfacial moduli are then related by

$$\mu' = G' \cdot h \quad (3)$$

$$\mu'' = G'' \cdot h. \quad (4)$$

A plot of interfacial shear modulus against LC layer thickness should give a straight line with G' and G'' respectively. This is valid as long as the LC layer thickness (h) does not exceed the thickness (d) of the concentric rings (Fig. 2). For larger h values, deviations can be expected.

According to eqs. (3) and (4), the averaged values of G' and G'' represent the slopes of the lines in figures 4A, B, where interfacial storage and loss moduli are plotted against the interfacial LC layer thickness. Eq. (1) predicts that $h = 0$ at $t = 0$, so that these lines pass through the origin.

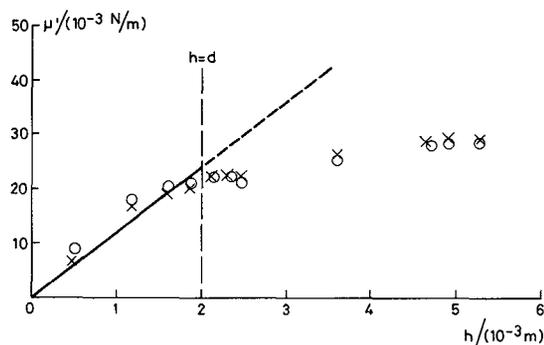


FIG. 4A. — Interfacial storage modulus (μ') (points) as a function of interfacial LC layer thickness for two frequencies at deformation $\gamma = 0.04$ and equilibrium bulk storage modulus (G') at the same frequencies and deformation (line) for the system water-Triton X 100-decanol. ○ and the line at $\omega = 0.38$ rad s $^{-1}$; × and the line at $\omega = 0.082$ rad s $^{-1}$.

As shown in figures 4A, B, the results of the interfacial shear measurements (indicated by points) and the bulk shear measurements (represented by lines) show a fair agreement.

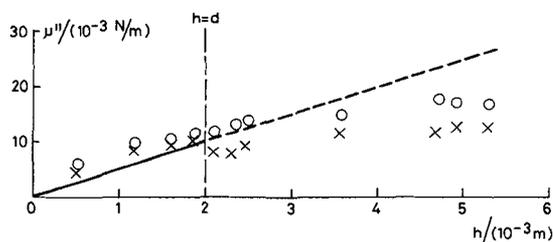


FIG. 4B. — As figure 4A for the interfacial loss modulus (μ'') and bulk loss modulus (G'').

Similar agreement was also found between interfacial and bulk measurements for the ternary system water-potassium octanoate-decanol. The LC phase, spontaneously formed between water + 5% (w/w) potassium octanoate and decanol, was compared with the equilibrium LC phase of the same potassium octanoate concentration. For the bulk rheological measurements, liquid crystalline samples were prepared by mixing the components; no precautions were taken regarding orientation of the material. However, the liquid crystalline layer was formed at the interface by spontaneous diffusion so that orientation may have occurred. According to the results presented in figures 4A, B, these effects do not strongly influence surface behaviour.

Nevertheless there are some slight differences between both results, which may be due to the following causes :

a) Inaccuracy of the measurements performed in the interfacial shear viscosimeter and the Weissenberg rheogoniometer. These errors are usually < 5%, except for very small phase angles.

b) Comparison of the interfacial moduli (μ) and the bulk moduli (G) is only possible at the same frequency and deformation. Therefore, interpolation between several bulk data was necessary. This causes only a minor error as in these systems changes of G' and G'' in relation to ω or γ are only slight.

c) Before the measurements in the interfacial shear viscosimeter are carried out, the two liquid phases have to be brought into contact. Disturbances at the interface during this process may cause a faster increase in LC phase thickness with time than would be expected from spontaneous diffusion only.

d) When the layer thickness exceeds the ring diameter ($h > d$), the interpretation of the results becomes incorrect. The values measured for the interfacial moduli are expected to be smaller than the bulk moduli. This is seen in figures 4A, B at high values for h .

Considering the above possible causes of differences the best agreement between the equilibrium and non-equilibrium data is expected for $h \approx d$.

5. Conclusions. — For simple systems, the formation of an LC phase at the interface between two liquid phases can be predicted from the phase diagram.

— The thickness of the liquid crystalline layer formed at the interface, increases linearly with the square root of time.

— The position of the layer relative to the original interface between two isotropic solutions can be calculated from the phase diagram.

— The results of interfacial shear measurements on the interfacial LC layer formed in these systems, can be explained by bulk properties of this mesophase. No large directional or superficial effects are found when comparing the interfacial shear measurements with the bulk measurements.

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