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Free-Surface Instability and Stratification of Critical Microemulsions.

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Abstract. - We have studied the influence of temperature gradients on the concentration distribution in a microemulsion near a consolute critical point. Temperature inhomogeneities much smaller than the distance to the critical temperature trigger convective flows along the free surface (liquid-vapour interface) and are the cause of a considerable stratification of the bulk sample. All these phenomena disappear if the vapour phase on top of the sample is replaced by a solid phase. We propose an explanation involving a thermodiffusion-induced superficial concentration gradient and the resulting Marangoni convection.

Several groups have been working on critical properties of microemulsions, *i.e.* systems made of a mixture of water, oil and a surfactant (in fact most often a mixture of a surfactant and a cosurfactant) [1]. Here we deal with microemulsions which can be thought of as equivalent to binary mixtures. Roughly speaking, these systems are suspensions of swollen micelles of water in oil or of oil in water. As a function of concentrations and of the temperature, one observes phase equilibria involving one isotropic liquid phase and a vapour phase (LV) or two isotropic liquids and a vapour phase (LLV), just as with true binary mixtures. Consolute (critical) points ending liquid-liquid coexistence lines have been evidenced in a variety of microemulsions and since then have motivated a large amount of work [2]. Most of the available data are concerned with the concentration fluctuations (critical opalescence) in the liquid phase of (LV) equilibria.

Although these fluctuations are very large close to the consolute point, one expects the liquid phase to be nearly homogeneous as an average, as long as phase separation does not occur. By «nearly» we in fact hint at gravity-induced concentration gradients (sedimentation) [3]. However, these gradients are always negligibly small in the experimental conditions we will discuss in this paper (we will be more quantitative on this point later).

In the course of a number of experiments we have carried out with water in oil critical microemulsions, we noticed that our samples were not at all homogeneous, in contrast with what we expected. A typical situation is illustrated in fig. 1. Here the sample is a mixture of

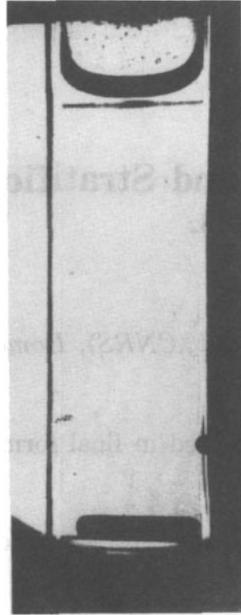


Fig. 1. - Example of a critical sample which has undergone a few thermal «shocks» (see text). The liquid is stratified in two zones separated by the flat dark line visible under the meniscus. The lower zone is very opalescent. The upper one is off the critical concentration and then clear. The width of the cell is 10 mm. The dark thing at the very bottom of the cell is a magnetic stirrer.

toluene (72.1), water (8.2), sodium dodecylsulfate (3.8) and butanol (15.9) (the composition is given in mass percentages). This system features a lower critical point (which means one goes from the LV equilibrium to the LLV equilibrium by raising the temperature) at $T_c \approx 305$ K. The sample is contained within a rectangular quartz cell, whose cross-section is (4×10) mm². The cell is located in a water bath, whose temperature is kept constant to within ± 0.01 K. Within the resolution of our thermometer (≈ 0.5 mK), we could not detect any sizeable static temperature gradient around the cell. Figure 1 is a Schlieren pattern of a LV equilibrium (here the Schlieren method has been used just as a phase contrast device). The curved black area on top is the liquid-vapour meniscus. The liquid phase has been first stirred at $T_c - T = 6$ K, then the temperature has been raised up to $T_c - T = 1$ K through a few steps. Basically, each step results in a transient horizontal temperature gradient across the cell, with a maximum along the walls. The observation is made after a few hours of equilibration at the final temperature. The striking feature in fig. 1 is a transition region which appears as a horizontal flat dark line right below the bottom of the meniscus. This line should not be confused with an interface separating two coexisting phases: it may be smooth (width $\sim (0.1 \div 1)$ mm) if a final temperature far from T_c is approached through many small steps. Its width is then at least 10^3 times larger than the correlation length of the concentration fluctuations ξ ; it may also appear sharp (not readily seen on the Schlieren pattern) if a few large steps are used to get close to T_c . In all cases the line slightly spreads out as time runs out.

Figure 2a) shows a cell which has been left at a short distance below the free surface of the water bath. Such a configuration just amounts to imposing a static vertical temperature gradient on the cell. The sample has been first stirred at $T_c - T = 4$ K and then left in the temperature gradient for 24 hours. The temperature decreases towards the top. The temperature gradient is about -0.5 K \cdot cm⁻¹ across the meniscus and decreases down to

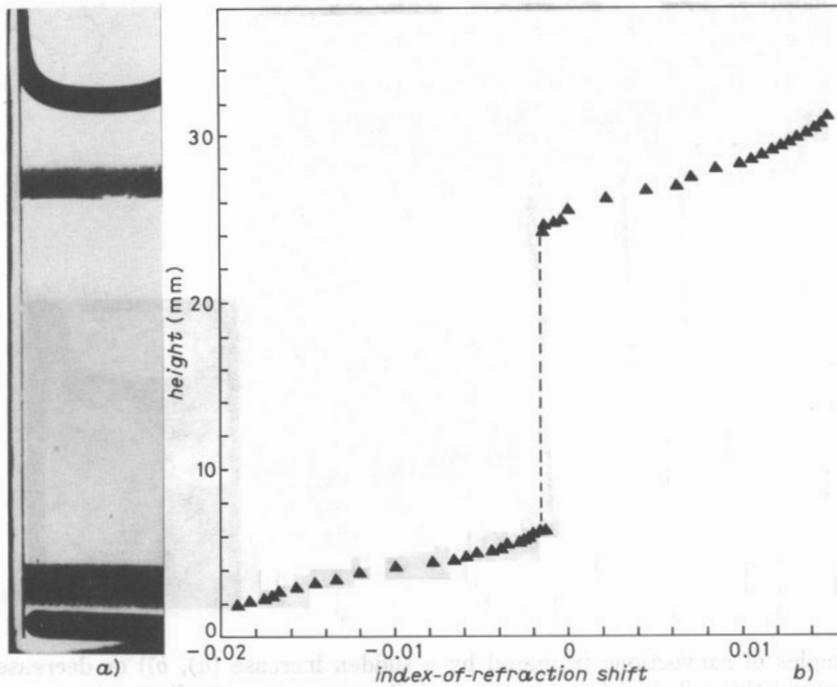


Fig. 2. – Example of a critical sample which has undergone a vertical static temperature gradient (see text). *a*) Example of a Schlieren pattern. *b*) Index-of-refraction profile (the average index over the whole cell is taken as the origin).

about $-8 \text{ mK} \cdot \text{cm}^{-1}$ at the bottom of the cell. Figure 2*b*) shows the index of refraction profile in the same cell after 72 hours, as given by the Schlieren patterns. The application of the temperature gradient results in a considerable stratification of the liquid in three zones. The concentration in the dispersed phase (essentially water and SDS) drastically decreases as a function of the height (z) in the sample.

As a rule, the water + SDS concentration in the vicinity of the LV meniscus always gets lower than the critical concentration, whatever the thermal history of the sample: static vertical gradient ($\partial T/\partial z < 0$) or transient gradient due to either an increase or a decrease of the water bath temperature. Besides, the amplitudes of the temperature gradients, needed to give rise to a sizable stratification, definitely decrease when one gets closer to T_c .

Figure 3 shows what we believe to be the common origin of all the above-described sample stratifications. A positive temperature jump ($\Delta T > 0$) triggers a flow along the LV interface, from the liquid-vapour-cell wall contact line towards the centre of the meniscus. An excess of mass results and a rain of small droplets falls down to the bottom of the cell (fig. 3*a*, *b*). A negative temperature jump ($\Delta T < 0$) triggers a centrifugal flow and a rain starting from the vicinity of the contact line (fig. 3*c*). These rains are transient phenomena and fade out after a few minutes. A long time after say $\sim 30 \text{ min}$ —a stratification like that of fig. 1 appears near the contact line. For a given value of ΔT the extent of the region above the transition line is an increasing function of the proximity to the critical temperature. These photographs have been made with very large temperature jumps ($|\Delta T| \sim 0.1 (T_c - T)$), just for producing highly contrasted flow patterns. The flow patterns are much less visible with definitely lower values of $|\Delta T|$ or $(T_c - T)^{-1}$, but the stratification scenario is always the same. We could also evidence transient centrifugal flows produced by a static vertical gradient ($\partial T/\partial z < 0$), see fig. 3*d*).

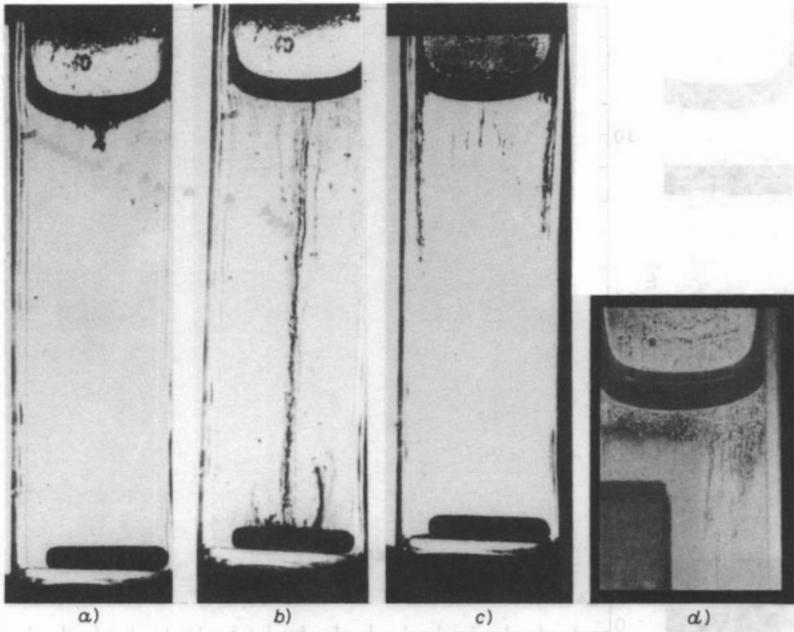


Fig. 3. - Examples of convections triggered by a sudden increase (a), b) or decrease (c) of the temperature around the cell, and by a static vertical temperature gradient (d).

Our observations are summarized in fig. 4. What we believe to be the basic parameter is the temperature distribution *along* the meniscus: in fig. 4a) the temperature is maximum along the contact line, a situation which is produced for instance by a positive temperature jump of the water bath; fig. 4b) shows the reverse situation which corresponds to a negative temperature jump as well as to a vertical static temperature gradient.

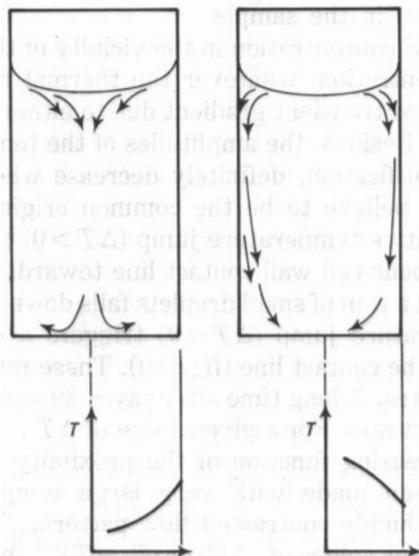


Fig. 4. - Sketches of the observed transient flow patterns produced by the two main types of temperature inhomogeneities *along* the meniscus.

All these phenomena disappear when there is no vapour phase above the liquid phase (L samples), in other words, when the liquid is entirely surrounded by glass (such a condition is approximately met by filling the liquid through a capillary tube on the side of the cell main body). We could check the absence of any thermal-gradient-induced flow, whatever the shape of the cell ceiling (flat and curved ceilings with a shape mimicking that of a LV meniscus have been used). There is no large stratification of the liquid bulk as with LV samples. Nevertheless cells which have been equilibrated for a few hours show a sizable concentration gradient in a very thin (~ 0.1 mm) region close to the top. We believe this gradient is just due to the sedimentation which always exists when LV or L samples undergo the influence of a gravity field. This view is consistent with the index of refraction profiles $n(z)$ we have calculated from the sedimentation equation [3], using the values of the osmotic compressibility and of the correlation length ξ in our system [4]. For instance for a 24 mm high cell at $T_c - T = 2$ K and 24 hours after stirring, we find a maximum value of $dn/dz \approx 1.2 \cdot 10^{-1}$ along the top and bottom boundaries of the cell. The amplitude of the gradient falls off below the resolution of our Schlieren set-up ($\sim 6 \cdot 10^{-4} \text{ cm}^{-1}$) at about 0.1 mm from the boundaries. These numerical values are unaltered if one takes into account thermodiffusion along the vertical. Qualitatively, thermodiffusion opposes to sedimentation if $\mu T/\mu z < 0$ because in our system the thermodiffusion constant is positive; however, the quantitative effect is always negligible [5]. Of course a much larger and deeper sedimentation is expected at thermodynamic equilibrium, but only after a huge time (~ 1 y).

Thus diffusion is a small and slow process that cannot account for the large and fast phenomena observed in LV samples. Convection, that singles out LV samples, is necessary to get the anomalous stratification. This may seem paradoxical since common sense intimates the homogenizing role of convective motions; nevertheless in some contexts these motions are known to cause stratification [6].

The fact that the presence of a vapour phase on top of a binary mixture near its consolute point drastically enhances the stratification of the liquid in a static temperature gradient had already been realized by Blagoi *et al.* with a $\text{CH}_4\text{-CF}_4$ mixture [7]. But as far as we know, it is the first time that a convective flow along the LV interface is observed and shown to be at the origin of the anomalous bulk stratification. Other observations have been reported of anomalous stratifications in liquid phases in contact not with a vapour phase but with one or two liquid phases. These cases include the middle and lower phases in different types of Winsor equilibria [8], and in ternary mixtures of alkanes near a tricritical point [9]. Although these situations are different from the one we have investigated, it is tempting to imagine that the reported anomalies originate from convective flows along one liquid-liquid interface *in lieu* of the liquid-vapour interface of our problem.

Drops falling from the free surface of LLV equilibria of binary mixtures close to their consolute point have been observed and attributed to the destabilization of «wetting layers» [10, 11]. Although such scenarios have never been evidenced with LV equilibria, the existence of a «prewetting layer» along the meniscus cannot be ruled out *a priori*. However, we expect the destabilization of such a layer to occur at the smallest wave vector allowed by the cell geometry [10], which, in practice, means one should see the growing-up of one large single drop below the meniscus with a size of the order of the cell thickness. All the flow patterns we could observe involve much shorter length scales and are always far from this picture of one single large drop.

What we believe to be the origin of the instabilities we report on can be summarized as a «thermodiffusion-mediated Marangoni convection». It is well known that any spatial nonuniformity of the interfacial tension of a fluid-fluid interface gives rise to a convective flow along the interface [12, 13] (this can be taken as a definition of the Marangoni convection). Let us assume, for simplicity, a flat free surface, x the position along this

surface, $\gamma(x)$ the surface tension and $T(x)$ the temperature distribution. To figure out the way in which $\gamma(x)$ depends on $T(x)$, we start from the equation proposed by Nagarajan *et al.* [14] for the surface tension (LV) of the water-isobutyric acid mixture, and we suppose this equation to be qualitatively valid in our experimental situation. Nagarajan's equation reads

$$\gamma(c, T) - \gamma_0 = [p + q(c - c_0)](T_c - T) + r|c - c_0|^{\mu/\beta}. \quad (1)$$

Here γ_0 is the surface tension at the consolute point, c the concentration and c_0 the critical concentration. μ is the critical exponent of the LL interfacial tension in the LL equilibrium, β is the coexistence curve exponent. p , q and r are constants.

$\gamma(x)$ depends directly on $T(x)$ through $(\partial\gamma/\partial T)_{c=c_0}$, and indirectly through $c(x)$. In fact, $c(x)$ depends on $T(x)$ through thermodiffusion [12] (or Soret effect):

$$\frac{dc}{dx} = -\frac{k_T}{T} \frac{dT}{dx}. \quad (2)$$

Here k_T is the so-called «thermodiffusion constant». Near T_c , $(\partial\gamma/\partial T)_{c=c_0}$ is regular, but k_T is expected to diverge as $|T - T_c|^{-\psi}$, where ψ is close to the correlation length critical exponent ν [15]. Although the surface tension of the uniform mixture does not vary very much near T_c , we, however, expect the surface tension profile $\gamma(x)$ to depend critically on the temperature profile $T(x)$. Assuming a linear temperature distribution $T(x) = T + (dT/dx)(x - x_0)$, we find from (1) and (2) for x sufficiently close to x_0

$$\gamma^{\text{crit}}(x) - \gamma_0 \sim (T_c - T)^{-\mu\nu/\beta} (x - x_0)^{\nu/\beta}, \quad (3)$$

where $\gamma^{\text{crit}}(x)$ is the critical part of $\gamma(x)$. With universal values for all the exponents ($\gamma = 1.24$, $\nu = 0.62$, $\mu = 1.30$, $\beta = 0.32$) we find a very fast variation of $\gamma^{\text{crit}}(x)$ near T_c ($\mu\nu/\beta \approx 2.4$). Since the experimental situation is never free of thermal gradients (static or dynamic), we expect a sizeable free surface driven convection to occur sufficiently close to T_c .

At this stage, our arguments are rough and even tentative. In particular, we did not attempt to describe more than the very first stage of the hydrodynamic processes leading to the quasi-steady bulk stratification. The experimental geometry is unappropriate for a quantitative evaluation of the flow patterns. However, we hope to test these ideas more decisively in a more sophisticated geometry, involving a laser-induced thermal lens near the free surface of the critical mixture.

* * *

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