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Transition from L_1 to L_2 in a ternary system (OBS-pentanol-water): a borderline case between continuous and discontinuous topological inversion

P. Bassereau, J. Marignan and J. Appell

Groupe de Dynamique des Phases Condensées (*), U.S.T.L., 34060 Montpellier Cedex, France and GRECO Microémulsions (C.N.R.S.)

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Résumé. — Le diagramme de phase du système ternaire OBS-pentanol-eau présente un étroit passage apparemment continu reliant les domaines d'existence de L_1 et de L_2 . Il présente aussi une petite région triphasique qui est habituellement plutôt caractéristique d'une situation où L_1 et L_2 sont séparées. Associés à ce caractère limite, des phénomènes physiques originaux sont observés et étudiés dans le passage étroit. Un scénario plausible pour l'inversion topologique de structure est proposé pour cette situation particulière.

Abstract. — The phase diagram of the ternary system OBS-pentanol-water presents an apparently continuous thin pathway connecting the L_1 and L_2 domains. It also shows a small triphasic region which, usually, is rather typical of disconnected L_1 and L_2 domains. Related to this borderline character, unique phenomena are observed and studied in the thin pathway. A plausible scenario for the topological inversion of structure is proposed for this particular situation.

1. Introduction.

Microemulsions are stable mutual dispersions of oil and water, stabilized by surfactant molecules which stand at the interface separating the water from the oil microdomains. The mixtures are clear and transparent, indicating that dispersion takes place at a length scale smaller than the light wavelength, and they are isotropic. There is no particular difficulty to understand the commonly admitted structure of the mixture when either water or oil is the main component : we have respectively oil droplets dispersed in the water continuous medium (L_1) or water droplets dispersed in the oil continuous medium (L_2) [1]. The difficulty arises when one deals with mixtures with comparable amounts of oil and water [2, 3] : what is the topology of the structure of the obtained isotropic mixture ?

Microemulsions usually involve four-component systems : water, oil, surfactant and a short chained alcohol (co-surfactant). In principle, the complete phase diagram should be represented in a three-dimensional space and is in general very complex. Because alcohol is poorly soluble in water, three component systems (water, surfactant, alcohol) often simulate, to some extent, the behaviour of true microemulsions and their phase diagram is indeed much simpler to study.

(*) Laboratoire Associé au C.N.R.S., UA 233.

Fig. 1. — Phase diagrams for three-component systems. Schematic after Ekwall [4] showing the monophasic domains : the isotropic phases L or L₁ and L₂, the lamellar liquid crystal LLC and the hexagonal phase E, (a) the chain of alcohol is short (butanol) : large continuous pathway from L₁ to L₂ (L); (b) the chain of alcohol is longer (pentanol) : L₁ and L₂ domains are separated by the LLC domain.

Fig. 2. — Phase diagram for the system under study at $T = 25^\circ\text{C}$, (a) general phase diagram (from [5]); (b) detail of the pathway from L₁ to L₂ beneath the lamellar liquid crystal LLC.

In particular, especially when the alcohol is short, the L₁ domain of the phase diagram is connected to the L₂ domain through a large pathway (Fig. 1a). The topological inversion of the structure L₁ to L₂ apparently occurs continuously and we face again the same topological question as in a true microemulsion in the intermediate domain.

On the other hand, if alcohol is longer chained, the situation is very different [4] (Fig. 1b) : the L₁ domain is clearly separated from the L₂ domain by a large lamellar liquid crystal domain. The topological inversion takes place discontinuously *via* phase separations, the topology of the intermediate phase (lamellar) being clearly bicontinuous.

The system we currently study in our group, *OBS-pentanol-water*, lies at the borderline between these two well defined situations (Fig. 2). A very thin, apparently continuous, pathway connects the L₁ and L₂ domains while a small triphasic domain appears which is usually observed when L₁ and L₂ are well separated by the lamellar.

Related to this borderline character, unusual phenomena are observed. In what follows, we

sum up the results of a preliminary experimental analysis of this unique behaviour and we suggest a plausible explanation for the structural inversion in this particular case, which might be of interest for the more general case of concentrated microemulsions.

2. Experimental.

2.1 PHASE DIAGRAM ANALYSIS. — The general phase diagram of the system OBS-pentanol-water, which is given in figure 2a, has been reported in previous articles [5]. It involves the three large monophasic domains : L_1 ; Lamellar ; L_2 .

In the present work, we especially focus our attention on the small part of the diagram which lies below the lower end of the lamellar domain where the L_1 and L_2 domains come close to each other. About 100 solutions were prepared in this particular zone. Special care was taken with the weighting of the components : the weight of all the samples was larger than 10 g and the components were weighted with an absolute accuracy which is better than 5 mg. Samples in the triphasic domain were further controlled using large samples (30 g) with the components weighted with the same accuracy. After preparation, the samples were kept in a thermostated room whose temperature was periodically checked : the temperature was found stable within an accuracy better than 0.1 °C over delays larger than one month. After one day temperature equilibration, the prepared samples were gently stirred in order to prevent artefacts due to phase separations initiated out of equilibrium ; then they were left undisturbed. The phase determination was performed after at least one month and involved normal light observation, polarized light observation and phase contrast microscopy.

The obtained phase behaviour is represented on a magnified scale, in figure 2b. This partial view of the diagram shows a very thin continuous pathway connecting the large domain of existence of L_1 and L_2 . It also shows a small triphasic domain where the three coexisting phases are very close to each other with respect to the relative concentration of the three components. The boundaries of the triphasic domain are not determined by titration of the three phases in equilibrium but by a simple optical observation. Eight different samples appeared triphasic and the evolution of the relative proportions of the three phases *versus* the overall composition is consistent with the triangular triphasic domain as drawn in figure 2b.

We also followed the variations of this part of the diagram with increasing temperature up to 30 °C. Without going into the details of the description, the main result is that, in the range 25 °C to 30 °C, increasing the temperature results in a very moderate progressive drift (of the order of one per cent in composition) of the monophasic domains towards the OBS rich corner. Otherwise the general phase pattern remains unaffected : we still observe a triphasic domain and a thin, apparently continuous pathway.

2.2 VANISHING OUT OF THE INTERFACE BETWEEN L_1 AND L_2 . — Proceeding carefully it is possible to syringe out amounts of the L_1 and L_2 phases from an equilibrated triphasic mixture. L_1 and L_2 phases are then successively and very slowly injected into the same test tube (L_2 over L_1). This is performed inside the thermostated room so that the thermal equilibrium remains in principle unperturbed during the whole operating process. Proceeding carefully, we obtain a sample consisting of two isotropic phases separated by a quite faint but horizontal and well defined interface. Within a few minutes, the interface spontaneously spreads into a thicker and thicker misty layer. After two hours, the whole sample is homogeneously misty. And within a few days, the whole sample becomes gradually clearer until it looks perfectly transparent and homogeneous. Then it looks apparently monophasic.

Actually, such a phase transformation could be induced by very small unavoidable temperature variations (smaller than 0.1 °C). Nevertheless, this behaviour has been observed reproducibly several times. This can hardly be related to erratic small temperature drifts.

After stirring, careful observations of the mixture in phase contrast microscopy reveal no detectable refraction index heterogeneity.

2.3 REFRACTION INDEX GRADIENTS INDUCED BY LOW SHEAR STRESSES. — This phenomenon occurs reproducibly, after equilibration, in apparently monophasic mixtures in the thin pathway as well as in samples obtained from a triphasic sample according to the procedure described just before. The slow displacement of a small magnetic stirrer immersed in the sample prior to equilibration induced elongated refraction index gradients in the equilibrated mixture. The phenomenon is similar to what is observed in a tea cup (with no milk) when stirring gently undissolved sugar. It is not observed just after vigorous stirring but reappears again after a few days equilibration.

2.4 LIGHT SCATTERING. — We performed light scattering experiments on samples in the thin pathway. The experimental apparatus is now classical (AMTEC spectrophotometer) and allows both intensity and quasielastic light scattering measurements with the same sample in the same place. In the quasielastic spectrum configuration, a real-time spectrum analyser (Rockland FFT 512/S) calculates the Fourier transform of the autocorrelation function of the photomultiplier's output current.

Fig. 3. — The scattered light intensity $I(q)$ as a function of the scattering wave vector q for three samples with $(\text{pentanol/OBS})_{\text{weight}} = 3$. (Δ) A typical sample (A) in the thin pathway (point A in Fig. 2b). Water content 76 weight %. ($\circ$) A check sample (B) on the L_1 side (point B in Fig. 2b). Water content 80 weight %. ($\bullet$) A check sample (C) on the L_2 side (point C in Fig. 2b). Water content 72 weight %.

After degassing and stirring, the sample is inserted into the cell holder and left still for 30 min at the properly regulated temperature (25 °C). A first set of measurement is then performed. A second one is performed again 24 h later.

The obtained angular dependence of the light scattered by a typical sample (in the thin pathway) is given in figure 3 (sample A). Compared to the curve obtained for check samples (same figure, samples B and C) in the large L_1 and L_2 regions it shows a rather unexpected feature. At high q values ($q > 1.5 \times 10^5 \text{ cm}^{-1}$) $I(q)$ is quite low and similar to what is obtained for the check samples. But for lower q values ($q < 10^5 \text{ cm}^{-1}$) $I(q)$ increases very steeply. The comparison with the check sample precludes the possibility of an artefact (micro-bubbles, dust particles, lack of reliability of the photo detection) related to the operating procedure. Because very low angles ($< 20^\circ$) cannot be explored under good conditions with the present apparatus, we cannot decide whether the increase of $I(q)$ corresponds to a true divergence or to the existence of a low angle finite maximum of $I(q)$. Anyway, the obtained $I(q)$ profiles indicate the existence of long spatial wavelength gradients of the refraction index in the clear transparent mixture.

The quasi-elastic light scattering patterns are also quite unique. Figure 4 represents the spectrum of the light scattered by sample A at an angle of 20° which is the lower angle for which reliable results can be obtained within the homodyne detection configuration. Figures 4a and 4b correspond to two distinct numerical analyses of the photomultiplier current involving diffe-

Fig. 4. — The spectrum of light scattered at an angle of 20° ($q = 5.9 \times 10^4 \text{ cm}^{-1}$) by the same typical sample (A) as in figure 4 : ● : experimental points. Continuous line : spectra corresponding to the fit by a single Lorentzian. (a) Large frequency scale, the halfwidth at halfmaximum — $(600 \pm 30) \text{ Hz}$ corresponding to a relaxation time for the refraction index fluctuations $\tau_1 \simeq 5 \times 10^{-4} \text{ s}$. (b) Narrow frequency/scale, the halfwidth at halfmaximum — $(0.6 \pm 0.1) \text{ Hz}$ corresponding to a relaxation time for the refraction index fluctuations $\tau_2 \simeq 5 \times 10^{-1} \text{ s}$.

rent frequency windows for the spectrum analyser. Clearly, two very different relaxation times ($\tau_1 \simeq 5 \times 10^{-4}$ s and $\tau_2 \simeq 5 \times 10^{-1}$ s), involving two different processes for the relaxation of spontaneous refraction index fluctuations, appear. Significantly, the dynamic light scattering patterns of the check samples (B and C) do not exhibit the long relaxation time τ_2 but only the short one τ_1 which is of the same order of magnitude as that of sample A. Therefore the long time τ_2 is distinctive of the particular structure of sample A.

The short time τ_1 for all samples shows the classical q^{-2} dependence indicating that it is probably related to a classical, thermally induced, diffusion of presumably « micellar objects ».

The relative intensity scattered by the A sample within the spectral width related to τ_2 decreases quickly when q increases : so the dependence of τ_2 on q can hardly be determined.

3. Analysis and discussion.

In principle, in a ternary system, the existence of the small triphasic domain is consistent with the two alternative configurations given in figure 5. Within the first one, the existence of the true continuous pathway involves a critical point denoted P_c in figure 5a. Clearly the expected critical opalescence is not observed in its vicinity. Moreover the light scattering patterns are certainly not typical of the vicinity of a critical point. On the other hand, within the second hypothetical configuration, a clear biphasic domain should be involved below the triphasic. What we observe is very different, the two phases, put into contact, spontaneously macro-emulsified in a first step, and then mixed together at a smaller length scale.

Fig. 5. — Possible configurations for the phase diagram below the small triphasic domain : (a) true continuous pathway between L_1 and L_2 with the existence of a critical point P_c ; (b) a biphasic domain exists.

In order to reconcile observations and principles, we propose the following explanation based on a structural assumption. This assumption is based on the point of view of Parodi [6] about the structure of concentrated microemulsions.

The lamellar phase exhibits long ranged orientational (optical birefringence) and translational (thin Bragg peaks) orders. The quantitative analysis of the X-ray data [5] indicates that the thickness of the hydrophobic lamellae is not composition dependent : ~ 20 Å. For compositions near the triphasic domain, the period of the lamellar phase is of about 74 Å.

We assume that the neighbouring L_1 and L_2 isotropic phases exhibit, at a local scale, a similar structure but with short range order only. The experimental work (X-rays) of Marignan *et al.* [5] strongly suggests that it is so for L_2 in the vicinity of the lamellar phase : the short range quasi-period in L_2 being of the same order of magnitude as the true periodicity in the lamellar phase. At the present time, as far as L_1 is concerned, the X-ray patterns cannot be interpreted as convincingly. According to this assumption, L_2 could be pictured as an assembly of flattened discoidal droplets of water embedded into an alcohol continuous medium. And L_1 would consist

Fig. 6. — Schematic picture of the structure of L_1 , L_2 and the interfacial after Parodi [6]. (1) L_1 : water is the continuous medium ; (3) L_2 : oil (or alcohol) is the continuous medium ; (2) interface between a L_1 and L_2 domain.

of similarly discoidal micelles immersed into continuous water. A schematic picture is given in figure 6 : both isotropic phases have similar local structures and only differ by their topology (direct and inverse topology). When both phases, which should coexist at thermal equilibrium, are put into contact, we expect a thick interface to form which also has a similar local structure (Fig. 6). Because the two phases and the interfacial region are not much different with respect to their composition and local structure, the interfacial tension is expected to be extremely low (quasi-zero tension). The initially plane and horizontal interface is therefore unstable with respect to the thermal fluctuations of its total area. This gives rise to the observed spontaneous emulsification, and further clarification of the sample.

According to this general picture, the clear mixture obtained after equilibration consists of a random distribution of micro-domains L_1 and L_2 : the total amounts of L_1 and L_2 are fixed by the overall sample composition, but the size and shape distribution of the micro-domains are probably polydispersed. The low angle apparent divergence of the light scattered intensity would then be related to the size distribution of the micro-domains. The short time τ_1 , in quasi-elastic light scattering, would be associated to the standard diffusion of the « micellar objects » in a given domain, while the long time τ_2 would be characteristic of the reorganization of the domains. This reorganization occurs through displacements of their interface and involves transfer of matter in order to adjust the local composition to the local topology. Such a process is expected to be slow and τ_2 is long.

Otherwise, the domains are bounded by a quasi-zero tension interface : they should be very easily deformable. They might account for the refraction index elongated gradients induced by gentle transient shear stresses.

4. Conclusion.

The above-described structural picture of the topological inversion through the thin pathway actually rather supports the phase configuration of figure 5b ; the remixing of the two isotropic phases, L_1 and L_2 , being related to the instability of the interface with respect to the thermal fluctuations of its overall area. A necessary prerequisite for such a process to be plausible is that the interfacial tension should be extremely low. In the present case, this conjecture is based on two arguments : the first one is the experimental observation of a first step of spontaneous emulsification ; the second one is related to the fact that the three phases (L_1 , lamellar, L_2) are very similar in composition. The inference that comparable compositions involve similar local structures may seem quite artificial. However, at a local scale, the spontaneous curvature of the surfactant film is expected to vary smoothly with the composition. Thus, two different phases with similar compositions should exhibit almost everywhere the same local curvature for the

surfactant film, and therefore similar structure at a local scale. They may however strongly differ with respect to the correlation length associated to the lamellar order : long-range order for the lamellar phase and short-range order for the two isotropic L_1 and L_2 phases. L_1 and L_2 can be pictured as lamellar phases where the long-range order is « killed » by a high density of « structural defects ». The nature of the structural defects should depend on the alcohol/surfactant ratio : in the L_1 phase the « defects » involve curvatures with convexity toward the water medium (smaller alcohol/surfactant ratio) and in the L_2 phase they involve high convexity towards the hydrophobic medium (higher alcohol/surfactant ratio) according to figure 6.

At the present time, it is often admitted that concentrated microemulsions are bicontinuous structures pictured as a random filling of some Voronoi or other arbitrary array with water and oil. In the case of the Talmon-Prager model [2] the Voronoi array is defined *via* a random distribution of points in space : it involves no particular scale length. In the case of the model of Jouffroy, Levinson and De Gennes [7], the array is a simple cubic network, the cell of which has a size related to the persistence length ξ ($\xi \sim \text{few } 10^2 \text{ \AA}$) of the surfactant film (finite flexibility of the film). Anyway, none of these descriptions involve an additional scale length of the order of several $10^3 \text{ \AA}$ related to microdomains with given topologies.

However, the microemulsion phase in quaternary diagrams generally has a larger part of its phase boundary close to the domain of existence of a lamellar phase. In the vicinity of this phase boundary, the present approach may well give a useful description of the structure which is intermediate between the long-range lamellar order and the totally random bicontinuous structure [8].

Anyway, the present Letter sums up a preliminary study. Several points should be explored in greater detail before setting firm conclusions. In particular the q dependence of the intensity of the scattered light indicates a lower boundary of about $5\,000 \text{ \AA}$ for the size distribution of the domains. Because of the density differences, the spatial statistical distribution of the domains should be in principle sensitive to the gravitational field and we expect a slow variation of the composition from the base to the top of a long vertical test tube. Within this framework, the next step of this experimental study is to measure the different light scattering parameters as functions of the height in a given long vertical sample (with composition in the thin pathway) at equilibrium.

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