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Interpretation of the Anomalous Critical Behaviour in a Quaternary Microemulsion.

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Abstract. – The new experiments presented in this paper show that the anomalous critical behaviour previously reported in a quaternary microemulsion is due as a matter of fact to a crossover of two critical phenomena. The temperature evolution of the phase diagram and the light diffusion data agree with this interpretation. The system investigated exhibits a phase separation at low and high temperatures. The high-temperature critical point is a consolute critical point characterized by Ising exponents. The critical behaviour found at low temperature is related to a transition from micellar to flow birefringent phases. This interpretation is in agreement with recent models.

1. Introduction.

Considerable experimental and theoretical effort has recently been devoted to the study of phase transitions and critical phenomena in liquid mixtures involving surfactants [1]. The aim of these investigations was to point out differences if they exist in between the critical points in these organized mixtures and the liquid-gas critical points of a pure compound. In most of the surfactant solutions the critical exponents are in agreement with those found in pure fluids or usual binary mixtures. However, for three particular cases deviations from the Ising values have been reported [2-4]. The critical points of aqueous solutions of the nonionic amphiphilic molecules $CH_3(CH_2)_{i-1}O(CH_2CH_2CH_2O)_jH$ (labelled C_iE_j), seem to belong to the 3D-Ising universality class for some i and j, while for others i and j, nonuniversal γ and ν values are obtained [4-7]. These observations have elicited intense theoretical interest [8-11]. However, very recent light scattering measurements [12] for the $C_{12}E_8$-water mixture are in agreement with the 3D-Ising values for some samples and lead to anomalous values for some others. Then, the critical behaviour appears to be dependent on the sample. This reduces the possibility of known non-Ising cases to the multicomponent systems [2, 3]. Criticallike behaviour reported by Dorshow *et al.* [2] for a five-component microemulsion with double 3D-Ising exponents is certainly due to an approach to a double

critical point as suggested by Sorensen [13]. Few years ago Bellocq *et al.* [3] have reported in a quaternary system (water, dodecane, SDS, pentanol) experimental evidence for a continuous variation of effective critical exponents γ and ν from 3D-Ising values to $\gamma = 0.42$ and $\nu = 0.21$ when approaching the critical end point of a critical line.

We report on new experiments on this system supporting the interpretation of variation of the critical exponents as crossover between two critical phenomena. This crossover results from the existence of a low-temperature critical point besides the high-temperature consolute critical point primarily considered as only responsible of the critical behaviour.

2. Experiments.

At constant pressure (P) and temperature (T), the phase diagram of the quaternary system (water, dodecane, pentanol, SDS) may be represented in the three-dimensional space pentanol concentration—dodecane concentration—X ratio (X being the ratio between water and SDS concentrations). One important feature found for this system at fixed T is a critical line P_C. As one takes into account the temperature variation, the critical line becomes a critical surface. The section at constant X for this surface gives a critical line P_C^1. Since the smallest values of γ and ν have been measured in the $X = 1.034$ plane we have performed a detailed analysis of the critical behaviour in this plane. Two samples chosen on the critical line P_C^1 and defined by their critical temperature $T_C = 37.7$ and $T_C = 30.9$ °C have been studied and will be, respectively, labelled *a*, *b*. A phase separation of these samples can be observed by raising temperature above the high consolute critical point at T_C but also by lowering temperature at T_D. The temperature range $\Delta T = T_C - T_D$ within which a critical mixture remains monophasic depends strongly on the critical temperature T_C. ΔT is, respectively, equal to 27.7 °C and 10.9 °C for samples *a* and *b*. Note that sample *a* is quite similar to the sample studied by Bellocq *et al.* The critical points have been approached by raising temperature. We measured the angular distribution of light scattered at $\lambda = 647.1$ nm from the two samples, as a function of T in the monophasic domain. The angular range covered was from 30° to 150°. Temperature was controlled within 0.01 °C. Figure 1*a*) shows the square of the correlation length ξ *vs.* temperature. For the sample *a* the values of ξ are already large far from T_C ($\xi \simeq 500$ Å) and increase strongly close to T_C. A fit assuming only one critical phenomenon gives the same value $\nu = 0.21$ as previously reported. The

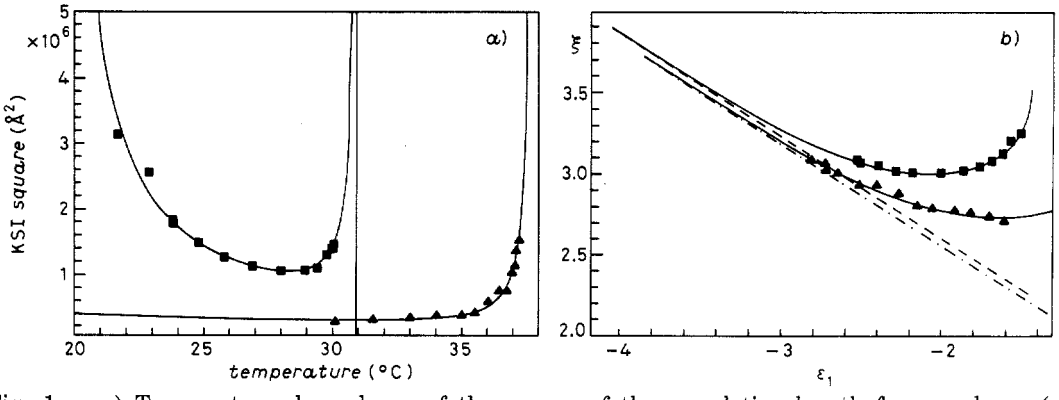

Fig. 1. – *a*) Temperature dependence of the square of the correlation length for samples *a* (▲) ($T_C^1 = 37.7$ °C, $T_C^2 = 0.0$ °C, $\xi_1 = 19.8$ Å, $\xi_2 = 168$ Å) and *b* (■) ($T_C^1 = 30.94$ °C, $T_C^2 = 19.31$ °C, $\xi_1 = 22$ Å, $\xi_2 = 164$ Å). The full lines are the fits according to eq. (1*a*). *b*) Log-log plot of ξ *vs.* ε_1. The dashed lines correspond to the behaviour expected for P_C^1. The full lines are the fit according to eq. (1*a*).

evolution of $\xi(T)$ is quite different for the second sample since ξ raises both close to T_C and T_D and cannot be well fitted assuming only one critical phenomenon. In order to check whether this anomalous behaviour was not an experimental artifact, we have prepared a third sample c with a critical temperature at $T_C = 34.3$ °C, *i.e.* in between the precedent values of T_C; moreover this last sample has been studied by turbidimetry at the same temperature stability and at the same wavelength. A similar increase is observed in fig. 2 for the turbidity close to T_C and T_D. These behaviours suggest the existence of a critical point at low temperature.

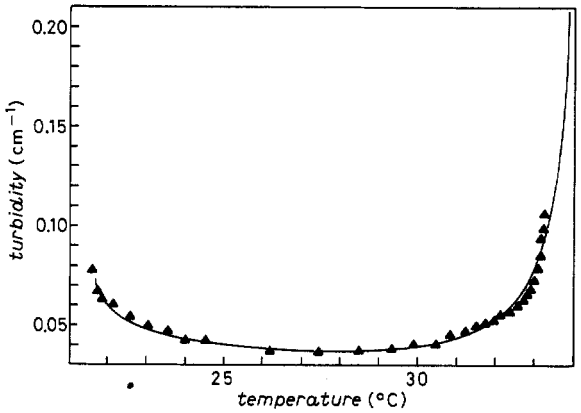

Fig. 2. – Turbidity *vs.* temperature for sample c. The full line is the fit according to eq. (2). $T_C^1 = 34.3$ °C, $T_C^2 = 21.5$ °C, $\xi_1 = 20$ Å, $\xi_2 = 345$ Å, $\chi_2/\chi_1 = 11.3$, $k\chi_1 = 8 \cdot 10^{-7}$ cm^{-1}.

3. Phase diagram.

The complex phase diagram of this quaternary system has been published elsewhere [14]. At 25 °C one identifies in the oil-rich part of the section $X = 1.034$ three distinct phases, L_2, L_2^* and D. The isotropic phase L_2 is the classical microemulsion phase, *i.e.* a dispersion of water droplets in oil. The structure of the flow birefringent L_2^*-phase has been recently elucidated [15]. It consists of a spongelike random bilayer continuous surface separating two oil-continuous regions. The D phase is an oily swollen lamellar phase. In order to understand the light scattering results, we have examined the temperature dependence of the phases L_2 and L_2^* observed in the section $X = 1.034$ close to the critical line P_C^1. Figure 3 shows partial diagrams obtained for four temperatures. As temperature is decreased the following changes are evidenced. Firstly, the critical points of P_C^1 continuously move toward the oil-rich region. Secondly, the mixtures L_2 located within the peninsula at low oil concentration exhibit a flow birefringence as the temperature is below 25 °C providing evidence of the continuity between L_2 and L_2^* domains. The main consequence of these changes is that the mixture marked by a cross in fig. 3, which is critical at 30 °C, remains a single phase in the temperature range comprised between 30 °C and 20 °C and then separates into two phases. At 20 °C, this mixture is found in the vicinity of the region where the phases L_2 and L_2^* become connected. Recent theories have predicted a second- or first-order phase transition from one structure to the other [16, 17]. Therefore in order to confirm the existence of a second critical point in the section $X = 1.034$, we have measured the correlation length ξ along the coexistence curve at 15 °C (fig. 4). We note a first maximum M_1 corresponding to a critical point of P_C^1 and a second maximum M_2 located close to the sharp edge domain where the transition from L_2 to L_2^* is expected. This last maximum corresponds to the critical

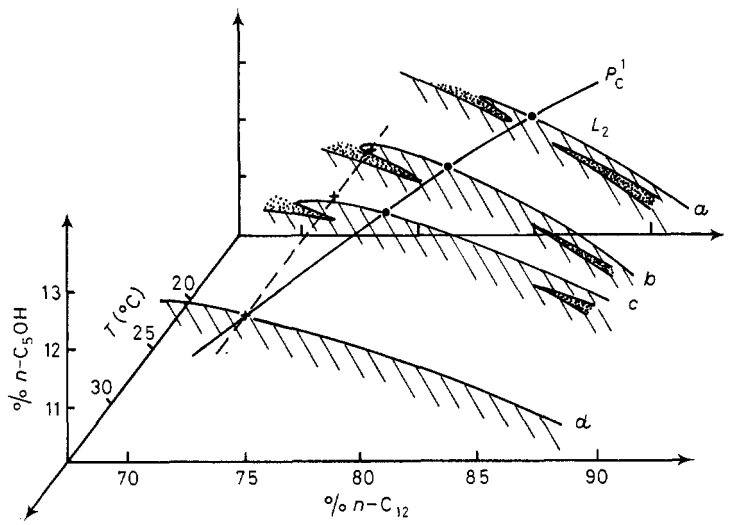

Fig. 3. – Temperature dependence of the phase diagram in the section $X = 1.034$. *a*) $T = 15$ °C; *b*) $T = 20$ °C; *c*) $T = 25$ °C; *d*) $T = 30$ °C. The dotted and hatched zones correspond, respectively, to the L_2^* phase and the multiphase regions. The dashed line describes the temperature path followed by the sample *b*.

behaviour found at low temperature (T_D) in the preceding experiments. However the associated critical points which define a critical line P_C^2 differ from critical consolute points since all diphasic mixtures close to P_C^2 have a very weak upper phase volume ([1]). This point which is at the confluence of the expected second-order line for the transition L_2-L_2^* and the first-order curve of coexistence between two isotropic phases should be a tricritical point [18].

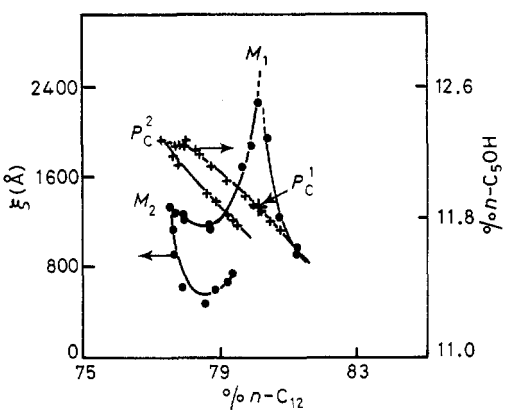

Fig. 4. – Partial phase diagram at 15 °C in the section $X = 1.034$. The full line is the limit of existence of the phases L_2 and L_2^*. The studied samples are marked by +, correlation length (●) is plotted *vs.* the dodecane concentration for the studied samples. The full line is a guide for the eye.

([1]) Close to a critical consolute point the system separates into two phases of equal volume and composition.

4. Discussion.

The above results suggest a competition between two critical behaviours related to the points of P_C^1 and P_C^2. The behaviour in the vicinity of the line P_C^1 is Ising-like (phase separation between two micellar phases), that in the vicinity of the points of P_C^2 is probably mean field. In order to account for this competition, we have fitted the light scattering data assuming ([2])

$$\xi_{\text{eff}}^2 = (\xi_1 \varepsilon_1^{-0.63})^2 + (\xi_2 \varepsilon_2^{-0.5})^2 , \tag{1a}$$

$$\chi_{\text{eff}} = \chi_1 \varepsilon_1^{-1.24} + \chi_2 \varepsilon_2^{-1} , \tag{1b}$$

where

$$\varepsilon_{1,2} = (T_C^{1,2} - T)/T_C^{1,2} \tag{1c}$$

and T_C^1, ξ_1, χ_1, T_C^2, ξ_2, χ_2 are, respectively, critical temperatures and prefactors associated to the two critical points of P_C^1 and P_C^2. Data of turbidity have been fitted assuming [19]

$$\tau = K \chi_{\text{eff}} \frac{2\alpha^2 + 2\alpha + 1}{\alpha^3} \ln(1 + 2\alpha) - \frac{2(1+\alpha)}{\alpha^2} \tag{2a}$$

with

$$K = \frac{\pi^2}{\lambda^4} \left(\rho \frac{\partial \varepsilon}{\partial \rho} \right)_T^2 k_B T \quad \text{and} \quad \alpha = 2 (q_0 \xi_{\text{eff}})^2 , \tag{2b}$$

where λ is the vacuum wavelength and ε the dielectric constant of the medium. The solid lines of fig. 1 and 2 are the best fits obtained. In the fits, T_C^1 which is the only experimental determined parameter is fixed, while T_C^2, ξ_i and χ_i are free parameters. The amplitude $\xi_1 \simeq 20$ Å associated to the points of P_C^1 is in agreement with well-known values for such micellar systems, ξ_2 is found of order of 170 Å for samples *a* and *b* and 345 Å for sample *c*. This disagreement is certainly related to the turbidity fit since more parameters have to be introduced in that case. However, ξ_2 is definitively larger than ξ_1 and is of the order of the characteristic size of the L_2^*-phase [15]. According to eq. (1*a*) with $\xi_2 \gg \xi_1$ the ε range where Ising exponents are expected is very sharp and is dependent on the difference $(T_C^1 - T_C^2)$. For example, Ising values are expected only if $\varepsilon < 10^{-4}$ for sample *b* (fig. 1*b*)). Let us note that the earlier measurements have been performed in the ε range $10^{-1} \div 10^{-3}$ and have lead to effective exponents. For sections of the phase diagram corresponding to larger X values the temperature distance between T_C^1 and T_C^2 is more important. Thus the crossover is less and less pronounced and effective exponents are more and more Ising-like.

5. Conclusion.

We have demonstrated by new experiments that the anomalous critical behaviour previously reported in a quaternary microemulsion is due as a matter of fact to a crossover

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([2]) One considers that the system can be described by two different order parameters weakly coupled.

of two critical phenomena. The temperature evolution of the phase diagram and the light diffusion data agree with this interpretation. At low temperature, a critical point has been found out which is related to a transition from micellar to flow birefringent phases. This interpretation is in agreement with recent models [17] (1). More generally the critical behaviour of mixtures involving surfactant seems now similar to that evidenced in usual binary mixtures.

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