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Light scattering study of a lower critical consolute point in a micellar system

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Résumé. — Nous avons étudié les solutions micellaires aqueuses de sulfate de dodécyle et de sodium, butanol et chlorure de sodium. En raison de l'écrantage des forces électrostatiques répulsives par les nuages ioniques et de l'existence de forces attractives entre les micelles (éventuellement reliées à l'hydratation), des points critiques inférieurs de démixtion peuvent être trouvés dans ces mélanges. Nos mesures par diffusion de lumière, de volume et de surface, sont en parfait accord avec les théories du groupe de renormalisation pour les phénomènes critiques. De plus, la région critique apparaît plus large que prévue par les modèles d'Ising décorés utilisés pour décrire les points critiques inférieurs.

Abstract. — We have studied aqueous micellar solutions of sodium dodecyl sulfate, butanol and sodium chloride. Due to the screening of electrostatic repulsive forces by the ionic atmosphere and to the existence of attractive forces (possibly related to hydration) between the micelles, lower critical consolute points can be found in these mixtures. Our data from surface and bulk light scattering are in perfect agreement with the renormalization group theories for critical phenomena. Moreover, the critical region happens to be wider than that predicted by the decorated Ising models used to describe lower critical consolute points.

1. Introduction.

The study of critical phenomena in micellar systems or in microemulsions, besides its intrinsic interest, is helpful for achieving a better knowledge of micellar interactions in these systems. A large number of papers have been devoted to this subject in the recent years [1-13]. The main conclusion of the studies on a large variety of systems is that the phase separation beyond the critical point is driven by the interactions between the structural elements (micelles) rather than between the individual molecular constituents. Another common observation is that the phase separation occurs upon heating and that the critical points are lower consolute points unlike in most binary mixtures of small molecules.

The existence of a lower critical consolute point in a micellar system can not be accounted for with the commonly considered interaction forces in these media : hard-sphere repulsion, electrostatic repulsion, Van der Waals attraction.

In aqueous micellar systems, the polar parts of the surfactant molecules are located at the outer surface of the micelles. Even with non-ionic surfactants, where the polar parts are not

charged, there is experimental evidence showing that the micelles do not interpenetrate when the critical point is approached [14]. In ionic surfactant micelles the outer volume containing no CH_2 groups has a non negligible thickness $1\text{--}2 \text{ \AA}$ [15]. Moreover the hard sphere radius is larger than the micellar radius : $R_{\text{HS}} \sim R_{\text{H}} + K^{-1}$, where K^{-1} is the Debye screening length [16]. In such conditions the Van der Waals attractive forces are not sufficiently strong to produce a phase separation (see appendix).

Moreover, unless the hard sphere radius varies with temperature, such interactions will lead to a phase separation when temperature is decreased.

Other types of forces, relevant from colloidal systems, have been recently evidenced [17]. Among them, the hydration forces originate from the increased structuring of the water around the polar parts of the surfactant molecules. These forces can have an attractive character : when two particles approach each other, part of the hydration water is released and transferred to the bulk, thus increasing the entropy of the system and decreasing its free energy [18].

A theoretical treatment for lower critical solution points in binary mixtures of small molecules (like nicotine + water) can be given by decorated lattice models [19-21]. They include a strongly directional interaction between the components of the mixture, such as a hydrogen bond, in addition to the usual non directional interactions. An extension of these models, due to G. R. Andersen and J. C. Wheeler [22], allows us to reasonably describe the asymmetry of the coexistence curves even for molecules (or molecular entities) disparate in volume like in polymer and micellar solutions. The critical exponents are non classical, but it must be pointed out that the temperature range $|T - T_c|$ where these critical exponents are valid is reduced compared to the case of upper critical points : typically 10^{-2} degrees compared to several degrees [23]. Beyond this range the properties of the system can still be described with power laws provided that an artificial temperature dependence of the exponents is introduced. Such temperature dependence of the exponents in fact reflects the temperature dependence of the interactions which give rise to the lower consolute boundary. (In an example presented in reference [22], the exponent β is equal to 0.32 within 10^{-2} degrees of T_c ; an apparent exponent of 0.42 can be defined around $T = T_c + 1^\circ$, increasing to 0.5 around $T_c + 3^\circ$). This might be the origin of the seemingly erratic variation in critical exponents near the lower critical boundary of non-ionic surfactant aqueous solutions [3].

However it must also be pointed out that these models could be less appropriate for micellar solutions than for binary mixtures of small molecules. Indeed, they do not include the possible evolution of size and shape of the aggregates with temperature. In particular simpler mean-field model can account for the dissymmetry of the coexistence curves by assuming that the aggregates are elongated. For spherical aggregates the critical concentration ϕ_c is between 10 and 20 % whereas experimental values as low as 2 % have already been reported in these systems. Moreover, the measured critical exponents are closer to the mean-field exponents when ϕ_c is small, and they only approach the non classical values when ϕ_c approaches 10 %.

Recently, lower critical consolute points have been observed in microemulsion systems, containing five components. In one case, it has been shown that the critical point was also a critical end point, because it was associated to a three-phase equilibrium [12]. A careful analysis of the phase diagram showed that many other critical points were present in the same composition region [24]. For this reason it was tempting to begin a study on a simpler system containing less components, without too much changing the interesting parameters, i.e. the structure and the interactions between the micelles.

2. Description of the system.

We previously performed a light scattering study of a series of microemulsions whose composition is reported in table I (series TB) [12]. We showed that the water rich microemulsions of the series contained droplets of oil (toluene) surrounded by surfactant molecules (sodium dodecyl

Table I. — *Compositions are given in wt %. S is the weight percentage of NaCl in the brine. T_1 is the temperature of the phase separation. See text for the other symbols.*

Sample	TB	B1	B2	B3	B4
Toluene	47.25	—	—	—	—
SDS	1.99	3.92	4.54	4.46	4.78
Butanol	3.96	7.77	8.12	8.13	8.42
Brine	46.8	88.31	87.34	87.41	86.80
S	3 to 10	5.5 to 8	6.6	6.6	6.6
T_1	20° ($S = 5.4$)	20° ($S = 6.6$)	25.2	24.85	23.2
T_c			25.0	24.85	23.0
μ			1 (± 0.2)	0.95 (± 0.2)	1 (± 0.2)
γ_0			0.13 dyn/cm	0.15 dyn/cm	0.19 dyn/cm

sulfate : SDS) and dispersed into water. The system also contains a salt (sodium chloride) and a surfactant or alcohol (butanol). The alcohol molecules are located not only in the surfactant layers but also in the toluene cores and in the aqueous continuous phase (a few per cent in the last two cases). Phase separation can be reached by increasing either the salt concentration S or the temperature. This is associated with structural changes that we will not discuss here [12].

We then decided to study a simpler system, removing the oil component. Indeed if the phase separation is due to hydration forces between droplets, these forces will only depend on the structure of the outer part of the droplet and not on the oil core properties.

The composition of the samples is indicated in table I. Series B1 corresponds to the same relative proportions of water, alcohol and SDS as the microemulsion series TB. The phase separation of water rich microemulsions is obtained for the salinity $S = 5.4$ whereas it is obtained for the salinity $S = 6.6$ in the series B1 without oil. Both points are close to critical as indicated by light scattering experiments. This can be considered as a confirmation of the dominant rôle of hydration forces ⁽¹⁾.

In order to better approach the critical point, we slightly modified the composition of the sample B1. The salinity was fixed at $S = 6.6$ and the concentration of SDS and butanol increased. For practical purposes we looked for a critical temperature around 24 °C. The composition of these samples is also reported in table I. The closest-to-critical sample is B3 which phase separates at $T_1 = 24.85$ °C into two phases of almost identical volumes (volume ratio : $r = 0.50 \pm 0.01$; this ratio decreases very slowly with temperature : $r = 0.46$ at $T = T_1 + 2^\circ$).

In these series of samples we are well above the critical micellar concentration of the surfactant (CMC). In the corresponding mixtures water + NaCl + butanol, the CMC as deduced from surface tension measurements is about 10^{-5} by weight.

3. Light scattering experiments.

Bulk light scattering measurements were undertaken both in the single phase and in the two-phase regions. If the sample composition is not exactly critical, the corresponding exponents in the one phase region might differ from the theoretical ones [28]. For these reasons most of the measurements were performed on the closest-to-critical sample B3.

⁽¹⁾ The size of the micelles in the systems without oil is expected to be smaller than in the microemulsions (radii ~ 100 Å). Indeed it is known that in systems without oil, only part of the alcohol swells the micelle. The remaining molecules dissolve in the aqueous phase and in the palissade layer of the micelles [25].

Both elastic and inelastic light scattering measurements were performed. The sample was held in a sealed cylindrical glass cell, temperature controlled to within ± 0.005 °C.

The elastic light scattering experiments were performed with an improved set-up where the intensity I of the light scattered at the angles θ and $\pi - \theta$ is alternatively detected and where we measure directly the ratio $I(\theta)/I(\pi - \theta)$ [24, 29]. This procedure considerably improves the accuracy on the measurements of the angular variations of the intensity.

A typical example of the performances of the set-up is given in figure 1. The line represents a fit with the Orstein-Zernike formula, which is expected to be valid in the critical region :

$$I(q) = \frac{I_0}{1 + q^2 \xi^2}, \quad q = \frac{4\pi}{\lambda} n \sin \frac{\theta}{2} \quad (1)$$

ξ is the correlation length of the concentration fluctuations; n is the refractive index of the solution and λ the wavelength of the light.

The experimental results were found to be in excellent agreement with the Orstein-Zernike formula, down to ξ values of about 100 Å. In such a case $I(0)/I(\pi) \sim 1.1$. These small ξ values were obtained far from the critical point for the samples B1 at low ($S \lesssim 6$) and high salinities ($S \gtrsim 7$). In these cases it becomes difficult to distinguish between the Orstein-Zernike function and the form factor for spheres which become very similar. Further experiments are in progress to measure independently the aggregation number of SDS molecules in the micelles (fluorescence experiments) and their size and shape (X-ray experiments). This will allow us to determine the limits of the critical region more precisely.

Fig. 1. — Angular variation of the scattered intensity for sample B3 $\varepsilon = 1.8 \times 10^{-4}$. The line is the fit with equation (1), which gives $\xi = 593$ Å.

We have also measured the autocorrelation function of the scattered light on the same samples. In all cases it was found to be exponential. We have related the time decay constant τ to the diffusion coefficient $\tau^{-1} = 2 D q^2$. In the critical region the angular variation of D is predicted by the Kawasaki formula :

$$D = D_0 \frac{3}{4 x^2} [1 + x^2 + (x^2 - 1/x) \operatorname{arctg} x] \quad (2)$$

with : $x = q\xi$

$$D_0 \cong 1.1 \frac{k_B T}{6 \pi \eta \xi} \quad (3)$$

η being the viscosity of the solution [30].

Again down to $\xi \sim 100 \text{ \AA}$ the agreement between theory and experiments is very good (see Fig. 2). The three different ξ values obtained from the angular variations of I , D and from D_0 are in excellent agreement ⁽²⁾. This strongly supports the interpretation of the data in terms of critical phenomena. A strong increase of the micellar radius can be excluded because it could not explain all the observed features. The critical domain is also found to be very large : 2 % for the salinity (samples B1) and several degrees for the temperature (samples B2-B4).

The behaviour of the correlation length *versus* the reduced temperature ε is shown in figure 3

Fig. 2. — Angular variation of the diffusion coefficient for sample B3 at the same temperature than in figure 2. Fit with equation (2) leads to $\xi = 613 \text{ \AA}$ and $D_0 = 1.51 \times 10^{-8} \text{ cm}^2/\text{s}$. From D_0 and equation (3) one gets the third determination $\xi = 600 \text{ \AA}$.

⁽²⁾ The value of ξ deduced from D_0 is less accurate in the two-phase domain than the two others, because of the uncertainty ($\sim 8\%$) on viscosity measurements requiring a phase separation procedure.

Fig. 3. — Correlation length *versus* reduced temperature for sample B3. In both one-phase (×) and two-phase region (upper phase ●, lower phase +), the lines are fits to equation (4). The quality of the fits is better in the one-phase region thus explaining the corresponding smaller error bars. The parameters ξ_0 and ν are reported in table II.

for both one-phase and two-phase regions. The data can be well fitted to power laws :

$$\xi = \xi_0 \varepsilon^{-\nu} \quad \varepsilon = (T - T_c)/T_c \tag{4}$$

The values for critical exponents and scale factors are reported in table II. We find a non-classical exponent (theoretical value $\nu \sim 0.63$) [27]. The ratio of the scale factors ξ_0 in the one-phase region and ξ'_0 in the two-phase one is also close to the theoretical prediction for Ising models $\xi_0/\xi'_0 \sim 1.95$ [31].

It can be noted that there is a small, but systematic difference between the correlation lengths measured in the upper and lower phases. We do not presently understand the origin of this difference.

We have made some complementary interfacial tension measurements between the two micellar phases above the phase separation temperature, by using surface light scattering methods [26].

Table II. — *Correlation length measurements. Sample B3.*

	Single phase domain	Two-phase domain	
		lower phase	upper phase
ν	0.62 ± 0.03	0.64 ± 0.04	0.63 ± 0.05
ξ_0	$(13 \pm 2) \text{ \AA}$	$(7 \pm 1.5) \text{ \AA}$	$(6.5 \pm 2) \text{ \AA}$

The samples were temperature controlled to within ± 0.05 °C. Even for samples whose composition is not exactly critical, the surface tension is expected to follow the power law [27] :

$$\gamma = \gamma_0 \varepsilon^\mu \quad (5)$$

where ε is the distance to the critical point and μ is the critical exponent. Indeed, this law is satisfied as soon as one follows a path in the phase diagram tangent to the coexistence curve [28].

When the composition is varied in order to approach the critical point (salinity S for the samples B1), ε has to be defined in terms of field variables, like chemical potentials of the different species, which are difficult to determine. We then rather relate the γ measurements to the density measurements of the two coexisting phases. The density difference follows also a power law [27] :

$$\Delta\rho = \Delta\rho_0 \varepsilon^\beta$$

from which one obtains $\gamma \propto (\Delta\rho)^{\mu/\beta}$.

The ratio μ/β in the B1 samples was found to be equal to 4 ± 0.1 as in the microemulsion samples TB [12].

This indicates that the exponents are non-classical ($\mu \cong 2$ v $\cong 4\beta$), since mean-field exponents are $\mu = 1.5$ and $\beta = 0.5$ ($\mu = 3\beta$).

When the temperature is varied at constant composition :

$$\varepsilon = (T - T_c)/T_c.$$

Then μ can be determined directly. It is given in table I for samples B2 to B5 together with the scale factor γ_0 . The variation of surface tension with temperature for sample B4 is represented in figure 4 together with the fit with equation (5). From these data one can deduce :

$$\mu = 1.0 \pm 0.2.$$

Fig. 4. — Surface tension *versus* reduced temperature for sample B4. Points are experimental; the line is the fit with equation (5), which leads to $\mu = 0.99$ and $\gamma_0 = 1.9 \times 10^{-2}$ dynes/cm.

We plan to improve the accuracy of this determination : the construction of a better temperature controlled cell is currently under way. However we can already conclude again that the measured exponent has not the mean-field value, although it is also slightly lower than the non-classical value $\mu \simeq 1.26$ [27].

4. Conclusion.

We studied a micellar system showing a lower critical consolute point. We saw no evidence of a large increase of the micellar size. Our results are rather consistent with the theories of critical phenomena. We observed a divergence of the correlation length ξ of the concentration fluctuations as T_c is approached. The critical exponents for ξ as well as those of the surface tension between the two-phases above T_c and of their density difference are all non-classical.

The scaling factors for the surface tension are unusually small, over 100 times smaller than the corresponding numbers for simple binary mixtures. This probably arises from the particular character of the surfactant molecules present in the mixture. The scale factor for the correlation length are on the contrary larger. This is however consistent with the fact that phase separation is not expected to be due to the interactions between individual components, but rather to interactions between the micelles which are already large objects.

The temperature range of the critical region is much larger than predicted by the decorated Ising models. As explained before, this could be particular to these models which do not incorporate the existence of aggregates. Further improvement of the theory is clearly needed to clarify this point.

Let us finally note that the mean-field theories recently proposed for elongated and flexible aggregates will not be appropriate here since our critical concentrations are close to the values for spherical aggregates ($\sim 10\%$) and because of the clearly non-classical values of the critical exponents.

Current experiments are under way in order to obtain more information about the size and the shape of the micelles close to the critical point.

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We gratefully thank A. M. Cazabat who pointed out to us that critical behaviour could be observed in quaternary mixtures derived from microemulsion systems, thus initiating this study.

Appendix.

The free energy per unit volume of a system of interacting spheres can be written phenomenologically as [32] :

$$F = F_{\text{HS}} + \frac{1}{2} \frac{kT}{v} A \phi^2$$

where F_{HS} is the free energy term relative to hard spheres, v the sphere volume, ϕ the sphere volume fraction and A a dimensionless parameter characterizing the strength of the interaction.

It is easy to show that this form of the free energy leads to a phase separation for $A < A_c \cong -21$. The critical volume fraction is $\phi_c \simeq 0.13$ in good agreement with the results from more sophisticated models [18].

On another hand, when the interaction forces are Van der Waals attraction between the hydrophobic cores of the micelles it can be shown that [32] :

$$A = \frac{1}{3} \frac{H}{kT} \left\{ \frac{1}{4} \ln \left(\frac{s-1}{s+1} \right) - s - s^2 \ln \left(\frac{s^2-1}{s^2} \right) \right\}$$

where H is the Hamaker constant and s the ratio between hard sphere radius and core radius : $s = R_{HS}/R_c$.

Typically $H \sim 5 \times 10^{-14}$ erg, $R_c \sim 17$ Å for an SDS micelle and $R_{HS} = R_c + l_p + K^{-1}$ where l_p is the size of the layer containing no CH_2 groups $l_p \sim 2$ Å and $K^{-1} \sim 3$ Å for $S \sim 6$; thus $R_{HS} \sim 22$ Å. It comes :

$$A = -5 \times 10^{-2} \gg A_c$$

A is still larger for a mixed alcohol – SDS micelle for which R_c is larger. To reach the value $A = A_c$ one should have $l_p + K^{-1} \sim 10^{-34}$ Å, i.e. the hydrophobic cores should be allowed to come into contact. This is very unlikely according to the existing experimental data (see text).

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