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Water/oil interface in L_2 phase : a small-angle X-ray scattering study

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Résumé. — Nous étudions la structure de micelles inverses du système ternaire aérosol OT-*n* heptane-eau par diffusion centrale des rayons X. La structure de la partie polaire à l'interface eau huile est précisée. Pour un rapport d'hydratation suffisant, la partie polaire hydratée piège une goutte d'eau « libre ». Les dimensions respectives de chaque zone sont déterminées. Des mesures de rayons de giration confirment ces modèles.

Abstract. — We have studied the structure of reversed micelles in the ternary system aerosol OT-*n* heptane-water by small-angle X-ray scattering. A structural model of the interface water/surfactant is proposed. At high water content, the film of hydrated surfactants surrounds a free water droplet. The size of the successive layers of the micelle is determined. The measurement of the radius of gyration seems to confirm our model.

1. Introduction.

In an organic solvent, water can be solubilized when a surfactant is added [1]. In an appropriate concentration range, the solution is made by a dispersion of water droplets surrounded by a film of surfactants in a continuous medium (the organic compound). The more common surfactant is the aerosol OT (AOT), owing to numerous industrial applications. A small-angle neutron scattering (SANS) study was presented in a previous paper [2]. It was shown that, in dilute solutions, inter-aggregate interferences can be neglected. A contrast variation allowed us to obtain the volume of the droplet, the aggregation number n and the area per polar head σ .

Nevertheless, we do not know the structure of the water/surfactant interface of these inverted micelles. The experimental determination of the number of water molecules bounded to the polar heads is needed to verify some theoretical model; for instance, to obtain contributions to the free energy of ionic amphiphile-water systems [3].

The aim of this paper is to try to obtain information on the internal structure of the micelles, using small-angle X-ray scattering techniques (SAXS).

2. Method and basic assumptions.

A schematic representation of an AOT inverted micelle is shown in figure 1. The aqueous core is surrounded by the polar heads of the surfactant molecules. The hydrophobic chains are in the organic solvent.

Fig. 1. — (a) The aerosol OT molecule; (b) inversed spherical micelle with an aqueous core.

We consider that, at low concentration, the L_2 phase is made up of monodisperse spherical droplets. Ultracentrifugation and small-angle neutron scattering studies [2] confirm this hypothesis [14].

The electron density profile of a normal micelle is well known [4]. But the representation of the contrast profile of reversed micelles is more doubtful. Two models can be proposed.

In the first one (Fig. 2, A), the electron density of the water core is constant and equal to $\bar{\rho}_{\text{pol}}$. The counterions Na^+ are considered to be evenly distributed in the core. ρ_{par} and ρ_0 are the electron density of the paraffinic region and the solvent, respectively.

In the second model (B), one distinguishes two kinds of water : i) the water of hydration for polar groups, and ii) free water in the droplet centre. Most counterions are bound to the polar heads [5] but some of them can be located in the free water.

The parameters ρ_{pol} , R_w , l_{pol} (Fig. 2) are determined by the method of Reiss-Husson and Luzati [6].

2.1 ELECTRON DENSITY OF THE INTERFACIAL REGION ρ_{pol} . — The integral of the scattered intensity gives the mean square value of the fluctuations of the electronic density [7] :

$$Q = 2 \pi \int_0^\infty s J_n(s) ds = \overline{(\rho(r) - \bar{\rho})^2} / \bar{\rho},$$

where $J_n(s)$ is the normalized scattered intensity [4] and $\bar{\rho}$ is the mean electron density of the sample (volume V).

This last equation allows us to determine ρ_{pol} when the values of the other electron densities are known (as in our case).

The last formula can be written as follows (Appendix I)

$$Q\bar{\rho} = (\rho_w^2 - \rho_0^2)(\Phi_0 + \Phi_{\text{pol}}^*) + (\rho_{\text{pol}} + \rho_w)(\rho_{\text{pol}}^* - \rho_w) \Phi_{\text{pol}}^* + (\rho_{\text{par}}^2 - \rho_0^2) \Phi_{\text{par}} + \rho_0^2 - \bar{\rho}^2. \quad (1)$$

2.2 RADIUS OF GYRATION MEASUREMENT. — The radius of gyration R_G is a function of the electron density

$$R_G^2 = \int r^2 \rho(r) dr / \int \rho(r) dr \quad (2)$$

R_G can be calculated if one knows the profile $\rho(r)$ and the geometrical parameters of the particle (Appendix II).

Fig. 2. — Schematic representation of a spherical micelle and its radial electron density in *n*-heptane. I : water region, its volume is v_w and its density is $\rho_w = 0.334 \text{ e}^-/\text{\AA}^3$. The volume of one water molecule is $29.9 \text{ \AA}^3$ at 25°C . II : polar region containing the polar heads, gegenions and water, its volume is v_{pol} and its electron density is ρ_{pol} . III : paraffinic region, its volume is v_{par} and its density is $\rho_{\text{par}} = 0.254 \text{ e}^-/\text{\AA}^3$. S_w : surface of discontinuity between ρ_w and ρ_{pol} . S_{pol} : surface of discontinuity between ρ_{pol} and ρ_{par} ($\sigma = S_{\text{pol}}/n \simeq 58 \text{ \AA}^2$ [2]). S_{par} : surface of discontinuity between ρ_{par} and ρ_0 ($\rho_0 = 0.237 \text{ e}^-/\text{\AA}^3$). Model B : R_w is the radius of the free water, $R_{\text{pol}} - R_w = l_{\text{pol}}$ is the thickness of the polar region. $R_{\text{par}} - R_{\text{pol}} = e$ is the thickness of the surfactant coat [12].

Inversely, R_G can be deduced from SAXS. In the very small-angle region (i.e. small value of the scattering vector s) the Guinier approximation gives us [7] :

$$R_G \simeq 0.80 \sqrt{-\beta}$$

where β is the slope of the Guinier plot $\log J_n$ versus $(2\theta)^2$ [11].

2.3 GEOMETRICAL PARAMETERS OF THE MICELLE. — At large s , the intensities obey Porod's law [8]. In our experimental configuration [4], if $s^3 J_n(s)$ is plotted as a function of s^3 , the experimental points align along a straight line with slope equal to zero. This asymptotic limit is related to the areas of the surfaces S_{ij} separating two regions with different electron density ρ_i and ρ_j

$$\lim_{s \rightarrow \infty} s^3 J_n(s) = \frac{1}{16 \pi^2} \sum \frac{(\rho_i - \rho_j)^2}{\bar{\rho}} \frac{S_{ij}}{V} = L_P. \quad (3)$$

This equation can be developed and gives (Appendix III) the value of R_w (model B) or R_{pol} (model A).

3. Experimental.

The molecular weight of the aerosol OT (sodium di-2-ethylhexylsulfosuccinate) is 444.5 g [2]. The water was tridistilled. The hydrocarbon solvent, obtained from Merck, is the *n*-heptane. Indeed, with such a solvent, a large amount of water can be solubilized : the molar ratio water/OBS can reach 70. On the other hand, the boundary of the L_2 phase in the phase diagram of the ternary system AOT/water/heptane is known [9]. Water can be considered to be insoluble in this solvent.

All the measurements were performed at 25 °C. A micellar solution is characterized by the molar ratio $\omega = (\text{water})/(\text{AOT})$ and the water volume fraction Φ_0 . The partial specific volume of AOT is obtained with a diapason device. One finds $v_{\text{AOT}} = 0.8621 \text{ cm}^3 \text{ g}^{-1}$ [10].

The ω values are : 8.5, 20, 30, 40, 49.5, 66.7. The volume fraction Φ_0 varies from 1 % to 15 %.

X-ray measurements were taken on a low-angle GDPA camera. The collimation system uses slits of negligible width and infinite height. The explored angular domain corresponds to $1.1 \times 10^{-3} \text{ \AA}^{-1} < s < 7 \times 10^{-2} \text{ \AA}^{-1}$. $s = 2 \sin \theta / \lambda$ is the scattering vector, $\lambda = 1.54 \text{ \AA}$ is the $\text{CuK}\alpha$ wavelength and 2θ is the angle between the scattered and the incident beam.

The resolution is about 14 Å and, at small s range, one can measure the radius of gyration in the region of 80 Å.

4. Results and discussion.

The experimental curves are smoothly decreasing and, at large s ($s > 3.3 \times 10^{-2} \text{ \AA}^{-1}$), the scattered intensities agree with Porod's law (Fig. 3). This behaviour allows us to make a good evaluation of the integral of the scattered intensity [11].

The X-ray diffraction spectra are treated using small-angle neutron scattering results [2] : the aggregation number n and the volume (v_0) of the micellar water pool.

Table I gives results obtained with samples (noted A_1 to A_{VI}), where $\omega = 49.4$.

$\bar{\rho}$, Φ_0 and Φ_{AOT} are deduced from the concentration of the solutions. The radius of gyration R_G is evaluated from experimental curves (Guinier plot) for dilute solutions ($\Phi_0 + \Phi_{\text{AOT}} < 6\%$) and corresponds to an extrapolation to zero concentration.

The other values of this radius (R_{GA} and R_{GB}) are calculated using equation (2).

Experimental results are presented in table II.

$\frac{\rho_{\text{pol}}}{\bar{\rho}_{\text{pol}}}$ is calculated from equation (1) according to model B. In model A, the polar electron density ρ_{pol} can be calculated from

$$\frac{\rho_{\text{pol}}}{\bar{\rho}_{\text{pol}}} = \frac{\rho_w v_0 + \rho_{\text{pol}}^* v_{\text{pol}}^*}{v_0 + v_{\text{pol}}^*}.$$

p is the number of water molecules bound to the polar heads in the region II : $p = \Delta v / 29.9 n$.

The main results depend on the ω value.

1) $\omega < 20$. — Let us compare the numerical value of ρ_{pol} deduced from the integral of the scattered intensity and the value of $\bar{\rho}_{\text{pol}}$. One can see that these two values are about the same. The radial electron density $\rho(r)$ is well represented by model A. This is emphasized by the calculated radius of gyration R_{GA} which gives a value very close to R_G .

One can give the following interpretation : at low water content, all of the water molecules participate in the solvation of the polar heads and the counterions Na^+ . This is in agreement with the behaviour of the interfacial area σ per polar group : σ increases if $\omega < 30$ [13] and becomes constant for $\omega > 30$.

2) $\omega > 40$. — The main result is that ρ_{pol} remains constant for all the values of ω . On the other hand, the value of $\bar{\rho}_{\text{pol}}$ is not consistent with model A. Indeed, $\bar{\rho}_{\text{pol}}$ is different from ρ_{pol} .

Fig. 3. — (a) Guinier plot of experimental curve : $\omega = 49.4$; solution A_{VI}; $R_G = 67.5 \text{ \AA}$. (b) Porod plot of experimental curve : $\omega = 49.4$; solution A_I; $L_P = 5.4 \times 10^{-6}$.

Table I. — *Experimental results for $\omega = 49.4$. Study of solutions A_I to A_{VI} leads to the following values : $\rho_{\text{pol}} = 0.42 \pm 0.01 \text{ e}^-/\text{\AA}^3$, $R_w = 55 \pm 10 \text{ \AA}$, $R_G = 66 \pm 1 \text{ \AA}$.*

Sample	$\bar{\rho}$ ($\text{e}^-/\text{\AA}^3$)	Φ_0	Φ_{AOT}	Φ_w	$10^3 Q$ ($\text{\AA}^{-3}$)	$10^6 L_P$ ($\text{\AA}^{-4}$)	$10^{-4} Q/L_P$ ($\text{\AA}$)	ρ_{pol} ($\text{e}^-/\text{\AA}^3$)	R_w ($\text{\AA}$)	R_G ($\text{\AA}$)
A _I	0.2640	0.1714	0.0736	0.0801	12.9	5.4	0.24	0.412	47.5	
A _{II}	0.2498	0.0803	0.0345	0.0343	6.8	2.6	0.26	0.416	53.4	
A _{III}	0.2454	0.0524	0.0225	0.0218	4.7	1.7	0.27	0.420	52.7	
A _{IV}	0.2442	0.0447	0.0192	0.0209	4.1	1.5	0.27	0.419	59.3	69.7
A _V	0.2433	0.0389	0.0167	0.0180	3.6	1.35	0.26	0.422	56.5	68.5
A _{VI}	0.2426	0.0345	0.0148	0.0160	3.2	1.2	0.26	0.425	62	67.5

Table II. — *Experimental results obtained by small-angle scattering on inverted micellar solutions AOT/water/n-heptane.*

ω	8.5	20	30	40	49.4	66.7
n	115	230	570	920	1 300	1 820
$10^{-6} v_0$ ($\text{\AA}^3$)	0.027	0.135	0.51	1.10	1.87	3.63
ρ_{pol}	0.57	0.44	0.41	0.42	0.42	0.42
$\overline{\rho_{\text{pol}}}$	0.563	0.438	0.406	0.388	0.378	0.367
R_w	0	0		43	55	82
R_{pol}	20	33	51	65	78	97
l_{pol}				22	23	15
p	(8.5)	(20)		25	23	25
R_G	17	27	40	55	66	80
R_{GA}	16.8	26.7		51	61	75
R_{GB}				54	65	80

Neutron : n and v_0 [2].

X-ray : for $\omega > 30$, model B yields experimental values,
for $\omega < 30$, this is not free water : $p = \omega$.

The uncertainties do not allow us to interpret results at $\omega = 30$.

For instance, let us, consider samples with $\omega = 49.4$. Table I shows that Q and L_p vary linearly with the concentration. As a consequence, the ratio Q/L_p remains quasi-constant in the studied concentration range which indicates that the size of the aggregate does not vary at constant ω . Our assumption seems to be valid.

Another argument is that the ratio Φ_w/Φ_0 is still constant.

ρ_{pol} can be determined with a good accuracy. This allows us to obtain the free water radius R_w with an uncertainty of about 20 %.

This result is based upon another assumption : in the relation $v_{\text{pol}} = v_{\text{pol}}^* + \Delta v$ (Appendix I) one considers that all the Na^+ ions are located in region II (Fig. 2). NMR Spectroscopy [5] shows that only 28 % of the Na^+ is dissociated from the sulfosuccinate head group. Moreover, a homogeneous distribution of the Na^+ in regions I and II involves a very weak variation $\Delta\rho_w$ of the electron density of the water with respect to ρ_{pol} .

A numerical evaluation can be given : taking the volume of Na^+ equal to $4 \text{\AA}^3$, one finds $\Delta\rho_w = 0.006 \text{ e}^-/\text{\AA}^3$ ($\omega = 49.4$) which corresponds to a relative change of the contrast of the order of 8 %. This other approximation seems to be justified.

Then, for $\omega \geq 40$, model B seems appropriate. This is true if one considers the ρ_{pol} value. This is also confirmed if R_G and R_{GB} are compared.

The number of water molecules bound to the sulfosuccinate head is about 25 and is independent of ω . As a consequence, the thickness l_{pol} of region II decreases when the micelles grow.

All these results are also consistent with the behaviour of the interfacial area per polar group ($\sigma = \text{const.}$ if $\omega > 30$).

3) If $\omega \simeq 30$, ρ_{pol} is very close to $\overline{\rho_{\text{pol}}}$. The experimental procedure is not precise enough to distinguish between model A and model B.

5. Conclusion.

Both small-angle neutron and X-ray scattering allow us to obtain a more precise description of micelles. It can be shown that the water pool can be divided into two regions where the structure of the water is quite different. For a complete hydration of the ion Na^+ and polar heads, about 25 water molecules are needed. This value is rather high compared with hydration numbers. This can be first explained by the model. Indeed, the electron density profile is surely smooth and our model is a crude approximation : the polar region is the region of the micelle where the electron density is different from ρ_w and from ρ_{par} . It must be noted that, even for normal micelles, the value of ρ_{pol} deduced from X-ray results are about 0.39 for similar polar groups [4]. This gives an apparent hydration number close to 20.

The presence of two carboxylic groups in the polar region can also explain this rather high value.

When the hydration ratio reaches a value of 30, free water appears in the water core.

It must be noted that the repartition of Na^+ ions is unknown. However, it can be shown that the main results of this study are valid whatever this repartition may be.

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Appendix I.

Let v_0 , v_w and v_{pol}^* , respectively be the volume of the water core, of the free water and of the polar region without hydration in the micelle, respectively Φ_0 , Φ_w and Φ_{pol}^* are the corresponding volume fractions.

One has

$$v_0 = v_w + \Delta v,$$

where Δv is the volume of the water of hydration in the micelle. We also have

$$v_{\text{pol}} = v_{\text{pol}}^* + \Delta v$$

and

$$\Phi_w + \Phi_{\text{pol}} = \Phi_0 + \Phi_{\text{pol}}^*,$$

which gives

$$(\rho_{\text{pol}} - \rho_w) v_{\text{pol}} = (\rho_{\text{pol}}^* - \rho_w) v_{\text{pol}}^*$$

and

$$\Phi_w = \Phi_0 - \Phi_{\text{pol}}^* \frac{\rho_{\text{pol}}^* - \rho_{\text{pol}}}{\rho_{\text{pol}} - \rho_w}.$$

Q can be written as follows

$$Q\bar{\rho} = (\rho_w^2 - \rho_0^2) \Phi_w + (\rho_{pol}^2 - \rho_0^2) \Phi_{pol} + (\rho_{par}^2 - \rho_0^2) \Phi_{par} + \rho_0^2 - \bar{\rho}^2.$$

This equation then leads to equation (1) using the values of Φ_w and Φ_{pol} introduced before.

Appendix II.

The calculation of the integral (2) leads to :

$$R_{GA}^2 = \frac{3}{5} R_{pol}^2 \frac{\rho_{pol} - \rho_{par} + (\rho_{par} - \rho_0)(1+b)^5}{\rho_{pol} - \rho_{par} + (\rho_{par} - \rho_0)(1+b)^3},$$

with $b = e/R_{pol}$ and $e = R_{par} - R_{pol}$ for model A and

$$R_{GB}^2 = \frac{3}{5} R_w^2 \frac{\rho_w - \rho_{pol} + (\rho_{pol} - \rho_{par})(1+a)^5 + (\rho_{par} - \rho_0)(1+a+b)^5}{\rho_w - \rho_{pol} + (\rho_{pol} - \rho_{par})(1+a)^3 + (\rho_{par} - \rho_0)(1+a+b)^3}$$

with $a = l_{pol}/R_w$ and $b = e/R_w$ for model B.

In all the cases, the length of the paraffinic chain is considered to be equal to 9 Å.

Appendix III.

We assume that the micelle is spherical. Then equation (3) can be developed and we obtain :

— Model B

$$\begin{aligned} 16 \pi^2 L_P &= \frac{1}{\bar{\rho} V} [(\rho_w - \rho_{pol})^2 S_w + (\rho_{pol} - \rho_{par})^2 S_{pol} + (\rho_{par} - \rho_0)^2 S_{par}] \\ &= \frac{3}{R_w} \frac{\Phi_w}{\bar{\rho}} [(\rho_w - \rho_{pol})^2 + (\rho_{pol} - \rho_{par})^2 (1+A)^{2/3} + (\rho_{par} - \rho_0)^2 (1+A+B)^{2/3}], \end{aligned}$$

with $A = \frac{\rho_{pol}^* - \rho_w}{\rho_{pol} - \rho_w} \frac{\Phi_{pol}^*}{\Phi_w}$ and $B = \Phi_{par}/\Phi_w$;

— Model A

$$\begin{aligned} 16 \pi^2 L_P &= \frac{1}{\bar{\rho} V} [(\rho_{pol} - \rho_{par})^2 S_{pol} + (\rho_{par} - \rho_0)^2 S_{par}] \\ &= \frac{3}{R_{pol}} \frac{\Phi_{pol}}{\bar{\rho}} [(\rho_{pol} - \rho_{par})^2 + (\rho_{par} - \rho_0)^2 (1+C)^{2/3}], \end{aligned}$$

with $C = \frac{\rho_{pol} - \rho_w}{\rho_{pol}^* - \rho_w} \frac{\Phi_{par}}{\Phi_{pol}^*}$.

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