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Organization of surfactant micelles adsorbed on a polymer molecule in water : a neutron scattering study

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Résumé. — Des particules complexes se forment dans l'eau par l'association spontanée de macromolécules de polyoxyéthylène (PEO) avec les petites molécules amphiphiles de dodécylsulfate de sodium (SDS). A cause de cette association le diagramme de phases des solutions diluées PEO + SDS montre 2 singularités : une concentration critique en SDS pour la formation des agrégats et une stoechiométrie. Nous présentons des expériences de diffusion de neutrons aux petits angles sur ces agrégats stoechiométriques ; nous utilisons la méthode de variation de contraste pour déterminer séparément la configuration du polymère et celle de l'amphiphile dans un agrégat PEO + SDS. Nous obtenons la structure suivante : (i) chaque agrégat contient une macromolécule de PEO, qui occupe un volume comparable à celui d'une pelote de PEO « libre » ; (ii) les molécules de SDS d'un agrégat sont associées en sous-unités, petites sphères de rayon $R = 20 \text{ \AA}$, semblables aux micelles formées par les solutions de SDS pur à faible force ionique ; (iii) ces sous-unités sont adsorbées sur les brins de la macromolécule (PEO) ; la distance entre sous-unités voisines dans un agrégat est contrôlée par l'équilibre entre leurs répulsions électrostatiques et l'énergie libre de la macromolécule (entropie de configuration + attraction pour les surfaces). Enfin les expériences de variation de contraste montrent que tous les agrégats présents dans les solutions stoechiométriques PEO + SDS ont la même composition.

Abstract. — Complex particles are formed in water by the spontaneous association of poly(ethylene oxide) macromolecules (PEO) with the small amphiphilic molecules of sodium dodecylsulfate (SDS). As a result, the phase diagram of dilute PEO + SDS solutions shows 2 singularities : a critical SDS concentration for the formation of the aggregates, and a stoichiometry. Small angle neutron scattering experiments on the stoichiometric aggregates are reported ; the contrast variation method is used to determine separately the configuration of the polymer and that of the amphiphile in a PEO + SDS aggregate. The following structure is obtained : (i) each aggregate contains a single PEO macromolecule whose radius of gyration is comparable to that of a « free » PEO coil ; (ii) the SDS molecules of the aggregate are clustered in subunits which are small spheres, 20 \AA in radius, similar to the micelles formed by pure SDS solutions at low ionic strengths ; (iii) these subunits are adsorbed on the PEO strands ; a distance between neighbouring subunits within the aggregate has been measured. Moreover, the contrast variation experiment shows that all the aggregates present in stoichiometric PEO + SDS solutions share the same composition.

1. Introduction. — That some molecules dissolved in water can spontaneously aggregate is well known : examples are the formation of micelles of amphiphilic molecules [1], the complexation of small molecules by

cage-like structures [2] or by macromolecules [3], and also the association of 2 types of macromolecules [4]. With these few examples the subject is usually considered to be exhausted, at least for artificial systems. Biological systems, on the other hand, show a limitless ability to produce complex particles such as viruses, lipoproteins, or mixed bile salt + lecithin micelles. Thus it is of interest to find out whether artificial particles of comparable complexity can be formed through

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the manipulation of intermolecular forces. In this respect, systems made of polymers and small amphiphilic molecules in water stand out as very good candidates. Firstly, in aqueous solutions, most water-soluble polymers will associate with some small amphiphilic molecules [5]. Secondly, this association presents an interesting competition between 3 types of forces, raising the hope that the type of aggregate formed can be controlled by altering the balance of these forces. The forces are [6] :

— F_1 attraction (or repulsion) between the monomers of the macromolecule when they are dissolved in water : this determines the volume of the polymer coil.

— F_2 attraction between the small amphiphilic molecules : this determines whether they tend to aggregate into micelles.

— F_3 attraction between the small molecules and the monomers of the macromolecule : this determines whether the small molecules will associate with the polymer.

A very frequent situation is where F_1 is repulsive and weak (water is a rather good solvent for the polymer), F_2 is attractive and strong (the small amphiphilic molecules form micelles), and F_3 is attractive and weak. Such is the situation for the interaction of some non ionic polymers with ionic surfactants. In this situation thermodynamic measurements indicate the formation of aggregates with remarkable properties : a critical amphiphile concentration which marks the onset of the adsorption of the amphiphilic molecules on the polymer, and a stoichiometry which marks the saturation of this adsorption [7].

2. Background for the PEO + SDS system. —

2.1 MATERIALS. — The aggregates studied in this work are made by the spontaneous association in water of poly(ethylene oxide) — in short PEO — with sodium dodecylsulfate — in short SDS. PEO is a non ionized, yet hydrophilic polymer ; when preparing the solutions of PEO in water some precautions must be taken to ensure that the polymer molecules do not remain trapped in microgels or microcrystallites [8] ; for this purpose we heated the polymer in water at 50 °C for 1 h. *All the PEO solutions used in this work were dilute, i.e. their concentration was well below the cross-over concentration C^* where the individual polymer coils begin to interpenetrate.* Table I lists the origins of the samples used in this work, their molecular weights as determined by viscosity measurements [9] and their polydispersities as measured by GPC in THF.

SDS is an anionic amphiphile whose solutions in water, above a critical micelle concentration of 8.1 mole/litre [10] form spherical micelles. The aggregation number of these micelles is close to 60, with a small dispersity of the weights $\sigma/M_n \sim 0.3$ [11]. About 25 % of their counterions are not condensed on the micellar surface, so that on the average each micelle carries 15 charges. Adding moderate amounts of salt (up to 0.2 M of sodium salts) lowers the c.m.c.

Table I. — *Characteristics of poly(ethylene oxide) samples.*

Product	M (visco)	M_w/M_n (GPC)
Fluka « 10 000 »	12 870	1.03
Serva « 40 000 »	38 000	1.06
Toyo Soda « SE 8 »	57 200	1.06
Toyo Soda « SE 15 »	135 000	
Toyo Soda « SE 30 »	235 000	
Toyo Soda « SE 70 »	505 000	
Toyo Soda « SE 150 »	1 200 000	

and induces a slight growth of the SDS micelles (aggregation numbers ~ 100), which nevertheless retain a globular shape and a small polydispersity. At higher ionic strengths (0.4 M and beyond) the micelles grow into elongated particles [12].

For the neutron scattering experiments we used perdeuterated SDS (SDS_d) as well as protonated SDS (SDS_p) (see section 3.1). SDS_d , prepared from dodecanol [13] and recrystallized in ethanol was obtained from Service des Molécules Marquées, CEN/Saclay, F 91191 Gif sur Yvette. SDS_p was purchased from BDH (grade « specially pure for biochemical work »). We found that the micelles of SDS_p in D_2O and of SDS_d in H_2O are identical in shape and size.

2.2 PHASE DIAGRAM. — In a number of thermodynamic experiments (equilibrium dialysis [14, 15], surface tension [7, 16, 17], dye solubilization [15, 18, 19], conductivity [16, 18]), dilute PEO + SDS solutions in water show a singular behaviour at 2 values of the SDS concentration. These singularities, labelled x_1 and x_2 , are displayed as dividing lines in a phase diagram of the solutions (Fig. 1). They mark the boundaries of 3 regions which can be explored successively by varying either the SDS concentration x or the PEO concentration y . For example, starting from a pure PEO solution, it is found that the first SDS molecules added dissolve into *free* DS^- and Na^+ ions and remain unassociated throughout region I. Then at x_1 the chemical potential of the isolated DS^- ions becomes equal to that of DS^- ions in PEO + SDS aggregates ; subsequently all the SDS added to the solution beyond x_1 is used to form PEO + SDS aggregates. This association continues through region II, and saturates at x_2 . Beyond this point there is a small transition region where the added SDS molecules again dissociate into free ions, thus raising their chemical potential until at x'_2 it becomes equal to that of DS^- ions in regular SDS micelles. Subsequently all the SDS added to the solution beyond x'_2 , forms regular SDS micelles. Thus in region III the solution contains the PEO + SDS aggregates formed in region II in equilibrium with regular SDS micelles and with a small number of unassociated ions.

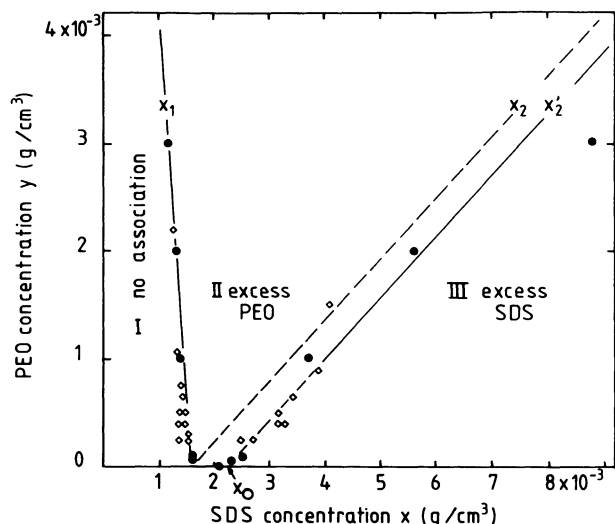


Fig. 1. — « Phase » diagram for the binding of SDS to PEO in dilute aqueous solution (no salt added). The lines correspond to the SDS concentrations x_1 and x_2 which mark respectively the beginning and saturation of this binding, as functions of the PEO concentration y : lozanges from reference [16], dots from reference [7]. As explained in reference [7], region I contains only unassociated PEO and SDS molecules; region II contains PEO + SDS aggregates which are not saturated with SDS; region III contains PEO + SDS aggregates in equilibrium with regular SDS micelles.

The concentration x_1 (onset of the aggregation of SDS molecules into PEO + SDS aggregates) has the properties of a critical micelle concentration (c.m.c.); however it is lower than the c.m.c. x_0 for a pure SDS solution. The ratio x_1/x_0 yields the difference in chemical potential $\Delta\mu$ between SDS molecules in pure SDS and those in PEO + SDS aggregates [7]. In contrast with the usual finding in the formation of mixed micelles (SDS + another small molecule), $\Delta\mu$ does not depend on the PEO concentration y and does not go to zero when it becomes very small (Fig. 1). This indicates that the composition of a PEO + SDS aggregate can never become close to the composition of a pure SDS micelle, even when there are very few PEO molecules in the solution. When the ionic strength of the solution is increased, the values of x_1 and x_0 are scaled down, but their ratio, and therefore $\Delta\mu$, does not change much with ionic strength (Fig. 2). Finally, $\Delta\mu$ is independent of the molecular weight of PEO for all polymers with $M_w > 10^4$. For smaller polymers $\Delta\mu$ falls and reaches zero abruptly at $M_{PEO} = 2\,000$ [18]. PEO polymers of lower molecular weights do not associate with SDS.

The saturation concentration x_2 has the properties of a stoichiometry. Indeed the quantity $x_2 - x_1$, which is the amount of SDS bound to PEO, remains proportional to the PEO concentration y (Fig. 1). Henceforth we shall call « stoichiometry » the value of $(x_2 - x_1)/y$ which is by construction independent of the PEO concentration. This stoichiometry must be

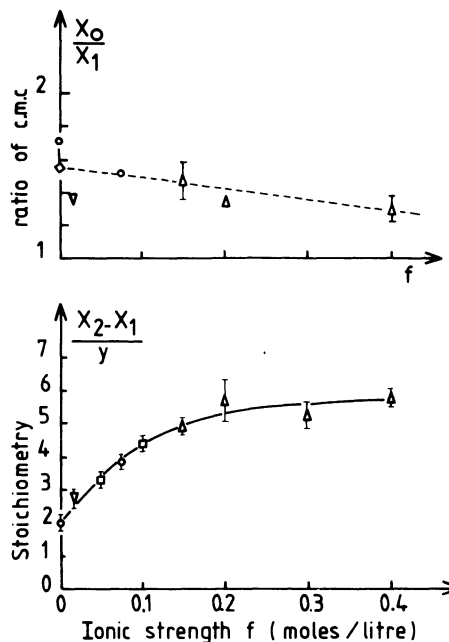


Fig. 2. — Top: ratio of the critical micelle concentrations x_1 for the formation of PEO + SDS aggregates and x_0 for the formation of pure SDS micelles. According to this ratio, the chemical potential of SDS molecules in PEO + SDS aggregates is lower than the chemical potential of SDS molecules in pure micelles by $\Delta\mu = 0.3 kT$. Bottom: stoichiometry of PEO + SDS solutions. The amount of SDS bound to PEO at saturation is measured by $(x_2 - x_1)$, or $(x'_2 - x_0)$; see figure 1. The ratio of this quantity to the PEO concentration y yields the composition of the stoichiometric aggregates.

an intrinsic property of the PEO + SDS aggregates; just like $\Delta\mu$ it remains roughly independent of M_{PEO} as long as $M_{PEO} > 10^4$. On the other hand, it does depend very much on the ionic strength: stoichiometric solutions at high ionic strengths contain substantially more SDS than stoichiometric solutions at low ionic strengths (Fig. 2).

2.3 PREVIOUS MODELS. — The first model proposed to describe the structure of these aggregates was based on the original observation of the saturation of the association at x_2 [16]: SDS molecules were thought to be adsorbed one by one along the polymer chain, with the saturation of the adsorption occurring at full coverage. This model, however, did not explain the similarity between the critical concentration x_1 for the formation of the aggregates and the c.m.c. x_0 of pure SDS solutions; neither did it explain the fact that short PEO polymers ($M\,2000$) do not associate with SDS.

Then NMR experiments [7] indicated that: (i) the aliphatic tails of the SDS molecules are actually segregated from water and clustered together, while their polar groups are located at the hydrocarbon/water interface; (ii) the polymer is in water, weakly adsorbed on this interface; (iii) the SDS/PEO layer formed in this way resists the addition of excess SDS

molecules or PEO monomers when the composition of the solution is moved away from the stoichiometric line.

Although the NMR results gave a good picture of the *local* structure of the PEO + SDS aggregates (arrangement of neighbouring molecules), they could not determine the size, shape, and internal organization of the aggregates; *a priori*, it was not possible to say whether the SDS molecules were aggregated into a sphere, or a spherocylinder, or a disk, or a ring, or into concentric shells, or even into a sponge-like structure. At this point a theoretical prediction was made for the association of « rigid » micelles with long polymers: S. Alexander predicted that the polymer should induce a clustering of the micelles or even a sol-gel transition [20]. In order to decide which of these structural models is adequate we turned to neutron scattering; a preliminary report of our results has been published previously [36]. In this paper we report a full determination of the structure of *stoichiometric* PEO + SDS aggregates made with polymers of large molecular weight ($M_w > 10^4$) in water with salt (0.1 to 0.8 M NaBr).

3. Neutron scattering techniques. — 3.1 CONTRASTS. — We are faced with the problem of determining the structure of 2-component (PEO, SDS) particles in solution. One way to do it is to observe separately the scattering from each component. This requires the use of the contrast matching method [21-24]. First one should make sure that the 2 components have very different indices of refraction for the radiation used in the experiment. In neutron scattering the appropriate quantity is the density of scattering length for each component:

$$\rho = b/v$$

where b is the sum of the scattering lengths of the nuclei of the molecule, and v its volume. Fortunately, H and D nuclei have scattering lengths of opposite signs, yielding a large difference in scattering length density between protonated and deuterated materials (Fig. 3). For this reason we used deuterated SDS (SDS_d) and protonated PEO as components of our aggregates. The next step is to find a set of solvents whose scattering length density can match either that of SDS_d or that of PEO. Figure 3 shows that the scattering length density of PEO can actually be matched by using a solvent made of 82% H_2O + 18% D_2O . In this solvent the PEO molecules do not produce any coherent scattering at small angles; the observed coherent scattering is produced by the SDS_d molecules; its intensity is proportional to the square of the contrast:

$$\kappa = v(\rho - \rho_s)$$

between them and the solvent. Conversely, the scattering length density of SDS_d is almost matched by D_2O ; in this solvent most of the scattering is produced

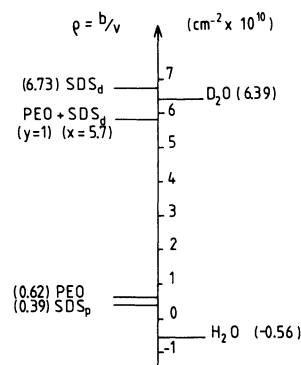


Fig. 3. — Densities of scattering length for the various molecules present in PEO + SDS solutions: b is the sum of the scattering lengths of all the atoms in one molecule, and v the volume of that molecule. The contrast which controls the scattering is proportional to squares of differences in densities $\rho = b/v$ between the various components. Zero contrast between PEO and the solvent can be obtained by using a mixture containing 82% H_2O and 18% D_2O , which matches the average scattering length density of PEO. Zero contrast between SDS_d and the solvent is almost achieved by using D_2O ; an exact matching of the average scattering length density of SDS_d would however require a solvent containing 4% more deuterium than D_2O .

by the PEO molecules. An exact cancellation of the scattering from SDS_d can be obtained in the limit of very low angles by extrapolating the data taken in a mixture of H_2O and D_2O to a solvent containing 4% more deuterium than D_2O . Even then the inhomogeneities in the density of scattering length of SDS_d (polar heads *vs.* hydrocarbon tails) would produce some scattering at finite angles. This is however a very small effect, as can be seen by comparing the scattering in D_2O from pure SDS_d with that of SDS_p [11].

3.2 DEUTERATION ARTEFACTS. — It is necessary to check that the isotopic substitution of H by D does not alter the structure of the aggregates. Both thermodynamic and neutron scattering evidences can be considered in this respect.

In neutron scattering we have compared the solutions of SDS_p in D_2O with those of SDS_d in H_2O : the micelles have the same size and shape in both cases [11]. We have also compared the scattering from SDS_p + PEO in D_2O with that from SDS_d + PEO in H_2O ; in both cases the composition is such that the scattering should be dominated by SDS; we find that both scattering curves show the same features.

In thermodynamic experiments we have compared the values of the concentrations x_1 and x_2 for SDS_p + PEO in H_2O with those for SDS_d + PEO in H_2O . The values found in both systems agree within experimental error ($\pm 10\%$). Moreover, it is known that the c.m.c. of SDS_p in D_2O is the same as that of SDS_p in H_2O [10].

Thus the H/D substitution seems safe in the case of PEO + SDS solutions in water; it may not be so

innocent in other cases. Indeed, in systems where 2 components are on the verge of separating, the H/D substitution could shift the affinities enough to produce major changes in the distribution of these components [25].

3.3 SCATTERING EXPERIMENTS. — The neutron scattering experiments were performed at ILL in Grenoble, France on the instruments D11, D17, and D1B. These instruments differ mainly by their range of scattering vectors $Q = (4\pi \sin \theta)/\lambda$ where 2θ is the scattering angle, and by the spread $\Delta\lambda/\lambda$ in the wavelengths of incident neutrons

$$\begin{aligned} \text{D11} &: 3 \times 10^{-3} < Q < 5 \times 10^{-2} \text{ \AA}^{-1} & \Delta\lambda/\lambda &= 8\% \\ \text{D17} &: 9 \times 10^{-3} < Q < 0.14 \text{ \AA}^{-1} & \Delta\lambda/\lambda &= 10\% \\ \text{D1B} &: 0.1 < Q < 1 \text{ \AA}^{-1} & \Delta\lambda/\lambda &= 1\%. \end{aligned}$$

For the PEO + SDS aggregates studied here, the D11 data cover the « Guinier » range (scattering controlled by the overall dimensions of the aggregates). The D17 data cover the « intermediate range » (scattering controlled by the internal structure of the aggregates). The D1B data cover the « asymptotic » range up to $Q = 1 \text{ \AA}^{-1}$, yielding a spatial resolution of 6 \AA ; however the range of useful data only extended up to $Q = 0.6 \text{ \AA}^{-1}$; beyond this point, peaks corresponding to intermolecular distances within the solvent or within the micelles appeared in the scattering curves. In other words, for such Q vectors it is no longer possible to define a contrast between the particles and the solvent.

The overlap between the Q ranges of these experiments enabled us to reconstruct a single scattering curve for the Q range $2 \times 10^{-3} < Q < 0.6 \text{ \AA}^{-1}$ (Fig. 4). One important factor in trying to match the

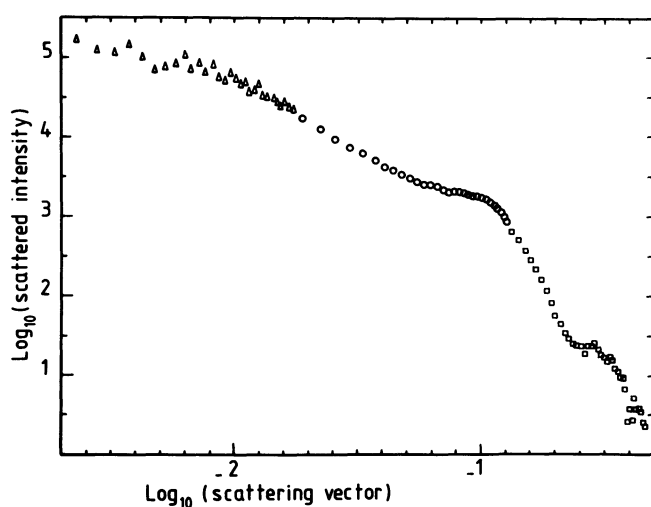


Fig. 4. — Scattering curve for SDS_d in $\text{PEO} + \text{SDS}_d$ aggregates. Polymer : $M_w = 135\,000$, $\gamma = 10^{-3} \text{ g/cm}^3$. Solvent : 82% H_2O + 18% D_2O + NaBr 0.4 M. The scattering vectors Q are defined by $Q = (4\pi \sin \theta)/\lambda$ where the scattering angle is 2θ . Triangles : data taken on D11. Dots : data taken on D17. Squares : data from D1B.

data from different instruments was found to be the quality of the data taken at very low angles. In this respect particular care was taken to optimize the collimation of the beam and prevent scattering by defects in the windows of the cells. The collimation was also a critical factor for obtaining credible data in the Guinier range ($QR < 1$) for large aggregates ($R \sim 200 \text{ \AA}$). In that instance we used a collimation distance (sample to source) of 40 m and a sample to detector distance of 20 m.

All data were treated according to standard ILL procedures for small angle scattering : radial averaging, background subtraction, and normalization of the efficiency of the detector cells by the scattering of H_2O .

3.4 ABSOLUTE SCALE. — The data were put on an absolute scale by comparing the scattering from the sample with the scattering from H_2O [23, 26]. Then the molecular weights of the various components in the scattering particles can be deduced from the absolute value of the intensity scattered at very low angles ($Q \rightarrow 0$) and concentrations ($C \rightarrow 0$). This procedure involves the use of a wavelength dependent correction factor $g(\lambda)$ which takes into account the inelastic effects in the scattering from H_2O ; we used the values of $g(\lambda)$ given by Jacrot and Zaccai [26]. With this procedure, the accuracy on the molecular weights is about 30% if good extrapolations to $Q \rightarrow 0$ and $C \rightarrow 0$ can be made.

4. Scattering data for stoichiometric aggregates. —

4.1 GUINIER RANGE. — This section describes the data obtained on the instrument D11 at Q vectors smaller than, or comparable to the dimensions of the aggregates. In this range the important experimental results are the variation of $I(Q)$ with Q^2 and the limit of $I(Q)$ for $Q \rightarrow 0$ [23]. The appropriate way to obtain these quantities is through a « Zimm plot » of $C/I(Q)$ vs. Q^2 ; this is shown in figure 5 for a dilute solution of SDS_p with a high molecular weight PEO in D_2O with NaBr (0.4 M). Of course the scattered intensities depend on the contrast [21-24], i.e. on the difference between the average scattering length density of the aggregates $\bar{\rho}$ and that of the solvent ρ_s . If the slope and $Q \rightarrow 0$ limit of the Zimm plot are measured as functions of the scattering length density of the solvent, then they can be related to the overall dimensions, molecular weight, and composition of the aggregates, as explained below.

4.1.1 Contrast variation. — For the scattering by one particle of volume V and average scattering length density $\bar{\rho}$ in a solvent of scattering length density ρ_s , the $Q \rightarrow 0$ limit of $I(Q)$ is :

$$I(Q \rightarrow 0) = AV^2(\bar{\rho} - \rho_s)^2$$

where the constant A contains all numerical factors of the experiment. The same applies for a solution of

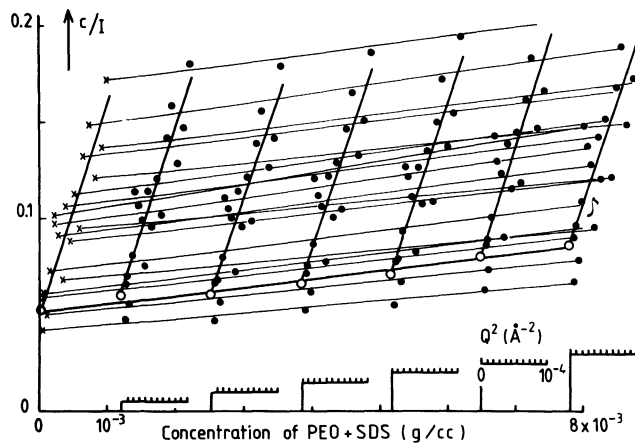


Fig. 5. — Zimm plot for stoichiometric aggregates made with SDS_p and a PEO of molecular weight 135 000 in $\text{D}_2\text{O} + \text{NaBr } 0.4 \text{ M}$. The 6 sets of data (dots) correspond to successive dilutions of the same sample along the stoichiometric line (Fig. 1). The stars are the results from extrapolations to $C = 0$ and the dots to $Q = 0$. In order to obtain data which allow such extrapolations to be made, it was necessary to use very low Q vectors (down to $2 \times 10^{-3} \text{ \AA}^{-1}$) and concentrations (down to 10^{-3} g/cc). Then the value of $I(C = 0, Q = 0)$ yields a mass of 664 000 for the whole aggregate; the slope of $C/I(C = 0, Q)$ vs. Q^2 yields a radius of gyration of $198 \pm 10 \text{ \AA}$, and the slope of $C/I(C, Q = 0)$ vs. C yields a second virial coefficient of

$$6 \times 10^{-5} \text{ cm}^3 \times \text{mole} \times \text{g}^{-2}.$$

N uncorrelated particles which all have the same composition. $I(Q \rightarrow 0, C \rightarrow 0) = N A V^2 (\bar{\rho} - \rho_s)^2$. For such a solution, $I(Q \rightarrow 0)$ should vanish when ρ_s matches $\bar{\rho}$; on the other hand, for a solution containing a mixture of particles with different compositions, there is no value of ρ_s which can cancel the scattered intensity at $Q \rightarrow 0$ [23, 24]. Our results (Fig. 6) show that $(I(Q \rightarrow 0)/C)^{1/2}$ is a linear function of ρ_s , in agreement with the above mentioned law for a stoichiometric solution containing only PEO + SDS aggregates of fixed composition. Moreover, from the value of ρ_s which matches $\bar{\rho}$ the composition of these aggregates can be calculated; this composition is found to be identical with the composition of the solution.

Similar considerations apply to the apparent radius R_{app} which can be deduced from the slope of the $C/I(Q)$ vs. Q^2 plot [21-24]. For a solution of particles which all have the same composition, this radius is related to the radius of gyration R_g of a homogeneous particle which would have the same volume by :

$$R_{\text{app}}^2 = R_g^2 + \frac{B}{\bar{\rho} - \rho_s} + \frac{E}{(\bar{\rho} - \rho_s)^2}$$

where B is the variation of scattering length density $\rho(r)$ within the particle (it is zero if the distributions of the various components in a particle all have the same radius of gyration), and E is non zero if the distribution of $\rho(r)$ does not have the same « centre of mass » as the volume of the particle. Our data, presented in figure 7,

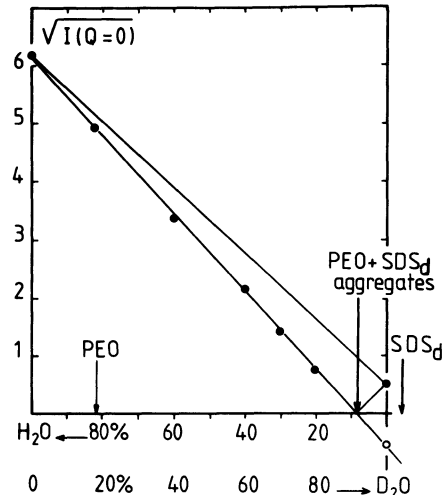


Fig. 6. — Contrast variation. The intensity scattered at $Q \rightarrow 0$ by a single aggregate is proportional to the square of the difference between its scattering length density $\bar{\rho}$ and that of the solvent ρ_s . Because the data for the intensity scattered by the whole solution follow the same law (lower line), it is argued that all the aggregates in the solution have the same $\bar{\rho}$, and therefore the same ρ_s . The upper line represents what would be expected in the opposite case where the solution would contain PEO and SDS molecules unassociated with each other. More generally, for a solution containing more than one type of aggregate, the scattered intensity could not be cancelled by any choice of solvent.

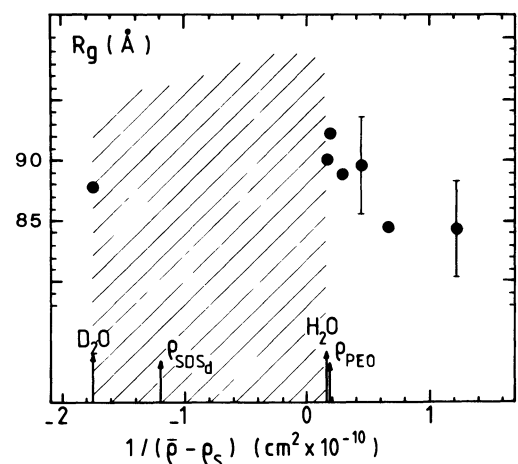


Fig. 7. — Contrast variation : in principle the apparent radius R_{app} of the aggregate can depend on the scattering length density of the solvent ρ_s . When $\rho_s = \rho_{\text{PEO}}$ the radius of PEO in the aggregate is measured; when $\rho_s = \rho_{\text{SDS}}$ the radius of SDS in the aggregate is measured.

show that R_{app} is practically independent from ρ_s ; thus only the first term in the expression of R_{app} is non zero. Therefore in a PEO + SDS aggregate the distributions of SDS and of PEO have the same centre of mass and the same radius of gyration.

4.1.2 *Molecular weights.* — The average mass M_w of the aggregates can be deduced from the small Q limit of the intensity at infinite dilution [23] :

$$\lim_{Q \rightarrow 0, C \rightarrow 0} I(Q)/C = BM_w(\bar{\rho} - \rho_s)^2 .$$

However, rather than the total mass of the aggregate, it is more interesting to know the mass of each component, SDS_d or PEO. These are also accessible from the data [26]. Indeed, in the solvent which matches SDS_d, only PEO scatters. Thus it is possible to use for ρ the scattering length density of PEO, and obtain as M_w the mass of PEO in the aggregate. Conversely, in the solvent which matches PEO, the mass of SDS_d in the aggregate can be determined. Our results are summarized in table II. They are in rough agreement with an analysis of the thermodynamic data (viscometric determination of the molecular weight of PEO, stoichiometry of the PEO + SDS solutions) based on the following assumptions : (i) each PEO + SDS aggregate contains a single PEO macromolecule ; (ii) in stoichiometric PEO + SDS solutions, all the aggregates share the same composition.

4.1.3 *Radii of gyration.* — We have seen (§ 4.1.1) that both PEO and SDS in an aggregate have the same radius of gyration ; this radius can be compared with that of the polymer alone in water. We find that at high ionic strengths a PEO + SDS aggregate has the same radius as PEO alone — for example 88 Å and 92 Å respectively in the case of aggregates made with the PEO of mass 38 000 in H₂O + 0.4 M NaBr.

The variation of these radii with the molecular weight M_w of the PEO molecule is presented in figure 8 : for PEO alone in water with salt the radii increase like $M_w^{0.6}$, as expected for a polymer in a good solvent [27] ; for PEO + SDS aggregates in H₂O + 0.4 M NaBr the M_w dependence is very similar.

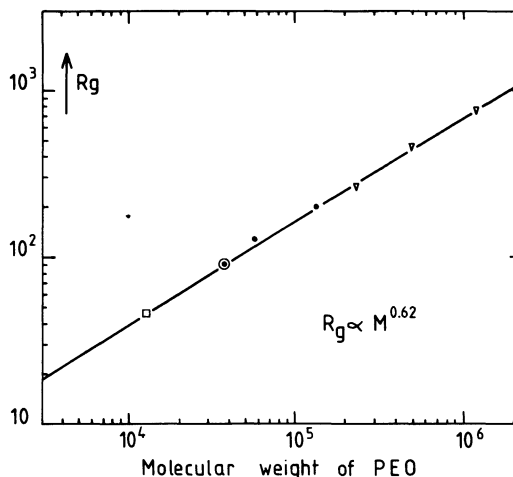


Fig. 8. — Radii of gyration of PEO + SDS aggregates compared with those of free PEO macromolecules. Dots : PEO + SDS_d in H₂O + NaBr 0.4 M. Circle : PEO alone in D₂O + NaBr 0.3 M. Square : PEO alone in D₂O + NaBr 0.075 M. The data for the 3 higher molecular weights (triangles) are the results of light scattering experiments on PEO in H₂O + NaBr 0.1 M by C. Strazielle.

4.1.4 *Interparticle scattering.* — Many of the Zimm plots obtained on PEO-SDS aggregates do not look like the one shown in figure 5. In solutions of lower ionic strength or higher concentrations the Zimm plots show some systematic deviations at low Q . These deviations are related to correlations between the positions of different aggregates ; such correlations exist when aggregates repel each other through long range electrostatic forces. In a solution containing identical particles whose positions are spatially correlated (but whose orientations are not), the scattering

Table II. — Mass of SDS in PEO + SDS aggregates.

1st column : molecular weight of PEO alone from viscosity data.

2nd column : mass of SDS in an aggregate, as obtained from the stoichiometry $(x_2 - x_1)/y$ multiplied by M_{PEO} (1st column).

3rd column : mass of SDS in a PEO + SDS_d aggregate from neutron scattering data in



For convenience the result is expressed as a mass of SDS_p.

4th column : total mass of a PEO + SDS aggregate as determined from neutron scattering with either SDS_d in H₂O + NaBr 0.4 M or SDS_p in D₂O + NaBr 0.4 M.

The accuracy of these values is $\pm 30\%$.

PEO alone visco	SDS in aggregate stoichiometry	SDS in aggregate neutrons	PEO + SDS neutrons
38 000	217 000	181 000	189 490
57 200	326 000		330 000
135 000	756 000		663 000

function can be written as :

$$I(Q) = \langle |A(Q)|^2 \rangle + \{ \langle |A(Q)| \rangle \}^2 \cdot S(Q)$$

where $\langle |A(Q)|^2 \rangle$ is the scattering function of an isolated particle and $S(Q)$ the structure factor for the correlations between particles. Then $S(Q)$ is a damped oscillating function of Q , whose oscillations are larger if the concentration of particles is high, or if the repulsions between them are strong. A practical consequence of these oscillations is that they prevent us from using the Guinier law to obtain the mass and radius of the particles in solutions of low ionic strength. In such conditions, single particle information can still be extracted from $I(Q)$ through a theoretical calculation of $S(Q)$ [37] or through a labelling of some of the particles [28]. This has not been done here.

4.2 INTERMEDIATE RANGE. — This section presents data obtained on the instrument D17 at Q values probing the internal structure of the aggregates ($QR_g > 1$, but also $Ql \ll 2\pi$, where l is the length of a SDS molecule). In this range the scattering curves from PEO and from SDS in a PEO + SDS aggregate are quite different from each other. This is to be contrasted with the results in the Guinier range (§ 4.1.1) where both curves show the same radius of gyration R_g . Thus the distributions of SDS and PEO inside the aggregate are not the same, even though they have the same overall dimensions (R_g) and the same centre of mass.

4.2.1 Scattering from PEO in a PEO + SDS aggregate. — In this range, the scattering from the polymer shows a monotonic decrease of $I(Q)$ with Q , which for large polymers follows a $Q^{-\alpha}$ law. Figure 9 shows the results obtained in $D_2O + 0.075$ M NaBr : the exponent α is 1.50 ± 0.10 ; in comparison the exponent for pure PEO in the same solvent is $\alpha = 1.67 \pm 0.10$. These exponents are related to the attractions or repulsions between monomers of the polymer [27] : $\alpha > 2$ if the monomers attract each other in the solvent, as is the case for collapsed polymer coils ; $\alpha < 2$ if the monomers repel each other, as is the case for polymers in a good solvent ; $\alpha = 2$ if this force vanishes, in which case the polymer coil should take a Gaussian configuration. Thus the configuration of PEO in a PEO + SDS aggregate dissolved in water with a small amount of salt resembles that of a polymer with strong repulsions between the monomers. In comparison, pure PEO in water is just typical of a polymer in a rather good solvent.

4.2.2 Scattering from SDS in a PEO + SDS aggregate. — In the intermediate range the scattering from SDS_d shows a prominent shoulder, which becomes a peak at low ionic strengths (Fig. 10). If the position of this peak is taken as a measure of a distance d within the aggregate, then $d = 2\pi/Q = 90 \text{ \AA}$ for aggregates in water with no salt added. As salt is added, the position of the peak shifts to higher Q values : a fit of

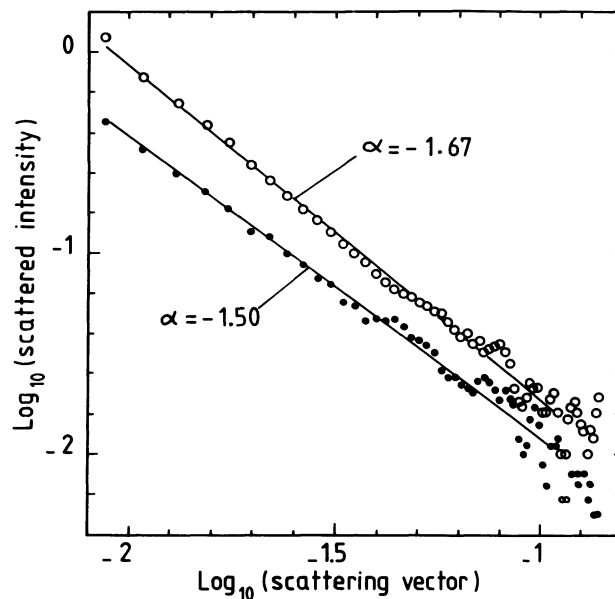


Fig. 9. — Log-Log plot of scattering curves obtained in the intermediate range ; the solvent is $D_2O + 0.075$ M NaBr, which matches approximately the scattering length density of SDS_d . Dots : PEO ($M = 171\,000$, $\gamma = 1.5 \times 10^{-3} \text{ g/cm}^3$) in PEO + SDS_d aggregates, slope $\alpha = -1.50$. Circles : PEO alone, same conditions, $\alpha = -1.67$. For a polymer with no repulsions between its monomers, $\alpha = -2$; for a rod, $\alpha = -1$.

the curve obtained with 0.8 M NaBr yields $d \sim 60 \text{ \AA}$. On the other hand, this position changes little with the molecular weight of the polymer ; it is also independent of the overall concentration of the solution.

This peak is observed for all contrasts where the scattering is dominated by the surfactant (either PEO + SDS_p in D_2O , or PEO + SDS_d in H_2O) ; it is not observed when the contrast of the surfactant is cancelled (PEO + SDS_d in D_2O).

It is also interesting to compare the scattering from SDS in a PEO + SDS aggregate with that from pure SDS micelles. Figure 11 shows the scattering curves of pure SDS solutions, with no salt added ; they also show a peak, which is produced by interferences between the micelles. The position of this intermicellar peak depends on the intermicellar distances, and therefore on the concentration of the SDS solution ; on the contrary, the peak shown in figure 10 for dilute PEO + SDS solutions does not depend on the total concentration of the solution.

4.3 ASYMPTOTIC RANGE. — This section presents the data obtained on the instrument D1B at Q vectors probing distances comparable to the dimensions of SDS molecules. In this range the scattering curve of SDS_d in PEO + SDS aggregates shows damped oscillations superimposed on an asymptotic Q^{-4} behaviour (Fig. 12). The Q^{-4} dependence is predicted by Porod's law for a sample which has sharp boundaries between 2 levels of scattering length density : that

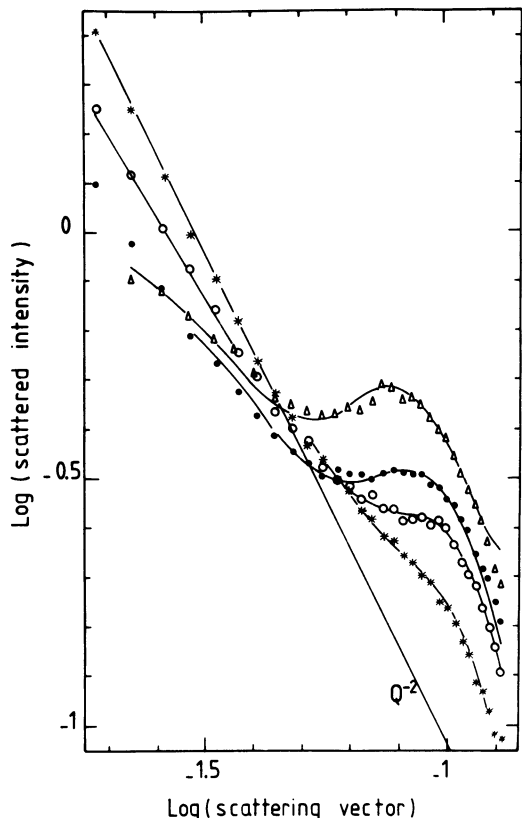


Fig. 10. — SDS_d in PEO + SDS_d aggregates made with the PEO of molecular weight 135 000. Log-log plot of the scattering curves in the intermediate range of *Q* vectors, with arbitrary shifts of vertical scales. The solvents contain 82 % H₂O + 18 % D₂O, to match the scattering length density of PEO, and differ by their ionic strengths. Triangles : no salt added. Dots : NaBr 0.05 M. Circles : NaBr 0.2 M. Stars : NaBr 0.8 M. It is argued that the peak observed at low ionic strengths is produced by interferences between subunits within the aggregate.

of the solvent, ρ_s , and a uniform level ρ for the scattering particles [29]. In the present case the polymer is matched by the solvent ($\rho_{PEO} = \rho_s$), so we conclude that the SDS_d molecules in PEO + SDS aggregates are clustered in particles which have a uniform density of scattering length, and sharp boundaries. We also find that the same holds true for regular SDS micelles. Thus, within the resolution of our experiment ($2\pi/Q_{max} = 6 \text{ \AA}$), there must be a well defined water/hydrocarbon interface in PEO + SDS aggregates as well as in regular SDS micelles; this is in agreement with the NMR results [7, 30]. The total area of this interface is :

$$S = \frac{1}{2\pi(\rho - \rho_s)^2} \lim_{Q \rightarrow \infty} \{ Q^4 I(Q) \} .$$

Also for scattering particles of uniform density, the total volume of the particles is :

$$V = \frac{1}{2\pi^2(\rho - \rho_s)^2} \int_0^\infty Q^2 I(Q) dQ .$$

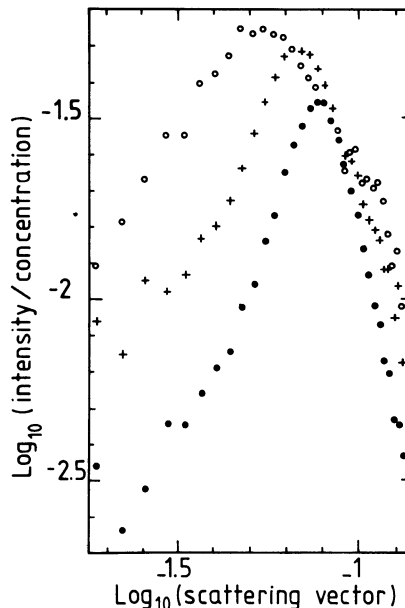


Fig. 11. — Log-Log plot of scattering curves obtained in the intermediate range for SDS_d alone in water (no salt added). Circles : $x = 10^{-2} \text{ g/cm}^3$. Crosses : $x = 5 \times 10^{-2} \text{ g/cm}^3$. Dots : $x = 10^{-1} \text{ g/cm}^3$.

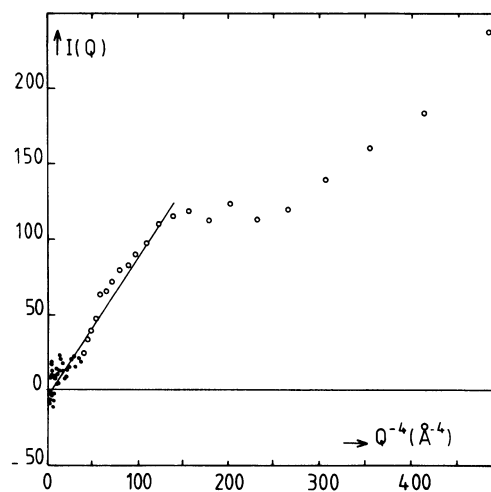


Fig. 12. — Asymptotic behaviour of the intensity scattered by SDS_d in PEO + SDS_d aggregates. Solvent : 82 % H₂O + 18 % D₂O + NaBr 0.1 M. Polymer : $M = 57\,200$, $y = 4.6 \times 10^{-3} \text{ g/cm}^3$. The points at the extreme right correspond to $Q = 0.2 \text{ \AA}^{-1}$, i.e. dimensions $\sim 30 \text{ \AA}$; the points at the extreme left to $Q = 1 \text{ \AA}^{-1}$, i.e. dimensions $\sim 6 \text{ \AA}$. The intensity tends towards zero (to the left) according to a Q^{-4} law, indicating that the scattering particles have sharp boundaries.

The ratio V/S yields a length, which is comparable to the « half thickness » of the particles. This length is 15 Å for SDS in PEO + SDS aggregates dissolved in water + NaBr 0.1 M; it is 17 Å for regular SDS micelles in the same solvent.

A more precise determination of the shape of the

scattering particles can be obtained from the damped oscillations of $I(Q)$ in the range 0.2 to 0.6 \AA^{-1} . As these oscillations are superimposed on a Q^{-4} dependence, they can best be shown by plotting $Q^4 I(Q)$ vs. Q . Such plots are shown in figure 13 for SDS_d in $\text{PEO} + \text{SDS}$ aggregates as well as for a pure SDS solution with $82\% \text{ H}_2\text{O} + 18\% \text{ D}_2\text{O} + 0.1 \text{ M NaBr}$ as a solvent. In both cases the curves can be fitted quite well by the theoretical scattering curve for a polydisperse solution of homogeneous spheres, with a Gaussian distribution of weights. The weight average radius of this distribution is controlled by the fit in the 0.05 to 0.15 \AA^{-1} region; it is found to be $21.5 \pm 0.1 \text{ \AA}$ for SDS in $\text{PEO} + \text{SDS}$ aggregates and $22.5 \pm 0.1 \text{ \AA}$ for SDS in a pure SDS solution. The polydispersity is given by the depth of the minimum at 0.22 \AA^{-1} ; it corresponds to a reduced standard deviation $\sigma^2/M_n = 0.3$, or to $M_w/M_n = 1.3$. Thus in both cases the SDS molecules must be aggregated in spherical micelles, with a rather sharp distribution of sizes.

At higher ionic strengths (0.8 M) pure SDS micelles are known to deform into elongated particles; this shows up in their scattering curves, which can no longer be fitted by the theoretical curves for spheres (Fig. 14). On the other hand, the curves for SDS in a $\text{PEO} + \text{SDS}$ aggregate remain quite close to the scattering curves for spheres, with a weight average radius $R = 23 \text{ \AA}$ and polydispersity $M_w/M_n = 1.4$ (Fig. 15). Conversely, one can try to plot the data in a representation which is appropriate for elongated particles: a plot of $\text{Log } QI(Q)$ vs. Q^2 (Fig. 16) shows that the micelles in SDS solutions with 0.8 M NaBr have a cylindrical shape, with a cylinder radius $R = 18 \text{ \AA}$, whereas the curve for SDS in $\text{PEO} + \text{SDS}$ aggregates does not

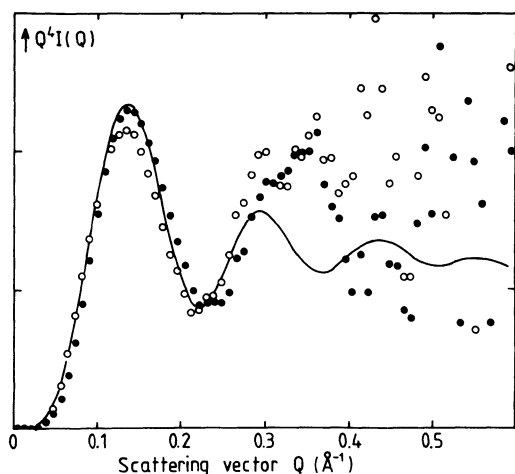


Fig. 13. — Comparison between the damped oscillations in the intensity scattered at large Q by pure SDS_d micelles (circles) and those of SDS_d subunits in $\text{PEO} + \text{SDS}_d$ aggregates (dots). Solvent: $82\% \text{ H}_2\text{O} + 18\% \text{ D}_2\text{O} + \text{NaBr } 0.1 \text{ M}$. Polymer: $M = 57\,200$, $\gamma = 4.6 \times 10^{-3} \text{ g/cm}^3$. Line: fit by polydisperse spheres, with an average radius $R = 22 \text{ \AA}$; the distribution of their weights has a width $\sigma/M_n = 0.3$.

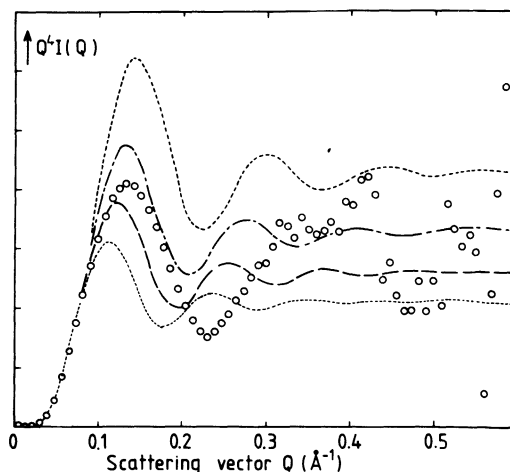


Fig. 14. — Damped oscillations at large Q for SDS_d micelles in $\text{D}_2\text{O} + 0.6 \text{ M NaBr}$. The lines are the theoretical scattering curves for spheres with average radii 22 , 24 , 26 , and 28 \AA ; their intensity scales have been adjusted to match the intensity scattered by the micelles at low Q . That a fit by spheres is no longer possible indicates that at this ionic strength the micelles have grown into elongated particles.

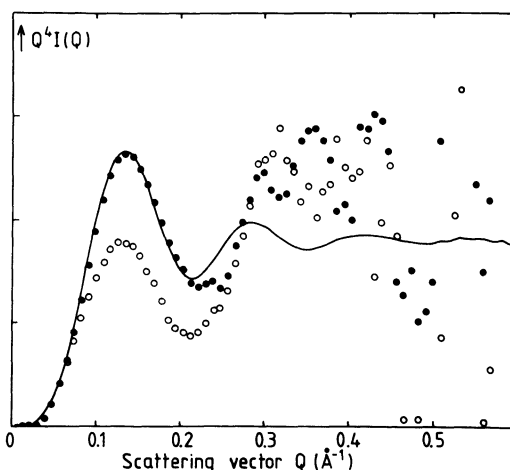


Fig. 15. — Damped oscillations at large Q and high ionic strength. Dots: SDS_d subunits in PEO ($M = 57\,200$) + SDS_d . Circles: pure SDS_d micelles. Solvent: $82\% \text{ H}_2\text{O} + 18\% \text{ D}_2\text{O} + \text{NaBr } 0.8 \text{ M}$. Line: fit by polydisperse spheres with an average $R = 23 \text{ \AA}$; the distribution of their weights has a width $\sigma/M_n = 0.4$.

follow the expected behaviour for cylinders. This establishes that the SDS molecules in $\text{PEO} + \text{SDS}$ aggregates remain clustered in spherical micelles even at high ionic strengths.

5. Structure. — 5.1 METHOD. — The contrast variation experiments described in § 4.1.1 and 4.1.2 indicate that *stoichiometric* $\text{PEO} + \text{SDS}$ solutions only contain one type of $\text{PEO} + \text{SDS}$ aggregate; all the PEO and all the SDS present in such solutions are used up in the formation of these aggregates. Thus

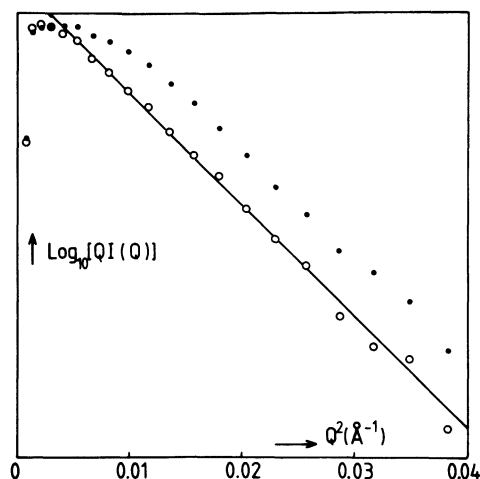


Fig. 16. — Scattering curves at high ionic strength, plotted in the appropriate representation for cylinders. Circles : SDS_p in $\text{D}_2\text{O} + 0.6 \text{ M NaBr}$. Dots : SDS_d in $\text{PEO} + \text{SDS}_d$ aggregates, solvent 82 % $\text{H}_2\text{O} + 18 \%$ $\text{D}_2\text{O} + \text{NaBr}$ 0.8 M. The data for the aggregates do not follow the straight line expected for cylinders.

the observed scattering curves do correspond to the structure of one type of particle, and not to an average over many types of particles. It is therefore legitimate to use the scattering curves to determine this structure.

Because the aggregates are randomly oriented in solution, the scattered intensity is isotropic (i.e. it only depends on the magnitude of the scattering vector \mathbf{Q}). It is not possible to obtain the 3-dimensional shape of these aggregates from such small angle scattering intensities alone [31].

The only exception to this rule is the case where the dissolved particles have true spherical symmetry; then a Fourier transform of the scattering curve can yield the radial distribution function of the particles; but the configurations of polymers in solution do not, in general, have spherical symmetry; the same must be assumed, *a priori*, for $\text{PEO} + \text{SDS}$ aggregates.

If however the aggregates could be assumed to have at least *some* simple symmetry, then the approach of Stuhrmann [32] could be followed : the density of scattering length $\rho(\mathbf{r})$ within an aggregate would be analysed in terms of spherical harmonics, and so would the corresponding factor $A(\mathbf{Q})$.

However the $\text{PEO} + \text{SDS}$ aggregates may well have no symmetry at all. For this reason the only tractable approach is to use the most distinctive features of the scattering curves, together with some basic knowledge on the shape of the molecules, to build a structural model; then check whether this model can reproduce the whole scattering curves (a trial and error routine) and whether it can also explain the properties of the particles; finally consider whether it is unique in this respect.

5.2 MODEL DESIGN. — We start by focussing on the state of aggregation of the SDS molecules. The experiments at large Q vectors indicate that, at all ionic strengths, the SDS molecules within a $\text{PEO} + \text{SDS}$ aggregate are assembled in spherical clusters whose size and shape are identical with those of spherical SDS micelles (§ 4.3). Yet when large PEO molecules are used ($M_w > 3 \times 10^4$) the molecular weight data as well as the stoichiometry indicate that the mass of SDS within an aggregate is much larger than that of a spherical SDS micelle (§ 4.1.2). Therefore there must be many such SDS clusters within one aggregate; from this point on these clusters will be called « subunits ». NMR experiments have shown that the polymer is in water, with some of its segments adsorbed on the surface of these subunits [7].

The data in the intermediate range are related to the organization of these subunits within the aggregate. When SDS_d is observed, the data show a peak at low ionic strengths, and a monotonic Q^{-2} dependence at high ionic strengths (Fig. 10). Thus the spatial distribution of the subunits within the aggregate is closer to a *homogeneous* distribution at low ionic strengths, and becomes *Gaussian* at high ionic strengths. For the polymer the data have been obtained at relatively low ionic strengths only; in this case the scattered intensity decreases monotonically as $Q^{-\alpha}$, with $\alpha = 1.50$ (Fig. 9). Thus the configuration of PEO within the aggregate resembles that of a polymer with strong repulsions between its monomers. These results are consistent with the idea of a competition between the electrostatic repulsions (subunit to subunit) and the free energy of the polymer coil (configurational entropy + attraction for the SDS surfaces). At low ionic strengths the electrostatic repulsions dominate; they restrict the variations in the density of subunits within the aggregate; most of the PEO segments are stretched out between these subunits, thus giving rise to the observed $Q^{-1.50}$ behaviour. At high ionic strengths the configurational entropy of the polymer takes over, producing a Gaussian density in space of its segments and of the subunits which are adsorbed on them.

Finally consider the overall parameters of the aggregate. The data obtained in the Guinier range for $\text{PEO} + \text{SDS}_d$ aggregates in $\text{D}_2\text{O} + \text{NaBr}$ 0.4 M yield the mass and dimensions of the polymer in the aggregate (§ 4.1.3). Accordingly the aggregate contains a single PEO macromolecule, whose radius of gyration is the same as that of a PEO molecule alone in D_2O (Fig. 8). Thus the adsorption of such polymers on the SDS/water interfaces does not produce a collapse of the polymer coils [33]. With the other contrast we observe that the distribution of SDS within the aggregate also has the same radius; thus the SDS subunits must be distributed throughout the polymer coil.

At this point it is possible to make a picture for the structure of a $\text{PEO} + \text{SDS}$ aggregate; such a 2-dimensional picture is shown in figure 17.

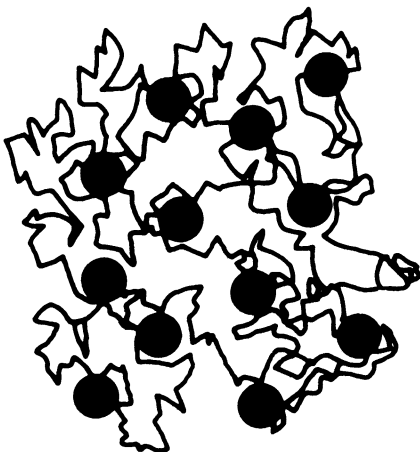


Fig. 17. — 2-dimensional representation of the structure of a PEO+SDS aggregate; the disks are the SDS subunits, and the polymer is adsorbed on their surfaces.

5.3 TESTING THE MODEL. — 5.3.1 *Is it internally consistent?* — The structural model proposed above has less parameters than what can be determined from the scattering curves. This redundancy should make it possible to perform some tests. In particular, one can think of 2 ways to calculate the number of subunits per aggregate. One way is to divide the mass M of the aggregate (as deduced from $I(Q \rightarrow 0, C \rightarrow 0)$) by the mass m of a subunit (as estimated from its radius). For aggregates made with PEO molecules of molecular weight 135 000 this would lead to about 38 subunits per aggregate. Another way is to choose a mathematical form for the spatial variations of the density of subunits within the aggregate, check that this form can reproduce the scattering curves in the intermediate range of Q , and then integrate this density over the volume of the aggregate, known from R_g . If the model is correct, this procedure should yield the same number of subunits as above. This calculation is in progress. At this stage, however it is instructive to point out that using a simplified procedure for this test can lead to an erroneous result. Suppose that one would assign the *average* distance between subunits within the aggregate to be equal to $d = 2\pi/Q$, where Q is the position of the peak observed in the intermediate range. The number of subunits which is obtained by integrating a uniform density defined by d over the volume of the aggregate is 5 times too large. This problem is caused by a misinterpretation of the peak. Indeed, this peak does not correspond to an *average distance*, but to the *smallest distance* of approach between subunits. Thus the failure of this simplified procedure indicates that in a PEO + SDS aggregate these 2 distances are very different from each other (on the contrary they are close to each other in a pure micellar solution). In turn, this indicates that the density of subunits within an aggregate is not uniform : it must be higher near the centre and lower at the periphery.

5.3.2 *Does it explain the properties of the aggregates?* — As mentioned in § 2.3, previous models for PEO + SDS aggregates (either random adsorption of isolated SDS molecules along the polymer chain, or mixed micelle models) had failed to explain how the solutions could show both a critical micelle concentration (c.m.c.) and a stoichiometry. The explanation for the c.m.c. was given previously [7]; it is related to the fact that the SDS molecules are clustered in micelle-like subunits; that this c.m.c. does not vary with the PEO concentration is in agreement with our finding that the number of PEO molecules per aggregate is always equal to one (§ 4.1.2).

The present model (SDS subunits within a PEO coil) also explains the stoichiometry; indeed there must be an optimal number of SDS subunits per aggregate. This number results from the balance between repulsion forces (subunit to subunit) and adsorption forces (polymer to subunit). If a solution contains more SDS than the stoichiometry set by this number, the excess SDS will have to form ordinary micelles unassociated with the polymer, as the electrostatic repulsions prevent any further increase in the number of SDS subunits of each aggregate. Conversely, in a solution containing less SDS than this stoichiometry, one can expect each PEO + SDS aggregate to be depleted in SDS subunits; this would imply that a smaller fraction of the PEO monomers would be adsorbed on the SDS/water interface.

6. **Variability.** — 6.1 EFFECT OF THE MOLECULAR WEIGHT OF PEO. — Our measurements of $I(Q \rightarrow 0)$ indicate that the mass of SDS within an aggregate is roughly ($\pm 30\%$) proportional to the molecular weight M_{PEO} of the polymer (Table II). This is in agreement with the results of thermodynamic experiments, which indicate that the stoichiometry is roughly the same for all the polymers used in this study (§ 2.2). On the other hand, the size of the SDS subunits remains the same regardless of M_{PEO} (§ 4.3); also, their distances from each other change little with M_{PEO} (§ 4.2.2). Thus changing M_{PEO} only affects the size of the aggregate and the number of SDS subunits which it contains, while leaving its internal structure unchanged.

6.2 EFFECT OF THE IONIC STRENGTH. — Ionic surfactants are very sensitive to salt, and pure SDS micelles are typical in this respect. In particular they grow into elongated particles when the salt concentration exceeds 0.4 M [10]. Similarly one might expect the subunits of a PEO + SDS aggregate to grow under the same conditions. Our results show that this does not happen : the SDS subunits remain small and spherical up to a salt concentration of 0.8 M (§ 4.3). This resistance is probably related to the adsorption of PEO monomers on the surface of the SDS subunits. Indeed, in order to grow, the subunits must reduce their area of surface per SDS molecule [35]. The addition of

salt promotes this reduction by screening the electrostatic repulsions between the polar groups of the SDS molecules; on the contrary adsorbed PEO monomers take up space on the surface of the subunit, thus preventing a reduction of the area of interface per SDS molecule. In this way, adsorbed PEO monomers play the same role as short chain alcohols adsorbed in SDS micelles.

On the other hand, the smallest distance d between subunits is sensitive to the ionic strength : it expands from 60 Å in solutions with 0.8 M NaBr to 90 Å in solutions with no salt added. The cause of this expansion was already indicated in § 5.2 : the ionic strength controls the balance between the electrostatic repulsions (subunit to subunit) and the free energy of the polymer (configurational entropy + attraction for the surfaces of the subunits).

This balance also controls the overall dimensions of the aggregate. Unfortunately, interferences between different aggregates prevent us from making precise measurements of their radius of gyration at low ionic strengths; nevertheless the available data suggest a slight expansion as the ionic strength is decreased from 0.4 M to 0.1 M.

7. Conclusions. — A model for the structure of stoichiometric PEO + SDS aggregates has been constructed on the basis of the neutron scattering data. In this model, the SDS molecules of an aggregate are clustered in subunits, which are themselves adsorbed on the polymer. A 2-dimensional representation of this model is shown in figure 17.

This structure appears to be quite stable; indeed, we have been unable so far to produce PEO + SDS aggregates with a different structure. Changes in the molecular weight of PEO only scale up or down the overall dimensions of the aggregate and the number n of SDS subunits which it contains (provided that $n \gg 1$). Changes in the ionic strength of the solution only produce a modest expansion or contraction of the aggregate, without modifying the size of the SDS subunits. Even the precipitation of the aggregates out of the solution requires larger amounts of mono- or divalent salts than in the case of pure SDS solutions.

At this point it is appropriate to return to our initial motivations and examine how one can make polymer + amphiphile aggregates with different struc-

tures. As explained in § 1, the same type of structure which we have found in PEO + SDS aggregates is likely to be found again in other systems which share the same balance of interactions (PEO monomer to PEO monomer, PEO monomer to SDS molecule, SDS to SDS). Accordingly, one can think of at least 3 ways to alter this balance :

(i) Instead of SDS, use another small amphiphilic molecule with different amphiphile to amphiphile interactions. For example, one could use some amphiphiles which are known to form exclusively disk shaped micelles. Alternatively, one could turn to amphiphilic molecules which do not cluster spontaneously into micelles, but nevertheless do associate with some water-soluble polymers [3].

(ii) Instead of PEO, use a polyelectrolyte with a charge opposite to that of the amphiphile, and instead of SDS a short chain amphiphile below its c.m.c. (Retaining a long chain amphiphile would probably lead to structures similar to those of PEO + SDS aggregates, as the hydrophobic amphiphile to amphiphile attractions would still overwhelm all other interactions.)

(iii) Use a polymer which is either much more expanded or much more compressed in water than PEO. A good candidate for the first option would be a very stiff polymer; for the second option a hydrophilic hydrophobic block copolymer could be used.

Acknowledgments. — The light scattering data on PEO alone in water are unpublished results from C. Strazielle; it is a pleasure for us to thank him for making them available to us. Most of the neutron scattering work was done at the high flux reactor of ILL in Grenoble, France, after some preliminary experiments performed at EL3 in Saclay; we gratefully acknowledge the material help and advice from ILL staff and members of the Laboratoire Léon Brillouin, including J. P. Cotton, M. Niehrlich, R. Oberthür, M. Rawiso, M. Roth, P. Timmins and C. Williams. Thanks are also due to D. Lecacheux, J. Lescq and L. Letot for the GPC measurements. This work was supported in part by a grant from D.G.R.S.T. N° 80.D.0707.

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