Erratum to: Solution behavior of aqueous mixtures of low and high molecular weight hydrophobic amphiphiles

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The original version of this article unfortunately contained mistakes. Several author corrections in different places were not carried-out due to technical problems. The correct version of the article is shown below.

Abstract Mixtures of a hydrophobic triblock copolymer (L121, PEO₅PPO₆₈PEO₅) and a hydrophobic anionic surfactant (AOT, Sodium bis(2-ethylhexyl)sulfosuccinate), each alone forming turbid vesicular solutions in water, aggregate to produce a thermodynamically stable, transparent and isotropic solution. Mixed AOT/L121 aggregates

could be confirmed by fluorescence, surface tension, differential scanning calorimetry (DSC) and isothermal titration calorimetry (ITC). In an isotropic region, where mixed aggregates are formed, there is a synergistic interaction between monomers of AOT and L121 in the mixture. In addition, Small Angle Neutron Scattering (SANS) experiments provided evidence that mixed aggregates have the shape of either spheres (with a certain polydispersity) or very short ellipsoids (axial ratio below 2), confirming a transition from giant multilamellar vesicles to small aggregates upon mixing the two hydrophobic amphiphiles. Upon dilution, the morphology changes to disk-like. From an examination of the results of all the methods the peculiar behavior of the mixed AOT/L121 system is explained.

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Introduction

It is known that mixing surfactants usually enhances the performance of products. Mixing can be also unavoidable as a result of fabrication processes. Therefore, it is important to understand the features of mixed systems, particularly in terms of their phase behavior and structure.

Poly(ethylene oxide)-Poly(propylene oxide) (PEO-PPO) amphiphilic block copolymers are versatile compounds whose hydrophile-hydrophobe balance can be tailored by changing the PEO (hydrophile) or PPO (hydrophobe) chain lengths or their molecular weights [1–4]. The change in the chain conformation and solvation with temperature or by addition of selective solvents also allows surface curvature changes that give rise to a very rich phase behavior and a variety of self-organizing structures; this subject has been studied extensively. Block copolymer nanostructures are often used in conjunction with ionic surfactants to modulate their functional properties [5–11]. Due to synergistic interaction with these surfactants, their performance improves as compared to that of individual components [12–14] in applications such as emulsification [15] and stabilization of dispersions [16]. Since the functionality of copolymer assemblies critically depends on the structure and the properties of mixed assemblies, clear understanding of the basic aggregation mechanism of block copolymer assemblies with different secondary species, such as ionic surfactants, proteins, etc., is crucial. This is also true for advanced applications such as the preparation of nanomaterials [17], in which mixing surfactants allows to tune the shape and curvature of the aggregates used as templates in order to obtain the desired structures.

In a previous report, for the mixtures of a hydrophobic triblock copolymer (L121, $\text{PEO}_5\text{PPO}_{68}\text{PEO}_5$) and a hydrophobic anionic surfactant (AOT, Sodium bis(2-ethylhexyl) sulfosuccinate), we found complete mixing of the two surfactants to form mixed aggregates. A phase diagram of this system is shown in Fig. 1 [18]. At both low and high AOT/L121 ratios, two liquid phases are present and samples look turbid, due to the presence of large vesicles. At intermediate AOT/L121 ratios, the solutions are single-phase, transparent and isotropic. Still, some questions remained opened concerning the main causes of this unexpected behavior.

Both micelle-to-vesicle and vesicle-to-micelle transitions are relevant for model biological membranes and delivery systems [19–21] in which the presence of PEO chains can provide enhanced circulation time [22]. Such transition has been reported previously in polymer-surfactant systems, but

mainly for mixtures where either the polymer or the surfactant is hydrophilic [23, 24]. In the present case both surfactant and polymer are hydrophobic, which imparts particular features to the system. To get more insight on the structure of the mixed L121+AOT aqueous solutions, we have further studied this system using small angle neutron scattering (SANS), tensiometry, fluorescence and differential scanning calorimetry (DSC) techniques.

Experimental

Materials

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was purchased from Sigma-Aldrich. The poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer Pluronic L121 was a gift from BASF Corp. The same batch of L121 was used in all experiments. The copolymer molecular formula can be represented as $\text{PEO}_5\text{PPO}_{68}\text{PEO}_5$. Pyrene (98%) was purchased from Fluka. All substances were used without further purification. Millipore-Q treated water was used for sample preparations except for SANS where D_2O was used.

Methods

Phase diagrams

Proper amounts of components were weighed in ampoules that afterwards were flame sealed, homogenised and kept in a water bath at several temperatures for equilibration. Phases were identified by visual observation through

Fig. 1 Phase behavior of AOT/L121/water systems as a function of AOT bulk mol fraction (X_{AOT}) in the AOT+L121 mixture (solvent-free basis). The total amphiphile (AOT + L121) concentration is kept constant at 5 wt%. I and II indicate one- and two-phase regions, respectively. Adapted from Ref. [18]

crossed polarisers, polarized optical microscopy (Leica Reichert Polyvar 2 instrument) and Small Angle X-Ray Scattering.

Small Angle X-ray Scattering (SAXS)

SAXS measurements were performed using a S3 MICRO instrument (Hecus X-ray Systems, from Graz, Austria) equipped with a GENIX microfocus X-ray source and a FOX 2D point-focusing element (both from Xenocs, Grenoble). The d spacings of liquid crystalline phases was determined by the Bragg equation, $d = 2\pi/q$, where q is the scattering vector.

Small-Angle Neutron Scattering (SANS) SANS experiments were carried out in the instrument installed in the Guide Tube (GT) laboratory, Dhruva reactor hall, BARC, Trombay, India. Details about the SANS instruments and analysis procedure can be found elsewhere [25, 26]. The Q range of the diffractometer is $0.18 - 3 \text{ nm}^{-1}$. Hydrogenated surfactant aggregates were contrasted against D_2O . Experiments were carried out at 25°C , and samples were loaded in 5 mm path-length rectangular quartz cells. To improve the statistics on the SANS patterns each measurement was taken for 8–10 hours.

In a SANS experiment one measures the differential scattering cross section ($d \sum(Q) / d\Omega$) per unit volume. For a system of monodisperse particles, it is given by [27]

$$\frac{d \sum(Q)}{d\Omega} = n(\rho_p - \rho_s)^2 V^2 P(Q) S(Q) + B \quad (1)$$

where n is the number density of the particles, ρ_p and ρ_s are, respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. $P(Q)$ is the intra-particle form (shape) factor and $S(Q)$ is the inter-particle structure factor. B is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample.

The SASFIT program (developed at Paul Scherrer Institute, Laboratory for Neutron Scattering, Villigen, Switzerland) was used for data fitting. For a 5 wt% total (AOT+L121) surfactant concentration, the $P(Q)$ contribution was tested for ellipsoidal aggregates as well as spherical aggregates and $S(Q)$ has been calculated using the model of Hayter and Penfold [28] which assumes screened Coulomb interactions between the charged aggregates. The micellar dimensions, aggregation number and fractional charge have been determined from the analysis. For the ellipsoidal aggregates, the semimajor axis (a), the semiminor axis (b), the fractional charge ($\alpha = z/N$, where z is the micellar charge in e^- and N is the aggregation number)

and the hard sphere radius are the fitting parameters in analysing the SANS data. For the spherical aggregates, the sphere radius (r), the polydispersity, the fractional charge and the hard sphere radius are the fitting parameters. For the ellipsoidal aggregates, the aggregation number is calculated by the relation $N = 4\pi ab^2 / (3\bar{V}_m)$, whereas for the spherical aggregates it is calculated by the relation $N = 4\pi r^3 / (3\bar{V}_m)$. In both cases $\bar{V}_m$ is the average surfactant monomer volume. The latter was calculated for each sample as an average surfactant monomer volume taking into account the corresponding contributions from AOT and L121, $\bar{V}_m = V_{\text{mAOT}} \cdot X_{\text{AOT}} + V_{\text{mL121}} \cdot X_{\text{L121}}$, where X_{AOT} and X_{L121} are the mole fractions of AOT and L121, respectively, in a water-free basis. For AOT, the molecular volume V_{mAOT} used was $650 \text{ \AA}^3$ [29] and for L121, V_{mL121} was $7100 \text{ \AA}^3$ [30]. In addition, a small contribution to the form factor was added taking into account the Gaussian chains from L121 for all the samples of the first series.

For a 0.5 wt% surfactant concentration, the form factor $P(Q)$ for a disk with radius R and height h was used. Neither polydispersity nor $S(Q)$ were considered, as the low concentration allowed to neglect the effect of interactions on the scattering intensity.

Steady State Fluorescence Steady state fluorescence of pyrene in water was measured using a Varian Cary Eclipse spectrometer. Pyrene was excited at a wavelength of 335 nm and the emission intensity from 350 to 500 nm was recorded. The excitation and emission slit openings were set at 5 and 2.5 nm, respectively. The scan speed was set at 600 nm/min. All spectra were averaged over two scans.

Equilibrium and dynamic surface tension The equilibrium surface tension of aqueous mixed surfactant solution was measured at 25°C by the Wilhelmy plate technique (K100 tensiometer, Krüss, Germany). Dynamic surface tension was measured by the maximum bubble-pressure method using a bubble pressure tensiometer BP2 (Krüss, Germany) at 25°C . Surface ages of bubbles were measured between 5 ms to 50 s.

Differential Scanning Calorimetry (DSC) DSC traces were recorded with a Setaram Micro DSC III. The samples ($\sim 0.5 \text{ g}$) were introduced in Hastelloy pans and heated at a rate of $1.5^\circ\text{C}/\text{min}$ under nitrogen atmosphere. A pan filled with Millipore water was used as a reference.

Isothermal Titration Calorimetry (ITC) ITC experiments were performed by a MicroCal ITC microcalorimeter. The syringe of calorimeter ($V \sim 0.3 \text{ mL}$) was filled with aqueous solutions of AOT or a mixture of AOT and L121 which

were then titrated into a cell containing 1.384 mL of water. Each experiment, performed at 25°C, consisted of 99 subsequent additions ($V=3\ \mu\text{L}$) of titrant solution.

Results and discussion

Phase diagram

The partial ternary phase diagrams of L121-AOT-water systems are presented in Fig. 2. Single AOT and single L121 aqueous systems form lamellar liquid crystals in water. At 25°C, a lamellar phase is found from ca. 15 wt% of AOT in water whereas the same liquid crystal is present from ca. 60 wt% L121 in water. Note that minute addition of AOT greatly stabilizes liquid crystal phases in the binary L121-water system; therefore, the liquid crystal region looks greatly expanded. Interestingly, mixing of the lamellar phases at certain AOT/L121 ratio results in single isotropic regions. In the dilute region, such an isotropic region is found between two multiphase regions in which vesicles or lamellar dispersions can be formed. The SAXS spectra for the lamellar liquid crystals at low AOT content showed three peaks at position ratios 1:2:3 corresponding to lamellar structures. On the other hand, the SAXS patterns for liquid crystal samples at high AOT content showed two well resolved peaks at position ratios 1:2 and one broad peak with a maximum at higher q values. In AOT aqueous systems, SAXS spectra also feature such a broad peak, which was attributed to the form factor of the defective AOT lamellar phase [31].

Fluorescence measurements

The pyrene emission dependence of the solvent polarity is expressed in terms of the ratio I_1/I_3 of the intensities of the first and the third vibronic bands. This ratio decreases with increasing hydrophobicity. Pyrene, having low water solubility, is expected to partition preferentially to the most hydrophobic regions of a self organized system in solution.

A simple mixing relationship [32] for the ratio of vibronic band intensities in the present binary mixed amphiphilic system would be

$$(I_1/I_3)_M = X_{\text{AOT}}(I_1/I_3)_{\text{AOT}} + (1 - X_{\text{AOT}})(I_1/I_3)_{\text{L121}} \quad (2)$$

where $(I_1/I_3)_M$, $(I_1/I_3)_{\text{AOT}}$, $(I_1/I_3)_{\text{L121}}$ are the ratios of intensities of the mixture, AOT micellar solutions, and L121 aqueous solutions above the aggregation concentration, respectively, and X_{AOT} is the mole fraction of AOT in the surfactant mixture. It is worth mentioning that in the present study the obtained experimental value for $(I_1/I_3)_{\text{L121}}$ is close to those reported for other plurionics with a similar

PPO chain length [33], but much higher than that of pure PPO, indicating that PPO chains in the aggregate could be somewhat hydrated.

As can be seen in Fig. 3, the actual values for $(I_1/I_3)_M$ are much higher than those given by Eq. 2 within a wide range of AOT mol fractions, which indicates that the contribution of L121 to the mixture is also higher than predicted. It suggests that the fluorescent probe is mostly surrounded by L121 lipophilic PPO chains in the micellar core. The I_1/I_3 ratio does not decrease significantly up to $X_{\text{AOT}} \approx 0.7$. After this value, which is close to the lower concentration boundary of the single phase region (see Fig. 1), there is sharp drop in the I_1/I_3 ratio. In some cases, vesicles or layers are less hydrated than aggregates and therefore such a drop would not be expected. There might be two reasons for such a behavior. One could be that the mol fraction of AOT inside aggregates increases, and therefore, the number of alkyl chains (more hydrophobic than PPO chains) surrounding pyrene molecules also increases. The other reason might be a change in micellar structure, which would cause pyrene molecules to be closer to the alkyl chains, and consequently, the PPO chains would change to a less extended conformation. Both possibilities will be discussed in the following sections.

Fluorescence measurements were also carried out in diluted samples to study the formation of aggregates. In Fig. 4, the I_1/I_3 ratios start to decrease from a given amphiphile concentration, reflecting a decrease in the polarity surrounding the probe, from an aqueous environment ($I_1/I_3 \sim 1.7$) to a less polar one with $I_1/I_3 \sim 1.3$, closer to that corresponding to PPO chains (see Fig. 3). Namely, the behaviour of I_1/I_3 is an indication of the formation of aggregates in which pyrene molecules are embedded; the onset of aggregation can be assigned to the first break point in the curves. The decrease in the I_1/I_3 ratios is not sharp as for single low molecular weight surfactants but takes place over a wide range of concentration (almost two orders of magnitude), which may indicate different stages in the association process and the presence of species with different molecular weights, as in the case of the block copolymers used in the present study.

The ratio of the fluorescence intensities of pyrene in the excimeric (I_e) and monomeric (I_3) states provides information about the local concentration of pyrene in the aggregates [34]. As can be seen in Fig. 4, the I_e/I_3 curves show a maximum, a behaviour that has been reported previously [33]. At low concentrations, pyrene molecules are distributed in the bulk solution, and therefore, the I_e/I_3 ratios are low. As the first aggregates are formed, there is a local increase in probe concentration as pyrene molecules migrate to such aggregates, which causes also an increase in I_e/I_3 ratio. A further increase in amphiphile concentration results in a larger number of aggregates and therefore

Fig. 2 Partial phase diagrams of AOT/L121/water system at 25°C in the dilute region (top) and concentrated (bottom) regions. L indicates a region in which lamellar liquid crystals are present. I and II indicates

single and multiphase regions, respectively. The insets in the bottom are SAXS spectra of representative samples; position ratios are indicated on the peaks. q is the scattering vector

Fig. 3 Variation of the pyrene polarity ratio I_1/I_3 at 25°C as a function of AOT bulk mol fraction in the AOT+L121 mixture (solvent-free basis). The total amphiphilic concentration (AOT + L121) is kept constant at 5 wt%. The continuous line represents a simple linear mixing relationship (Eq. 2). The dashed lines are the boundaries of the isotropic, single-phase region

Fig. 4 Plot of I_1/I_3 (filled symbols) and I_2/I_3 (open symbols) ratios as a function of total amphiphile concentration. Circles: $X_{AOT}=0.81$; Triangles: $X_{AOT}=0.94$

pyrene molecules will also be distributed in a larger volume; as a consequence, the I_e/I_3 ratio decreases after the maximum. Contrary to previous results on single PEO-PPO copolymer systems, in the present case, the I_e/I_3 maximum does not coincide with the first break in the I_1/I_3 curves but more with the second, which suggests that in the present mixed system the singular points in each curve might indicate different aggregation states, as will be discussed in the next section.

Critical aggregation concentration determination

Surface tension measurements were used to determine the critical aggregation concentration (cac) of mixed AOT+L121 solutions. It should be emphasized here that for all experiments the same L121 product lot was used to reduce the effect of composition changes. Two breaks were observed in the surface tension isotherm (Fig. 5). The appearance of two breaks has been ascribed to the broad distribution of the molecular weight of polymer, a change of molecular conformation at the air/water interface, or the formation of two types of aggregates [35, 36]. There are reports on discrepancies between the results on cac of Pluronic solutions estimated by different techniques [37]. However, in the present case, the first break in Fig. 5 correspond to that found in I_1/I_3 curves of Fig. 4, and the second break occurs at approximately the same concentration as that of the maximum in I_e/I_3 curves in that figure. Therefore, fluorescence and surface tension results are in agreement in the present case. It is possible then that first AOT, L121 and pyrene molecules associate in some kind of structures that are more “open”, so that the local pyrene concentration is not much different to that of the bulk solution but still the probe “feels” a different environment. This kind of association could be similar to the well-known pearl-necklace model for surfactant/polymer interactions [38]. The second kind of association will be closer to typical aggregates in which local pyrene concentration is

Fig. 5 Representative surface tension curves for two different X_{AOT} values. The total amphiphilic concentration (AOT + L121) is kept constant at 5 wt%. Circles: $X_{AOT}=0.81$; Triangles: $X_{AOT}=0.94$

different from that of the bulk. We followed the criteria of Alexandridis et al [35], and took the second break as the concentration corresponding to the formation of mixed micellar-like aggregates (cac^*).

The mixed critical aggregation concentration (cac^*) of an ideal surfactant mixture is given by [39]

$$\frac{1}{cac^*} = \frac{X_{AOT}}{cac_1} + \frac{(1 - X_{AOT})}{cac_2} \quad (3)$$

where X_{AOT} is the bulk mole fraction of surfactant 1 (AOT) in total mixed solute, and cac_1 and cac_2 are the critical aggregation concentrations of pure components 1 and 2, respectively. Fig. 6 shows that the cac values for AOT+L121 mixtures deviate negatively from the ideal cac^* values at medium to high AOT fractions. Such a negative deviation is related to favorable mixing, i.e., synergistic interaction between monomers of AOT and L121 in the mixture, as observed in other Pluronic-Ionic surfactant mixed systems [40].

The AOT mol fraction in aggregates (x_1) can be estimated by solving the following equation derived from the regular solution theory pseudophase separation model [43]

$$\frac{x_1^2 \ln(X_{AOT}cac^*/x_1cac_1)}{(1 - x_1)^2 \ln[(1 - X_{AOT})cac^*/(1 - x_1)cac_2]} = 1 \quad (4)$$

where cac_1 and cac_2 are the $cacs$ of AOT and L121, respectively. A plot of x_1 as a function of X_{AOT} is presented in Fig. 7. In most range of AOT bulk fractions, L121 molecules are a majority inside the aggregates. Above $X_{AOT} \approx 0.8$, the mol fraction of AOT in aggregates (near the cac) sharply increases. This behavior is similar to that observed with fluorescence measurements at high surfactant concentrations, which also suggested an increase in the x_1 at about the same value for X_{AOT} . The values of interaction

Fig. 6 Critical aggregation concentrations (cac) from surface tension measurements at 25°C as a function of AOT mol fraction in the AOT+L121 mixture (solvent-free basis). The total amphiphilic concentration (AOT + L121) is kept constant at 5 wt%. The line corresponds to an ideal mixture. The values for pure AOT and pure L121 were obtained from Ref. [41] and Ref. [42], respectively

parameter β derived from the application of the regular solution theory pseudo phase separation model [43] to the *cac** experimental data showed a large variation with composition, as can be observed in Fig. 7. β is highly negative, reflecting the asymmetry of the system.

Small-angle neutron scattering (SANS) measurements

SANS curves from 5 wt% micellar solutions of L121 and AOT mixtures with varying AOT mole fractions in the AOT+L121 mixture (X_{AOT}) at 25°C are shown in Fig. 8. Some of the raw data were briefly introduced recently by some of the authors of the present paper [44]. All the distributions show well-defined peaks characteristic of suspensions of charged particles with strong repulsive intermicellar interactions. It is observed that an increase in the AOT/L121 ratios results in a large decrease in the scattering intensities and a shifting of the peak position to higher Q values, reflecting a change in aggregate dimensions. It is to be noted here that the peak in SANS arises from a corresponding peak in the inter-particle structure factor $S(Q)$ the position of which at $Q_m (\approx 2\pi/d)$ depends on the inter-particle distance d . Therefore, a shift in the peak position towards lower Q values suggests an increase in micellar size and *vice-versa*. As a consequence, the present SANS results indicate that the mixed aggregates of AOT and L121 decrease in size as X_{AOT} increases.

We used the radius of gyration as a fixed parameter, calculated [45] from the contour length L and the Kuhn statistical segment length k as $R_g = (Lk/6)^{1/2}$. From the bond lengths and angles, the contour length per one ethylene oxide unit is 3.5 Å, while the Kuhn length for poly(ethylene oxide) is about 10 Å [46]. From these values $R_g = 5$ Å is obtained for the hydrophilic chains of 5 EO units, which agrees with other theoretical calculations [47] and values calculated by extrapolation of experimental data

Fig. 7 Aggregate mole fraction of AOT (x_1 , filled circles) and interaction parameters (β , open circles) versus bulk mole fraction (X_{AOT}) in L121 + AOT aqueous systems derived from data in Fig. 6. The line is the best fit to a cubic polynomial

of longer chains [48, 49]. The fitting model would be similar to a “crew-cut” morphology [50], with large hydrophobic cores and relative thin hydrophilic coronas. We cannot completely rule out that part of PPO chains are also hydrated, which would increase the value for R_g . In any case, the parameters in Table 1 changed only slightly upon varying R_g .

The values obtained from the fit are shown in Table 1, and they correspond to relatively small aggregates. Absolute values of the parameters for prolate ellipsoids should be taken with precaution, as the fitting of the theoretical model is far from perfect; however, data have been included to compare with that coming from the spherical model. The estimated values for the axial ratio (a/b) were also relatively small (1.7–1.8) and change very little with X_{AOT} . The studied samples showed low viscosity, which rules out the presence of highly elongated or entangled aggregates [51]. Cryo-TEM pictures (not shown) did not give evidence of very long aggregates either. In fact, and as can be seen in

Fig. 8 SANS data for AOT+L121 solutions at various AOT mole fractions (X_{AOT}) and the corresponding fitted curves (solid lines) for prolate ellipsoids (a), and polydisperse spheres (b). The total amphiphile concentration (AOT + L121) is kept constant at 5 wt%. Curves have been multiplied by the indicated factors for clarity of presentation

Fig. 8, experimental data were better fitted by the spherical model with a polydispersity close to 0.2, a value similar to that reported for other pluronic-ionic surfactant systems [13, 52]. The sizes estimated from SANS are larger than those derived from Dynamic Light Scattering in our previous report [18], but there is an agreement in the decreasing tendency of the size with increasing X_{AOT} .

According to an earlier report [53], AOT aggregates at 1 wt% in water have the shape of prolate ellipsoids with $a=20.6\text{ \AA}$ and $b=12.6\text{ \AA}$ (axial ratio=1.64); namely, addition of L121 induces micellar swelling. Since the hydrodynamic radius of L121 unimers in water (at 10°C) is $19\text{ \AA}$ [54], the copolymer seems to be in a more extended conformation when incorporated into the mixed aggregates, namely, the AOT hydrophobic chains would be acting as a relatively good solvent for PPO. In fact, we found that PPO with the same molecular weight of the PPO block of L121, and octane (similar to the alkyl chain of AOT) are mutually soluble in all proportions, which could be expected from the proximity of their solubility parameters.

Table 1 also shows that the fractional charge (α) increases with AOT content, as expected. The α values are higher in the case of the spherical model, and are comparable to those reported for pure AOT micelles in water [53]. No major changes in the size and geometry of aggregates were observed when temperature was increased from 30 to 50°C (see supplementary material (ESM 1)).

It is apparent that there is an optimum range of AOT/L121 mixing ratios for the formation of quasispherical

aggregates. For $X_{AOT}<0.7$ (low concentration boundary of the single phase in Fig. 1), there is not enough AOT to solubilize the hydrophobic PPO chains, therefore, phase separation is favoured. For $X_{AOT}>0.94$ (high concentration boundary of the single phase in Fig. 1), the entropy penalty derived from the compression of the PPO chains within the small aggregates would be too high and again, the system would tend to phase separate. Trying to get more insight on the role of L121 on the phase transitions, we observed the phase behaviour at 25°C of aqueous mixtures of AOT with PPO with the same molecular weight as that of the L121 hydrophobic block, keeping the total concentration as that used in the AOT+L121 system (i.e., 5 wt%). We found a single phase isotropic region, but much narrower than that for AOT+L121 systems (between $X_{AOT}=0.5$ and $X_{AOT}=0.7$); namely, L121 does not simply act as a swelling hydrophobe.

According to an earlier article by Fan et al. [55], in mixtures of AOT with pentaethyleneglycol dodecyl ether (C_{12}E_5), only vesicles are formed and no vesicle-micelle transition was detected. Since L121 and C_{12}E_5 have the same PEO chain length (L121 in both ends of the molecule), it seems that L121 long hydrophobic chain is determinant for the vesicle-micelle transition. The critical packing parameter [56] $P=\nu/(Sr)$, where ν and r are the molar volume and length of the amphiphile hydrophobic moiety, respectively, and S is the effective surface area per surfactant molecule, is also appropriate for a qualitative analysis of the results. For single L121 or AOT molecules in water, S is small and ν relatively high, therefore structures with low curvature and high P , such as vesicles, are favoured. In order to have quasispherical aggregates with $P\approx 1/3$, either high S or high r values are needed. In the present case, there is swelling of the micellar cores by the solubilization of PPO chains (increase of effective r) while relatively high S values are induced by the electrostatic repulsion between AOT head groups. Hence, this synergism is the driving factor for the formation of quasispherical aggregates.

We have also performed SANS measurements for 0.5 wt% solutions of L121 and AOT mixtures as shown in Fig. 9, so as to keep the micellar volume fraction low and thereby minimize intermicellar interactions (the contribution of structure factor was neglected in the calculations).

With the increase in X_{AOT} value, there is a decrease in the low- Q scattering while the intensity at higher Q regions ($Q>2\text{ nm}^{-1}$) remains practically unchanged. The decrease in low- Q scattering is again consistent with the decrease in the micellar size with the increase in fraction of AOT, which is clearly observed when comparing the micellar volumes (see Table 2). However, the scattering patterns at low concentrations corresponded to disk-like aggregates, indicating a shape transition from short prolate ellipsoids (or spheres) to disks upon dilution. Such a transition also results in an increase in the aggregation numbers (see Table 2). At

Table 1 Structural parameters of mixed micellar aggregates obtained from the SANS distribution

X_{AOT}	b^a (Å)	r^b (Å)	α^c (e-/molecule)	Aggregation number
Model: Prolate ellipsoid ^d				
0.60	48		0.12	248
0.71	44		0.12	250
0.81	37		0.18	187
0.91	29		0.24	131
0.94	26		0.26	108
0.96	20		0.45	53
Model: polydisperse spheres ^d				
0.60		44	0.29	111
0.71		42	0.27	114
0.81		37	0.33	104
0.91		29	0.42	75
0.94		26	0.48	60
0.96		19	0.92	29

^a Semi-minor axis

^b Sphere radius

^c Fractional charge

^d Total (AOT+L121) concentration = 5 wt%

Fig. 9 SANS data for AOT+L121 solutions at various AOT mole fractions (X_{AOT}) and the corresponding fitted curves (solid lines) for disks. The total amphiphile concentration (AOT + L121) is kept constant at 0.5 wt%. Curves have been multiplied by the indicated factors for clarity of presentation

0.5 wt%, single AOT in water has been reported to have ellipsoidal shape [53] whereas single L121 forms vesicles or lamellar structures [54]; namely, again there is a morphological change when the single surfactant systems are mixed.

DSC measurements

The DSC trace of L121 in water, Fig. 10, shows an endothermic peak having a small shoulder, with an onset temperature 14°C and an associated enthalpy of 474 kJ/gmol. The presence of this composite peak is attributed to the formation of vesicles or a dispersion of a lamellar liquid crystal in a two-step process [57]. It is known that the enthalpy change of pure L121 solutions is related with the aggregation process, and results from the dehydration of PPO chains [57]. Below a certain temperature (i.e. 14°C), L121 is in a monomeric state. Note that such state can not be observed in the phase diagram of Fig. 2 since it was constructed at 25°C. When AOT is added the onset of the peak is shifted to lower temperatures and the enthalpy associated with the peak decreases; peak broadening is also observed. Therefore, adding AOT induces the formation of aggregates at lower temperatures. Such a decrease in aggregation temperature and enthalpy of aggregation has also been found when nonionic surfactants are added to block copolymers [58, 59]. On the other hand, the shoulder observed in the DSC curve of L121 aqueous solution also disappears upon addition of AOT, which suggest that the nature of the transition is different. Actually, the formation of micelles in other Pluronic aqueous solutions is reflected by a single peak, as in the present case when AOT is added. In L121 + sodium dodecyl sulfate (SDS) mixed systems, the micellization enthalpy also decreases upon adding the ionic surfactant, but the onset temperature actually

increases [57]. AOT is much less hydrophilic than SDS, and therefore the effect should be different. It seems that AOT favours the formation of mixed aggregates with L121 at low temperatures. The decrease in the aggregation enthalpy upon addition of AOT is clearly observed in Fig. 10 (bottom) and could be attributed to the formation of smaller aggregates and to a decrease of the dehydration enthalpy as the fraction of PPO chains in the aggregates decreases, which supports SANS results.

Results on ITC measurements are presented in Fig. 11. In Fig. 11a, the curve for pure AOT (enthalpogram) shows a sigmoidal shape. Initially, the surfactant undergoes disaggregation followed by monomer dilution. Heat changes result from the disaggregation of surfactant aggregates and dilution of monomers. At the state of aggregation and above, the solution undergoes aggregate dilution (and not further disaggregation) with an appreciable change in the enthalpy that remains nearly constant with increasing surfactant interaction [60]. The difference between the final and initial part of enthalpogram corresponds to the enthalpy of aggregation, ΔH_{agg} , as it is shown in Fig. 11a. The obtained value of 3.68 kJ/mol is slightly higher from the value of 3.12 kJ/mol obtained by calorimetry by Chatterjee et al. [41].

The aggregation concentration is determined according to the Phillip's criterion [61] from the first derivative of the reaction heat against surfactant concentration (Fig. 11a). Estimated value of 2.55 mM is in good agreement with the values (2.72 mM, 2.68 mM) reported in the literature [41].

The calorimetric behavior is very much different for mixed AOT+L121 systems (Fig. 11b). Here curves do not present clear sigmoidal features and were analyzed by a data treatment as it has been described by Bouchemal et al recently [62].

The start of transition (ST) and end of transition (ET) has been determined as it is shown in Fig. 11b for $X_{AOT}=0.3$. Linear fits of the data sets in the lower and upper concentration domains were performed and the intercepts of the two straight lines were determined. The difference between this two intercepts yields the enthalpy of the transition (aggregation). This procedure yields values of about 60 ± 5 kJ/mol and 180 ± 10 kJ/mol for the surfactant

Table 2 Structural parameters of mixed micellar aggregates obtained from the SANS distribution

X_{AOT}	Radius (Å)	height (Å)	Aggregation number
0.60	96	73	633
0.71	92	76	768
0.80	91	50	627
0.94	127	44	1863

Model: Disk. Total (AOT+L121) concentration = 0.5 wt%

Fig. 10 DSC traces of AOT-L121 aqueous mixtures. X_{AOT} values are shown besides each curve (top). Transition enthalpies derived from DSC curves (bottom). The total surfactant concentration is 5 wt%. The data for $X_{AOT} = 1$ is taken from ITC measurements (see discussion below)

mixtures with $X_{AOT} = 0.6$ and 0.3 , respectively. As it can be seen from Fig. 10 they are slightly lower from those obtained by DSC technique, but the difference can be ascribed to the error made by the linear fits and the extrapolation of the ITC data, although kinetic effects cannot be completely ruled out. Note that aggregation takes place at very low concentrations, so that the locus of the transition from monomer to aggregates cannot be observed in the phase diagram of Fig. 2a.

Nevertheless, the enthalpy change increases as X_{AOT} decreases, i.e. as L121 content increases. Actually, the shape of the curves suggest the presence of at least two processes (indicated by the breaks in the straight dotted lines in Fig. 11b), in qualitative agreement with the surface tension results shown in Fig. 4.

Dynamic surface tension measurements

Dynamic surface tension (DST) measurements were carried out as a function of X_{AOT} at different total surfactant concentrations (5 wt%, 0.5 wt%, and 0.005 wt%) at 25°C . At high total surfactant concentrations (e.g. 5 wt% and 0.5 wt%), the DST data showed almost no change with time

and the values were close to those at equilibrium (see supporting material). At lower total surfactant concentration (0.005 wt%), the DST curves are different: an induction region (at short times), followed by a decreasing region are clearly visible in the DST curves, see Fig. 12 (top). Usually, the reduction of dynamic surface tension involves several mechanisms and a typical surface tension vs time curve can be divided into four regions [63]: an induction region (short times), a rapid fall region, a mesoequilibrium region, and an equilibrium region (at a long time). However, we have observed only the first two regions for the dilute samples. A relatively long induction time (~ 1000 ms) can be attributed to the low cmc of the systems [64, 65]. When a new interface is created, the surface tension is high but as the time passes the adsorption of surfactant molecules at the gas-liquid interface cause a decrease in the surface tension. Minute observation of the DST curves reveals that with increasing mixing fraction of AOT (X_{AOT}) the induction region tends to shorten indicating a faster diffusion to the surface.

We define a normalized dynamic surface tension $\gamma_n = (\gamma_t - \gamma_\infty) / (\gamma_0 - \gamma_\infty)$, where γ_t , γ_0 and γ_∞ are the

Fig. 11 Reaction heat as a function of total amphiphile concentration in AOT (a) and AOT+L121 (b) aqueous systems at 25°C

surface tensions at time t , at $t \rightarrow 0$ and at equilibrium, respectively. The following equation is used for fitting the experimental data [64]

$$\gamma_n = \sum_{i=1}^n a_i \exp(-t/\tau_i) \quad (5)$$

where a_i is a constant and τ_i is a relaxation time. In the present case, the experimental data could be fitted to a single exponential with a single relaxation time, which is plotted in Fig. 12 (bottom). The normalized DST and their exponential fit are supplied as supplementary material (ESM 1). The decrease of relaxation time with increasing X_{AOT} also suggests the faster diffusion of surfactant molecules to the surface.

Oil solubilization

To further explore the properties of mixed L121+AOT aggregates, solubility studies of a model oil were carried out. As it is shown in Fig. 13, the aromatic hydrocarbon *p*-xylene can be solubilized in the isotropic region of Fig. 1, which is the typical of micellar aggregates with a swollen core. The amount of solubilized oil increases with the AOT

Fig. 13 Solubilization of *p*-xylene in AOT+L121 aqueous mixtures at 25°C. The total amphiphilic concentration (AOT + L121) is kept constant at 5 wt%. The line is only a visual guide

Fig. 12 Dynamic surface tensions at 25°C for different values of X_{AOT} in AOT+L121 aqueous mixtures (top), and relaxation time as a function of X_{AOT} from the fitting of data in (a) using Eq. 5 (bottom). The surfactant concentration is fixed at 0.005 wt%

fraction. Mixing with L121 increases the micellar solubilization of *p*-xylene with respect to the binary AOT + water systems [65]. At $X_{AOT} > 0.85$, the solubilization capacity of the mixtures is higher than that of SDS or that of other pluronics with the same hydrophobic chain length as L121 [66]. According to the theory of Nagarajan [66], it could be explained in terms of a favourable change in the solubility parameters of the mixture with respect of that of the solubilize (*p*-xylene), namely, there is a synergistic effect.

Conclusions

A bilayer-micelle-bilayer transition takes place in a mixture of two hydrophobic amphiphiles, Pluronic L121 and AOT, which results in the formation of a transparent isotropic solution when mixing two turbid dispersions. Experimental evidence from SANS points to the existence of relatively small, quasispherical aggregates in the isotropic solutions, which decrease in size when the AOT fraction is increased; however, upon dilution, the aggregates change to disk-like. The inner core of aggregates is occupied by the PPO hydrophobic chains of the copolymer that seem to be in an extended confirmation. Such a conformation, together with the repulsion between charged AOT groups, leads a decrease in the effective packing parameter, thus favouring the formation of quasispherical aggregates. This synergistic effect is also reflected in a faster adsorption at the air-solution interface and improved solubilisation capacity.

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