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Incorporation of sparingly soluble species in mesostructured surfactant–polymer films

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Abstract

Recently we have investigated the formation of novel thick, solid, mesostructured films of polymer/surfactant mixtures which form spontaneously at the air–solution interface. Here we report studies of the effect of adding a series of sparingly soluble species to the precursor solution, to alter the mesostructure of cetyltrimethylammonium bromide/polyethylenimine films and to investigate the incorporation of small molecules within the films. Small-angle neutron scattering confirmed that cyclohexane and decane evenly swell the micelles in film forming solutions, while cyclohexanol extends the prolate micelles along their long axis. Although the presence of these additives in solution did not greatly affect the formation of the film, it was observed that they did influence the structure of the films. Films produced with decane consisted of a cubic phase rather the conventional 2-D hexagonal phase, whilst both cyclohexane and cyclohexanol enhance the level of ordering in low MW polymer films. Benzene was found to have no significant effect on the film.

Keywords: Surfactant–polyelectrolyte interactions; Film; Nanostructure; SANS; Reflectivity; Encapsulation

1. Introduction

In recent publications we have reported the formation and structure of spontaneously forming surfactant-templated mesostructured films [1–3]. These films are formed by the mixing of cationic surfactants with polyethylenimine (PEI) and, depending on the conditions used, the films can be both macroscopically thick and highly ordered. If a crosslinking agent is used the films become robust enough to be removed from the air/water interface and dried [2], forming a solid, mesostructured polymer–surfactant membrane. In this paper we investigate the addition of sparingly soluble species to the film forming solutions for two reasons: to determine whether they can be incorporated into the film, and to determine whether the incorporation has any effect on film structure. As with any mesostructured system it is highly desirable to be able to tune the properties of the film by varying the internal nanostructure and incorporation of sparingly soluble molecules which alter micelle shape is one method to achieve this [4–7]. Incorporation of such species could also result in use of these membranes in encapsulation/release applications, e.g., for hydrophobic species such as scents, pesticides or therapeutic agents.

In previous experiments we observed that largely stepwise changes in film parameters, such as the long range order and size of the mesostructure, occurred when micellar parameters (alkyl chain length and micelle composition) were changed [1,8]. On the other hand, when parameters related to the intermicellar phase (pH and polymer molecular weight) were changed, the film parameters varied in unexpected ways [1,2]. Given that altering micellar parameters yields more predictable variation in the films we have done further experiments in this area. One common method of adjusting the shape and size of surfactant micelles is through incorporation of water-insoluble, or sparingly soluble, species into the micelle [9,10].

In general the incorporation of sparingly soluble species will affect surfactant micelles in one of two ways. Highly water insoluble additives, such as long chain n-alkanes, are incorporated into the micellar core, swelling the micelle and leading

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to shifts in micelle structure from ellipsoidal to spherical or from rod-like to spheroidal [9,11–15]. Alternatively, polarisable additives, such as alcohols and aromatics, are incorporated into the palisade layer of the micelle, close to the aqueous phase [10,16]. This often leads to a reduction in the curvature of the micelle surface and the formation of, for instance, rods instead of spheres [13,17,18]. With this in mind we therefore report here structural studies of solid cetyltrimethylammonium bromide (CTAB)/PEI films produced from solutions containing *n*-decane, cyclohexane, cyclohexanol or benzene.

Considerable previous work has been done on the incorporation of sparingly soluble material into surfactant micelles in solution. Of the species reported here, only the effect of cyclohexanol has not been examined in detail, however a number of studies have shown that the behaviour of structurally complex alcohols is similar to that of the equivalent 1-alcohol [10,12]. The comparison of cyclohexanol with cyclohexane, a more extensively studied additive, is also of interest.

It was initially believed that cyclohexane behaved in the same manner as long chain *n*-alkanes [16,18–21], however it was soon found that it can affect surfactant micelles in a manner similar to more soluble compounds [9,13]. Although hydrophobic additives will not be in close contact with the water phase (as is the case with alcohols and aromatics) [20], it has been postulated that shorter alkanes like cyclohexane will preferentially mix with the surfactant alkyl chains rather than be pseudo-phase-separated in a hydrocarbon rich core [22]. Using a theoretical approach Aamodt et al. have calculated that at low additive concentrations even relatively long alkanes, such as *n*-octane, mix with the surfactant alkyl chains [23]. It was also shown that as the concentration of alkane increases, the fraction pseudo-phase-separated in the micelle core increases [23]; this is true for all solubilised species [10,17].

As stated above, aromatics tend to be incorporated into the palisade layer of the micelle. It is believed that this state is stabilised by the formation of π-cation bonds between the surfactant headgroups and the polarisable benzene ring [24], with the benzene molecules being incorporated between the surfactant headgroups. This intercalation increases the average distance between the surfactant headgroups, leading to a lower charge density on the micelle and a decrease in the micellar curvature [6,17]. The high degree of segregation of such sparingly soluble species into the micelles in solution suggests that it should be possible to incorporate these "filled" micelles into our CTAB/PEI films.

From our previous studies on the CTAB/PEI system it is known that in solution, in the presence of polymer, the micelles have a prolate ellipsoid shape, while in the film the micelles are rod-like and produce a two-dimensional hexagonal phase of surfactant micelles encased in polymer [1,2]. We would therefore expect species that reduce the micellar curvature to elongate the micelles in the solution (perhaps even forming rod-like micelles), and also therefore increase the average length of the micelles in the film. On the other hand, swelling agents such as decane would be expected to increase the size of the micelles in solution, and also therefore swell the micelles in the film. In this paper a series of scattering measurements are performed on CTAB/PEI systems with the above species. Both bulk sensitive (small angle neutron scattering (SANS)) and surface sensitive (X-ray and neutron reflectometry and grazing incidence X-ray diffraction (GID)) techniques were used.

2. Experimental

The CTAB and cyclohexane were purchased from Acros, cyclohexanol from Fluka, benzene from Fisher, while the PEI and *n*-decane were from Sigma–Aldrich. The deuterated analogues of CTAB, decane, cyclohexane and cyclohexanol were purchased from CDN isotopes. All the chemicals were used without further purification and ultrapure Milli-Q water or D_2O (Sigma) were used as the solvent.

For all the solutions the concentration of CTAB was 0.037 M, and the concentration of polymer was 15 g/l. Two polymers were used, a $M_W \sim 2000$ Da copolymer type PEI (short or S-PEI) and a $M_W \sim 25{,}000$ Da hyper-branched type PEI (medium or M-PEI), see Ref. [2] for details. Under the conditions used here the polymer was ~3% charged giving a solution pH of ~10, however no pH adjustment was made to solutions without polymer. For all the measurements the temperature was kept at 25–30 °C, this was above the Krafft temperature of the surfactant in the mixed system. The amount of each species added was calculated as a percentage of the total number of methylene groups in the micelle core, i.e., a 30% decane system will have a decane concentration of 0.0254 M. For cyclohexanol the alcohol functional group was excluded from this calculation. Note that for the SANS experiments, due to the expense of deuterated materials and solvents the sample volumes prepared were deliberately low (4 ml maximum per sample, which were prepared from 15 ml stock surfactant/30% hydrophobe solutions that were then diluted further to achieve the lower hydrophobe loadings). Thus the absolute amounts of species added were very small, (i.e., between 130–150 µl, added using a microsyringe) leading to significant inaccuracies in the added amounts of hydrophobic species for these experiments. Solutions for reflectometry experiments were each ~30 ml, thus measurement errors are less significant for these experiments.

The GID and X-ray reflectometry experiments were performed on the Troika II (ID 10B) beamline at the European Synchrotron Radiation Facility, Grenoble, France, with a monochromatically selected X-ray wavelength of ~1.55 Å [2]. For the GID two angles of incidence were used, 0.13° and ~0.89°, see Ref. [2] for details. For each sample an X-ray reflectometry profile was measured first over about 1 h, followed by the two GID patterns (each requiring 1 h) and then a second reflectometry profile (1 h). Thus by the end of the second reflectivity profile the films were over 4 h old. The films are generally visible to the naked eye at the surface of the solution within 5 min after the solution is poured into the trough and remain visible until removed at the end of the measurement. In the absence of any other species, variation of the CTAB/PEI film mesostructure with time does occur within the first hour, as reported in our earlier work [2]. After approximately one hour the evolved film mesostructure is generally stable, for films containing only CTAB and PEI, unless the ambient conditions are changed.

Crosslinking the polyelectrolyte fixes the mesostructure which is present in the film at the point where crosslinking occurs, [2] thus the film structure can be stabilised by this reaction. Consequently identifying the "transient" phases formed in these non-equilibrium systems is important since it enables us to determine when best to crosslink and fix the desired structures. (These phases are present for at least several tens of minutes, if not hours, allowing time for the crosslinking to be initiated and freeze in the desired structures.) However in the present paper we restrict our report to the evolution of phases in CTAB/PEI films containing sparingly soluble species, since we require information on these systems without the additional perturbation of crosslinking.

The neutron experiments were performed on the LOQ, SURF and CRISP instruments at the ISIS Pulsed Neutron and Muon source, Rutherford Appleton Laboratories, Chilton, England. The incident angle used for the reflectometry experiments was 1.5°, with data being collected between 0.048 and 0.613 $Å^{-1}$ in Q_Z $(=2\pi/d = (4\pi/\lambda)\sin\theta$, where d is the lattice spacing). For each sample a series of 15 min scans were performed and where no changes with time were observed these profiles could be combined to reduce the associated errors.

For the SANS experiments protonated CTAB was used with protonated or deuterated additive in 100 or 60% D_2O. At least three of the possible four contrasts were measured for each sample. Data were collected between 0.09 and 0.285 $Å^{-1}$ in Q for 30 min, corrected for background and reduced to one dimension by radial averaging using the Collette program on LOQ. The profiles were modelled simultaneously using a procedure written by Dr. Steve Kline at the NIST Centre for Neutron Scattering for the Igor PRO platform (WaveMetrics) [25], with the Hayter–Penfold formalism being used to account for the interactions between the charged micelles [26]. Several models for the micelle shape were initially investigated (prolate and oblate ellipsoids, cylinders), and the final selection made on the basis of a selection of fits giving the lowest χ^2. The model chosen was that of a uniform ellipsoid and, in line with our earlier results on the shape of CTAB micelles in the presence of PEI [1] and with the literature [17,27,28] the shape of the micelles was thereafter constrained to a prolate ellipsoid. Prolate ellipsoids have one major semi-radius (A) and two degenerate minor semi-radii (B), e.g., A > B; the volume of the ellipsoid is therefore: $V = (4/3)\pi AB^2$. For the model the temperature (298 K), dielectric constant (80) and micellar charge (25, measured by Berr [27]) were all fixed, whilst the variables fitted were the SLD contrast (between the micelle and the intermicellar phases), volume fraction, micelle radii, salt concentration and incoherent background. Values of the SLD contrast were initially calculated for the expected compositions of the intermicellar phase and micelle cores, based on the prepared solutions. These were used as starting values for fitting, and in the case of the samples in 100% D_2O, provided an upper bound for physically reasonable results. The final fits with lowest χ^2 values all had fitted contrasts which were equal to or lower than those calculated for the samples in 100% D_2O. For samples in 60% D_2O the fitted values also were compared with the calculated values to ensure that the fitting was physically reasonable.

Table 1

Micelle radii, aggregation numbers (N), volume fractions of sparingly soluble species in the CTAB micelles calculated from the fitted SLD contrast values and the expected volume fraction, and the excess volume fractions taken from the modelled SANS data[a]

Additive	%	Radii (Angstroms^{-1})		N	Additive (%)		EVF (%)
		A	B		Calc.	Expected	
No polymer							
Cyclohexane	10	37.1	24.1	150	0.2	10.4	24
	20	36.6	23.9	144	0.5	20.7	25
	30	38.7	29.0	200	11.9	30.9	21
Cyclohexanol	10	37.0	24.2	152	0.8	10.2	23
	20	37.0	24.2	149	2.7	20.3	22
	30	37.1	23.9	140	6.0	30.5	22
Decane	30	39.3	27.8	192	8.3	32.6	23
S-PEI							
No additive[b]	–	38.4	23.8	163	–	–	18
Cyclohexane	10[c]	36.7	24.5	164	–	–	–
	20[c]	37.5	25.5	176	–	–	–
	30	39.0	28.4	201	10.7	30.9	20
Cyclohexanol	10	37.1	24.3	155	0.6	10.2	22
	20	36.7	24.1	148	4.9	20.3	19
	30	36.7	23.3	138	7.3	30.5	17
Decane	10	37.1	24.9	161	1.6	11.2	22
	20	37.5	25.4	173	3.1	22.0	19
	30	36.3	27.3	179	5.2	32.6	22
M-PEI							
No additive[b]	–	34.9	25.3	139	–	–	32
Cyclohexane	10	37.0	24.7	128	1.4	10.4	37
	20	36.9	25.0	132	3.5	20.7	34
	30	37.7	26.0	138	6.3	30.9	35
Cyclohexanol	10	37.1	24.3	116	0.0	10.2	42
	20	36.5	23.8	113	2.6	20.3	38
	30	36.4	23.5	108	5.3	30.5	36
Decane	30	38.6	28.5	154	6.3	32.6	40

[a] The errors associated with the radii are ±2 Å and ±1 Å for the radii, respectively, ±5 for N, and ±5% for volume fractions.

[b] No data with deuterated additive was available for these samples.

[c] These results were taken from [1], where a $M_W \sim 750{,}000$ Da polymer was used instead of M-PEI.

The fitted contrasts were used directly to calculate the content of additives in the micelles given in Table 1 above.

3. Results and discussion

3.1. SANS results

The most important aim of the SANS experiments reported here was to determine that the presence of the polymer in solution did not impair uptake of the hydrophobic species into the micelles. We also used the SANS experiments to compare the shape of micelles in solution with the mesophases found in the films formed at the air–solution interface, thus we have not attempted to determine a full solution-phase diagram for these systems but merely to correlate solution behaviour with film structures. In modelling our SANS profiles we were able to achieve good fits using a simple ellipsoid model and thus

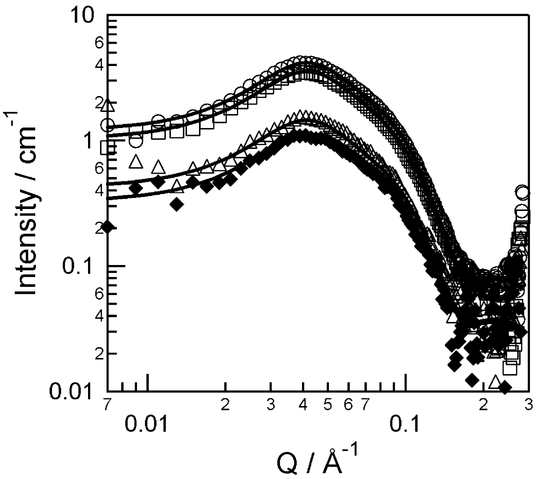

Fig. 1. SANS data for 15 S-PEI:CTAB: 30% cyclohexanol: (circles) 100% D_2O, H-cyclohexanol, (squares) 100% D_2O 30%, D-cyclohexanol, (triangles) 60% D_2O, 30% H-cyclohexanol, (diamonds) 60% D_2O, 30% D-cyclohexanol. The lines are simultaneous fits to the data using the model described in the text.

attempts to determine the location of the different additives and/or polymer in the micelle through the use of a more complex model were not justified by the data available. Sample fits to the SANS data are shown in Fig. 1.

According to Berr a 0.1 M CTAB solution in 100% D_2O contains prolate micelles with core radii of 37.8 Å (A) and 20.1 Å (B), with a 'Stern layer' thickness of 6.5 Å and an aggregation number of 164 [27]. Aswal et al. more recently fitted data from a 0.05 M CTAB solution in 100% D_2O as uniform prolate micelles (using a similar Hayter–Penfold type interaction as used here) and found radii of 33.7 (A) and 24 Å (B). However using NMR measurements Hedin et al. obtained core radii of 36.5 and 25.7 Å for a 0.1 M CTAB solution [17]. Relative to these three studies the radii of the micelles containing the various sparingly soluble species (albeit at a lower CTAB concentration) are closest to those reported by Hedin et al. (Table 1) and are larger than the equivalent values reported in the absence of such species, suggesting the sparingly soluble species have swollen the micelle despite the presence of the polymer in solution, as expected.

Along with the micelle radii determined by the uniform ellipsoid model, Table 1 also gives values for the aggregation number (N) of the additive containing micelles and an estimation of the amount of this species in the micelle (as a percentage of the total volume). N was calculated from the total volume fraction and the micellar volume by assuming that all the surfactant in the system is incorporated into the micelle, whilst the percentage of additive was calculated from fitted SLDs using values for the SLD calculated from molecular structure and densities for the protonated and deuterated species. The final variable in Table 1, the excess volume fraction, was determined by subtracting the volume of the surfactant alkyl chains (using the molecular volume of the alkyl chain determined by Berr et al. [27,29] multiplied by N) and the volume of additive (from the just calculated additive volume fraction) from the fitted micelle volume. This is a direct determination of amount of non-surfactant alkyl chain and non-additive components present in the modelled ellipsoid, presumably it corresponds to a mixture of surfactant headgroups, solvent, and (where present) polymer.

A complete data set was not collected for the pure CTAB (no polymer, no additive) system, however using radii values of 36.9 and 24.1 Å (which are comparable to the literature and similar to those samples with low hydrophobe loading), an aggregation number of ∼150, and the theoretical SLD contrast, a good fit on a single CTAB in 100% D_2O SANS profile was obtained. It is therefore likely that the above values are accurate for pure CTAB micelles under our conditions.

Relative to these values, the size of the CTAB micelles is increased at high decane concentrations; this is consistent with the general interpretation that such molecules will swell the micelles [5]. The same also occurs for cyclohexane, in line with the results of Törnblom and Henriksson, which show (in polymer-free solutions) a swelling of CTAB micelles containing cyclohexane at additive contents above 10% [22]. Below 10% Törnblom and Henriksson showed that there was a lengthening of the surfactant micelle; this was not observed here, presumably due to the absence of a system with a suitable additive content (6–9%). The swelling of both the cyclohexane and decane containing micelles is accompanied by an increase in the aggregation number, which is consistent with theoretical predictions of Aamodt et al. [23].

When cyclohexanol is incorporated into CTAB micelles it appears to induce a slight elongation of the micelles with increasing additive content, more obviously there is a concomitant decrease in the aggregation number. Although the use of cyclohexanol as an additive is rarely reported in the literature the results shown here are comparable to those given for other alcohol/surfactant systems, in particular Zana has reported a significant drop in the aggregation number of tetradecyltrimethylammonium bromide micelles with increasing concentrations of 1-hexanol [30].

One unusual feature observed in all systems is the significantly lower calculated additive contents than theoretically expected. The experimental values for the nominally 20 and 10% solutions do however roughly scale with the amounts in the 30% solutions, as expected since these were prepared by dilution from the 30% stock solution. Given that all of the additives have low calculated volume fractions, factors such as evaporation of the additive and variant partitioning of the additive in the intermicellar phase can be discounted since these would depend on the volatility or hydrophobicity of particular species. Possibly some phase separation occurs within these systems, however this was not observed in the cells during the experiments and these solutions were all completely clear, not cloudy, although the small amounts of additives (i.e., 8–10 µl per ml of solution) compared to the overall solution volume could make it difficult to see this effect. Importantly however there appears to be no difference between the amounts of sparingly soluble species found in solutions with the polymer present compared to those without PEI. Thus the addition of polymer to the solutions makes little difference to the extent of solubilisation of these species in the micelles.

The inclusion of polymer in the intermicellar phase does however have some effect on the micelles. In a previous publication it was shown that pure CTAB micelles became elongated and narrower as the polymer concentration increased [1]. The effect was greatest for polymer concentrations higher than 15 g/l and in the present study there does not appear to be any significant variance in the micelle radii upon the inclusion of the polymer. There is however a significant variation in the micelle aggregation number and the excess volume fraction (Table 1). Whilst short PEI gives values close to those from the polymer free systems, the medium PEI systems give a significant variation in both values. The results for M-PEI are also similar to a previously reported CTAB/15 g/l (750,000 Da) PEI/additive free system (Table 1) [1], and so it appears that when a high MW polymer is used, the polymer becomes partially incorporated into the surfactant micelle.

The most likely reason for this is the more hydrophilic nature of the shorter polymer, which has previously been found to be a dominant factor affecting the properties of this system [2]. It could be that the more hydrophobic higher MW polymers are incorporated into the palisade layer of the micelles. Alternatively the polymer could be more closely bound to the micelle surface, excluding water from this region. Again, importantly, it is clear from the results in Table 1 that the effect of the different additives on the CTAB micelles is unchanged in the presence of either polymer.

3.2. *GID and reflectometry results*

From previous experiments it is known that, in the absence of additive, CTAB/PEI films are composed of rod-like micelles encased in a polymer matrix [3]. For a soft matter system these films possess a relatively high level of ordering and subsequently peaks corresponding to a two-dimensional hexagonal phase (or wormlike phase) are observed in the diffraction patterns. As the films are not rigidly crystalline it is likely that these ordered phases coexist with disordered regions (that would give little or no scattering) [2].

Another principal feature of these films is the MW dependence of the degree of ordering. Films prepared using high MW polymers are thicker but less ordered, displaying a diffraction ring in their GID patterns. On the other hand, films prepared with short PEI, although thinner, can have a very high level of ordering and primarily display a single diffraction spot in their GID patterns although patterns can contain up to 8 diffraction spots [2,3]. This spot is indicative of a highly ordered film, in which the crystallites are aligned with the air/water interface. This high level of ordering in pure CTAB/PEI films which are not crosslinked can be, however, short-lived, as, particularly at lower polymer concentrations and for low molecular weight PEI, there is a loss of structure with time. This has been attributed to competition between local crystallite growth and global film development [2].

For most of the additive containing films reported here the GID patterns exhibit the standard 2D hexagonal phase structure, with the M-PEI films producing diffraction rings and the S-PEI films producing up to four diffraction spots in their lower angle pattern (Fig. 2, Table 2). The M-PEI films show the standard improvement of structure with time which is also seen for higher molecular weight PEI films which do not contain additives [2]. In additive-free films the *d*-spacing is also observed to increase slowly with time, possibly due to water swelling the polymer regions of the initially formed mesophase. However, in contrast to the additive-free films, those films containing additives are on the whole more stable in *d*-spacing during our measurements. The exceptions to this are the decane containing films.

Table 2
d-Spacings (Å) from the low (0.13°) and high (~0.89°) incident angle GID patterns and X-ray and neutron reflectometry profiles[a]

Additive	%	X-ray	GID	GID	X-ray	Neutron	
		Refl. 1	(low)	(high)	Refl. 2	Initial	Final
S-PEI							
No additive	–	48.8	50 (S)	50 (wS)	51.6	49.0	52.0
Benzene	27	47.3	49 (S)	NS	–	53.5	50.7
Cyclohexane	10	–	–	–	–	50.4	50.4
	20	–	–	–	–	50.4	50.4
	30	47.3 (2P)	50 (3S)	NS	74.1	51.1	51.1
Cyclohexanol	10	–	–	–	–	51.1	51.1
	20	–	–	–	–	49.6	51.1
	30	46.8 (4P)	50 (2S)	47 (4S)	52.3	49.6	51.1
Decane	10	–	–	–	–	51.9	60.2
	20	–	–	–	–	51.9	60.2
	30	NS	60 (R)	65, 58, 52 (3R)	61.7, 55.6, 51.1	51.1	54.2
M-PEI							
No additive	–	53.5[b]	60 (R)[b]	54 (R)[b]	–	51.1	52.6
Benzene	27	48.9	49 (bwR)	50 (R)	48.9 (2P)	–	–
Cyclohexane	30	50.0	49 (wR)	50 (R)	48.9 (2P)	52.6	52.6
Cyclohexanol	10	46.8	52 (RwS)	49 (R)	48.3 (2P)	49.6	52.6
	20	–	–	–	–	49.6	49.6
	30	–	–	–	–	51.1	52.6
Decane	30	52.9	54 (bR)	53 (bR)	52.9	–	–

Columns are given in chronological order as the data was taken during the experiment. The first X-ray reflectivity pattern was started within 10 min of pouring the solution into the trough, GID (low) started 1 h later, GID (high) after 1 further hour and the second X-ray reflectivity pattern was started 3 h after the solution was poured into the trough. The first neutron reflectivity profile was collected for 15 min starting immediately after solution poured into trough, the final neutron reflectivity profile for 15 min starting 45 min after solution was poured into the trough.

[a] For the GID patterns R denotes a ring, S a spot, while b and w indicate broad and weak diffraction features, respectively. For X-ray reflectivity P indicates the presence of multiple peaks. In cases where multiple peaks are present the spacing given is that of the first order peak since the others are directly related to this spacing by integer factors as expected for aligned 2D hexagonal phases. NS indicates that no diffraction features were seen, and a dash that the profile was not measured. The error associated with the X-ray reflectometry and GID data is ±0.6 Å and ±5 Å, respectively, and for the neutron reflectivity is ±0.8 Å.

[b] X-ray data from Ref. [2] for a CTAB/750,000 Da PEI film.

The PEI/30% decane system in particular shows a dramatic divergence from the behaviour observed for the other films. As

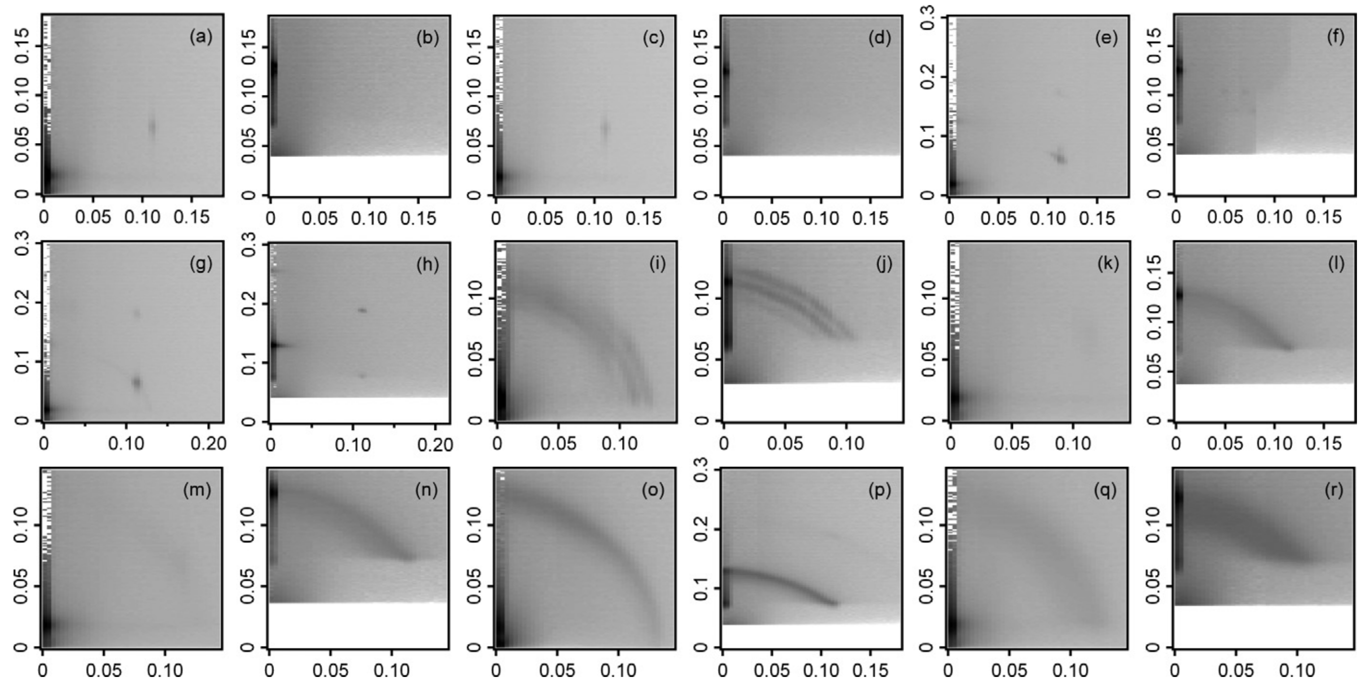

Fig. 2. GID patterns for the CTAB/PEI films at different incident angles (x-axis–Q_{XY} (Å^{-1}), y-axis–Q_Z (Å^{-1})). Left to right, top row: S-PEI (no additive), (a) 0.13° and (b) 0.89°; S-PEI/27% benzene, (c) 0.13° and (d) 0.94°; S-PEI/30% cyclohexane, (e) 0.13° and (f) 0.94°; middle row: S-PEI/30% cyclohexanol, (g) 0.13° and (h) 0.95°; S-PEI/30% decane, (i) 0.13° and (j) 0.80°; M-PEI/27% benzene, (k) 0.13° and (l) 0.90°; bottom row: M-PEI/30% cyclohexane, (m) 0.13° and (n) 0.89°; and M-PEI/30% cyclohexanol, (o) 0.13° and (p) 0.92°; M-PEI/30% decane, (q) 0.13° and (r) 0.86°.

is most evident in the second S-PEI/30% decane GID pattern the phase structure of this film is that of a cubic *Pm3n* phase (Fig. 2). This phase can be composed of spherical or ellipsoidal micelles and the formation of these instead of rod-like micelles within the films is consistent with the change from rod-like to spheroidal micelles expected upon the incorporation of the additive [9,11,12]. *Pm3n* cubic phases can also form from entangled rod-like micelles but in this case it seems more likely that the spheroidal micelles observed in solution simply pack together in the film rather than rearrange, although there is insufficient information available here to distinguish the possible cubic phase structures. In a previous paper we reported the formation of a cubic phase in a system containing CTAB, 60 g/l S-PEI and a crosslinking agent; this yielded a lattice parameter of 23.9 Å [2]; for the S-PEI/30% decane system the lattice parameter is 26.1 Å, indicating that the micelles have been swelled by the decane, as expected given the SANS results (Table 1). Notably, in the S-PEI/30% decane films although the cubic phase is not aligned with the air/water interface like the hexagonal phase, intense diffraction rings were produced which indicate that the overall ordering within the films is high. Given that film thickness is highly dependent on the polymer MW and that decane is incorporated into the micelle interior (where it cannot interact with the polymer) it seems unlikely that this increased scattering is due to the film being thicker. A more probable explanation is that the film is internally more ordered; this could result from the inherently greater organisational flexibility of the spheroidal micelles.

We have assumed, from the positions and breadths of the rings/peaks in the GID and reflectometry profiles of the other decane containing films (Table 2), that these films also have a cubic phase structure. Ruggles et al. observed a similar hexagonal to cubic phase transition upon the addition of decane to dodecyltrimethylammonium bromide templated silica films, although in that case, when CTAB was used as the surfactant there was instead a swelling of the hexagonal phase [5].

More subtle variations in the structure of the films is observed with the addition of the other additives. For both of the PEI/30% cyclohexanol films there is significant improvement in the intensity of the diffraction features (Fig. 2). The low angle pattern of the M-PEI/30% cyclohexanol film displays the greatest ordering of all medium PEI films, while the number and intensity of the spots in the second diffraction pattern of the S-PEI/30% cyclohexanol film is greater than that observed for the additive free films. As with decane films, this improved diffraction intensity is most likely due to the presence of a more ordered film rather than a thicker film. The probable cause of this improvement is an increase in the length of the rod-like micelles in the presence of cyclohexanol. Such an increase would be consistent with the SANS data, that showed an elongation of the micelles. It is also consistent with the literature, which suggests that cyclohexanol should stabilise the rod-like phase [10], and which in turn will increase the rod length and potentially improve the long-range ordering.

Given the intensity and number of spots in the second GID pattern of S-PEI/30% cyclohexanol relative to that of the additive free film (Fig. 2), the addition of cyclohexanol, along with improving the mesoscale ordering of the film, also appears to shift the thermodynamic equilibrium within the films to favour the preservation of the initially formed crystallites [2]. Thus adding this sparingly soluble species improves both the structure and the persistence of that structure in the films.

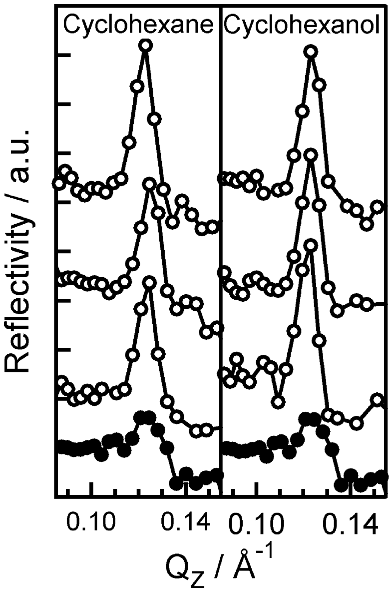

Fig. 3. Neutron reflectometry profiles (45–60 min) for the (protonated) CTAB/S-PEI/cyclohexane and CTAB/S-PEI/cyclohexanol films on 100% D_2O. Bottom to top: No additive, 10, 20 and 30% additive films. The error bars have been excluded for clarity.

The strong diffraction from the S-PEI/cyclohexanol films is also evident in the neutron reflectometry results (Fig. 3, Table 2) and shows that even very small concentrations of cyclohexanol significantly improve the ordering within the films. Interestingly, similarly strong diffraction is observed for the S-PEI/cyclohexane films; this is somewhat surprising as the SANS results show the surfactant micelles to be swollen rather than elongated (Table 1). It may be that the actual volume percentages of cyclohexane incorporated into the micelles within the film is lower than 10%, where it has been proposed that cyclohexane causes an elongation of the micelles [22], though this would raise the question of the location of the 'missing' additive. Another possible explanation is that the effect of the polymer on the micelle (which also leads to elongation of the micelles in solution [1]) is significant enough in the films to drive the system as a whole to form rod-like micelles in the presence of the cyclohexane. In this situation the cyclohexane would likely be forced into the palisade layer as no increase in the d-spacings was observed (Table 2). Ultimately though, cyclohexane does not preserve the structure of the films in the same way as cyclohexanol as there is no structure in the second GID pattern of the S-PEI/30% cyclohexane film, and the ordering in the M-PEI/30% cyclohexane patterns is not significantly improved.

Relative to all the other additives the influence of benzene was minimal (Table 2). This is also surprising as benzene, like cyclohexanol, is expected to stabilise and lengthen rod-like micelles. The reason for the absence of any effect may be due to the mechanism by which benzene interacts with the cationic surfactant. It is believed that the aromatic ring, when located in the palisade layer, is polarised to form a charge-dipole complex with the surfactant headgroups [24,31]. This is similar to the charge-dipole interaction formed between the surfactant and the polymer and it is possible that these two interactions compete with each other to negate any potential increase in ordering.

4. Summary

The addition of small amounts of hydrocarbons or alcohols to the film forming solutions of CTAB and PEI has been shown to influence the properties of the micelle network in the film. A cubic phase was formed in the presence of decane, while enhanced ordering in films prepared using low molecular weight PEI was also observed when cyclohexane or cyclohexanol were present. From the SANS measurements it was observed that the actions of the additives and the polymer on the CTAB micelles are independent of each other. These experiments show that it is possible to incorporate hydrophobic species within the micelles within the polymer–surfactant films while still forming a continuous membrane at the interface. Further development of these membranes as encapsulation systems is under investigation.

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