

# Formation of robust, free-standing nanostructured membranes from cationic surfactant mixtures and hydrophilic polymers

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A new type of surfactant templated polymer film, which spontaneously forms at the air/water interface into micron-thick structures, was prepared from a water-soluble polymer and a cationic surfactant mixture; the film is stable, highly ordered and robust, requiring no cross-linking agents to fix the structure.

Surfactant aggregates (micelles, vesicles *etc*) are used in numerous applications because of their ability to encapsulate hydrophobic molecules within an aqueous solution. Conversion of these surfactant encapsulated materials into solid-state films may be achieved in a number of ways, such as by the Langmuir–Blodgett method, evaporation, precipitation or using layer-by-layer assembly. Phospholipid vesicles have recently been incorporated into polymer films using a modified layer-by-layer assembly.<sup>1</sup> However, these methods have a number of drawbacks, such as requiring a high level of engineering, producing very thin films, and/or requiring the use of a solid support to ensure contiguity of the film. Here we report the spontaneous formation at the air/water interface of robust, ordered, micron-thick films of surfactants with a biocompatible polymer that can be removed from the surface without a solid support. These robust films are stable and prepared without using a cross-linking agent, representing a significant advance over our earlier work in this area.<sup>2</sup> These films were prepared using a cationic surfactant mixture (containing oppositely charged surfactants) that can act as a mimic of a biological membrane or vesicle, and could therefore potentially be used for encapsulation membranes for topical drug delivery.<sup>3</sup>

Cationic mixtures prepared from equimolar amounts of two oppositely charged surfactants tend to precipitate out of solution,<sup>4</sup> however on either side of the equimolar line vesicles are frequently formed in the low-concentration region (1–2 wt%).<sup>5</sup> Vesicle formation is aided by using surfactants with different alkane chain lengths, and it has been postulated that surfactant composition varies across the inner and outer layers of the vesicular bilayer.<sup>6</sup> Already there have been studies on cationic vesicles with added drug molecules,<sup>7</sup> interacting with hydrophobically modified biocompatible polymer,<sup>8</sup> or with DNA or charged polymers.<sup>1,9</sup>

We observed formation of thick, robust, membrane-like films when cationic vesicles of cetyltrimethylammonium bromide (CTAB, Acros) and sodium dodecyl sulfate (SDS, Acros) are mixed with water-soluble polymers. We report here as an example, films prepared using the biocompatible polymer polyacrylamide (PAAm, Aldrich ~10 000 Da; see Fig. 1). In these experiments

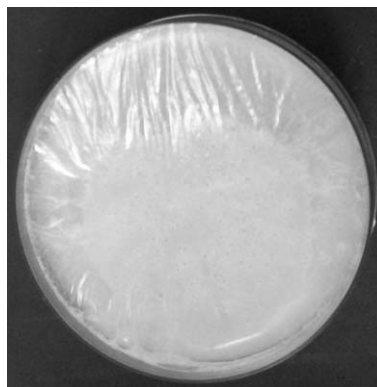


Fig. 1 Picture of a two months old 60 : 40 CTAB/SDS/PAAm film in a 62 mm wide polystyrene dish.

$5.00 \times 10^{-5}$  mol of surfactant was added for each gram of water or 1 wt% PAAm solution, giving a total surfactant concentration of 1.64 wt% for a 60 : 40 CTAB/SDS mole ratio solution. Preliminary SANS measurements on this cloudy solution suggest the presence of polydisperse CTAB/SDS vesicles in the solutions, as expected.

Visual observation of the CTAB/SDS system (both with and without PAAm) showed that, even at the extremes of the mole fraction range examined (98 : 2 to 10 : 90 CTAB/SDS), when solutions of the two surfactants were mixed there was an instantaneous clouding of the solution. Clouding was not always uniform, indicating a phase separation, however stirring for a few seconds resulted in a contiguous (and apparently stable) phase.

When mixed with only one surfactant no film was formed on the PAAm solution, yet upon incorporation of the second surfactant in the CTAB-rich region, even at mole fractions as high as 97 : 3 CTAB/SDS a visible film was observed. Between fractions of 80 : 20 and 55 : 45 the properties of the films appear to be the same, and within this region the films were, in appearance, similar to the skin formed on top of hot milk; they were contiguous, rubbery and had some resilience to tearing. After removal from the interface and drying the PAAm films become more rigid and brittle but are nonetheless still highly contiguous. To avoid confusing these thicker films with the Gibbs monolayer films that are present in standard surfactant solutions we will use the term skin to describe the macroscopically thick films. For the 97 : 3 system the time taken for the skin to form was ~2 days, however as the fraction of SDS was increased the skins became more substantial and the skin formation time dropped to ~10 h for the 60 : 40 system. As expected, some precipitation of material occurred when the mole fraction reached 50 : 50, and at this point

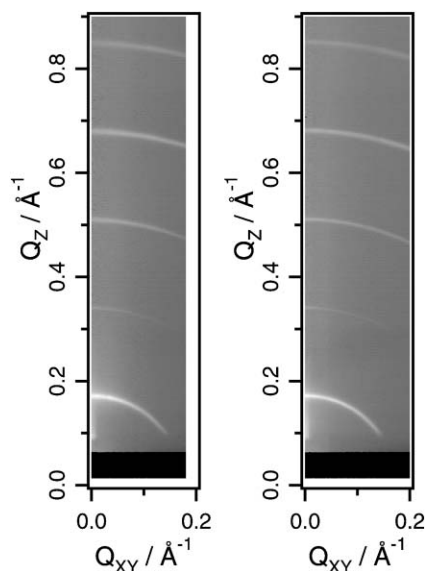
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no skin formation was observed. Notably, as the fraction of SDS was increased beyond the equimolar point skin formation did not recommence despite the presence of vesicles in the solution. Therefore the use of positively overcharged cationic mixtures is necessary for skin formation.

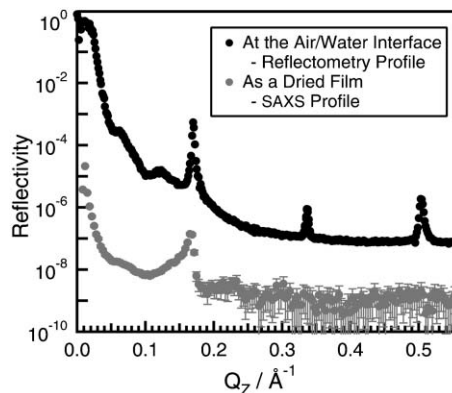
When a skin was present there was a significant reduction in evaporation rates, such that even after two months an average 60 : 40 CTAB/SDS/PAAm solution would contain over 40% of its initial mass (30 g) of water (Fig. 1). When still in contact with the subphase below the skins were also able to self-repair – a new skin forms over exposed areas on time scales near to the initial film formation time. In Fig. 1 a partially dried skin is also clearly visible. This formed when the solution level dropped, separating the solution from the skin that stayed attached to the container at the original solution height. Following skin formation it was also possible to draw segments of the skin off of the surface, and these dry within a day under ambient conditions. When dry the skin is micrometers thick, is rigid and brittle but capable of supporting its own weight and resilient to the application of light forces.

In the absence of PAAm a film is still formed by the 60 : 40 CTAB/SDS system, and was visible to the naked eye, although no proper skin is formed and the film does not affect the rate of evaporation dramatically. This suggests that the properties of the CTAB/SDS vesicles are important to the formation of the skins but that aggregation with the polymer is necessary for the formation of a contiguous skin. The presence of an ordered, thick film/skin in 60 : 40 CTAB/SDS solutions with and without PAAm was verified by grazing incidence X-ray diffraction (GID) † (Fig. 2).

Intense, sharp diffraction peaks are observed showing that a highly ordered, and therefore significant, film was present. From the regular spacing of the peaks, the mesophase consists of a series of layered bilayers so the film is composed of a randomly oriented lamellar phase or close-packed multilamellar vesicles. The repeat spacing of this layer for the polymer free system was calculated to be 37.1 Å, this is close to the bilayer spacing of equimolar CTAB/SDS determined by Tomašić *et al.* of 38.2 Å,<sup>10</sup> but much



**Fig. 2** GID patterns for 60 : 40 CTAB/SDS without (left) and with (right) PAAm.



**Fig. 3** X-Ray reflectometry and SAXS profiles of a 60 : 40 CTAB/SDS/PAAm skin. For clarity the reflectivity values for the dried skin were multiplied by 1000.

shorter than the bilayer spacing of crystalline CTAB (51.9 Å<sup>11</sup>), suggesting interdigitation of the surfactant alkyl chains.

Upon the addition of polymer this spacing is unchanged and the level of structure is also the same. This is significant as it is unlikely that there could be penetration of polymer into the bilayer structure without a dramatic change in one of these values. The pure CTAB/SDS lamellae or vesicles must be surrounded and interlinked by the polymer to form the skins. Using the first diffraction peak in the reflectometry profile of the 60 : 40 CTAB/SDS/PAAm skin (Fig. 3) and the Scherrer equation, the average crystallite size was 750 nm. For such a material this is extremely large and indicates that the lamellae contain ~200 ordered bilayers. GID patterns taken at higher incident angles, probing deeper into the skin, show similar levels of structure.

Also shown in Fig. 3 is the small angle X-ray scattering (SAXS) † pattern of the dried film. Notably the single peak observed in the pattern is at 37.4 Å, almost exactly the same as the spacing of the peak for the skin at the air/water interface; clearly therefore the bilayer structures in the skin have a very low water content even at the air/water interface. Dehydration at the air/skin interface has previously been observed in polymer/surfactant skins and is probably the reason for the evaporative resistance of the skins.<sup>2</sup> TGA measurements on dried skins show they contain ~8 wt% water, while fresh skins harvested onto a glass slide raised from below the skin, lose ~60 wt% below 100 °C. About 20 wt% is lost below 45 °C, attributed to rapidly evaporating subphase solution from the bottom surface of the wet skin which is not part of the solid skin network. Thus the wet skins are ~40% water, probably in a gradient from the drier top surface to the wetter liquid interface.

In summary we report the formation of highly ordered and unusually robust nanostructured membranes which self-assemble over arbitrarily large areas, are easily recovered after growth and retain their structure when dried. We have prepared these films using many polymers including poly(ethylene oxide) and poly(ethylene imine), making it a generally applicable technique for preparation of membranes having potential application as encapsulation or delivery systems.

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## Notes and references

† The GID and reflectometry data were collected on the Troika II beamline (ID10B) at the European Synchrotron Radiation Facility, Grenoble, France. The SAXS results were collected on a PANalytical/Anton Paar SAXSess system with a PW3830 generator. Igor Pro (Wavemetrics) was used for data handling.

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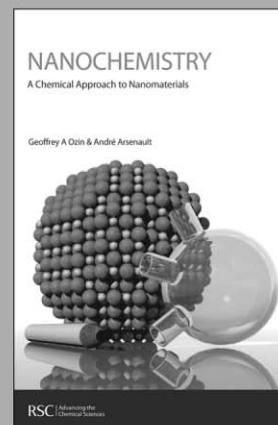
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