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Stomatosomes, blastula vesicles and bilayer disks: Morphological richness of structures formed in dilute aqueous mixtures of a cationic and an anionic surfactant

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ABSTRACT

Cryogenic transmission electron microscopy (cryoTEM) was used to study the structures formed in mixtures of sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) in dilute aqueous solutions with 0–300 mM NaBr. The DTAB mole fraction, X, was in the range 0.2–0.4, limited at 25 °C by precipitation of solid DTA–DS at $X = 0.38$ without salt to $X = 0.25$ at 300 mM NaBr. At a total surfactant concentration of 100 mM the samples separated into two liquid phases (the bottom phase birefringent) within a narrow (±0.01 mole fraction units) composition range. At the mid-point X varied from 0.32 without salt to 0.22 at 300 mM NaBr. Elemental analysis of C, S, O, and N in the separated phases of a sample with 100 mM NaBr and $X = 0.26$ showed the top phase to contain almost only SDS at a low concentration, 14 mM, and the bottom phase 175 mM total surfactant, with $X = 0.27$. Elemental analysis on samples without added salt gave erratic results, indicating problems in the physical separation of the phases. The cryoTEM survey of the separated phases revealed similar problems. Without salt both phases showed similar structures, whereas the top phase in the sample with added salt was void of structures larger than small micelles. The cryoTEM survey revealed a variety of structures being simultaneously present in most samples. A general trend with increasing X was an evolution from globular micelles, over disks, bands, branched bands transforming into sparse webs, perforated bilayer structures, and finally smooth bilayers. Increasing salt and total surfactant concentrations resulted in the emergence of structures with smaller mean curvature at lower X. Perforated bilayers were found in samples with 100 mM or less of added salt, and usually persisted to DTAB contents where precipitates appeared. The porous bilayers seemed to derive from sparse webs of band-like structures, and the hole size decreased with increasing X and salt concentration. Two types of recurrent structures were noticed: blastula aggregates, seemingly an intermediate structure transforming crumpled bilayers into vesicles of similar size (diameter 400–500 Å), observed over a broad range of conditions, and at 100 mM total surfactant concentration and 50 mM added salt or more a type of regular disks with a diameter of 180 ± 30 Å.

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1. Introduction

Formation of vesicles from mixtures of an anionic and a cationic surfactant was demonstrated by Hargreaves and Deamer in 1978 [1], and has later been shown to occur quite generally [2–10]. Usually equimolar mixtures give precipitates at room temperature (exceptions are known [11,12]) and the vesicles are found within two lobes in the quasi-ternary phase diagram, with excess of one or the other of the surfactants. The vesicle lobes have larger extensions in mixtures of surfactants that differs in chain length than in symmetrical mixtures, and the vesicle lobe is more extended on the side with the more soluble component in excess [13].

Mixtures of sodium dodecylsulfate, SDS, and dodecyltrimethylammonium bromide, DTAB, have been carefully studied and the positions of the vesicle lobes in the composition diagram established [14]. An interesting liquid–liquid phase coexistence occurs in many systems within a narrow composition region, often starting within the vesicle lobe and extending to higher total surfactant concentrations. A well-studied example is SDS and dodecyltriethylammonium bromide, DTEB [15,16]. Both phases display a complex rheological behavior [17]. Such a phase separation has been mentioned in DTAB/SDS but not established. In numerous investigations of this system at various proportions and concentrations

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of the surfactants and with added salt, structures of mixed micelles and vesicles have been characterized by SANS [18,19] and cryogenic transmission electron microscopy (cryoTEM) [4,14]. The kinetics of formation of vesicles has been studied [20], and the enthalpy of mixing determined from micro-calorimetric measurements [21].

Much is known, thus, about the dilute DTAB/SDS system. What prompted us to undertake the present study was two issues: the nature of the two liquid phases that separate within a narrow composition region, and the evolution of perforated bilayer structures. With respect to the liquid–liquid phase separation, a surprising conclusion from the investigations by Zhao et al. of the DTEB/SDS system [15–17] was that both phases contained appreciable amounts of aggregates formed from mixtures of the two surfactants, as evidenced by the surface tension and peculiar rheological properties. In mixtures of DTEB and sodium dodecanoate it was even reported that both phases contained vesicles. [16] In contrast, an early report on liquid–liquid phase separation, in this case in SDS and octyltrimethylammonium bromide, seemed to indicate that the surfactants were mainly found in one of the phases (however, the report was not quite clear on this point: "the top layer was surfactant rich while the lower layer contained a larger concentration of NaBr") [22]. This has been taken as an example of an associative phase separation, as would be expected [23], whereas the results from Zhao et al. suggest a segregative behavior. A more detailed study of the morphologies of the aggregates formed would clarify this question.

Perforated vesicles, called *stomatosomes*, and other perforated bilayer structures were first clearly identified in a study of the solubilization of lecithin vesicles by a cationic surfactant, CTAB [24], in the presence of salt, and later documented from a number of systems; for overviews see [25,26]. Although difficult to discern in the published cryoTEM micrographs, such perforated vesicles were found in the study of DTAB/SDS mixtures by Kamenka et al. [4]. Since the conditions for the emergence of perforated bilayer structures still are obscure, we hoped that this simple system would allow measurements under controlled conditions: at different ratios of the surfactants, and at different total surfactant concentrations and concentrations of added salt. Some progress was made but the system turned out to be more complicated morphologically than anticipated. Among the various structures observed was an unusual type recently found by others in a freeze-fracture electron microscopy study and called *blastula aggregates* by them [27]. Clusters of small and fairly monodisperse vesicles, corresponding to such structures, were observed in many of the samples.

Bergström et al. [18,19,28,29] have made comprehensive SANS investigations of micelles and other structures found in dilute DTAB–SDS mixtures, with and without added NaBr. The measurements were made at 40 °C to avoid precipitates. To compare the morphologies found by cryoTEM with the structures deduced from the SANS results, some samples with compositions as used in the SANS study were investigated by vitrification from 40 °C.

2. Materials and methods

2.1. Materials

Sodium dodecyl sulfate (SDS, >99%, special pure) from BDH laboratory (UK), dodecyltrimethylammonium bromide (DTAB, >99%) and sodium bromide (NaBr, >99%) from Sigma (Germany), were used as received. Millipore water was used as a solvent in all cases.

2.2. Sample preparation

Surfactant stock solutions, prepared by dissolving weighed amounts of dried materials in NaBr solutions of the desired concentration, were mixed to obtain the desired anionic/cationic surfactant mole ratio. The catanionic surfactant solutions were stirred with a vortex mixer, and left to equilibrate for more than 3 weeks at 25 °C. Samples investigated at 40 °C were kept at this temperature for 20 to 44 h before measurements. The samples were examined between crossed polarizers. In phase separated samples the birefringence was different (usually only one phase birefringent) in the two phases, with a clear interface in between.

2.3. Cryogenic transmission electron microscopy (cryoTEM)

The electron microscopy investigations were performed with a Zeiss 902A instrument, operating in zero-loss bright field mode at 80 kV. Specimens were prepared in a chamber with controlled temperature and humidity. A drop of the sample solution was placed onto an EM grid coated with a perforated polymer film. Excess solution was removed by blotting with a filter paper, leaving a thin film of the solution spanning the holes of the polymer film on the EM grid. The thin film was vitrified by rapidly plunging the grid into liquid ethane held just above its freezing point. The vitrification was normally performed immediately after the blotting, in order to minimize the time spent by the thin film in the atmosphere of the preparation chamber. It is our experience that the thinned film rapidly responds to even minute differences in water activity between the film and the environment. The vitrified specimen was kept at −165 to −170 °C during both transfer to the microscope and investigation. Images were chosen carefully to represent a typical impressions of all images obtained from the same sample. Details on the procedures and interpretations have been published [30].

The investigation by cryoTEM was very extensive. Not only were a large number of samples investigated, but often several grids for each sample. On each good grid numerous vitrified films spanning different holes in the perforated polymer film were examined. Usually ten to thirty micrographs were saved from each sample. Obviously only a small fraction of these can be presented here. In the selection the technical quality of the pictures is important. A minimum requirement is that it should be possible to print the images. Otherwise we have strived to choose representative examples. Still, it is inevitable that the selection process is somewhat subjective.

2.4. Elemental analysis

Mikro Kemi AB, Uppsala, Sweden, made elemental analysis for N, S, O, and C on each of the carefully separated phases of a few phase separating samples.

3. Results and discussion

In the mixtures SDS was always in excess, and only SDS was present as free surfactant at appreciable concentrations in the aqueous sub phase, although in most cases at amounts negligible compared with the total SDS in the systems studied. The cationic surfactant can be regarded as only present in mixed micelles and other aggregates. The aggregates are thus negatively charged with an average charge per surfactant given by

$$Q_n = 1 - 2X \tag{1}$$

with the mole fraction of DTAB, X, given by

$$X = [\mathrm{DTAB}]/C_t, \tag{2}$$

where C_t is the total concentration of surfactant. The total concentration of NaBr in the solution is the sum of the added salt and that released as DTAB associates with an excess SDS in aggregates,

$$C_{s,n} = C_s + [\mathrm{DTAB}] = C_s + XC_t, \tag{3}$$

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