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Quantification of counterion binding to and its effects on aqueous dispersions of dialkyl cationic surfactants

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ABSTRACT

Dialkyl cationic surfactants, such as dioctadecyl dimethyl ammonium bromide (DODAB) form vesicles upon dispersion in water. In order to study the influence of the surfactant's counterion, the same dialkyl surfactant was prepared with a fluoride counterion (DODAF). Visually, quite transparent dispersions were prepared when fluoride was selected as counterion, whereas more turbid dispersions were obtained using the bromide surfactant. LR-NMR revealed that the permeability of the DODAF dispersions for water was much larger, which indicated that these rather contained uni- or oligolamellar vesicles, whereas the DODAB dispersions were multilamellar. These observations seemed to indicate an increasing degree of surface charge neutralization by the heavier anions, in line with the Hofmeister series, which was indeed confirmed by electrophoretic light scattering measurements. In order to further quantify the surfactant-counterion interaction, HR-NMR diffusometry measurements were performed on dispersions of a dialkyl cationic surfactant with methyl sulphate counterion in deuterated water. The diffusion data showed that the mobility of this organic anion increased when adding different sodium halides, with a stronger effect from fluoride over chloride and bromide to iodide, which clearly indicated the gradual displacement of the methyl sulphate counterion from the vesicular surface by the stronger binding anions.

1. Introduction

Cationic surfactants are widely used for technical applications. One of the major applications of dialkyl cationic surfactants is as fabric softeners [1–5]. In this application, a concentrated vesicular dispersion of typically 5 to 20% of dialkyl cationic in an aqueous medium is added in the final (rinsing) step of the washing cycle. On the one hand, this cationic surfactant is meant to impart softness by adsorption to the fabrics. In addition, the vesicular dispersion mostly contains additional ingredients, such as perfume components, which are meant to give a pleasant odour to the fabrics.

Charge effects are important in the whole life cycle of the cationic vesicular dispersions. First of all, it is well known that smaller, less multilamellar structures can be prepared with less energy input if the surfactant used is more highly charged [6]. In addition, the adsorption process is largely driven by electrostatic interactions with negatively charged groups on the fabrics, which favours adsorption of more highly charged cationics [7].

The surface charge density of the cationics used largely depends on the chemistry of the cationic group, which in its turn may be pH-dependent (e.g. for amines). Moreover, it is well known that the electrolyte used may play an important role as different counterions are known to have more or less affinity for charged groups. Thus, the well-known Hofmeister series describes the binding affinity of ions [8,9]. Cavalli deduced from Langmuir monolayer studies that the anion binding affinity for quaternary ammonium groups increased in the sequence $F^- < Cl^- < Br^- < I^-$ [10]. As counterion binding reduces the effective size of the hydrated polar head group by reducing the electrostatic repulsion between neighbouring head groups, in some cases, counterion binding can even affect the surfactant association behaviour. Thus, didodecyl dimethylammonium with either acetate or hydroxide counterions has been reported to form an extensive solution phase prior to the liquid-crystalline phase, which is in clear contrast to the phase behaviour of the same surfactant containing either chloride or bromide counterions [11–13]. Nascimento et al. observed a similar effect for dioctadecyldimethylammonium: also in this case, the larger

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and more hydrated acetate anion seemed to be much less strongly bound as compared to chloride or bromide [14].

In this contribution, dialkyl cationics with different counterions were used. Thus, DODAF was prepared by replacing Br^- by F^- and its properties were compared to the original DODAB. Moreover, considering a dialkyl cationic with an organic counterion, the mobility of the latter can be followed by diffusion NMR, which indirectly also enables to quantify the interaction with inorganic anions.

2. Materials and methods

2.1. Materials

The cationic surfactant dimethyl dioctadecylammonium bromide (DODAB, 99% pure) was purchased from Acros organics (Geel, Belgium), whereas a mixture of the isomers bis-(2-hydroxypropyl)-dimethylammonium methylsulfate fatty acid ester, (2-hydroxypropyl)-(1-methyl-2hydroxyethyl)-dimethylammonium methylsulfate fatty acid ester, and bis-(1-methyl-2hydroxyethyl)-dimethylammonium methylsulfate fatty acid ester, was supplied by Evonik.

Deuterium oxide (D_2O > 99.8% atomD) was purchased from Armar Chemicals (Switzerland). All sodium salts used were of analytical grade.

2.2. Preparation of DODAF

DODAF was prepared by precipitation of AgBr upon titration of a DODAB solution in isopropanol/water with aqueous AgF as described by Woiterski et al. [15]. A 789 mM AgF (99+ %, Acros Organics, Geel, Belgium) solution was first prepared in ultrapure water. The DODAB solution contained 4.01 g DODAB (6.35 mmol) in 375 ml isopropanol (100%, VWR chemicals, Fontenay-sous-Bois, France) and 125 ml ultrapure water. The AgF solution was slowly added to the DODAB solution. The AgBr precipitate formed was removed by centrifugation (Sigma 3-16P, Sigma, Newtown, USA) at 4000 rpm during 15 min. The supernatant was subsequently centrifuged during 30 min at 8000 rpm (Beckman, L7-55 Ultracentrifuge; 55.2 Ti rotor). The solvent from this supernatant was removed in a rotavapor (RV 10 basic, IKA, Staufen, Duitsland) at 40 °C; the vacuum level was adjusted to ensure that the solution remained below the boiling point. After freezing at −20 °C, the remaining gel-like material was lyophilized (alpha 1-2 LD plus, Christ, Germany) under vacuum to a white powder.

2.3. Preparation of vesicular dispersions

The dispersions were prepared by first hydrating the lipids in water and stirring at 60 °C (i.e. above the phase transition temperature) during 1 h, using a magnetic stirrer. For NMR analysis, the dispersions (in deuterated water) were subsequently sonicated using a Sonifier 250 (Branson, Canada) tip sonicator. The 13 mm tip was immersed approximately two thirds of the sample height. The power monitor indicated 20%. In the beginning and after every two minutes of sonication, the sample was left to rest in a water bath at 55 °C during one minute. A 50% duty cycle was selected to prevent heating of the sample. The sonication time was always 10 min in total. Samples for SAXS analysis were prepared by extruding stirred dispersions (in deuterated water) 5 times at 65 °C through a 450 nm filter in order to obtain unilamellar vesicles.

2.4. Characterization of vesicular dispersions

The phase transition temperature was determined from the inflection point in the plot of the relative density (i.e. ratio of the density of the sample to that of pure water) of a 5 mM vesicular dispersion as a function of temperature. Density measurements were performed on a DMA 5000 (Anton Paar, Austria), based on an oscillating borosilicate U-tube. The temperature was controlled by a Peltier element within 0.002 °C. The scan rate was about 0.25 °C/min.

The electrophoretic mobility of the vesicular dispersions was determined at 25 °C by electrophoretic light scattering using a Zetasizer IIc (Malvern Instruments).

Rheological measurements were performed with a Brookfield Viscometer LV-DV-II+ pro (Middleborough, USA) with small sample adapter and cylindrical spindle (SC4-18). The viscometer was PC-controlled via the Rheocalc v3.3 software. The temperature was controlled with a Julabo F12 water bath with temperature control (Julabo Labortechniek GmbH, Seelbach, Germany). The rotational speed was increased every 30 s, whereby the shear stress, and shear rate were measured just before every increase in rotational speed; the latter was selected to ensure that torsion data could be obtained within the range from 10 to 90% of the maximum value.

Small angle X-ray scattering (SAXS) experiments on cationic dispersions in D_2O were performed on the beamline ID02 at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France) as described in detail by Saveyn et al. [16]. The wavelength was 0.1 nm, corresponding to a photon energy E of 12.4 keV. In order to make an accurate background subtraction, samples were contained in a temperature controlled flow-through quartz capillary cell with a diameter of 1.5 mm. The background with the capillary filled with D_2O was measured in an identical manner. The background subtracted intensity is depicted as $I(q)$.

2.5. Diffusion NMR

LR-NMR measurements were performed at 5 °C on a benchtop Maran Ultra spectrometer (Oxford Instruments, UK) operating at a frequency of 23.4 MHz. The samples were filled in 18 mm diameter glass NMR-tubes (Oxford Instruments, UK) so that a height of about 15 mm was obtained. Pfg-NMR experiments were conducted using an inversion recovery-stimulated echo pulse sequence characterized by a time duration Tau (40,402 μs), with which it is possible to suppress the NMR contribution of the lipophilic phase. The relaxation delay was set at 10 s. The diffusion time (Δ) was set to 0.06 s or 0.22 s, the gradient duration (δ) was fixed at 1.5 ms, while the gradient strength (G) was varied in 20 steps from 0 to 3.17 T/m. Measuring the echo intensity of the NMR-signal as a function of the gradient strength, a mono-exponential decay is obtained for a sample with free diffusing water, whereas a quasi biexponential decay is recorded for samples containing a fraction of free diffusing water and a fraction of restricted diffusing (enclosed) water.

All the HR-NMR experiments were performed on a Bruker Avance II spectrometer operating at a ^1H frequency of 700.13 MHz and equipped with a 5 mm ^1H TXI-Z gradient probe with a maximum gradient strength of 57.7 G/cm. Measurements were performed at 25 °C and the temperature was controlled to within ± 0.01 °C with a Eurotherm 3000 VT digital controller. Diffusion coefficients were measured by pfg-NMR with convection compensated double stimulated echo experiments using monopolar smoothed rectangular shaped gradient pulses and a modified phase cycle to minimize phase distortions due to unwanted gradient echos. The fraction of bound counterions was determined as described in detail by Sabatino et al. [17]. Using this methodology, the bound fraction X_{bound} follows from the methyl suphate diffusion coefficient in the absence (D_{free}) and presence of vesicles (D_{obs}):

$$X_{\text{bound}} = \frac{D_{\text{free}} - D_{\text{obs}}}{D_{\text{free}} - D_{\text{vesicles}}}$$

In this equation, the diffusion coefficient of the vesicles is mostly negligibly small and hence the above equation can be simplified:

$$X_{\text{bound}} \approx \frac{D_{\text{free}} - D_{\text{obs}}}{D_{\text{free}}}$$