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Clouding in fatty acid dispersions for charge-dependent dye extraction

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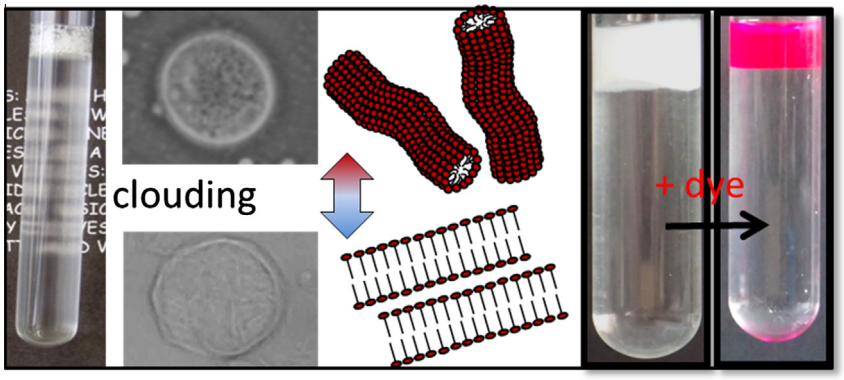
GRAPHICAL ABSTRACT



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ABSTRACT

The clouding phenomenon in non-ionic surfactant systems is a common feature that remains rare for ionic detergents. Here, we show that fatty acid (negatively charged) systems cloud upon cooling hot dispersions depending on the concentration or when adding excess guanidine hydrochloride. The clouding of these solutions yields the formation of enriched fatty acid droplets in which they exhibit a polymorphism that depends on the temperature: upon cooling, elongated wormlike micelles transit to rigid stacked bilayers inside droplets. Above this transition temperature, droplets coalesce yielding a phase separation between a fatty acid-rich phase and water, allowing extraction of dyes depending on their charge and lipophilicity. Positively charged and zwitterionic dyes were sequestered within the droplets (and then in the fatty acid-rich upper phase) whereas the negatively charged ones were found in both phases. Our results show an additional case of negatively charged surfactant which exhibit clouding phenomenon and suggest that these systems could be used for extracting solutes depending on their charge and lipophilicity.

1. Introduction

The clouding phenomenon in aqueous micellar solutions of non-ionic surfactants is a common feature [1,2]. It is characterized by a change in the sample turbidity that generally occurs upon heating. The initial clear surfactant solution made of micelles becomes cloudy at a temperature called the cloud point. There exist numerous references on the theory of the clouding phenomenon, one of these suggest that clouding originates from attractive interactions between micelles [3], leading to a liquid–liquid phase separation [4]. This is the reason why it mainly occurs

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in non-ionic surfactant systems and would typically not happen for ionic ones because of dominating electrostatic repulsions between micelles. However, in some cases, when these repulsions can be screened out by increasing for instance the ionic strength or by using bulky counter-ions, the clouding may also occur in ionic surfactant systems [5–11]. The clouding phenomena have been mainly studied in the literature in the case of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS). Recently, this has also been observed in sodium oleate (an unsaturated fatty acid, $C_{18:1}$) dispersions upon addition of triethylammonium chloride [7]. However, clouding in saturated long chain fatty acid (sLCFA, namely myristic acid: $C_{14:0}$, palmitic acid: $C_{16:0}$ and stearic acid: $C_{18:0}$) systems has never been reported [12]. sLCFA are of particular interest compared to synthetic surfactants mainly because they are greener, bioavailable in large amounts, biodegradable and exist under various forms: with different chain lengths, possibly bearing double bonds and/or hydroxyl groups along the chain that may trigger the self-assembly [12,13]. sLCFA are also widely used in catanionic systems, in combination with a cationic surfactant [14–17]. Aqueous dispersions of 'pure' sLCFA have been studied for decades [18], in the soap form (sodium or potassium), they self-assemble into micelles at high temperature but crystallize upon cooling below their Krafft point [19–21]. Recently, other soaps were produced in water using tetrabutyl ammonium [22,23] or choline [24–26] counter-ions instead of sodium or potassium. The strong advantage here is that these dispersions no longer crystallized. These counter-ions allowed decreasing the Krafft point of sLCFA yielding stable aqueous micellar dispersions even when samples are kept at 4 °C. However, there is no report on clouding phenomenon in these above mentioned systems. These systems are similar to catanionic systems [12,14] except that the positively charged moiety is a soluble counter-ion. Latter, guanidine hydrochloride (GuHCl) has been shown to prevent the crystallization of sodium salts of sLCFA [27,28]. Equimolar mixtures of GuHCl and sodium soaps of sLCFA formed micelles at high temperature and stacked bilayers that no longer crystallized at lower temperature. It has been proposed that the guanidine moiety strongly interacts with the carboxylate group of the sLCFA, probably via electrostatic and bidendate interactions [13,29–31], thus preventing re-protonation of the sLCFA carboxylate ion and then, crystallization [21]. Only 'low' sLCFA concentration (=10 mg/mL) and equimolar ratios (sLCFA sodium salts vs. GuHCl) had been investigated in our previous works [27,28] and no clouding had been observed in these experimental conditions.

We are still investigating these fatty acid systems (sLCFA/NaOH/GuHCl), varying the concentration and the ratio of each component and we observed that some samples clouded. We report herein these findings, showing that excess of GuHCl or sufficiently high sLCFA concentration lead to cloudy systems upon cooling hot dispersions, yielding the formation of sLCFA-rich droplets. The sLCFA within these droplets are shown to exhibit a transition upon cooling from elongated wormlike micelles to rigid stacked bilayers. We further study the sequestration of about 30 dyes in these sLCFA droplets and observed that it depends on their charge and lipophilicity.

2. Materials and methods

Protonated (Sigma–Aldrich, Saint Quentin Fallavier, France) or deuterated (Eurisotop, Saclay, France) fatty acids (myristic acid: $C_{14:0}$, palmitic acid: $C_{16:0}$ and stearic acid: $C_{18:0}$) were massed in a tube and ultra-pure water was added in amounts depending on the desired concentration. Then, the desired volume of a 1 M stock solution of guanidine hydrochloride (GuHCl, Sigma–Aldrich, Saint Quentin Fallavier, France, ref: G4505) and NaOH were added. All samples were submitted to at least 3 cycles of freeze thawing and further kept at −20 °C. Prior to being used, each sample was heated at 80 °C for 10 min. For samples for which GuHCl is in excess, the additional volume in excess was poured and sample tubes were again submitted to the above-mentioned procedure for homogenization. Dyes were dispersed in distilled water at a concentration of 2 mg/mL and typically, 100 μL of that stock solution were added to a 5 mL sample of sLCFA (10 mg/mL) droplets. Nile red (Sigma–Aldrich) was used at a concentration of 1 mg/mL in chloroform and 10 μL were added to a 5 mL dispersion of droplets at 10 mg/mL sLCFA.

2.1. Solid state NMR

For NMR experiments, perdeuterated sLCFA (Eurisotop, Saclay, France) was used and samples were prepared in the same way as previously mentioned except that only 1 mL was produced. Samples were placed into a 100 μL ZrO_2 rotor (Cortecnet, Paris, France). Deuterium NMR experiments were carried out in the static mode at 76.8 MHz for deuterium on a Bruker Avance II 500 WB spectrometer (Bruker, Wissembourg, France) with a CP-MAS dual 4 mm $^1H/^2H$ probe. Quadrupolar-echo sequences [32] were performed to record time-dependent signals that were Fourier transformed with 100–200 Hz Lorentzian filtering to yield wide line spectra. Pulse durations and echo time delay were respectively 2.75 μs and 40 μs, spectral window was 500 kHz and 4 k acquisitions were accumulated with a repetition time of 1.5 s. Temperature was controlled to ±1 °C.

2.2. Microscopy

Observations were made at room temperature at 20× magnification using an optical microscope in the phase contrast mode (Nikon Eclipse E-400, Tokyo, Japan) equipped with a 3-CCD JVC camera allowing digital images (768 × 512 pixels) to be collected. A drop of the lipid dispersion (about 20 μL) was deposited on the glass slide surface (76 × 26 × 1.1 mm, RS France) and covered with a cover slide (22 × 22 mm, Menzel-Glaser, Germany). The glass slides were previously cleaned with ethanol and dried.

Epifluorescence images were acquired (at 20× magnification) with a Nikon Eclipse 800 microscope equipped with a Coolsnap HQ2 digital camera (Photometrics) using the Metavue 7.7.1 software (Roper Scientific, France).

2.3. UV–visible experimental procedure

Spectra were recorded on a Cary (Varian) UV–visible spectrophotometer at 25 °C with samples prepared as described above. In the case of basic fuchsin, toluidine blue, rhodamine 6G, brillant blue R and rhodamin B, 100 μL of the upper phase was diluted in 1 mL of pure water. The lower phase was taken using a Pasteur pipette to prevent any contamination by the upper phase and used without further dilution. In the case of calcein, bromophenol blue, xylene cyanol and bromocresol purple, 500 μL of both phases were poured in a different sample tube and diluted with 1 mL ethanol.

2.4. Small-angle neutron scattering (SANS)

Small-angle neutron scattering (SANS) experiments were performed at Laboratoire Léon-Brillouin (laboratoire mixte CEA/CNRS, Saclay, France) on the spectrometer PACE. The neutron wavelength was set to 5 or 13 Å with a mechanical velocity selector, the detector being positioned at 1, 3 or 5 m, respectively. The scattering wave vector, Q, then ranges from typically 0.003 to 0.5 $Å^{-1}$, with a significant overlap between the three configurations. The samples, prepared with deuterated water, were held in flat quartz cells