

Characterization of reverse microemulsion formed with functionalized surfactants based on ferricyanide ions



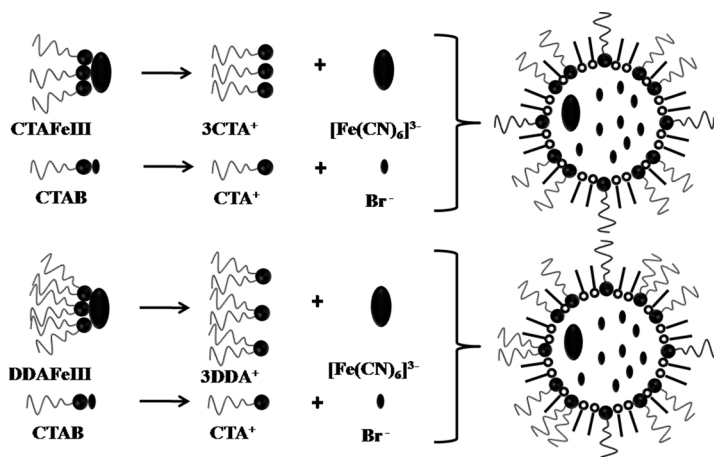
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GRAPHICAL ABSTRACT



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ABSTRACT

Schulman's titration (ST) and dynamic light scattering (DLS) were employed to obtain structural parameters of the reverse microemulsions formed by the functionalized surfactants cetyltrimethylammonium ferricyanide (CTAFcIII) and didodecyldimethylammonium ferricyanide (DDAFcIII). From the ST, the amount of surfactant and cosurfactant per droplet can be calculated, and if the droplets are spherical, it is possible to determine the droplet radius taking into account geometrical parameters. DLS measures the collective diffusion coefficient of the droplets, and then by means of the Stoke-Einstein equation, the droplets radius can be calculated. When the amount of water in the microemulsions is lower than 15 wt%, both techniques yield similar droplet radii, regardless of the functionalized surfactant used, which indicates that the microemulsions contain spherical droplets in this range of water concentration. When the amount of water reaches 20 wt% the radii obtained by DLS are larger than the one deduced from ST, suggesting that at this water concentration, the droplets are not

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spherical. These results are useful to understand the behavior of bulky functionalized surfactants and their possibility to be applied in the synthesis of nanoparticles based on ferricyanide ions.

1. Introduction

Microemulsions are homogeneous and thermodynamically stable dispersions of two or more immiscible liquids and their structural aspects have been reviewed recently [1]. For the case when water droplets are dispersed in an oil medium (w/o) they are classified as reverse microemulsions (RMEs) [2,3]. For their formation one typically requires surfactants with a bulky hydrophobic part, e.g. double chain surfactants. However, many other surfactants are not able to form RMEs due to their chemical structure; in those cases, the addition of a short chained alcohol as co-surfactant is necessary [4–6], where one can control the size of the droplets via the amount of added cosurfactant.

Recently, RMEs have been employed to synthesize nanoparticles of controlled size and shape [7–9]. In principle the role of the RMEs is to contain the necessary ions in its aqueous core, thereby delivering them in well-defined portions to the proceeding reaction to form the nanoparticles. In most of the proposed systems, the size of the RME droplets affects directly the size of the obtained nanoparticles [8–10]. Thus, the characterization of RMEs is pivotal to have a better understanding about their effects on the nanoparticles. In that context, dynamic light scattering (DLS) and Schulman's titration (ST) have been widely used in the characterization of RMEs [11–16]. DLS is used to measure the mutual diffusion coefficient of droplets and then, by means of the Stoke-Einstein equation, the hydrodynamic radius can be calculated. On the other hand, ST (also known as dilution method) has been employed to determine the amount of cosurfactant at the water-oil interface and, as long as the droplets in the RME are spherical, it is possible to calculate the size, aggregation number and droplets concentration [17–19].

In previous works, nanoparticles of hexacyanoferrates of different transition metals via RMEs formed with the functionalized surfactant (FS) cetyltrimethylammonium ferrocyanide (CTAFcII) were obtained [20]. To the same finality, in this work we propose two novel FSs: cetyltrimethylammonium ferricyanide (CTAFcIII) and didodecyltrimethylammonium ferricyanide (DDAFcIII). The RMEs formed with these FSs were characterized by DLS and ST. The main aim was to identify whether the presence of CTAFcIII or DDAFcIII modifies the structural properties of the formed RME droplets. With these surfactants it is easier to insert the ferricyanide ions inside the droplets without further salts addition [20]. The results obtained in this work are the first step to understand the behaviour of the FSs and their effect on the structure of the RME droplets.

2. Materials and methods

Potassium ferricyanide (J. T. Baker, 99.8%), hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich, > 98%), didodecyltrimethylammonium bromide (DDAB, Santa Cruz Biotechnology), hexanes (Golden Bell, ACS) and *n*-pentanol (Jamek, > 98%) and bi-distilled water were used as received. The FSs CTAFcIII and DDAFcIII were synthesized by mixing an aqueous solution 40 mM of potassium ferricyanide with an aqueous solution 40 mM of CTAB or DDAB, respectively. The yellow precipitates were washed several times until no colour was observed in the supernatant. The products were dried at 40 °C under vacuum.

Two RME systems were studied: i) CTAB-CTAFcIII-*n*-pentanol/hexane/water and ii) CTAB-DDAFcIII-*n*-pentanol/hexane/water. Three different surfactants FS-CTAB mixtures (*s*-mix) containing 30, 15 and 5% of FS were tested. The amount of *n*-pentanol in the blend *s*-mix/*n*-pentanol was fixed to a mass ratio of 1:1. For simplicity, the blend *s*-mix/*n*-pentanol is considered as surfactants, whose mass is $m_S = m_{\text{pentanol}} + m_{s\text{-mix}}$. The mass of hexane in the RMEs (m_H) was established according to the ratio $S = m_S / (m_S + m_H)$. The mass fraction of water in the RMEs is defined by $w = m_w / (m_w + m_S + m_H)$.

2.1. Phase diagrams

The pseudo-ternary phase diagrams were constructed by mixing the surfactants and hexane, so different *S* values were obtained, succeeded by a titration with water. A Thermo Scientific Orion 4-Star plus pH/Conductivity meter was used to perform a conductimetric titration with water. Viscosity of samples was measured on a rotational rheometer ARG2 TA instruments. Afterwards, different samples within the RME region were stored at room temperature (25 °C) and observed for 5 days to decide about their phase assignment. The RME region was constructed by considering only the samples that remain transparent.

2.2. Schulman titration (ST)

The RMEs were formed by weighing the required amount of each component to form a clear and stable system; afterwards, the samples were placed in a thermal bath at 25 °C. The ST were performed by adding hexane until the sample became turbid, more hexane was added as excess; then *n*-pentanol was added until a clear and stable system was formed again. This procedure was repeated several times on the same sample.

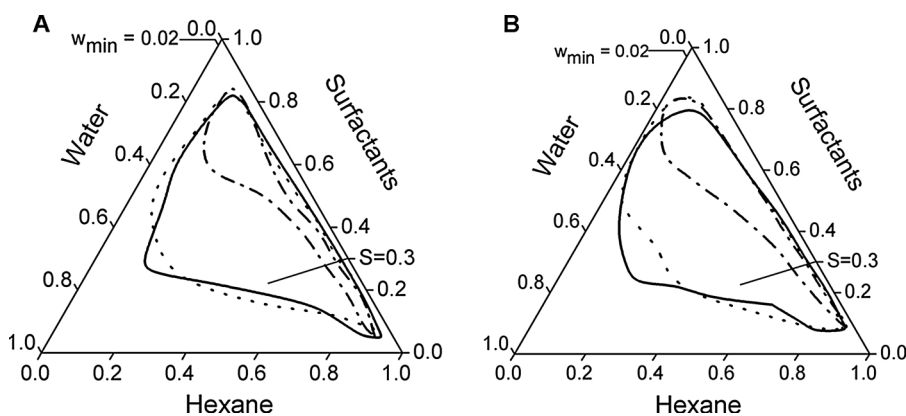


Fig. 1. Pseudo-ternary phase diagrams for the systems (A) CTAB-CTAFcIII/ *n*-pentanol/ hexane/ water and (B) CTAB-DDAFcIII/ *n*-pentanol/ hexane/ water at different *s*-mix: 5% (solid line), 15% (dotted line) and 30% (dash-dotted line). The closed sections correspond to the RME phase. The straight line is the path followed for the ST. w_{\min} represents the minimum water fraction necessary to form the RME phase.

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