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Rheological investigation of thermal transitions in vesicular dispersion

Luigi Coppola, Mohamed Youssry *, Isabella Nicotera, Luigi Gentile

Department of Chemistry, University of Calabria, 87036 Rende, Italy

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ABSTRACT

The thermal behavior of unsonicated dispersions of a double-chained surfactant, Dioctadecyldimethylammonium bromide (DODAB), has been studied over a wide concentration range using DSC and dynamic rheology. All dispersions are characterized by the pre- and main transition peaks at 35 °C and 43 °C, respectively. But, only above 10 mM DODAB, a third endotherm at 52 °C appears which may correspond to the (ULVs + L_α fragments) → MLVs transition. The thermal-induced MLV's size is proportionally dependent on the concentration. In addition, and in agreement with DSC data, dynamic rheology has proven to be an indirect way to elucidate the structural transitions in these DODAB vesicular dispersions.

1. Introduction

Quaternary ammonium surfactants are some of the most common double-chained amphiphiles that prefer to assemble in water into bilayered structures with near-zero curvature due to geometric considerations. These structures vary from vesicles to lyotropic lamellar phase, and in some cases, sponge phase. Since their discovery in the mid 1960s, vesicles have attracted increasing attention. They consist of one or more amphiphilic bilayers(s) that surround an aqueous core. Their encapsulation properties lead to a wide range of applications, for example within pharmaceutical science [1], as membrane mimetic systems [2], and as templates for chemical reactions [3,4].

Dioctadecyldimethylammonium bromide (DODAB) is a double-chained quaternary ammonium surfactant that forms unilamellar vesicles (ULVs) in water [5]. Among various preparation methods, the "hot-water" method [6] offers a simple procedure to prepare DODAB cationic vesicles by simply dissolving the DODAB in hot water above 50 °C, i.e., chain melting (main) transition, T_m.

Over the last two decades, much effort was done to investigate the phase behavior of dilute DODAB dispersions (0.1–10 mM DODAB) using a variety of experimental techniques. It includes differential scanning calorimetry [6–14], turbidity [14,16], static light scattering [17], fluorescence [9], surface pressure [18], and electron spin resonance (ESR) [10,18,19]. In general, the DSC thermograms of the unsonicated DODAB dispersions are dominated by two endotherms; the pre- and main transition peaks. However, discrepancies are found in the literature for the temperatures at which the pre- (35–36 °C), and main (42.7–45 °C) transitions occur, although the unsonicated dispersions were prepared by the same method within the concentration range 1–10 mM DODAB [6–14]. Nevertheless, the transition temperatures are independent of the concentration as shown in this contribution over a large concentration range 0.5–80 mM DODAB. Moreover, Benatti et al. [9] reported the presence of a third endotherm (post transition) at 52.2 °C for 1 mM DODAB dispersion, although other studies showed this transition only at 10 mM DODAB [11,15].

The main transition (T_m) is ascribed to gel to liquid-crystalline phase transition in which the alkyl chains transform from solid-like to liquid-like state [11,20]. In the unsonicated dispersions, the unilamellar vesicles (ULVs) transform into multilamellar vesicles (MLVs) above T_m [11]. The origin of pre- and post transitions is still not fully understood. The pre-transition has been attributed either to changes in the chain conformations [21], structural transformations within the headgroups [22], or intervesicular interactions [6].

Although DSC is the favored method for detecting the thermal transitions occurring in surfactant solutions, several other techniques can provide complementary information on detecting and understanding such transitions. Among these techniques, rheology has proven its power in detection of the transition through following the dynamic moduli with the temperature [23–25]. In this contribution, we reinvestigate the thermal behavior of DODAB dispersions over large concentration range using DSC and dynamic rheology. We see how the dynamic temperature sweep tests confirm the transition temperatures in excellent accordance with the DSC data; moreover, the frequency sweep tests around these transitions are an indirect method to elucidate the microstructural changes in DODAB dispersions. Such experiments offer abundant information about the thermally-induced structural transitions without any limitations that face other powerful methods like scattering techniques.

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* Corresponding author.
E-mail address: youssry@unical.it (M. Youssry).

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2. Experimental

2.1. Materials and preparation

Dioctadecyldimethylammonium bromide (DODAB; >98%, Aldrich) was used as purchased. Ultra pure Millipore water was used for the samples preparations.

Among different methods, we used the "hot-water" method to prepare the vesicular dispersions due it its good reproducibility as previously mentioned [6]. In a flask, a weighted amount of DODAB was added to water and shaken while being held in hot water (>50 °C) until dissolving the DODAB. Then, the flask was cooled to room temperature and the volume of solution made up to the mark.

2.2. Differential scanning calorimetry (DSC)

DSC measurements were conducted using a Setaram Micro-DSC III high-sensitivity calorimeter. Two steel 1.2 mL twin cells were used; one containing the sample and the other water as reference. All the upscan and downscan experiments were done at a scan rate of 1 °C/min. The dispersion was left at 15 °C for at least 1.5 h before starting the upscan.

2.3. Dynamic shear experiments

The dynamic measurements have been performed in a strain-controlled rheometer (Rheometrics RFS III, USA) equipped with couette geometry (inner radius 17 mm, gap 5 mm). The temperature was controlled by a Peltier system with accuracy of ±0.1 °C. Dynamic strain sweep tests were firstly applied to ensure that measurements were within the linear viscoelastic region prior to the temperature and frequency sweep measurements. The temperature sweep measurements were conducted at frequency of 1 Hz and strain amplitude of 1% using a scan rate of 1 °C/min. After filling the geometry, the samples were left at 20 °C for 3 h before starting the measurements. The frequency sweep measurements were performed at different temperatures to compare the viscoelasticity of the dispersions around the transitions.

The linear viscoelastic behavior of a material can be characterized by the determination of the complex shear modulus [26]:

$$G^*(\omega) = G'(\omega) + G''(\omega) \tag{1}$$

where G' (ω) and G'' (ω) are the elastic and the viscous moduli, respectively, and ω is the angular frequency. Such viscoelastic material can be modeled by a number of Maxwell elements in parallel. Each element consists of a spring and dashpot in series, characterized by spring modulus g and a relaxation time τ. The generalized Maxwell model in terms of G' (ω) and G'' (ω) can be written as [26]:

$$G'(\omega) = \frac{G_0\omega^2\tau^2}{1+(\omega\tau)^2} \tag{2}$$

$$G''(\omega) = \frac{G_0\omega\tau}{1+(\omega\tau)^2} \tag{3}$$

$$|\eta^*| = \frac{\eta_0}{\sqrt{1+(\omega\tau)^2}} \tag{4}$$

3. Results

Unlike all the previous studies, we extend our investigations over a wider concentration regime (0.5–80 mM DODAB). Based on visual inspections, with increasing the concentration of DODAB, it is possible to distinguish two different concentration regimes (Fig. 1). Turbid dispersions are obtained up to 2 mM DODAB, above which the dispersions appear as milky fluids over 10–20 mM DODAB. Above 40 mM DODAB, highly viscous milky dispersions are formed as shown in the upper part of Fig. 1.

Additional information can be drawn from the DSC thermograms as depicted in Fig. 2. All the thermograms of freshly prepared mixtures are characterized by two distinct endotherms at 35 and 43 °C. Moreover, starting from 10 mM DODAB an additional endotherm appears at 52 °C which becomes more pronounced as the concentration increases in good agreement with the results found previously [11,15]. In addition, it is worth to note that the enthalpy values (ΔH) of both pre- (35 °C) and main (43 °C) transitions increase with the concentration until 10 mM DODAB, beyond which they suffer a reduction as shown in Table 1. In contrast, the enthalpy values of post transition at 52 °C increase with the concentration. All transition temperatures are independent of surfac-

Fig. 1. Phase behavior of DODAB dispersions over the concentration range 0.1–80 mM at room temperature. The numbers on the photos express the concentration. Lower photos illustrate the transformation from turbid dispersions into milky ones with the concentration. Upper photos show the viscoelasticity of the dispersions.