



Study of the micelle-to-vesicle transition and smallest possible vesicle size by temperature-jumps

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ABSTRACT

We have investigated the temperature induced micelle-to-vesicle transition in a binary non-ionic surfactant/water system, for which the spontaneous curvature decreases with increasing temperature. Temperature jumps with variable rate were performed in a microwave oven, from a micellar phase at 5 °C to a lamellar phase region at 35 °C, passing a liquid–liquid two phase region where dilute and concentrated micellar solutions coexist. It is shown that the obtained vesicle size decreases with increasing heating rate through this two phase region. Moreover, we demonstrate that there exists a minimum vesicle radius, R_v^* , as is also predicted by theory. In the present system we find $R_v^* \approx 50$ nm, in reasonable agreement with a theoretical estimate.

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1. Introduction

Bilayer vesicles are one class of such objects which are important not only from a fundamental point of understanding bilayer stability in cell membranes [1,2] but also as carriers in applications such as drug-delivery [3]. They can be formed either by the fragmentation of larger lamellar domains ("top-down" approach) [4–6], or by the "bottom-up" aggregation of smaller micelles [7,8,4,9]. The latter approach is less common because not many systems allow for a simple transformation from stable micelles to stable bilayers. Additives can be used in the stabilization of vesicles by addition of amphiphilic copolymers, shown to improve both stability and size of charged vesicles [10]. For studying the micelle-to-vesicle transition nonionic surfactants, belonging to the alkyl poly(oxyethylene glycol) mono ether family with the general formula $\text{CH}_3(\text{CH}_2)_{n-1}(\text{OC}_2\text{H}_4)_m\text{OH}$ (C_nE_m) are particularly useful model systems as the surfactant monolayer spontaneous curvature, H_0 , can be easily tuned, by simply adjusting the temperature. The binary phase behavior of these kind of surfactants with water are generally strongly dependent on the temperature. In several C_mE_n /water systems a micellar L_1 phase is stable at lower temperatures ($H_0 > 0$) while a lamellar phase, L_α , forms at elevated temperatures where $H_0 \approx 0$. In between in temperature, the micellar phase show a miscibility gap, $L'_1 + L''_1$, where a dilute micellar solution (L'_1) coexists with a concentrated micellar phase (L''_1). This liquid–liquid two phase region has a lower critical temperature,

often referred to as the cloud point. Thus, with a suitable C_mE_n surfactant a micelle-to-vesicle transition can be induced by an increase in temperature. However the temperature shift needed is of the order of 10–20 °C or more, and the heating path involves passing through the miscibility gap where rapid micelle aggregation takes place in the process of forming the concentrated phase.

A first attempt to study such a temperature induced micelle-to-vesicle transition was done in the C_{12}E_4 /water system [9]. The temperature jump was slow, of the order of a minute, but it was recognized that the final vesicle size depends on the heating rate. It was also shown by static light scattering that there is rapid micelle aggregation into clusters (presumably of composition near the composition of the dense L''_1 phase) as the sample passes through the $L'_1 + L''_1$ region. After the sample passes the three phase line $L'_1 + L''_1 + L_\alpha$, the micelle clusters or aggregates transform into vesicles, in a similar fashion as for charged surfactant systems. It was concluded that the vesicles were formed from these micellar clusters and that it was the size of the micellar clusters that dictated the size of the vesicles formed. The size of the clusters when they transform into vesicles, in turn depend on the time taken for the sample to traverse the $L'_1 + L''_1$ region, i.e. for how long the aggregation process has been going on. Within a simple colloidal aggregation model a broad Gaussian vesicle size distribution is expected with a standard deviation given by (taken from Ref. [9]):

$$\sigma = \left(\frac{tk\phi}{4\pi\delta} \right)^{1/2} \quad (1)$$

where t is the aggregation time, i.e. the time taken to transverse the $L'_1 + L''_1$ region, k is the aggregation rate constant, ϕ is the surfactant

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volume fraction and δ is the bilayer thickness. σ can be obtained by a dynamic light scattering experiment, where at low q the z-averaged hydrodynamic radius $R_{H,z} = 2\sigma$. An agreement with experiment was found in that $R_{H,z}$ increases with increasing t and ϕ , but it was concluded that the rate was approximately two orders of magnitude lower than the diffusion limited case.

The final step of the proposed mechanism of the micelle-to-vesicle transition involves the transition from a bilayer sheet, or disc, into a vesicle. However, small bilayer discs are stable relative to vesicles. Similar mechanisms have been proposed in charged mixed surfactant systems where a line tension energy acting in favor of vesicle forming is balanced against a curvature energy needed to be overcome for vesicles to form [11]. Within the harmonic approximation [12] the vesicle curvature free energy is size independent, $G_{c,ves} = 4\pi(2\kappa_b + \bar{\kappa}_b)$ where κ_b and $\bar{\kappa}_b$ are the bending and saddle splay moduli of the bilayer, respectively. Flat discs, on the other hand carry a line energy, G_L , with line tension γ , associated with an unfavorably curved surfactant packing at the edge of the discs. This line energy is proportional to the disc circumference and for circular discs $G_L = 2\pi\lambda R_d$, where R_d is the disc radius. Small discs are not observed experimentally for single component surfactants or lipids. Due to the line energy they are expected too unstable relative to coarsening by e.g. Ostwald ripening or coalescence and will eventually reach the size where they spontaneously close into vesicles [11,13]. This implies the existence of a minimum vesicle radius, R_v^* , that can be estimated by $R_v^* = 2(2\kappa_b + \bar{\kappa}_b)/\lambda$. Modeling the rim of the disc as a cylinder of radius $\delta/2$, split in half, an explicit expression for R_v^* was derived in terms of the curvature elastic properties of the surfactant monolayer [9]:

$$R_v^* = \frac{4\delta}{\pi} \left(\frac{2(1 - \delta H_0/2) + \frac{\bar{\kappa}_m}{\kappa_m}}{(1 - \delta H_0)^2} \right) \quad (2)$$

where κ_m and $\bar{\kappa}_m$ now are the bending and saddle splay moduli, respectively, of the surfactant monolayer and H_0 is the monolayer spontaneous curvature. In Fig. 1 we show the water–C₁₂E₄ phase diagram (data taken from Ref. [14]), illustrate the temperature jump and summarize a few key results from the study of Bryskhe et al. [9]. The red arrow in the phase diagram of Fig. 1a illustrate the temperature jump studied by Bryskhe et al. Fig. 1c shows the time dependence of the scattered light intensity together with the temperature profile. Note the sharp peak in the scattering intensity indicating (i) a rapid aggregation within the $L'_1 + L''_1$ region and (ii) that a transformation of the aggregates into vesicles occur rapidly as soon as the three phase line at 22 °C is crossed. A similar scattering behavior has been seen in charged surfactant system [15]. Static light scattering patterns at 2 °C and 45 °C are compared in Fig. 1b. Note the much higher intensity at 45 °C and the q^{-2} power law consistent with polydisperse vesicles. Finally, in Fig. 1d the two key events are illustrated. (i) The initial nucleation and growth of the L''_1 phase, involving micelle aggregation and the formation of a dense interconnected network. (ii) The transformation of the L''_1 phase particles into vesicles, occurring rapidly as soon as the three phase line is crossed. The temperature jumps were slow, samples were heated by shifting it from a cold to a warm thermostat, and the obtained vesicle sizes were consequently much larger than the expected R_v^* . In order to further investigate how the vesicle size depends on the heating rate and the possible existence of a minimum vesicle size, we have in this paper extended the study to more rapid temperature jumps, using microwave heating. The remaining of the paper is structured as follows. First, we present the methods used, including calibration results for the microwave heating. Then we present and discuss the results from temperature jump experiments varying both the heating rate and surfactant concentration. At the ends of the paper the final conclusions are summarized.

2. Experimental

2.1. Temperature jumps

Different heating rates to be used in the temperature jumps where achieved by heating vials filled with sample in a standard microwave oven in the presence of a water sink, which size, volume and placement was varied to adjust the heating rate. This set-up resulted in reproducible T -jumps and the corresponding temperature vs. time profiles are shown in Fig. 2, for the four different heating rates used. The four different heating rates are termed 6, 35, 60, and 90 s, respectively, corresponding to the time taken to reach the target temperature 35 °C. The heating profiles shown in Fig. 2 were obtained by the following sample handling procedure. Samples (1.5 mL) cooled to $T = 4.8 \pm 0.1$ °C, in order to equilibrate at a temperature corresponding to the micellar L_1 phase for C₁₂E₄/water, were heated in the microwave for a selected time after which the temperature was measured at the top and in the bottom of the vial. We note that immediately after heating an uneven temperature distribution between top and bottom of the vials was recorded which was more pronounced for the slower heating rates, 60 and 90 s. However, the heating methods all gave reproducible results and were shown reliable for achieving the desirable T -jumps and heating. In case of the slowest T -jump, 90 s, in Fig. 2 one can see that this heating rate is initially equal to the 60 s heating curve. This results in samples for the 60 s and 90 s setups passing the unstable two-phase $L'_1 + L''_1$ region in the phase diagram of C₁₂E₄/water (marked as the grey-shadowed region in Fig. 2, $T = 8$ – 22 °C) at very similar rates. This somewhat negative result that two of our heating rates are in principle the same, however, provided us with a convenient test of our hypothesis that the time upon traversing the two-phase region is actually what determines the vesicle final size and should result in the same vesicle sizes.

2.2. Dynamic light scattering

Dynamic light scattering (DLS) measurements were performed using an ALV/DLS/SLS-5000F CGS-8F compact goniometer equipped with a solid state, diode pumped, Ng:YAG laser with a wavelength $\lambda = 532$ nm and a constant power of 400 mW. An attenuator (Newport Coop.) is implemented in the setup in order to vary the power. The majority of the DLS measurements were conducted at a fixed scattering angle $\theta = 90^\circ$ which corresponds to a q -value of 0.022 nm^{-1} , q being the magnitude of the wave vector defined as $q = 4\pi n \sin(\theta/2)/\lambda$, n is the refractive index of the solvent. In all measurements the temperature was kept fixed to 35 °C. Two multiple-delay time digital correlators (ALV-5000/E and ALV-5000/FAST) with 320 exponentially spaced channels is used to construct the normalized intensity auto-correlation function. Diffusion coefficients were extracted from the initial short-time decay of the auto-correlation function by a second order cumulant analysis [16]

$$g^{(1)} = Ae^{-q\Gamma^{(1)}(q)t - q^2\Gamma^{(2)}(q)t^2 + \dots} \quad (3)$$

$\Gamma^{(1)}(q)$ is for noninteracting spherical particles the Stokes–Einstein expression for the dilute-limiting diffusion coefficient

$$D_0 = \frac{6\pi\eta R_H}{k_B T} \quad (4)$$

η is the viscosity of the solvent and R_H the hydrodynamic radius.

2.3. Materials

The nonionic surfactant C₁₂E₄ was obtained from Nikko Chemicals Co., Tokyo, and used as received. A stock solution was

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