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Characterization of mixed micelles of cationic twin tail surfactants with phospholipids using fluorescence spectroscopy

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Abstract

The pyrene fluorescence measurements have been carried out for various binary mixtures of micelle forming (L-α-diheptanoylphosphatidycholine, DHPC) and vesicle forming (L-α-dimyristoylphosphatidycholine, DMPC) phospholipids with different twin tail alkylammonium surfactants. The mixed micelle formation in all binary mixtures has been evaluated and it has been observed that the mixed micelle formation between the unlike components of phospholipid and cationic surfactants takes place due to the synergistic interactions. The influence of hydrophobicity of series of twin tail cationic surfactants has been studied on the degree of synergism.

Keywords: Mixed micelles; Phospholipids; Twin tail cationic surfactant; Synergism; Fluorescence measurements

1. Introduction

The surface active compounds (surfactants) have attracted a significant interest in last couple of decades due to their potential industrial applications [1–3]. This has lead to the synthesis of new surfactants with better surface activity. A category of twin tail surfactants is relatively new group of highly surface active chemical compounds and their fundamental behavior is of significant interest [4–6]. Although, there are plenty of gemini surfactants reported [6–8], a comprehensive study related to their mixed micellar properties with phospholipids is still lagging. Present work is step forward in this direction, where the mixed micelle behavior of these twin tail surfactants with two different kinds of phospholipids has been carried out.

The purpose of choosing these phospholipids is simply based upon the fact that L-α-diheptanoylphosphatidycholine (DHPC) is micelle forming phospholipid due to its readily soluble nature in pure water, whereas L-α-dimyristoylphosphatidycholine (DMPC) is a vesicle forming phospholipid due to extremely low water solubility. The mixed micellar properties of DHPC with gemini surfactants are expected to be much different from those of DMPC, since the mixed micelle formation mechanism in both the cases must be different. Previous studies have suggested [9–13] that DHPC exists in monomeric form and at a particular concentration it forms the micelles while this is not the case with DMPC, where direct vesicle formation takes place. In order to compare the mixed micelle properties between both phospholipids with common cationic gemini surfactants, DMPC should have to be dissolved in micellar solution so as to produce the mixed micelles and then to compare their nature with that of DHPC. Apart from this, the cationic surfactants have been selected on the basis of their variable spacer chain length, and variable one of the twin tails while keeping the other one constant at $C = 12$.

2. Experimental

2.1. Materials

The lipids, L-α-diheptanoylphosphatidycholine (DHPC) (99% pure, Avanti polar) and L-α-dimyristoylphosphatidycholine (DMPC) (99% pure, Sigma) (see Scheme 1), were obtained as lyophilized powders. Cationic twin tail surfactants (dialkyldimethylammonium bromide, 12-0-*m*, where *m* is 8,

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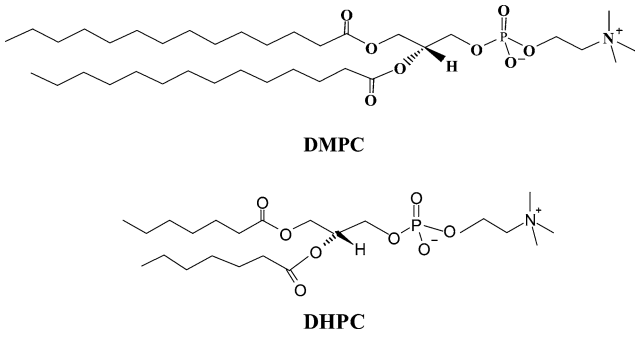

Scheme 1.

10, 12, and 16), synthesized according to the method reported elsewhere [14]. Cationic gemini surfactants, trimethylene-1,3-bis(dodecyldimethylammonium bromide), (12-3-12) and hexamethylene-1,6-bis(dodecyldimethylammonium bromide), (12-6-12) were synthesized according to method reported elsewhere [15,16]. All cationic surfactants were fully characterized by NMR and IR, and were recrystallized several times from ethanol before use. The fluorescence probe pyrene (Py) (99% pure, Sigma) was used as such. Double distilled water was used in the preparation of all solutions. All solutions were prepared by mass within the accuracy of ±0.01 mg. The mole fractions were accurate to ±0.0001 units.

2.2. Fluorescence measurements

In the case of binary mixtures of twin tail surfactants with DHPC, the desired mole fraction range was covered by mixing precalculated amounts of the stock solutions of both components in aqueous phase. The composition of the solution was expressed in molar fraction (α_{DMPC}) of the respective lipid (Eq. (1)).

$$\alpha_{\mathrm{lipid}} = \frac{[\mathrm{lipid}]}{[\mathrm{surfactant}] + [\mathrm{lipid}]}. \tag{1}$$

The aqueous stock solutions of DMPC + surfactant were prepared first by weighing the appropriate amounts of surfactants in clean glass vials and then adding the desired amount of DMPC. This solution was stirred for 10–15 min to ensure the complete solubilization of DMPC in surfactant solution and was kept for overnight in order to attain equilibrium before performing the fluorescence titration in pure water containing fixed amount of fluorescence probe. The mixed micelle formation studied by adding successive amounts of stock solutions in reference solution in the form of titrations.

The critical micelle concentration (cmc) values for each binary surfactant mixture were obtained by monitoring the I_1/I_3 intensity ratios of pyrene. Fluorescence emission spectra of these solutions were recorded employing an excitation wavelength of 334 nm, and the intensities I_1 and I_3 were measured at the wavelengths corresponding to the first and third vibronic bands located at ca. 373 and 384 nm. The ratios I_1/I_3 were plotted as a function of the total surfactant concentration. The cmc was taken from the break in I_1/I_3 curve (see Fig. 1). The errors in cmc values were estimated to be less than 10%. All the steady-state fluorescence measurements were recorded on

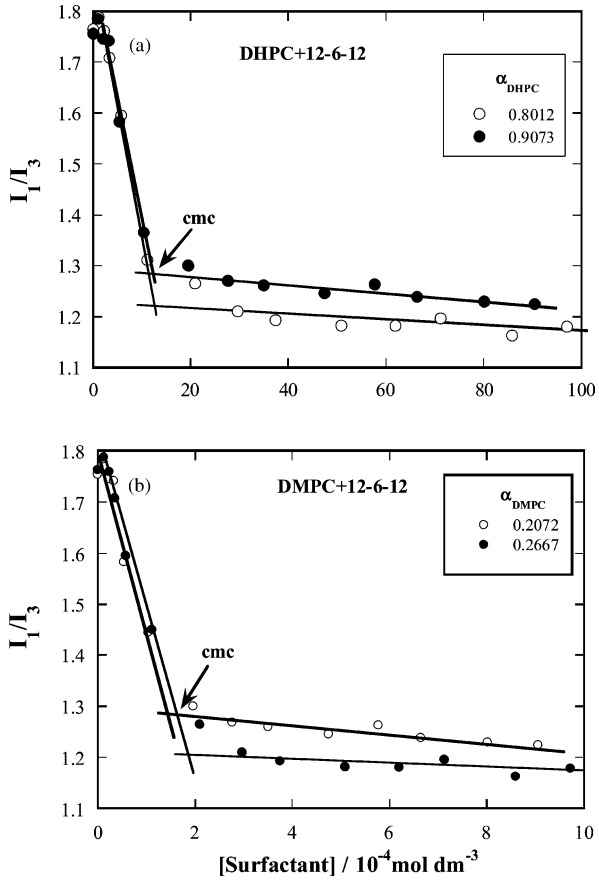

Fig. 1. Variation of the pyrene intensity I_1/I_3 ratios with the total surfactant concentration in water (arrow denotes the cmc value) of (a) DHPC + 12-6-12 and (b) DMPC + 12-6-12.

Table 1
Values of critical micelle concentrations (cmc/10^{-4} mol dm^{-3}) of various surfactants

Surfactants	cmc	Literature values
12-0-8	11.5 ± 0.7	10.8 [10]
12-0-10	5.20 ± 0.27	5.40 [10]
12-0-12	1.80 ± 0.02	2.00 [10]
12-0-16	0.89 ± 0.09	–
12-3-12	10.1 ± 0.6	9.40 [10,11]
12-6-12	11.1 ± 0.7	10.5 [10,11]
DHPC	19.0 ± 0.8	20.0 [21,22]

a Hitachi F-2500 fluorescence spectrophotometer at 25 °C by circulating the thermostated water by using the Julabo F-25 water thermostat bath. The concentration of Py was fixed at 10^{-6} mol dm^{-3}, which is expected not to influence the mixed micellization process in any way since the values of pure components agree well with the literature values (Table 1).

3. Results and discussion

3.1. Mixed micelles of DHPC and cationic twin tail surfactants

Fig. 1 represents some of the typical examples of the mixed micelle formation process of both phospholipids with differ-