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Effects of interactions on the formation of mixed micelles of 1,2-diheptanoyl-*sn*-glycero-3-phosphocholine with sodium dodecyl sulfate and dodecyltrimethylammonium bromide

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Abstract

Mixed micelles of the phospholipid 1,2-diheptanoyl-*sn*-glycero-3-phosphocholine (DHPC) with sodium dodecyl sulfate (SDS) or dodecyltrimethylammonium bromide (DTAB) in aqueous solutions and the effects of interactions between the components were studied by fluorescence and NMR measurements. The regular solution theory (RST) was applied to analyze the experimental critical micelle concentration values determined from the fluorescence spectra of pyrene in the mixed micelles. Negative values for the interaction parameter (β_{12}) were obtained for both DHPC + SDS and DHPC + DTAB mixtures, with the value being more negative in the former case. The negative β_{12} values for the two systems imply that the interaction between the phospholipid and the two ionic surfactants is attractive in nature, being more intense in the case of DHPC + SDS. The interaction parameter, β_{12}, varies with composition of the mixtures indicating changes in packing. The proton NMR shifts are quite different for the two systems and also vary with composition. An interpretation of these experimentally determined chemical shifts in terms of the degree of compactness attributed to electrostatic and steric interactions in the mixed micelle supports the conclusions derived from the fluorescence cmc experiments.

Keywords: Diheptanoyl phosphatidylcholine; Mixed micelles; Sodium dodecyl sulfate; Dodecyltrimethylammonium bromide

1. Introduction

Aggregates of synthetic lipids and their mixtures with ionic surfactants are model systems for investigating aggregated assemblies of phospholipids that occur naturally in biological systems [1,2]. In the human digestive tract, phospholipids form mixed micelles with bile salts and are hydrolyzed by the phospholipase enzymes [3–5]. Although several studies exist on the mixed micelle formation between conventional surfactants and long chain phospholipids upon a breakdown of the vesicular structures [6–9], little is known about direct mixed micelle formation between phospholipids and detergents. Hence, it is important to elucidate the nature of mixed micellization on the basis of different categories of the surfactants. Furthermore, information on the properties of these mixed aggregates remains scarce. Characterization of assemblies containing lipids, undertaken here, is motivated by their biological significance [10] and is believed to be a relevant first step toward better understanding of phospholipase enzymology where phospholipid containing mixed micelles serve as substrates.

In the present work, we report studies of binary combinations of a micelle forming phospholipid diheptanoylphosphatidycholine (DHPC, Fig. 1) [11,12] with two ionic surfactants: sodium dodecyl sulfate (SDS) and dodecyltrimeth-

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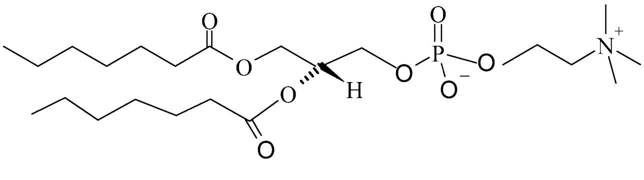

Fig. 1. Chemical structure of the phospholipid 1,2-diheptanoyl-*sn*-glycero-3-phosphocholine (DHPC).

ylammonium bromide (DTAB). Micelles are formed directly upon mixing DHPC and SDS and DHPC and DTAB. The choice of surfactants was based on the fact that the ionic surfactants, SDS and DTAB, are expected to interact more strongly with zwitterionic DHPC in view of the electrostatic interactions than the surfactants of any other category. We have specifically selected two ionic surfactants with identical hydrophobic tail in order to distinguish between the effect of anionic and cationic head groups on the mixed micellization with DHPC. Critical micelle concentration (cmc) measurements and proton NMR shift studies were carried out with the goal of understanding the effects of headgroup interactions on the structural organization of the constituent components in the mixed micelles. The results from these experiments are examined for a mutually consistent interpretation. Interactions in mixed micelles are conventionally studied by cmc measurements [13]. Electrostatic and steric interactions between headgroups play a major role in the formation of mixed micelles [13]. At cmc, where the aggregation numbers are small, electrostatic interactions have been shown to play the dominant role [13]. In this work, ^{1}H NMR is used to probe the compactness of the mixed micelles at concentrations well above the cmc in order to determine the effects of steric as well as electrostatic interactions.

2. Materials and methods

2.1. Materials

DHPC (lyophilized powder from Avanti Polar Lipids Inc., >99%), sodium dodecyl sulfate, SDS (Sigma, 99%), and dodecyltrimethylammonium bromide, DTAB (Aldrich, 99%), were used as received. Pyrene (Aldrich) was purified by recrystallizations from ethanol. Nanopure water from Sybron/Barnstead Nanopure II was used as solvent.

2.2. Critical micelle concentration (cmc) from pyrene fluorescence measurements

The cmc values for each binary surfactant mixture were obtained by monitoring the pyrene I_1/I_3 ratio ([pyrene] = 0.5 µmol L^{-1}) [14–16]. Different binary stock solutions with a total surfactant concentration (S_t) of 10, 20 and 30 mM were prepared for the two systems investigated. The composition of the solutions was expressed in molar fraction (X_i) of the respective surfactant, defined as

$$X_i = \frac{[S_i]}{[S_i] + [S_j]}, \tag{1}$$

where $[S_i]$ and $[S_j]$ are the molar concentrations of the surfactants i and j in the mixed solution. 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 maximum of the second derivatives of the least-square sigmoidal best fits of the experimental data as represented in Fig. 2a with the example of SDS. The estimated errors in cmc values were less than 15%. All the steady-state fluorescence measurements were recorded on an FS 900 CT steady-state T-geometry fluorometer of Edinburgh Analytical Instruments (EAI). The apparatus uses a 450 W steady-state xenon lamp as the excitation source and is equipped with thermostat cells housing. For some of the samples, the cmc was checked by surface tension measurements, using a Krüss K12 tensiometer and the Wilhelmy plate technique [17].

2.3. NMR measurements

^{1}H NMR spectra were recorded on a Bruker AC200E instrument. Measurements were conducted on mixtures of SDS and DHPC (SDS + DHPC) and DTAB and DHPC (DTAB + DHPC) at various compositions. The total surfactant concentration was kept at 50 mmol L^{-1}. All chemical shifts were measured relative to the sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), which acted as an internal standard [18]. Deuterium oxide (D_2O; 99.9%) from Aldrich was used as solvent instead of water to weaken the water signal for all solutions. Only the chemical shift differences were considered in this study. The downfield shift (to lower magnetic fields) of the resonance relative to the first component is represented by a negative sign ($-\Delta\delta$) and an upfield shift (to higher magnetic fields) is shown by a positive sign ($+\Delta\delta$) [18]. In terms of the micelle structure, an increase in the compactness of the micelle gives rise to an increased shielding of the proton from the magnetic field. Therefore a positive or upfield shift in the proton resonance signifies tighter packing of the monomers in a micelle [18]. Conversely, a negative shift means a deshielding or a loosening of the micelle.

3. Results and discussion

3.1. Critical micelle concentration and synergism

The cmc values obtained for pure SDS and DTAB are 8.3 and 15.6 mmol L^{-1}, which are in good agreement with