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Solubilization of hydrophobic molecules in nanoparticles formed by polymer–surfactant interactions

Gilat Nizri, Shlomo Magdassi *

Casali Institute of Applied Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Abstract

The interaction between the anionic surfactant, sodium dodecyl sulfate, and the polyelectrolyte, poly(diallyldimethylammonium chloride), may lead to formation of nanoparticles dispersed in water. The morphology of the resulting nanoparticles and their ability to solubilize hydrophobic molecules were evaluated. As shown by SEM and AFM imaging, the particles are spherical, having a diameter of about 20 nm. The solubilization within the nanoparticles was tested with pyrene, a fluorescence probe, and Nile Red, a solvatochromic probe. It was found that for Nile Red the solubilization within the nanoparticles is at lower polarity than for SDS micelles, and from pyrene solubilization it appears that the hydrophobicity of the nanoparticles depends on the ratio between the SDS molecules and the charge unit of the polymer.

Keywords: SDS; PDAC; Surfactant; Polymer; Nanoparticles; Solubilization; Pyrene; Nile Red; CAC; CMC

1. Introduction

Polymer–surfactant interaction in aqueous solutions has been intensively studied [1–8], due to the growing applications of these systems in various fields, such as detergents, hair care products, foams, emulsions, mineral recovery, and DNA transfections.

So far, most of these interactions have been elaborated in systems containing nonionic polymers and ionic surfactants. The surfactant in these systems is weakly bound to the polymer chains, whether as a single molecule or as an aggregate.

Interactions between a charged polymer and an oppositely charged surfactant usually result in phase separation owing to strong electrostatic forces. These forces may induce precipitation of a polymer–surfactant complex at certain surfactant concentration range. However, as reported by Dubin and Oteri [9] for systems containing PDAC, SDS, and a nonionic surfactant (Triton X-100), aggregation could occur without accompanying precipitation at specific ranges of the ionic strength and the mole fraction of anionic surfactant (basis total surfactant). Nanoparticle formation was also reported by Thünemann et al. [10] in interactions between an amphoteric polyelectrolyte and an anionic surfactant. Nanoparticles in the size range 3–5 nm were formed at a molar ratio of 1:1 of the cationic group on the polymer and the anionic surfactant. The structure suggested was that of micelles coated by (“dressed by”) the ampholyte polymer.

In a previous paper [11] we showed that nanoparticles (35–150 nm) may be formed by interaction of an anionic surfactant, sodium dodecyl sulfate (SDS), with the cationic polyelectrolyte polydiallyldimethylammonium chloride (PDAC) in aqueous solution. Nanoparticles of various sizes and surface potentials having organized internal structure were obtained, depending on the SDS/PDAC molar ratio, r (referred to the PDAC monomeric charge unit). In the present paper we investigate SDS–PDAC nanoparticles by an atomic force microscope and study their solubilization ability by using hydrophobic probes, Nile Red (NIR), and pyrene. NIR (Fig. 1a) (9-(diethylamino)-5H-benzo[α-phenoxazin-5-one) is a highly fluorescent, solvatochromic dye, in which the absorbance and emission maxima are

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* Corresponding author. Fax: +972 2 6584350.
E-mail address: magdassi@cc.huji.ac.il (S. Magdassi).

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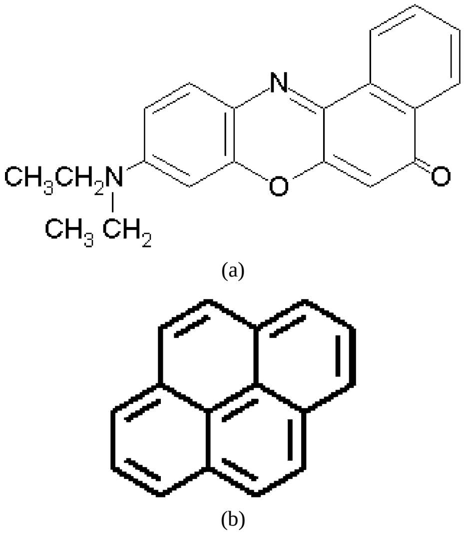

Fig. 1. Structure of Nile Red (a) and pyrene (b).

shifted to higher wavelengths with increasing polarity of the medium [12]. Nile Red is extensively applied to examine the structure, dynamics, and environment in biological and microheterogeneous systems, and was recently reported as a probe for microemulsions [13,14]. Therefore, NIR enables us to obtain information about its solubilization site in the nanoparticles.

Pyrene (Fig. 1b) shows interesting photophysical properties due to the long lifetime of its monomers and its efficient formation of excimers. Pyrene is one of the few condensed aromatic hydrocarbons, which shows significant fine structure (vibronic bands) in its monomer fluorescence spectra in solution. The vibrational fine structure intensities undergo significant perturbations on going from nonpolar solvents to polar solvents with high permanent dipoles. The five predominant peaks of pyrene are numbered I–V, and peak III shows maximum variations in intensity relative to peak I [15]. This 3/1 ratio will be used as an indication for the polarity of the environment in which the pyrene is solubilized, and also for determination of the critical association concentration, CAC, of SDS/PDAC systems.

2. Materials and methods

2.1. Materials

The following materials were used with no further purification: PDAC of molecular weight 100,000–200,000 g/mol, from Aldrich as a 21.8% (w/w) aqueous solution; SDS (minimum 98.5%, by gas chromatography) from Sigma; Nile Red from Fluka; and pyrene (minimum 97.5% by HPLC) from Aldrich.

Muscovite mica films were obtained from Pelco International and were freshly cleaved prior to spin coating.

2.2. Nanoparticle preparation and probes solubilization

SDS and PDAC stock solutions were prepared in deionized water, and SDS–PDAC particles were prepared as described in a previous paper [11]. Typically, 5 ml of SDS solution of the required concentration and 5 ml of PDAC solution (0.2% w/w) were poured simultaneously into a vial and were stirred immediately. Thus, the final PDAC concentration was kept constant, 0.1% w/w (6.8 mM, based on the monomer), in all experiments, while the SDS/PDAC molar ratio was varied.

In NIR solubilization experiments, the vials contained the hydrophobic probe, prior to the addition of the polymer and surfactant. The probe was placed in the vials as an ethanol solution in a volume of several microliters, depending on the required final concentration during the solubilization experiment. The ethanol was evaporated prior to the solubilization experiments. In pyrene solubilization experiments, pyrene was first dissolved in ethanol, and then a PDAC aqueous solution was prepared using a small portion of the pyrene solution after evaporation, according to the procedure of Kogej and Škerjanc [16]. The pyrene-containing PDAC solution was used to prepare SDS–PDAC samples by mixing with SDS solution. The pyrene concentration in all samples was 1×10^{-6} M. The samples were shaken for 48 h in a shaker at 25 °C, except the samples for the CMC evaluation, which were shaken for a week.

2.3. Ultrafiltration

Separation of the nanoparticles from the micelles was performed using Ultrafree microcentrifuge filters (Sigma) made of polysulfone membrane with 300 KD cutoff. Samples were twice centrifuged and resuspended with deionized water before absorbance or fluorescence spectra were measured.

2.4. Absorbance and fluorescence spectra

Absorbance spectra of the samples were taken using a Cary 100Bio spectrophotometer, a 1-cm polystyrene cell, and a scan rate of 600 nm/min.

Fluorescence spectra of samples were taken using a Cary Eclipse fluorimeter, a 1-cm quartz cell, and a scan rate of 1200 nm/min. In NIR experiments, excitation and emission slits were both fixed at 5 nm, and λ_{ex} was 500 nm. In the pyrene experiments the excitation and emission slits were fixed on 10 and 2.5 nm, respectively, and λ_{ex} was 335 nm.

2.5. Spin coating

A custom-made spinner was used for spin-coating experiments, which were carried out at room temperature. The sample was dispensed onto the central portion of the spinning surface (mica film for AFM imaging, and aluminum stab for SEM imaging), which was accelerated to a speed of