



Comparing the spectral properties of pyrene as free molecule, label and derivative in some colloidal systems



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ARTICLE INFO

Article history:

Received 18 October 2013

Received in revised form 10 February 2014

Accepted 14 February 2014

Available online 6 March 2014

Keywords:

Pyrene

Pyrene label

Pyrene derivative

Fluorophore solubilization

Nonionic surfactant

Hydrophobically modified poly(acrylic acid)

ABSTRACT

This paper investigates the behavior of pyrene as free molecule (probe), label and derivative in some colloidal systems. Aqueous octaethylene glycol mono *n*-dodecyl ether (C₁₂E₈) with or without poly(acrylic acid) (PAA), and a hydrophobically modified polyacrylate are considered. The effect of C₁₂E₈ on PAA labeled with pyrene is also studied. As a probe, pyrene has a typical behavior in the absence or presence of PAA. The labeled PAA has the peak corresponding to the sandwich excimer even in the absence of surfactant. The pyrene derivative is 4-(*N,N'*-diphenyl-hydrazine)-3,5-dinitrobenzoic acid 2-oxo-2-pyren-2-yl-ethyl ester. Its fluorescence emission is low and bathochromically shifted by 9 nm with respect to pyrene. The low fluorescence emission of derivative is due to its self-quenching. The data reveal that pyrene probe is located in the free or polymer-bound micelles. The labels on PAA create hydrophobic domains and shrink the polymer coil. By surfactant addition, labeled pyrene is solubilized in micelles palisade layer, closer to the ethylene oxide (EO) chains. The derivative is also located into the micellar palisade layer, in the proximity of the EO groups. The fluorophore behavior is discussed in relation to the critical points of surfactant and polymer–surfactant systems.

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1. Introduction

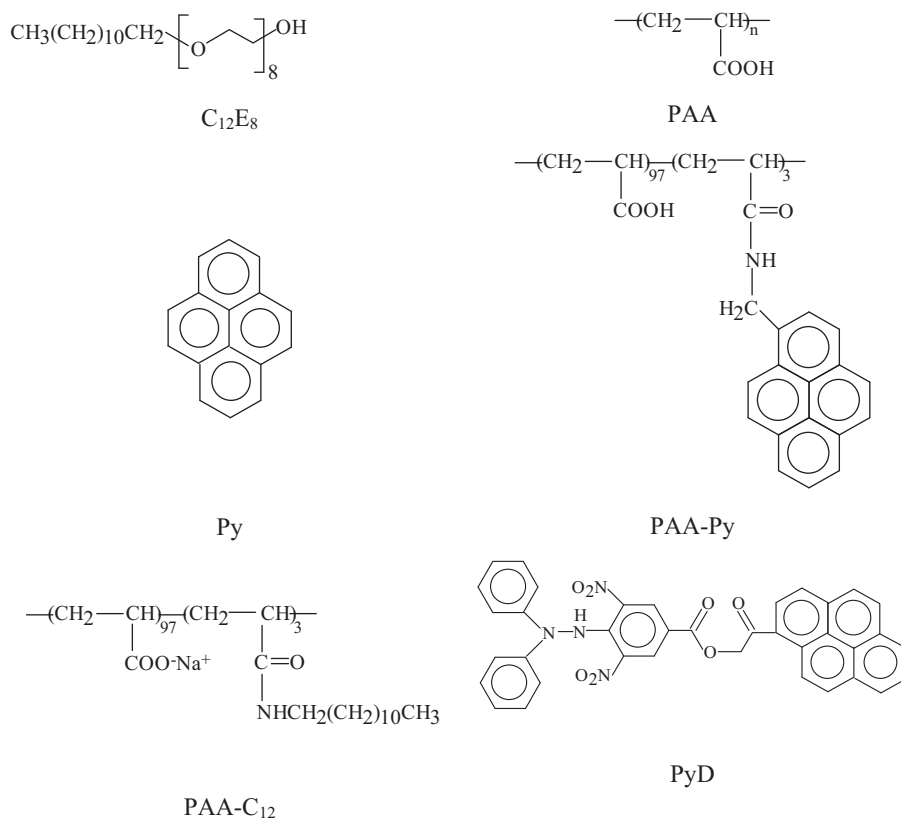
The surfactant–polymer mixtures are extensively studied due to their large applicability in pharmaceutical formulations, personal care and food products, household and industrial detergents, paints and coatings, oil drilling and enhanced oil recovery fluids, etc. [1–5]. The understanding of forces leading to the formation of surfactant–polymer complexes and characterization of these aggregates represent a challenge for researchers. Among the methods used for this purpose, the molecular spectroscopy has a key role. The fluorescence technique has become a very popular method due to the great variety of the available fluorophores (simple molecules or their derivatives utilized in order to enhance or, on the contrary, to quench the fluorescence), easiness of use, and very small quantities involved in the experiments. However, the most important clue is the great sensitivity of fluorophore to microenvironment changes, providing detailed information about the properties of the investigated system (like micropolarity, microviscosity). By

tailoring the fluorophore structure (derivatization, attaching a lateral chain, immobilizing on a polymer chain) one obtains suitable chemosensors for biological, environmental or other purposes [6–11]. Depending on application, the fluorophore can be probe or label. As a probe, the fluorophore is added as such into the system. As a label, it is chemically attached to an appropriate substance (surfactant, polymer or another molecule of interest). Irrespective of being a probe or a label, the fluorophore positioning in the system is the key issue.

Among the combinations of various kinds of polymers and surfactants in aqueous solution, we studied the systems of ethoxylated nonionic surfactants and polymeric acids. These systems show interaction through hydrophobic attraction and multiple hydrogen bonds, and their critical aggregation concentration (CAC or *T*₁) is lower than the critical micelle concentration (CMC) [12–19]. The data were acquired by a score of methods including fluorescence spectroscopy of pyrene (Py). Pyrene is a commonly used probe because its emission spectrum is strongly sensitive to the environment [20–26].

The aim of this paper is to investigate the behavior of pyrene as such, label and derivative, in aqueous solutions of octaethylene glycol mono *n*-dodecyl ether (C₁₂E₈) with or without poly(acrylic acid)

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(PAA). The pyrene and its derivative are also studied in aqueous solution of hydrophobically modified sodium polyacrylate (PAA-C₁₂).

2. Experimental

2.1. Materials

All the substances used in the study were of reagent grade. The nonionic surfactant octaethylene glycol mono *n*-dodecyl ether, PAA (MW = 150 000 g/mol) and pyrene were the same as reported [12–19]. PAA was labeled with 3 mol% pyrene (PAA-Py) based on a previously described procedure [27]. The same PAA was hydrophobically modified with 3 mol% dodecyl chains (PAA-C₁₂) after Magny recipe [28]. The synthesis and characterization of PAA-Py and

PAA-C₁₂ are presented in the Supplementary Material. The home-made pyrene derivative (PyD) was the 4-(*N,N'*-diphenylhydrazine)-3,5-dinitrobenzoic acid 2-oxo-2-pyren-2-yl-ethyl ester, being prepared as described in [29]. The chemical structures of the compounds are presented in Scheme 1.

2.2. Measurements

Steady-state fluorescence measurements were done on a FluoroMax 4P spectrofluorometer, from Horiba Jobin Yvon. The excitation wavelengths were as follows: Py – 335 nm, PyD – 359 nm and 335 nm and PAA-Py – 344 nm. From the recorded spectra, the corresponding sample blanks measured under identical conditions were subtracted off. Excitation spectra were taken with emission at 375 nm for monomer and 480 nm for excimer. The absorption

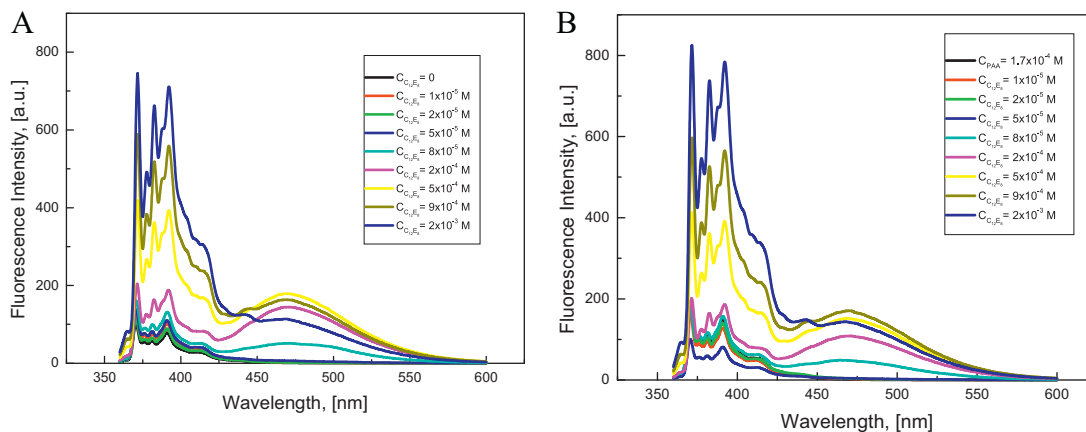


Fig. 1. Pyrene emission spectra in surfactant (A) and surfactant–polymer mixtures (B).

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