



Formation of micelles of Pluronic block copolymers in PEG 200

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ABSTRACT

The formation of micelles of Pluronic block copolymers in poly(ethylene glycol) (PEG) was studied using fluorescence, solubilization measurements, and frozen fracture electron microscopy (FFEM) methods at 40 °C. It was discovered that surfactants L44 (EO₁₀PO₂₃EO₁₀), P85 (EO₂₆PO₄₀EO₂₆), and P105 (EO₃₇PO₅₆EO₃₇) can form micelles in PEG 200 (PEG with a nominal molecular weight of 200), and the critical micellization concentration (CMC) decreases with increasing molecular weight of the surfactants. The size of the micelles formed by these Pluronic block copolymers is in the range of 6–35 nm. The CMC values in PEG 200 are higher than those in aqueous solutions.

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1. Introduction

Amphiphiles tend to self-assemble into micelles in suitable solvents. Micellar solutions show excellent properties in chemical reactions [1], drug delivery [2,3], and the synthesis of nanomaterials [4,5]. The study of the properties of micellar solutions has been an interesting topic for many years [6–9].

Triblock copolymers, poly(oxyethylene)/poly(oxypropylene)/poly(oxyethylene) (PEO–PPO–PEO), are an important class of surfactants with the commercial name of Pluronics. Ethylene oxide units are hydrophilic and propylene oxide units are hydrophobic [10]. By varying the PO/EO ratio and/or the molecular weights of the surfactants, one can obtain triblock copolymers with different properties, which can meet the specific requirements for different processes. In addition, the surfactants are environmentally more acceptable and have been used widely in detergency, dispersion, stabilization, emulsification, lubrication, pharmaceuticals, and bioprocessing [11–14]. The micellization of this kind of surfactants in water has been studied extensively. For example, Mortensen and Pedersen [15] studied the structural properties of aqueous solutions of EO₂₅PO₄₀EO₂₅ (P85) using small-angle neutron scattering experiments. They reported that the hydrophobic nature of PPO can cause aggregation of the polymers into spherical micelles with core sizes of 4–5 nm at ambient temperature [15]. Kabanov et al. [16] studied the micellization of F68, P85, and F108 in aqueous solutions with surface tension and fluorescent probe methods, and the average hydrodynamic diameter of the studied micelles

is in the range of about 15 to 35 nm, depending on the type of Pluronics. By using time-resolved fluorescence measurements Verma et al. [17] investigated the effect of the size of triblock copolymers on the nature of the water molecules in the corona region of the micelles. They found that the micelles formed by F88 (EO₁₀₃PO₃₉EO₁₀₃) were more hydrated and the water molecules in the corona were more liable than those of P123 (EO₂₀PO₇₀EO₂₀), which have different EO and PO block length.

Apart from the extensive investigation of microemulsions with water as the continuous phase, micellization of some surfactants (e.g., sodium dodecyl sulfate and hexadecyltrimethylammonium bromide) in organic solvents, such as formamide [18,19], ethylene glycol [20], and chloroform [21], has also been studied. The nonaqueous microemulsions have some obvious advantages in applications, especially when water-sensitive substances are involved.

The general formula of poly(ethylene glycol) (PEG) is H(OCH₂–CH₂)_nOH. Because of their wide availability, nonvolatility, nontoxicity, biodegradability, and low price, PEGs have been used in large quantities in the pharmaceutical, cosmetics, and food industries. In addition, PEGs as green solvents have many potential applications [22–24]. It is interesting to study the micellization of surfactants in PEG because its volatility is extremely low, and it is greener than commonly used organic solvents. To the best of our knowledge, micellization of surfactants in PEGs has not been reported. In this work we investigated the micellization of PEO–PPO–PEO surfactants in PEG 200 (with a nominal molecular weight of 200 g/mol). We believe that these greener micellar systems, which consist solely of nontoxic and nonvolatile reagents, have potential applications in different fields.

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2. Materials and methods

2.1. Materials

The PEO–PPO–PEO block copolymers L44 (EO₁₀PO₂₃EO₁₀), P85 (EO₂₆PO₄₀PEO₂₆), and P105 (EO₃₇PO₅₆EO₃₇) were provided by BASF Corporation. PEG 200 (A.R. grade) was purchased from Beijing Chemical Reagents Company. Pyrene was provided by Fluka. *n*-Decane was supplied by Acros.

2.2. Fluorescence study

A fluorescence method is often used to determine the onset of micellization in Pluronic block copolymer solutions [25,26]. Pyrene probes are sensitive to changes in the polarity of the microenvironment. Emission peak 1 at 372 nm shows significant intensity enhancement in polar solvents, whereas peak 3 at 383 nm shows very limited intensity variation with polarity. Therefore, the intensity ratio of the two peaks, I_1/I_3 , is closely related to the polarity of the probe microenvironment. The first inflection of the curve I_1/I_3 vs surfactant concentration is often designated as the CMC [27]. In this work, the fluorescence spectra of the solutions were determined using a Hitachi F-2500 spectrofluorometer. The temperature-controlled sample cell used and the procedures were similar to those reported previously [28]. In the experiment, a surfactant solution with a fluorescent probe (pyrene) was loaded into the sample cell, which was maintained at 40 °C. The concentration of the probe in the solutions was 4.5×10^{-6} mol/L. The excitation wavelength was 335 nm and the emission wavelength ranged from 350 to 460 nm. The excitation slit and scan rate were 5.0 nm and 60 nm/min, respectively. At each condition, the experiment was repeated at least five times, and the repeatability for the pyrene fluorescence intensity ratio (I_1/I_3) was better than $\pm 0.3\%$.

2.3. Solubilization of *n*-decane

The fact that micelles can solubilize relatively large amount of sparingly soluble compounds has been used to determine the onset of micelle formation [29,30]. Micellization can be known through the observation of discontinuity for solubilization to some hydrophobic compounds. Solubility of decane in the PEG 200/surfactant solutions was studied in this work by a conventional direct observation method. In the experiments the sealed vials containing surfactant/PEG 200 solutions of different concentrations were placed in a constant-temperature water bath (40 °C). The solubility of decane in the solution was determined by the sequential addition of decane to the vials. The solution became turbid if an excess amount of decane was added in the solution. Under each condition, the experiment was repeated at least five times, and the repeatability was better than $\pm 2\%$.

2.4. Freeze fracture electron microscopy

Freeze fracture electron microscopy (FFEM) is a useful technique for studying the size and shape of micelles. The formation of the micelles and their sizes were also examined by freeze fracture electron microscopy (FFEM). The experiment consisted of three steps: freezing of the sample, fracturing and replication, and obtaining the transmission electron microscope (TEM) images. In the experiments, about 4 ml of the sample was placed on a 0.1-mm-thick copper disk and covered with a second copper disk. The copper sandwich with the sample was frozen by plunging this sandwich into liquid propane at -453 K (cooling rate on the order of 3000 Ks⁻¹). For fracturing, the samples were clamped under liquid nitrogen inside the vacuum chamber of the freeze-etching apparatus (Balzers/BAL-TE, Liechtenstein). Fracture was achieved by

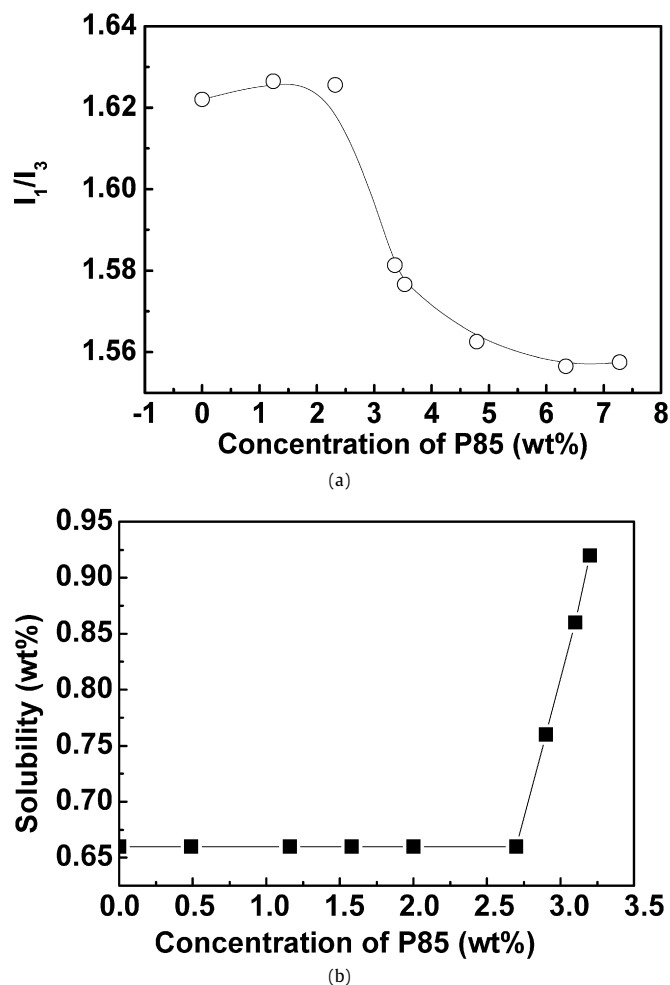


Fig. 1. Pyrene fluorescence intensity ratio I_1/I_3 versus concentration of P85 in PEG 200 (a) and solubilization of decane (total solution basis) as a function of P85 concentration (b) at 40 °C.

displacing a microtome arm cooled by liquid nitrogen, which had been cooled with liquid nitrogen. The now-exposed fracture face was immediately shadowed unidirectionally by Pt/C deposited at a 45° angle. The replicas were examined by Jeol-2010 transmission electron microscopy (TEM).

3. Results and discussion

3.1. Micelle formation of P85

Fig. 1a shows I_1/I_3 versus concentration of P85 (PEO₂₆PPO₄₀PEO₂₆) at 40 °C. It is obvious that the curve has a reverse S form, which is similar to other systems that form micelles [31,32]. The value of I_1/I_3 decreased dramatically when P85 concentration was increased to 2.7 wt%, indicating that the probe was in a more hydrophobic microenvironment. The significant decrease of the ratio I_1/I_3 is attributed to the formation of micelles with a hydrophobic core formed by hydrophobic PPO chains where pyrene partitions preferentially. It can be deduced that the CMC of the surfactant in PEG 200 at 40 °C is 2.7 wt%.

n-Decane is a typical nonpolar compound, and its solubility in PEG 200 is small. Therefore, it is a suitable compound to study the formation of micelles by the solubilization method. To further confirm the formation of the micelles, we studied the solubility of *n*-decane in the surfactant/PEG 200 solution. Fig. 1b is a plot of the solubilization of decane in the micelles as a function of the concentration of P85 in PEG 200 solution at 40 °C.

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