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Self-diffusion study of micelles in poly(oxyethylene)–polydimethylsiloxane diblock copolymer and poly(oxyethylene) alkyl ether systems

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Abstract

Self-diffusion constants of amphiphilic molecules in D_2O solutions of mixed poly(oxyethylene)–polydimethylsiloxane diblock copolymer (POE–PDMS, $Si_mC_3EO_n$) and poly(oxyethylene) dodecyl ether ($C_{12}EO_n$) were measured by pulsed-field-gradient NMR method. In the D_2O/$Si_{25}C_3EO_{51.6}$/$C_{12}EO_8$ or D_2O/$Si_{52}C_3EO_{51.6}$/$C_{12}EO_8$ systems, small and large micelles coexist in a wide range of $Si_mC_3EO_{51.6}$ fraction in total amphiphiles, whereas such a coexisting phenomenon does not take place in the D_2O/$Si_{5.8}C_3EO_{51.6}$/$C_{12}EO_8$ system. The coexisting phenomenon also takes place in the D_2O/$Si_{25}C_3EO_{51.6}$/$C_{12}EO_5$ system although the range of mixing fraction is limited. By obtaining each contribution of surfactant and copolymer molecules to the attenuation decay of the echo signal from the proton of the poly(oxyethylene) chain, we could evaluate the composition of the mixed micelles in the D_2O/$Si_{25}C_3EO_{51.6}$/$C_{12}EO_8$ system. The copolymer content in the mixed micelle increases proportionally to the copolymer mole fraction in the aqueous solution. From the series of self-diffusion measurements, we can conclude that the miscibility of $Si_mC_3EO_n$ and $C_{12}EO_n$ in aqueous micelles becomes poor and the coexisting phenomenon takes place when the PDMS chain becomes much longer than the dodecyl chain of $C_{12}EO_n$ or the POE chain of $C_{12}EO_n$ becomes long. Furthermore it is also revealed that very few silicone copolymer molecules can be incorporated in small surfactant micelles.

Keywords: Micelle; Self-diffusion study; POE–PDMS block copolymer; Poly(oxyethylene) alkyl ether; Coexisting micelles; Micelle composition

1. Introduction

Poly(oxyethylene)–polydimethylsiloxane diblock copolymer (POE–PDMS, $Si_mC_3EO_n$) forms various self-organized structures in water and these structures are varied mainly by the relative block ratio [1,2]. Kunieda et al. reported that the structural change is also induced by mixing with a short-chain nonionic surfactant (C_mEO_n) [3]. They used $Si_{25}C_3EO_{51.6}$ as a POE–PDMS, which has on the average 25 units of dimethylsiloxane and 51.6 units of oxyethylene with C_3 spacer chain between POE and PDMS chains. The concentration–temperature phase diagram of the water/$Si_{25}C_3EO_{51.6}$ system contains a lamellar and a solid phase only. When a part of copolymer is substituted for $C_{12}EO_5$, the phase behavior shows more varieties. Micellar, discontinuous cubic, lamellar, bicontinuous cubic and reverse hexagonal phases appear with increasing concentration of the copolymer–surfactant mixture. It is interesting to note that two lamellar phases coexist in a certain range of copolymer–surfactant ratio. The coexistence of two lamellar phases is also found in the system with POE–POP–POE triblock copolymer (so-called Pluronic) and C_mEO_n [4]. In the Pluronic–C_mEO_n system, the range of mixing ratio for two lamellar regions in the phase diagram increases with the increase in the difference in molecular weight between copolymer and surfactant [5]. These findings mean that amphiphilic block copolymers and surfactants are not miscible in self-organized structures due to the difference in molecular weight. Borovinskii and Khokhlov theoretically predict a phase separation with the formation of pure A micelles in one phase and complex A–C micelles in the other phase in

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the melt mixture of two diblock copolymer A–B and C–B with the condition that the length of C-chain is much longer than A-chain [6]. They also predict the equilibrium coexistence of A–C mixed micelles and pure micelles of shorter-chain block copolymer in a dilute solution of A–B and C–B block copolymers [7]. There are several experimental observations for the coexistence of two kinds of micelles (comicellization) in some block copolymer solutions. After the beginning work to detect the comicellization of poly(α-methylstyrene-*block*-2-(4-vinylphenyl)ethanol) solution by Honda et al. [8], some groups reported it in some block copolymer solutions detected by light scattering method [9–11]. Zheng and Davis reported the coexistence of small and large micelles in the dilute aqueous solution of poly(oxyethylene)-type nonionic surfactant with POE–PBO diblock copolymer or POE–PEE–POE triblock copolymer through cryo-TEM observation [12]. PBO and PEE denote polybutadiene and poly(ethyl ethylene), respectively. Kunieda et al. also reported comicellization in aqueous solutions of poly(oxyethylene)–polyisoprene block copolymer and C_mEO_n [13]. Hence the comicellization in the water/POE–PDMS/C_mEO_n can also be expected although a macroscopic phase separation does not take place in the micellar-phase region [3].

In this context, we studied the miscibility of POE–PDMS and C_mEO_n in micelles as a function of copolymer–surfactant ratio and the chain length of polydimethylsiloxane and poly(oxyethylene) in C_mEO_n by the pulsed-field gradient NMR (PFG-NMR) method. Since the copolymer and the surfactant employed in this study produce different proton NMR signals, the PFG-NMR method simultaneously gives us self-diffusion constants of both the components and is, therefore, a suitable method to study the possible comicellization systems.

2. Materials and methods

2.1. Materials

Poly(oxyethylene)–polydimethylsiloxane diblock copolymer $(CH_3)_3SiO–((CH_3)_2SiO)_{m-2}–(CH_3)_2SiCH_2CH_2CH_2–(OCH_2CH_2)_nOH$ was kindly supplied from Dow Corning-Toray Silicone Co Ltd., Japan. It is abbreviated as $Si_mC_3EO_n$ and is regarded as a copolymer. Table 1 is the list of copolymer used in the present study. Molecular weight (M_S), polydispersity index (M_w/M_n), molar volume of copolymer and poly(oxyethylene) block (V_S, V_{EO}), and volume percent of poly(oxyethylene) part in the whole copolymer molecule (f) are also shown. Main impurity is unreacted polydimethylsiloxane, which was removed by washing the copolymer with hexane at least three times. Note that the self-diffusion constants obtained in this study are always the averaged values since the POE–PDMS copolymers employed in this study have chain distributions for both PDMS and POE chains. Homogeneous penta(oxyethylene) dodecyl ether ($C_{12}EO_5$) and octa(oxyethylene) dodecyl ether ($C_{12}EO_8$) were obtained from Nikko Chemicals Co.

Table 1
Poly(oxyethylene)–polydimethylsiloxane diblock copolymer

m	n	M_S	M_w/M_n (PDMS)	M_w/M_n (POE)	V_S ($cm^3\,mol^{-1}$)	V_{EO} ($cm^3\,mol^{-1}$)	f (%)
5.8	51.6	2761	1.02	1.13	2515	2011	79.96
25	51.6	4185	1.20	1.13	3996	2011	50.33
52	51.6	6187	1.07	1.13	6079	2011	33.08

2.2. Methods

2.2.1. Sample preparation

All the samples were obtained by weighing the ingredients in glass test tubes. The weight fraction of D_2O was kept at 0.98. These samples were mixed well by a vortex mixer.

2.2.2. Self-diffusion measurement

Self-diffusion constant were measured by the pulsed-field gradient NMR method (PFG-NMR method) [14] on a Bruker DMX-200 spectrometer with Bruker field gradient probe operating at proton resonance frequency of 200 MHz. A stimulated echo pulse sequence [14] was used for the measurement. The temperature was kept at 25 °C with an accuracy of ±0.1 °C.

The spin-echo amplitude, I, of a given NMR resonance is described as follows:

$$I = I_0 \exp(-kD),$$
$$k = \gamma^2 G^2 \delta^2 (\Delta - \delta/3), \tag{1}$$

where I_0 is the echo amplitude in absence of gradient, γ is the gyromagnetic ratio, G is the magnetic field gradient, δ is the duration of the gradient pulses, D is the self-diffusion constant of the molecule, and Δ is the gradient pulse interval. Experiments were carried out at constant Δ, 100 ms and at appropriate G (0.065–0.36 $T\,m^{-1}$) and δ (1–3 ms), depending on the samples. The logarithm of relative spin-echo intensities (I/I_0) was plotted against k value and a self-diffusion constant was obtained from the slope of a least-square fit. (The correlation coefficients, r^2, for both single and double exponential echo decay were always better than 0.997.) The self-diffusion constant of $C_{12}EO_n$ and $Si_mC_3EO_n$ were obtained from the spin-echo signal from methylene proton on the alkyl chain (at around 1.2 ppm) and methyl proton on the PDMS chain (at around 0 ppm), respectively.

3. Results

3.1. Self-diffusion constants in $D_2O/Si_mC_3EO_{51.6}/C_{12}EO_8$ system

Self-diffusion constants of poly(oxyethylene)–polydimethylsiloxane diblock copolymer ($Si_mC_3EO_{51.6}$, $m = 5.8, 25, 52$) and octa(oxyethylene) dodecyl ether ($C_{12}EO_8$) in D_2O were measured by the PFG-NMR method at 25 °C and the results are presented in Fig. 1. The self-diffusion constants are plotted against the weight fraction of $Si_mC_3EO_{51.6}$ in total amphiphiles ($Si_mC_3EO_{51.6} + C_{12}EO_8$), which is denoted as W_P. The total amphiphile ($Si_mC_3EO_{51.6} + C_{12}EO_8$) concentration was kept at 2 wt%.