



## Electron Spin Resonance Study on the Miscibility of Poly(ethylene glycol) with Cationic Dodecyl Trimethylammonium Bromide Micelle

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**Abstract:** The interaction of poly(ethylene glycol)(PEG) with cationic dodecyl trimethyl ammonium bromide (DTAB) micelle was studied with electron spin resonance (ESR) by determining line widths of ESR spectra and coupling constant of nitrogen( $A_N$ ). The degree of ESR line shape change such as line widths and coupling constant indicated that PEG mixes well with DTAB micelle due to a great hydrophobic interaction with surfactant alkyl chains. This suggests that the PEG can be used as non-ionic surfactant to disperse the exposed oil in the ocean.

### INTRODUCTION

Water problem is becoming a serious global problem. The contamination of the environment by numerous chemicals from industry, agriculture and domestic usage must be suppressed. Such chemicals as insecticides, pesticides, chlorinated organics, and some surfactants are difficult to be decomposed by biodegradation by bacteria. Therefore they accumulate in nature and persist for a long time. Also many of surfactants widely used in various applications can cause severe problems for the natural aquatic environment.<sup>1</sup> Their biodegradation and bioelimination by bacteria is slow. Several days or even weeks are required for the complete biodecomposition of surfactants.<sup>2-5</sup>

Non-ionic surfactants have recently been in great demand for a variety of application because of its mildness and miscibility with oil. Their presence in the environment requires the development of a waste treatment technique. In recent literature, various reports have dealt with heterogeneous photocatalysis mediated method.<sup>6-8</sup> In spite of the such an effort, non-ionic surfactants such as p-nonylphenyl poly (oxy ethylene) ether, poly(ethylene oxides) (PEO) derivatives have been used as a milding agent and surfactant for the oil spill to disperse the exposed oil in the ocean. Recently, much attention has been focused on the utilization of non-ionic surfactants for the oil spill problem because of excellent ability to disperse exposed oil in the ocean and easy biodegradability and photodegradability.<sup>12</sup> Such a dispersing ability of non-ionic surfactant of oil is based upon the great hydrophobic interaction in the water.<sup>4</sup> Winnick *et al.* have studied the interaction of sodium dodecyl sulfate micelle and non-ionic PEO with pyrene at both ends of the PEO chain by measuring the fluorescent properties of the bound pyrene.<sup>9</sup>

Electron spin resonance(ESR) has been used to investigate the micro-environment of nitroxide spin probes in micelles and vesicles by measuring nitrogen coupling constant and ESR line width.<sup>10</sup> The coupling constant( $A_N$ ) is affected by the local polarity of the nitroxide. A more polar environment gives larger values of  $A_N$  due to greater electron density at nitrogen. The line widths are controlled by the rotational and lateral diffusion of the spin probes which is affected by the viscosity, orderness, and temperature of the spin probe environment in micelles and vesicles.<sup>11-13</sup>

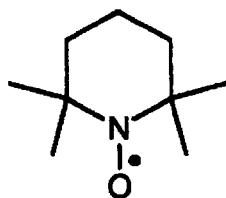
The larger ordering parameters of x-doxystearic acids(x-DSA) at the interface regions of micelles or vesicles compared to the hydrocarbon region indicated orientation of x-DSA with its polar headgroup at the interface. This results in a broader line width and a slower tumbling rate for the spin probe consistent with a longer relaxation time.

In the present study, the interaction of the cationic dodecyl trimethyl ammonium bromide(DTAB) micelle with non-ionic poly(ethylene glycol)(PEG) was studied with ESR by determining the line widths and coupling constant of  $\alpha$ -DSA spin probes solubilized into the micelles. The ESR line widths of the low and high magnetic field lines of the nitroxides are measured and compared to determine the relative viscosity changes of the nitroxide environment as a function of the nitroxide. The nitrogen coupling constant are also determined to obtain relative information on the interaction of DTAB micelles and non-ionic PEG surfactant.

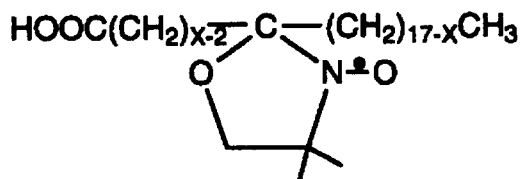
## **EXPERIMENTALS**

### ***Materials.***

PEG(average molecular weight of 200) was obtained from Aldrich and used without further purification. DTAB was obtained from Aldrich and used after recrystallization from ethanol three times, followed by washing with diethyl ether and drying at 50 °C under a moderate vacuum. Stock solution of 0.1 M DTAB surfactant was prepared in the purified water from Nanopure (resistivity was 18.3 M $\Omega$  cm) after bubbling with dry nitrogen gas for 15 min. Stock solution of 13 mM for each doxylstearic acid and tempo nitroxide of which structures are shown in Figure 1 and they were obtained from Sigma Chemical Co. were prepared in chloroform.



**Tempo (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical)**



**x-Doxylstearic acid**

**Fig. 1.** The structures of nitroxide spin probes.

A 17  $\mu$ L quantity of each spin probe stock solution was transferred into a 1.6 cm (o.d.) by 1.25 cm (i.d.) test tubes, and then the chloroform was evaporated by bubbling nitrogen gas into the surface of the solution. Then 1 mL of a 0.1 M stock DTAB micellar solution was added to the test tubes, and each quantity of PEG was added into the 1 mL x-DSA/H<sub>2</sub>O/DTAB micellar solutions to result in 0.5, 10, 40 mM concentration of PEG in micellar solutions. These solutions were used for up to 2 days. The spin probe concentration was  $2.2 \times 10^{-4}$  M. The samples was introduced into 1.0 mm (i.d.) by 1.1 mm (o.d.) Pyrex disposable micropipets (CMS Co.) for ESR experiments.

### ***Electron Spin Resonance Experiments.***

ESR spectra were recorded at room temperature on a Bruker ESP 300 ESR X-band spectrometer with 100-kHz magnetic field modulation and 1.97 mW microwave power to avoid power saturation. The magnetic field were measured with a Varian E-501 gaussmeter, and frequencies were directly measured with a Hew-Lett Packard 5350 B microwave frequency counter. Each ESR spectrum was averaged for seven scans. The ESR line widths for the low and high magnetic field lines were measured for the peak-to-peak distance of the first-derivative ESR spectrum. The nitrogen coupling constant ( $A_N$ ) was determined for half of the peak-to-peak distance of the low and high magnetic field lines. The mean values are obtained from triplicate measurements.

## **RESULTS AND DISCUSSION**

The location and degree of interaction of PEG polymer chains with surfactant assemblies like micelles, vesicles and reverse micelles are partially understood. The interaction of non-ionic surfactants with oil is critically affected by the degree of hydrophobic interaction of them. The interaction of PEO with sodium dodecyl sulfate (SDS) micelles already has been studied by the measurement of conductance and surface tension.<sup>13</sup> The plots of surface tension and conductance as a function of the SDS concentration showed two transition points. These were interpreted in terms of a polymer-surfactant complex at the first point and micelle formation with binding between the surfactant ionic head group and the polymer at the second transition point. The interaction of PEO with vesicles has also been studied for dipalmitoylphosphatidylcholine vesicles by viscosity change.<sup>14</sup> It was reported that polymer addition increased the vesicle surface viscosity. The PEO/SDS system has

also been studied by  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{23}\text{Na}$  NMR.<sup>15</sup>

Micelles containing polymer at their surface or interior have higher viscosity than the micelle or polymer solutions themselves.<sup>16-18</sup> So an increasing concentration of PEG in the micellar solution increases the viscosity due to PEG interaction with the micelle. The increasing viscosity can be probed by a paramagnetic nitroxide group located near the micellar interface.

The correlation time of nitroxide group spin probes in micelles is related to the order parameter of the interface region and the rotational diffusion tensor.<sup>12</sup> Previous studies have shown that detailed line shape simulations can give the order parameter and rotational diffusion tensor of nitroxides in vesicles, but this time-consuming analysis is not necessary to establish the trends with PEG concentration investigated

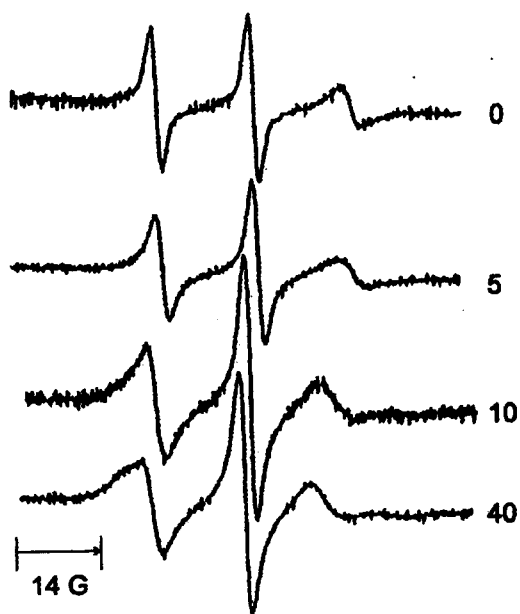


Fig. 2. The first derivative ESR spectra of 5-DSA/DTAB/H<sub>2</sub>O/PEG (mM) at room temperature.

here. Some representative correlation times in ammonium pentadecafluorooctanate micelles are  $1.1 \times 10^{-9}$  s for 5-DSA and  $2.3 \times 10^{-10}$  s for 16-DSA.<sup>10b</sup>

These values indicate that the x-DSA nitroxide in micelles are typically in the fast tumbling range ( $\tau_c = 10^{-9}$  s) in micelles. As PEG is added to the micellar solution, the local viscosity of the nitroxide environment increases as shown by increasing ESR line widths in Table 1.<sup>18,19</sup> Baglioni *et al.* confirmed a relationship between the rotational correlation time and the viscosity in such surfactant systems.<sup>11</sup>

Table 1. The First Derivative ESR Line Widths to  $\pm 0.02$  G for Low and High Magnetic Field Lines of Tempo and x-DSA in 0.1 M DTAB/H<sub>2</sub>O Micelles With Different Concentration of PEG at Room Temperature.

[PEG]	ESR line	tempo	5-DSA	7-DSA	12-DSA	16-DSA
0 mM	low	1.56 G	2.51 G	2.51 G	1.69 G	1.81 G
	high	2.21	3.42	3.41	2.25	3.32
5	low	1.57	3.12	3.22	1.78	2.41
	high	2.22	5.93	6.25	2.39	4.01
10	low	1.58	3.43	3.43	1.79	2.53
	high	2.23	6.25	6.47	2.39	4.32
40	low	1.59	4.50	3.95	1.81	2.73
	high	2.25	6.38	6.28	2.43	3.76

Thus, the increasing line widths of 5-, 7-, and 16-DSA nitroxide spin probes with increasing concentration of PEG as shown Figure 2 and Table 1 indicate that

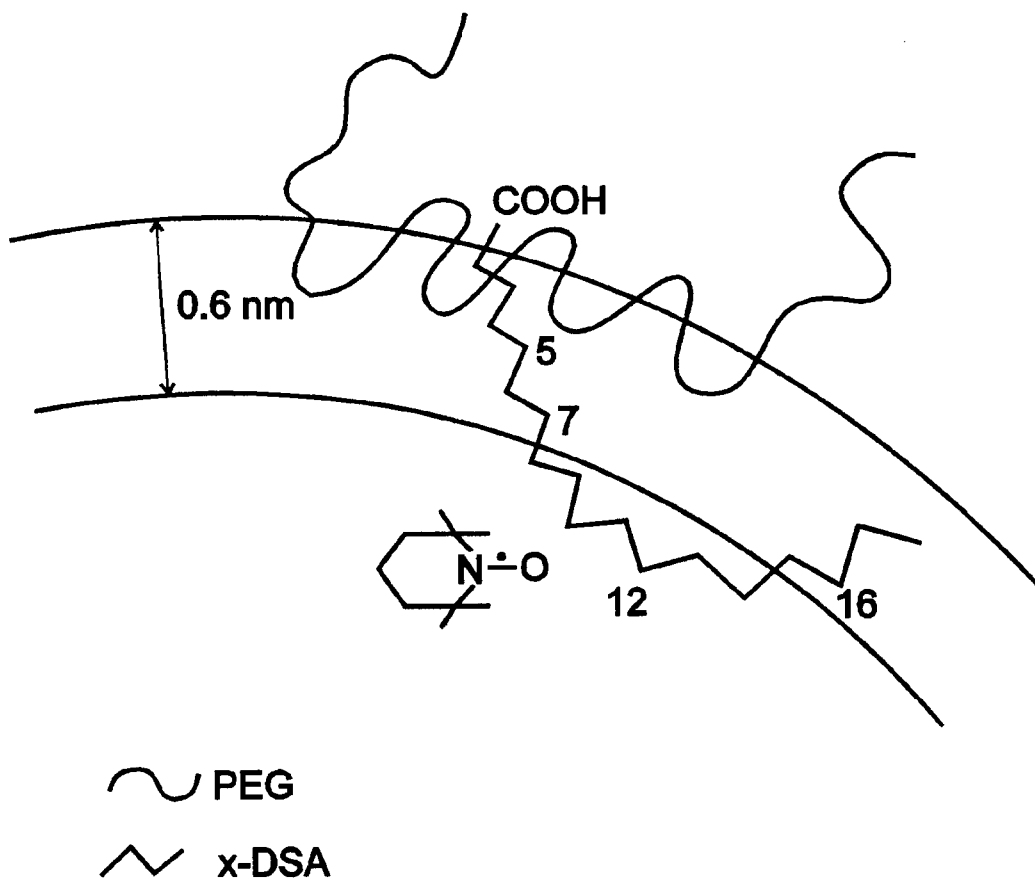


Fig. 3. Schematic drawing of the location of PEG non-ionic surfactant at the interface of DTAB micelle relative to nitroxide spin probes.

the PEG is located near the micelle interface region of which location the nitroxide moieties of these x-DSA spin probes are found. On the other hand, the constant ESR line widths of tempo, and 12-DSA with increasing PEG concentration indicate that the locations of the nitroxide moiety of these spin probes are farther from the PEG location near the micellar interface. This is schematically shown in Figure 3.



Table 2. Nitrogen coupling constant to 0.01 G of tempo and x-DSA nitroxide in 0.1 M DTAB/H<sub>2</sub>O micelle with different concentration of PEG at room temperature.

[PEG]	tempo	5-DSA	7-DSA	12-DSA	16-DSA
0 Mm	15.22 G	15.62 G	15.59 G	15.31 G	15.41 G
5	15.22	15.54	15.54	15.29	15.38
10	15.22	15.50	15.48	15.29	15.38
40	15.21	15.44	15.42	15.29	15.36

The difference among the various x-DSA with PEG concentration is also supported by a small decrease in the nitroxide coupling constant for 5- and 7-DSA in constant value for tempo, 12-DSA and 16-DSA with increasing PEG concentration as shown in Table 2. This indicates that the polarity of the nitroxide moiety in the micelle is slightly decreased with increasing PEG concentration.

Conclusively, the degree of the interaction of non-ionic surfactant PEG with DTAB micelle indicates the miscibility between them. ESR line shape change with increasing concentration of PEG clearly showed that PEG is mixed well with DTAB micelle due to great hydrophobic interaction of PEG with DTAB surfactant chains.

## CONCLUSIONS

Non-ionic PEG surfactant is milding surfactant molecules. The miscibility of PEG with DTAB micelle is studied with Tempo and x-DSAs by measuring ESR line widths and coupling constant( $A_N$ ). The increasing PEG concentration added into DTAB micelle solution increased ESR line widths of 5-, 7-, and 16-DSA nitroxide spin probes.

On the other hand, The ESR line widths of Tempo and 12-DSA nitroxide spin probes was almost constant with increasing concentration of PEG in DTAB micelle. These indicate that nitroxide spin probes of Tempo and 12-DSA located in the hydrophobic core region of DTAB micelle. The nitroxide spin probes of 5-, 7-, and 16-DSA are located at the interface of DTAB micelle. So, the interaction of PEG with DTAB micelle results in the interrelation of PEG molecule between headgroups of DTAB micelle. This interpretation is also supported by the decreased nitrogen coupling constant of nitroxides with increasing concentration of PEG. All of the results indicate that PEG is mixed well with DTAB micelle by intercalation between headgroups.

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## FIGURE CAPTIONS

Figure 1. The structures of nitroxide spin probes.

Figure 2. The first derivative ESR spectra of 5- DSA/DTAB/H<sub>2</sub>O/PEG (mM) at room temperature.

Figure 3. Schematic drawing of the location of PEG non-ionic surfactant at the interface of DTAB micelle relative to nitroxide spin probes.

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