

Location of Phenothiazine in Sodium Dodecyl Sulfate/*n*-Pentanol/Water Microemulsions

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The location of phenothiazine (PTZ) in sodium dodecyl sulfate (SDS)/*n*-pentanol (*n*-C₅H₁₁OH)/water microemulsions is studied by cyclic voltammetry at a Pt electrode. The results indicate that PTZ exists in the membrane phase of microemulsion droplets with its N atom or S atom toward the polar head of the surfactant. In addition, we examine the effect of the compositions and structures of the microemulsions, pH, temperature, and the inorganic salts on the location distribution for PTZ in the membrane phase of the microemulsions. The results show that the location distribution for PTZ in the membrane phase of the microemulsions is mainly dependent on the hydrogen bond between the –NH in PTZ and *n*-pentanol (or the –SO₄[–] of SDS) and on the electrostatic interaction between the S atom (or N atom) in PTZ and the polar head of SDS.

Introduction

Microemulsions are clear, thermodynamically stable fluids of water, oil, and surfactants and are considered as less toxic, less expensive alternatives to many solvents.¹ In practice, the three-component microemulsion system, composed of surfactant, cosurfactant, and water, is often used as the basic system of microemulsions.^{2,3} These microheterogeneous fluids can solubilize both polar and nonpolar reactants, so they play important roles in biology, material, the environment, and other related fields.⁴ To apply microemulsions more widely, investigation of the explicit locations of organic compounds in the system is very important and interesting.⁵ Plenty of methods such as electron spin resonance (ESR),⁶ fluorescence spectra,⁷ ultraviolet spectroscopy,⁸ small-angle X-ray scattering (SAXS),⁹ and NMR spectroscopy¹⁰ have been proposed to estimate the location of organic materials solubilized in micelles.

Phenothiazine (PTZ) is a typical and useful organic compound with an N atom which makes it easy to lose one electron to form the cation radical.¹¹ In addition, being a hydrophobic

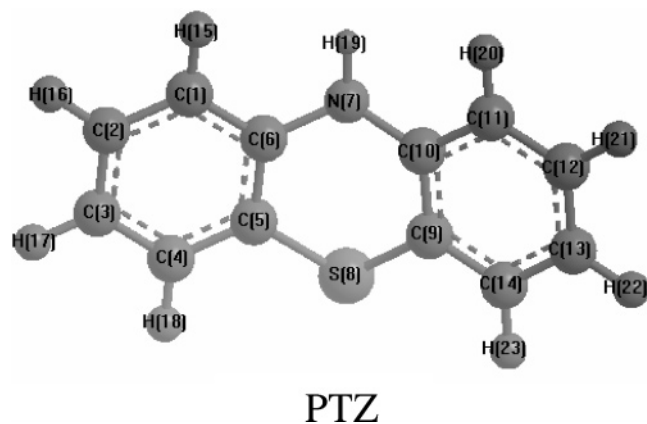
resembles that of many drugs and biologically active molecules, making it an interesting model for drug-delivery applications.

In our previous studies,¹² we have used fluorescence spectroscopy to study the location of phenothiazine (PTZ) in O/W and W/O microemulsions and found that the PTZ molecules exist in the membrane phase of O/W and W/O microemulsions. But we cannot use fluorescence spectroscopy to decide which polar moiety of PTZ is near to the polar head of the surfactant in the membrane phase of the microemulsion. Electrochemical techniques, such as polarography, rotating disk voltammetry (RDV), cyclic voltammetry (CV), and so on, have been successfully applied as the popular tools in the study of the physical–chemical properties of microemulsions.^{13,14} In the present Article, the location of PTZ in SDS/*n*-C₅H₁₁OH/H₂O microemulsions, and the influence of the compositions and structures of the microemulsions, pH, the inorganic salts, and temperature on the location distribution for PTZ, are studied by cyclic voltammetry, and some interesting information is obtained.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS, sigma, 98%) was recrystallized twice in ethanol. The purity of the surfactant was examined, and no surface tension minimum was found in the surface tension curve. Phenothiazine (PTZ, 99%), pyrene (99%), and *n*-pentanol (*n*-C₅H₁₁OH, 99%) were all from Aldrich. The NaCl, KCl, CaCl₂, MgCl₂·6H₂O, AlCl₃·5H₂O, NaOH, and HCl used were analytical reagent grade (Shanghai Chemical Co., China). The water used was deionized and distilled twice.

Electrochemical Measurements. Cyclic voltammetric experiments were carried out with a CH Instruments 660a electrochemical workstation (Zhenghua, Shanghai). The electrochemical cell was a standard three-electrode configuration similar in design to that described elsewhere.¹⁵ The working electrode (Shanghai Rex Instrument Factory, China; model 213) was a platinum plate (area 0.24 cm²). A saturated calomel electrode (SCE, Jiangsu Electroanalytical Instrument Factory, China; model 232C) was used as the reference electrode, and a platinum plate was used as the auxiliary electrode. Besides acting as a surfactant to form the microemulsion, the anionic



molecule with two polar moieties of an N atom and an S atom, as can be seen from the structure of PTZ, its chemical structure

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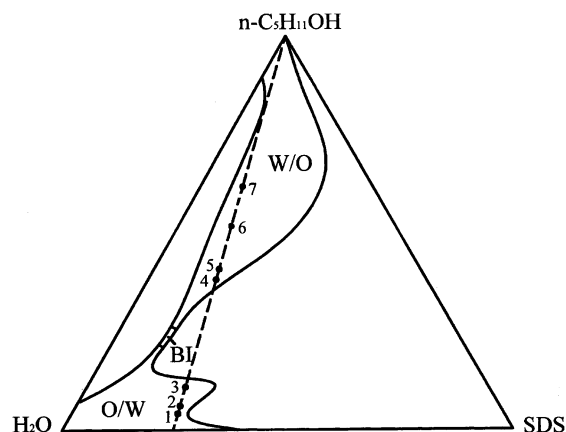


Figure 1. Partial phase diagram of the SDS/*n*-C₅H₁₁OH/H₂O system.

surfactant SDS can also act as the supporting electrolyte because of its ionic property under the high content (from 10 to ~25 wt %). Tetrabutylammonium perchlorate (TBAP, 0.01 M) was used as the supporting electrolyte when the electrochemical measurements were conducted in *n*-pentanol. The cyclic voltammograms for PTZ were obtained at 25 ± 0.1 °C, and the sweep rate was 100 mV/s.

Measurement of Fluorescence Spectroscopy. Fluorescence spectra of pyrene in microemulsions were measured at 25 °C in the presence or absence of PTZ using an RF-5301 PC spectrofluorophotometer (SHIMADZU). The emission spectra were measured in the wavelength range of 350–600 nm with the excitation wavelength being 338 nm. The pyrene concentration was 1.0 × 10⁻⁶ M.

UV-Irradiation Measurement. The sample was irradiated by a high-pressure mercury lamp (150 W).

Measurement of pH. The pH of the microemulsions was adjusted with HCl at low pH, <7.0, and with NaOH at high pH, >7.0. The pH of the microemulsion was determined with a pH meter (Shanghai Rex Instrument Factory, China; model PHS-3C), which was standardized with Aldrich buffers. Prior to the measurements, the microemulsions were bubbled with nitrogen to avoid any contribution in the measured pH from CO₂, dissolved from the atmosphere.

DFT Quantum Calculation. Density functional theoretical (DFT) calculations of phenothiazine were carried out at the level of B3LYP/6-31G (d) with the GAUSSIAN 03 program.¹⁶

Results and Discussion

Location of Phenothiazine in SDS/*n*-C₅H₁₁OH/H₂O Microemulsions. The partial phase diagram of the SDS/*n*-C₅H₁₁OH/H₂O system determined in our previous studies¹⁷ is shown in Figure 1, where O/W, BI, and W/O represent oil in water, bicontinuous, and water in oil microemulsions, respectively, and the numbers 1–7 show the compositions of the samples used in this Article.

Parts a and b of Figure 2 illustrate the cyclic voltammogram of PTZ at a Pt electrode in SDS/*n*-C₅H₁₁OH/H₂O O/W and W/O microemulsions, respectively. Since the anodic peak potential (E_{pa}) is independent of the sweep rate ν (Figure 2, parts a and b) and the anodic peak current i_{pa} is proportional to the square root of the potential sweep rate $\nu^{1/2}$ (Figure 3, parts a and b), the electrochemical process for PTZ at a Pt electrode is a diffusion-controlled process. According to the peak separation ($E_{pa} - E_{pc}$) between the peak potentials in the positive and negative scans, the number of electrons involved in the electron transfer, n , can be obtained from the Nernst eq at 25 °C¹⁸

$$\Delta E_p = E_{pa} - E_{pc} = \frac{56}{n} \text{ mV} \quad (1)$$

in which E_{pa} is the anodic peak potential and E_{pc} is the cathodic peak potential. It can be seen from Table 1 that the value of ($E_{pa} - E_{pc}$) is close to 56 mV in the O/W microemulsion and is higher in the W/O microemulsion. Considering the fact that there is no obvious peak for PTZ in pure *n*-pentanol with TBAP as the supporting electrolyte (Figure 2c), the electrochemical reaction of PTZ at a Pt electrode does not take place easily in pure *n*-C₅H₁₁OH, which causes the higher ($E_{pa} - E_{pc}$) in the W/O microemulsion in which *n*-C₅H₁₁OH is a continuous phase. Thus, the electrochemical process for PTZ is a diffusion-controlled reversible one-electron-transfer (both n_1 and $n_2 \approx 1$) process in the O/W microemulsion and a diffusion-controlled quasi-reversible one-electron-transfer process in the W/O microemulsion.

PTZ is hardly soluble in water, so PTZ can only exist in the O/W microdroplet in SDS/*n*-C₅H₁₁OH/H₂O O/W microemulsions and in the membrane phase of W/O microdroplet or oil continuous phase in SDS/*n*-C₅H₁₁OH/H₂O W/O microemulsions. In our recent study,¹² the interaction between chloroform and PTZ in O/W and W/O microemulsions has been studied by the fluorescence spectroscopy method. Obviously, there is

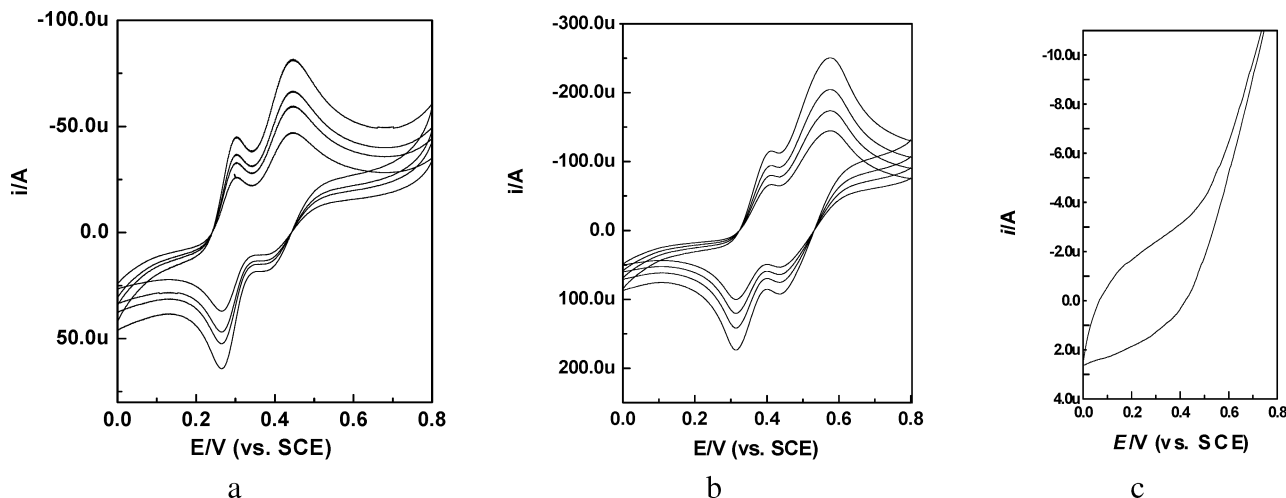


Figure 2. The cyclic voltammogram of 4.1 mM PTZ in SDS/*n*-C₅H₁₁OH/H₂O microemulsions with the *n*-C₅H₁₁OH content being 10.0 wt % (a) and 52.0 wt % (b) when the weight ratio of SDS/H₂O is 25.5/74.5. Sweep rate (ν /(mV·s⁻¹), from bottom to top): 50, 80, 100, 150. (c) The cyclic voltammogram of 4.1 mM PTZ in pure *n*-pentanol with tetrabutylammonium perchlorate as the supporting electrolyte.

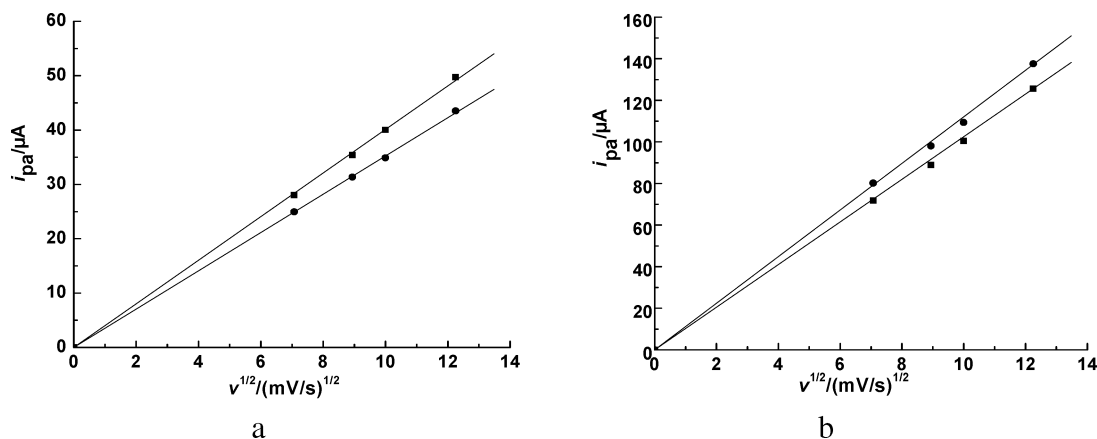


Figure 3. Dependence of the peak current i_{pa} of the anodic peak with a lower anodic peak potential (■) and higher anodic peak potential (●) for 4.1 mM PTZ on the square root of the potential sweep rates $v^{1/2}$ in SDS/*n*-C₅H₁₁OH/H₂O microemulsions with the *n*-C₅H₁₁OH content being 10.0 wt % (a) and 52.0 wt % (b) when the weight ratio of SDS/H₂O is 25.5/74.5.

TABLE 1: Voltammetric Parameters for PTZ in SDS/*n*-C₅H₁₁OH/H₂O Microemulsions

microemulsion sample ^c	SDS/H ₂ O (wt/wt)	<i>W</i> _{<i>n</i>-C₅H₁₁OH} (wt %)	structure	first oxidation peak ^a		second oxidation peak ^b		$i_{pa1}/(i_{pa1} + i_{pa2})$
				E_{pa1} (V)	$E_{pa1} - E_{pc1}$ (mV)	E_{pa2} (V)	$E_{pa2} - E_{pc2}$ (mV)	
1	25.5:74.5	4.2	O/W	0.270	59	0.418	59	0.56
2	25.5:74.5	6.2	O/W	0.283	59	0.432	59	0.55
3	25.5:74.5	10.0	O/W	0.302	59	0.445	59	0.53
4	25.5:74.5	38.4	W/O	0.371	60	0.520	79	0.51
5	25.5:74.5	41.1	W/O	0.382	63	0.535	82	0.50
6	25.5:74.5	52.0	W/O	0.411	65	0.573	86	0.48
7	25.5:74.5	62.0	W/O	0.420	68	0.618	88	0.44

^a E_{pa1} and E_{pa2} represent the lower and higher oxidation peak potentials, respectively. ^b E_{pc1} and E_{pc2} represent the lower and higher reduction peak potentials, respectively. ^c Consistent with that shown in Figure 1.

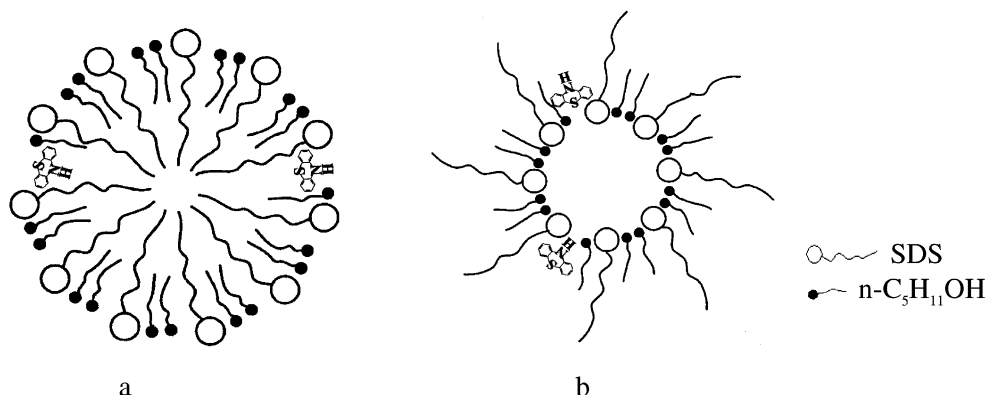


Figure 4. Schematic illustration of the location of PTZ in the SDS/*n*-C₅H₁₁OH/H₂O O/W (a) and W/O (b) microemulsion.

strong interaction between chloroform and PTZ in benzyl alcohol. However, in O/W microemulsions, there is no interaction between chloroform and PTZ. Since chloroform exists in the core of the O/W microdroplet, hence PTZ can only exist in the membrane phase of the O/W microdroplet. In W/O microemulsions, the interaction between chloroform and PTZ is very weak. Since chloroform exists in the oil continuous phase, consequently, PTZ also exists in the membrane phase of the W/O microdroplet. Therefore, the oxidation peaks in Figure 2, parts a and b, are caused by PTZ molecules located in the membrane phase of the microemulsions.

Then, why are there two oxidation peaks in Figure 2, parts a and b? Since the process of PTZ^{•+} losing one electron to form PTZ²⁺ needs much more energy ($E_{PTZ^{2+}} - E_{PTZ^{•+}} \approx 0.50$ V) and does not take place easily,^{11,19} the anodic peak potential separation less than 0.20 V between the two oxidation peaks (Figure 2, parts a and b, and Table 1) indicates that the two

peaks are both caused by PTZ losing one electron to form PTZ^{•+}. Hence, the two peaks in Figure 2, parts a and b, reveal that PTZ exists in the membrane phase of SDS/*n*-C₅H₁₁OH/H₂O microemulsions in two ways, i.e., it can exist in the membrane phase of the microemulsion with the N atom or the S atom toward the polar head of SDS (Figure 4). This is consistent with the result obtained by Hu and Kevan who used ESR to study the location of derivatives of PTZ in cetyltrimethylammonium micelles and found that the derivatives of PTZ can exist in the membrane phase of the micelle with the N atom or the S atom toward the polar head of surfactants.²⁰

Since PTZ^{•+} is produced by losing an electron from the N atom in PTZ molecules, the high negative electron density around the N atom can cause the easy formation of PTZ^{•+} and, hence, a low E_{pa} value.²¹ The negative electron density around the N atom in the PTZ molecule with the N atom toward the polar head of SDS is higher than that with the S atom toward

the polar head of SDS, because the polar head of SDS is electron negative. Therefore, the PTZ molecule with the N atom toward the polar head of SDS loses an electron more easily and has a lower anodic peak potential (E_{pa1}), while that with the S atom toward the polar head of SDS has a higher anodic peak potential (E_{pa2}). Furthermore, the higher micropolarity for the N atom in PTZ with the N atom toward the polar head of SDS also causes the formation of $PTZ^{+\bullet}$ to be easier and, hence, a lower E_{pa1} .

It is evident that PTZ can reside in the membrane phase of microemulsions with the N or the S atom toward the polar head of SDS since PTZ has two polar moieties of an N atom and an S atom. In addition, as can be seen from the structure of PTZ, $-NH$ in PTZ easily forms a hydrogen bond with *n*-pentanol and $-SO_4^-$ of SDS. Obviously, the hydrogen bond action can induce PTZ to reside in the membrane phase of the microemulsion with the N atom toward the polar head of SDS. At the same time, we have calculated the Mulliken atomic charge of PTZ by DFT quantum calculations. The Mulliken atomic charge (with hydrogen summed into the heavy atoms) of 7N is -0.412953 , and that of 8S is $+0.172105$. Thus, there exists an electrostatic repulsive interaction between the N atom in PTZ and the $-SO_4^-$ of SDS and an electrostatic attractive interaction between the S atom in PTZ and the $-SO_4^-$ of SDS. Hence, the electrostatic interaction between the S atom (or N atom) in PTZ and the $-SO_4^-$ of SDS can induce PTZ to reside in the membrane phase of the microemulsion with the S atom toward the polar head of SDS. Therefore, the above factors lead to the location distribution for PTZ in the membrane phase of the microemulsions all together.

Effect of the Composition and Structure of Microemulsions. If i_{pa1} denotes the peak current of the anodic peak with a lower anodic peak potential (E_{pa1}) and i_{pa2} denotes the peak current of the anodic peak with a higher anodic peak potential (E_{pa2}), the value of $i_{pa1}/(i_{pa1} + i_{pa2})$ can indicate the molar fraction of the PTZ molecules with the N atom toward the polar head of SDS. Table 1 shows that more PTZ molecules tend to reside in the membrane phase with the N atom toward the polar head of SDS in the O/W microemulsion, and more PTZ molecules tend to reside with the S atom toward the polar head of SDS in the W/O microemulsion. As can be seen from Figure 4, PTZ resides in the outer part of the membrane phase in the O/W microemulsion and in the inner part of the membrane phase in the W/O microemulsion. Compared with that in the O/W microemulsion, PTZ cannot reside in the membrane phase very close to the polar head of SDS in the W/O microemulsion, because the arrangement of molecules (including surfactants and *n*-C₅H₁₁OH molecules) in the inner part of the W/O microemulsion is more compact than that in the outer part of the O/W microemulsion. Hence, the hydrogen bond between the $-NH$ in PTZ and the $-SO_4^-$ of SDS (or *n*-C₅H₁₁OH) forms more easily in the O/W microemulsion than that in the W/O microemulsion, and more PTZ molecules reside in the membrane phase with the N atom toward the polar head of SDS in the O/W microemulsion.

Table 1 also shows that $i_{pa1}/(i_{pa1} + i_{pa2})$ is decreased with the increase of *n*-C₅H₁₁OH content for both O/W and W/O microemulsions, which indicates that the molar fraction of PTZ molecules in the membrane phase with the N atom toward the polar head of SDS is decreased with the addition of *n*-C₅H₁₁OH. As we all know, the hydrogen bond between the $-NH$ in PTZ and *n*-C₅H₁₁OH can make more PTZ molecules tend to reside with the N atom toward the polar head of SDS in the membrane phase of microemulsions. But the addition of *n*-C₅H₁₁OH can also make PTZ molecules farther away from

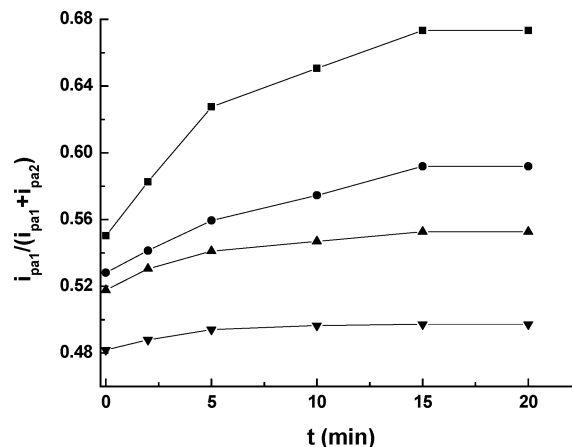


Figure 5. Dependence of $i_{pa1}/(i_{pa1} + i_{pa2})$ for 4.1 mM PTZ in the SDS/*n*-C₅H₁₁OH/H₂O microemulsion on the UV-irradiation time (the weight ratio of SDS/H₂O being 25.5/74.5 and the *n*-C₅H₁₁OH content as follows: ■ 6.2 wt %, ● 10.0 wt %, ▲ 38.4 wt %, ▼ 52.0 wt %).

the polar head of SDS because of the volume effect, and hence, the hydrogen bond between the $-NH$ in PTZ and *n*-C₅H₁₁OH (or the $-SO_4^-$ of SDS) becomes weaker, resulting in fewer PTZ molecules with the N atom toward the polar head of SDS. In the present study, the latter effect plays an important role and makes more PTZ molecules reside in the membrane phase with their S atoms toward the polar head of SDS.

Effect of UV-Irradiation. Figure 5 shows the dependence of the location distribution of PTZ in the SDS/*n*-C₅H₁₁OH/H₂O microemulsion on the UV-irradiation time. As shown in Figure 5, $i_{pa1}/(i_{pa1} + i_{pa2})$ increases with the UV-irradiation time. Upon illumination, $PTZ^{+\bullet}$ forms following the photoionization process (eq 2)²², and there exists an electrostatic attractive interaction between the cation radical $PTZ^{+\bullet}$ and the $-SO_4^-$ of SDS, which will cause more PTZ molecules to reside with the N atom toward the polar head of SDS in the membrane phase of the microemulsions.



(PTZ* represents the excited PTZ) (2)

Figure 5 also shows that $i_{pa1}/(i_{pa1} + i_{pa2})$ increases more slowly with the *n*-C₅H₁₁OH content after UV-irradiation. On one hand, the hydrogen bond between PTZ and *n*-pentanol becomes stronger with the addition of *n*-pentanol, which makes the negative electron charge density in the N atom in PTZ decrease. On the other hand, the *n*-pentanol molecules make PTZ move away from the polar head of SDS, and hence, the negative electron density around PTZ is decreased. The lower electron densities in the N atom and around the N atom both make the formation of photoinduced $PTZ^{+\bullet}$ more difficult, so the effect of the UV-irradiation on the location distribution of PTZ in the membrane phase of the microemulsion is less obvious in the microemulsion with higher *n*-C₅H₁₁OH content.

Effect of Inorganic Salts. Figure 6 shows the dependence of the location distribution of PTZ in the SDS/*n*-C₅H₁₁OH/H₂O O/W microemulsion on the inorganic salt concentration. As shown in Figure 6, $i_{pa1}/(i_{pa1} + i_{pa2})$ decreases with the addition of inorganic salt, which indicates that the molar fraction of PTZ molecules in the membrane phase of the O/W microemulsion with the S atom toward the polar head of SDS increases with the addition of inorganic salts. The salts are NaCl, KCl, CaCl₂, MgCl₂, and AlCl₃.

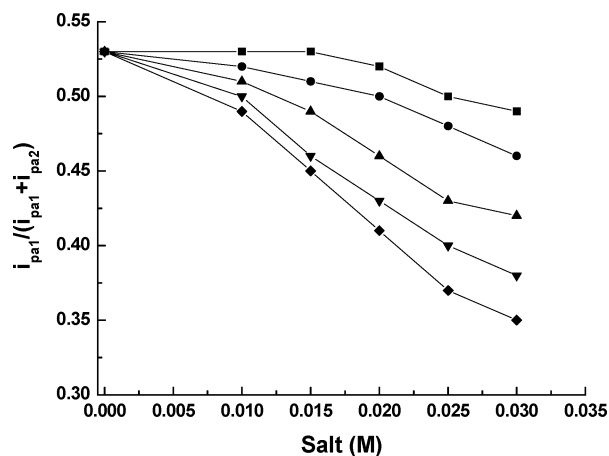


Figure 6. Dependence of $i_{pa1}/(i_{pa1} + i_{pa2})$ for 4.1 mM PTZ in the SDS/ n -C₅H₁₁OH/H₂O O/W microemulsion on the salt concentration (the weight ratio of SDS/H₂O being 25.5/74.5 and the n -C₅H₁₁OH content being 10.0 wt %, ■ NaCl, ● KCl, ▲ CaCl₂, ▼ MgCl₂, ◆ AlCl₃).

In general, the addition of salts leads to the decrease of the negative charge density of microdroplets of microemulsions because of the enhanced screen of the electrostatic interactions.^{23,24} The low negative charge density around the $-\text{SO}_4^-$ of SDS weakens the hydrogen bond between the $-\text{NH}$ in PTZ and the $-\text{SO}_4^-$ of SDS, which causes more PTZ to reside in the membrane phase of the O/W microemulsion with the S atom toward the polar head of SDS. The decrease of the electrostatic interaction between the $-\text{SO}_4^-$ of SDS and the N atom (or S atom) in PTZ causes more PTZ molecules to reside in the membrane phase of the O/W microemulsion with the N atom toward the polar head of SDS. But this does not matter much here.

In Figure 6, the effect of the counterion on the location distribution of PTZ in the membrane phase of the microemulsions increases in the order $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$. For the cation with higher charge and smaller radius, the effect of the screen of the electrostatic interaction is more obvious, so the effect of Al^{3+} on the location distribution for PTZ is the most obvious. For the cations with the same charge, the adsorption quantity of the cation with the smaller radius in the microdroplet is larger and the effect of the screen of the electrostatic interaction is more obvious. Therefore, the radius of Mg^{2+} is smaller than that of Ca^{2+} , resulting in a more obvious effect of the location distribution for PTZ in the presence of the former. However, the effect of K^+ on the location distribution for PTZ is more obvious than that of Na^+ , although the hydrated radius of Na^+ is lower than that of K^+ . Recently, Morten et al. have studied the salt partitioning in the SDS microemulsion. They have found that Na^+ partitions more strongly toward the excess water phase while K^+ shows more preference for the microdroplet composed of anionic surfactant with Na^+ as the counterion.²⁵ So, the effect of Na^+ on the negative charge density of the SDS microdroplet is less obvious than that of K^+ .

Surprisingly, the opposite effect of salts on the location distribution of PTZ is observed in the W/O microemulsion. Table 2 shows the effect of 0.01 M salts on the location distribution of PTZ in SDS/ n -C₅H₁₁OH/H₂O W/O microemulsions. The concentration of the salt remains less than 0.01 M to keep the W/O microemulsion stable. As shown in Table 2, $i_{pa1}/(i_{pa1} + i_{pa2})$ increases with the addition of salts, which indicates that the molar fraction of PTZ molecules in the

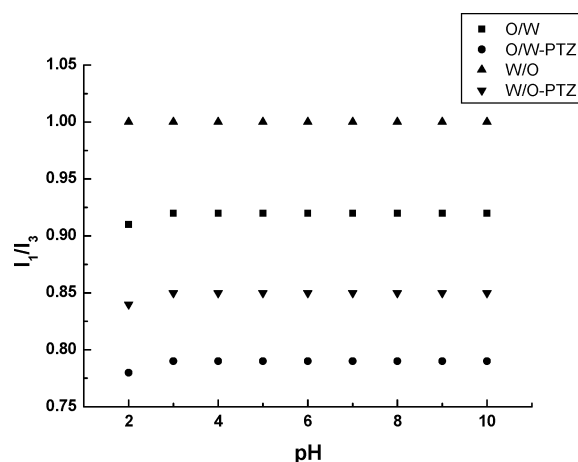


Figure 7. Dependence of I_1/I_3 for pyrene in the SDS/ n -C₅H₁₁OH/H₂O microemulsion on pH (the weight ratio of SDS/H₂O being 25.5/74.5 and the n -C₅H₁₁OH content being 10.0 wt %, ■ in the absence, ● in the presence of PTZ; 52.0 wt %, ▲ in the absence, ▼ in the presence of PTZ).

TABLE 2: Effect of Inorganic Salts on $i_{pa1}/(i_{pa1} + i_{pa2})$ for 4.1 mM PTZ in the W/O SDS/ n -C₅H₁₁OH/H₂O Microemulsion (the Weight Ratio of SDS/H₂O Being 25.5/74.5 and the Content of n -Pentanol Being 52.0 wt %)

salt (0.01 M)	NaCl	KCl	MgCl ₂	CaCl ₂	AlCl ₃
$i_{pa1}/(i_{pa1} + i_{pa2})$	0.48	0.50	0.51	0.50	0.54

membrane phase of the W/O microemulsion with the N atom toward the polar head of SDS increases with the addition of salts.

Just as discussed above, the hydrogen bond between the $-\text{NH}$ in PTZ and the $-\text{SO}_4^-$ of SDS (or n -C₅H₁₁OH) in the W/O microemulsion is weaker than that in the O/W microemulsion, so the “hydrogen bond” effect is not an important factor in determining the location distribution of PTZ in the membrane phase of the W/O microemulsion. The decrease of the negative charge density of the microdroplet with the addition of salts leads to the decrease of the electrostatic interaction between the N atom (or S atom) and the polar head of SDS, which plays an important role here. And hence more PTZ molecules reside in the membrane phase of the W/O microemulsion with the N atom toward the polar head of SDS.

Effect of pH. Figure 7 shows the effect of pH on the intensity ratio (I_1/I_3) of pyrene in SDS/ n -C₅H₁₁OH/H₂O O/W and W/O microemulsions with and without PTZ molecules. Pyrene is often used as the probe to determine the microenvironmental polarity of microemulsions by observing its fine fluorescence structure. The intensity ratio of the first peak to the third peak (I_1/I_3) of the fluorescence spectrum of pyrene shows the microenvironmental polarity where the probe exists. It is well-known that pyrene exists in the membrane phase of O/W and W/O microemulsions closer to the polar head of the surfactant.²⁶ With the addition of PTZ, the decrease of I_1/I_3 for pyrene in O/W and W/O microemulsions also indicates that PTZ molecules reside in the membrane phase of microemulsions.

Figure 7 reveals that the intensity ratio (I_1/I_3) of pyrene is almost unchanged with varying pH ranging from pH 2.0 to 10.0 in SDS/ n -C₅H₁₁OH/H₂O O/W and W/O microemulsions, which indicates the microenvironment property of pyrene remains almost unchanged, so the O/W and W/O microemulsions with and without PTZ are stable in the pH range from 2.0 to 10.0. Figure 7 also indicates that PTZ is still located in the membrane phase of the O/W and W/O microemulsions rather than the aqueous domain even at pH 2.0 when PTZ has protonated.

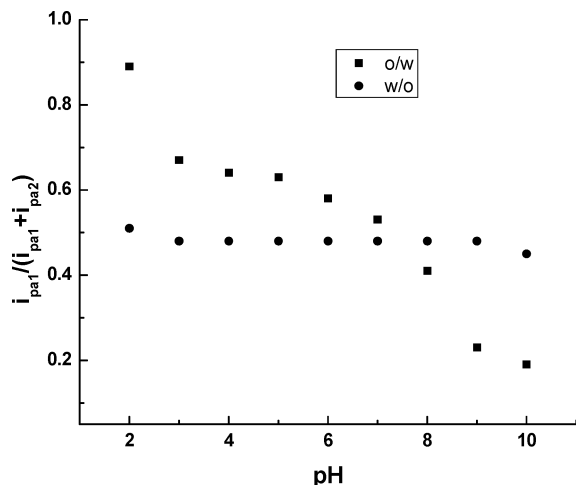


Figure 8. Dependence of $i_{pa1}/(i_{pa1} + i_{pa2})$ for PTZ in the SDS/*n*-C₅H₁₁OH/H₂O microemulsion on pH (the weight ratio of SDS/H₂O being 25.5/74.5 and the *n*-C₅H₁₁OH content as follows: ■ 10.0 wt %, ● 52.0 wt %).

Figure 8 shows the dependence of the location distribution of PTZ in SDS/*n*-C₅H₁₁OH/H₂O O/W and W/O microemulsions on pH. As shown in Figure 8, $i_{pa1}/(i_{pa1} + i_{pa2})$ decreases with increasing pH in O/W microemulsions, which indicates that the molar fraction of PTZ molecules in the membrane phase of the O/W microemulsion with the S atom toward the polar head of SDS increases with pH.

In O/W microemulsions, below pH 7.0, H⁺ partitions toward the microdroplet, and the hydrogen bond between H⁺ and N atom in PTZ forms easily. The stronger hydrogen bond between H⁺ and the N atom in PTZ makes more PTZ molecules reside in the membrane phase of O/W microemulsions with the N atom toward the polar head of SDS. In addition, PTZ begins to partially protonate with the continuous decrease of pH, so there exists an electrostatic attractive interaction between the partially protonated PTZ and the polar head of SDS apart from the hydrogen bond between PTZ and H⁺, which also leads more PTZ molecules to reside with the N atom toward the polar head of SDS. At pH 2.0, the very high value of $i_{pa1}/(i_{pa1} + i_{pa2})$ may be attributed to the fully protonated N atom in PTZ at low pH. Furthermore, H⁺ can work as counterion to decrease the negative electron density of the microdroplet of microemulsions and weaken the hydrogen bond formed between the -SO₄⁻ and the -NH in PTZ, which does not play an important role here.

Above pH 7.0, the OH⁻ partitioning to the O/W microdroplet of the microemulsions weakens the hydrogen bond between *n*-C₅H₁₁OH and PTZ because the hydrogen bond between OH⁻ and *n*-C₅H₁₁OH forms more easily,²⁷ which will cause more PTZ molecules to reside in the membrane phase of the O/W microemulsion with the S atom toward the polar head of SDS at higher pH.

In contrast to what is observed in the O/W microemulsion, no significant effect of pH on the location distribution of PTZ is observed in the W/O microemulsion. As can be seen from Figure 8, $i_{pa1}/(i_{pa1} + i_{pa2})$ is almost unchanged within the range from pH 3.0 to 9.0 in W/O microemulsions. $i_{pa1}/(i_{pa1} + i_{pa2})$ increases slightly at pH 2.0 and decrease slightly at pH 9.0 in W/O microemulsions. Just as in the O/W microemulsion, at pH 2.0 the hydrogen bond between PTZ and H⁺, and the electrostatic attractive interaction between the partially protonated PTZ and the polar head of SDS, both cause the increase of $i_{pa1}/(i_{pa1} + i_{pa2})$ in W/O microemulsions. At pH 10.0, the weaker

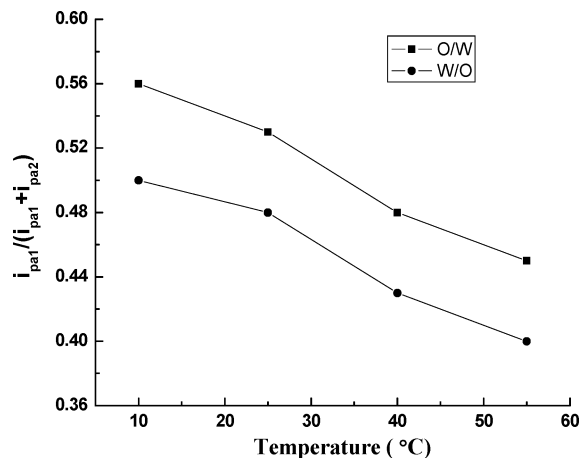


Figure 9. Dependence of $i_{pa1}/(i_{pa1} + i_{pa2})$ for PTZ in SDS/*n*-C₅H₁₁OH/H₂O microemulsions on the temperature (the weight ratio of SDS/H₂O being 25.5/74.5 and the *n*-C₅H₁₁OH content as follows: ■ 10.0 wt %, ● 52.0 wt %).

hydrogen bond between *n*-C₅H₁₁OH and PTZ caused by OH⁻ causes the decrease of $i_{pa1}/(i_{pa1} + i_{pa2})$ in W/O microemulsions.

Then, why is the effect of pH on the location distribution of PTZ slight in W/O microemulsions? In general, W/O microemulsions appear to exert a “buffering” effect,^{28,29} and there is a pH gradient in the W/O microdroplet, so the H⁺ or OH⁻ concentration is lower in the membrane phase of the W/O microemulsion than that in the water pools.³⁰ In addition, PTZ resides in the membrane phase in the W/O microemulsion farther away from the polar head compared with that in the O/W microemulsion, so the effect of pH on the location distribution in W/O microemulsions is much less obvious than that in O/W microemulsions.

The above discussions also reveal that the hydrogen bond between the -NH in PTZ and *n*-C₅H₁₁OH (or the -SO₄⁻ of SDS) is a key factor in determining the location distribution of PTZ in the membrane phase of the microemulsion.

Effect of Temperature. Figure 9 shows the dependence of location distribution of PTZ in the SDS/*n*-C₅H₁₁OH/H₂O O/W and W/O microemulsions on the temperature. As shown in Figure 9, $i_{pa1}/(i_{pa1} + i_{pa2})$ decreases with the increase of temperature, which indicates that the molar fraction of PTZ molecules in the membrane phase of the microemulsion with the S atom toward the polar head of SDS increases with temperature.

It is well-known that the hydrogen bond forms easily at low temperature, so the hydrogen bond between the -NH in PTZ and *n*-C₅H₁₁OH (or the -SO₄⁻ of SDS) becomes weaker with the increase of temperature, which causes fewer PTZ molecules to reside in the membrane phase of the microemulsion with the N atom toward the polar head of SDS. Generally, the aggregation number of the microdroplets of the microemulsions increases, but the charge density of the microdroplets of the microemulsions decreases with the increase of temperature.³¹ Thus, the electrostatic interaction between the polar head of SDS and the N atom (or S atom) in PTZ becomes weaker with the increase of temperature, which causes more PTZ molecules to reside in the membrane phase of the microemulsion with the N atom toward the polar head of SDS. But, this does not matter much here.

Conclusions

In SDS/*n*-C₅H₁₁OH/H₂O W/O and O/W microemulsions, PTZ molecules exist in the membrane phase of the microemulsion

either with the N atom or with the S atom toward the polar head of SDS, which explains the two oxidation peaks in the cyclic voltammogram. The compositions and structures of the microemulsions, the salt, pH, UV-irradiation, and temperature all affect the distribution of the two locations for PTZ in the membrane phase of the microemulsions. The added $n\text{-C}_5\text{H}_{11}\text{OH}$ and increased temperature cause more PTZ molecules to reside in the membrane phase of the microemulsion with the S atom toward the polar head of SDS. The inorganic salt causes more PTZ molecules to reside with the S atom toward the polar head of SDS in the O/W microemulsion and with the N atom toward the polar head of SDS in the W/O microemulsion. At low pH, PTZ tends to reside in the membrane phase of the microemulsion with the N atom toward the polar head of SDS because of the stronger hydrogen bond between PTZ and H^+ , and at high pH, PTZ tends to reside in the membrane phase of the microemulsion with the S atom toward the polar head because of the weaker hydrogen bond between PTZ and $n\text{-C}_5\text{H}_{11}\text{OH}$ caused by OH^- . The UV-irradiation causes more PTZ molecules to reside in the membrane phase of the microemulsion with the N atom toward the polar head of SDS. Our results suggest that cyclic voltammetry may provide a powerful means for investigating the exact location of electroactive guest molecules with two or more polar moieties in heterogeneous host systems including micelles, microemulsions, liquid crystals, phospholipid bilayers, etc.

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