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The Catalysis of Sodium Dodecyl Sulfate/1-Pentanol/Water W/O Microemulsion on the Photoisomerization of *trans*-Stilbene

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Abstract: The photoisomerization of *trans*-stilbene was studied in the water in oil (W/O) micro-emulsion formed by SDS (sodium dodecyl sulfate), *n*-$C_5H_{11}OH$ (1-pentanol) and H_2O. The experimental results show that after 2-minute UV-irradiation, the yield of *cis*-stilbene is higher in W/O microemulsion than in homogeneous solvent—*n*-$C_5H_{11}OH$.

Keywords: *trans*-Stilbene, 1-pentanol, photoisomerization, microemulsion.

In recent years, great attention has been paid to the application and research of photochromic materials in high-technology area[1]. *cis-trans* Photoisomerization is an important reaction in photochromics. However, it should be noted that the low transition yield and (or) the slow reaction rate for many photoisomerization reactions limit their applications. Thus, how to improve the sensitivity of these reactions to light is very interesting and important. It is well known that the rate and the yield for *cis-trans* photoisomerization are closely related to the nature of the medium, such as the polarity, rigidity, viscosity, and so on[2]. Microemulsion, a kind of molecular organized assembly, is optically transparent, isotropic and thermodynamically stable mixture[3]. Their physical properties, for example, the viscosity, structure and polarity, can be easily adjusted by changing their composition. However, up to now, the reports on the photochemical behaviors of organic compounds in microemulsions are few, although many meaningful results have been obtained by using microemulsion as microreactor in other fields[4].

Thus, in the present paper, we use SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion[3] as micro-reactor for *cis-trans* photoisomerization in order to improve its photo-sensitivity. *trans*-Stilbene is chosen as the reactant since its photoisomerization reaction is often used as a model for the dynamic study of photoisomerization reactions[2].

Experimental

SDS was obtained from Sigma (98%) and was recrystallized twice in ethanol. 1-Pentanol (*n*-$C_5H_{11}OH$) was in analytical grade from Shanghai Chemicals. trans-Stilbene (TS, Fluka, 97%) was used as obtained. Water used was deionized and distilled twice. Pyrene was obtained from Sigma. A 125-W high-pressure mercury lamp (Shanghai

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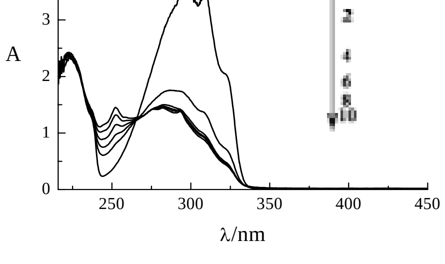
Yaming lamp factory) was used as the excitation source and the photoisomerization was carried out in a quartz cells. Fluorescence intensity was measured by a Shimadzu RF-540 fluorescence spectrophotometer at (30±0.1)℃ with a slit of 1.5 nm. UV-Vis absorption spectra of TS were measured by using a Shimadzu UV-2501 ultraviolet spectrophotometer at room temperature. The medium in which the photoisomerization of TS was carried out was used as the reference solution.

Results and Discussion

When the weight ratio of SDS/n-$C_5H_{11}OH/H_2O$ is 15/68/17, the microemulsion shows water in oil (W/O) structure[3]. **Figure 1** shows the Uv-vis spectra of TS with different UV-irradiation time in the above microemulsion. With the increase of irradiation time, the absorbance value at 296 nm (A_{296}) reduces gradually and the absorbance value at 250 nm (A_{250}) rises accordingly. The maximum absorption wavelength for TS is at 296 nm and that for *cis*-stilbene (CS) is at 250 nm[5]. Meanwhile, the molar extinction coefficient for CS at 296 nm is 10 times smaller than that for TS and the molar extinction coefficient for CS at 250 nm is 10 times larger than that for TS[5]. Thus, the concentration of CS is increased gradually with UV-irradiation time and A_{296} can reflect the concentration of unreacted TS[6]. Moreover, the existence of the isosbestic point (266 nm) and the constant absorbance value in 220 nm (**Figure 1**) indicated that there were no other products formed[7]. Further study shows that when the concentration of TS (C_{ts}) is smaller than 1.8×10^{-4} mol/L, the plot of A_{296} *versus* C_{ts} in SDS/n-$C_5H_{11}OH/H_2O$ W/O microemulsion obeys Lambert-Beer’s Law. Since C_{ts} before UV-irradiation (**Figure 1**) is 1.2×10^{-4} mol/L, the absorbance at 296 nm at different UV-irradiation time ($A_{296}(t)$) can be used to calculate the concentration of TS ($C_{ts}(t)$) according to eq. 1. Then, the CS yield (%CS) can be obtained by eqs. 2~3. Here, ε is the molar extinction coefficient of TS at 296 nm, $C_{ts}(0)$ the concentration of TS before UV-irradiation, $A_{296}(0)$ the absorbance of TS at 296 nm before UV-irradiation and $C_{cs}(t)$ the concentration of CS after t-minute UV-irradiation.

Figure 1 UV-vis absorption spectra of TS (1.2×10^{-4} mol/L) *versus* irradiation time in SDS/n-$C_5H_{11}OH$ /H_2O W/O microemulsion



$$A_{296}(t) = \varepsilon \cdot C_{ts}(t) \cdot l \tag{1}$$

$$C_{cs}(t) = C_{ts}(0) - C_{ts}(t) \tag{2}$$

$$\%CS = \frac{C_{cs}(t)}{C_{ts}(0)} = \frac{A_{296}(0) - A_{296}(t)}{A_{296}(0)} \tag{3}$$

If *n*-$C_5H_{11}OH$ was used as solvent, the isosbestic point (266 nm) and the absorbance at 220 nm were also irrelevant with the irradiation time (Figure not shown), showing in this case, there were no other product, except for CS.

Table 1 Fluorescence parameters and CS yield (%CS) after 2-minute UV-irradiation in the two different media

Medium	% CS	I_f (TS)
n-$C_5H_{11}OH$	30	106
W/O microemulsion*	52	77

*weight ratio of SDS/*n*-$C_5H_{11}OH/H_2O$ is 15/68/17

Table 1 lists the CS yield after 2-minute UV-irradiation. The data shows that the yield for CS in SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion is obviously higher than that in *n*-$C_5H_{11}OH$. Further study indicates that the fluorescence intensity (I_f) of TS in *n*-$C_5H_{11}OH$ is different from that in SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion (**Table 1**). Since *n*-$C_5H_{11}OH$ exists as the oil continuous phase in SDS/*n*-$C_5H_{11}OH/H_2O$ W/O micro-emulsion, **Table 1** indicates that TS can be located in the membrane phase of this microemulsion. The effect of TS on the microenvironmental polarity of pyrene also states the above conclusion. The fluorescence spectrum of pyrene is formed by five peaks, which are marked 1 through 5 from the shortest wavelength peak. By the intensity ratio of the fist peak to the third peak (I_1/I_3), which is sensitive to pyrene environment, the microenvironmental polarity of microemulsions could be measured[8]. **Table 2** shows that the value of I_1/I_3 in SDS/*n*- $C_5H_{11}OH/H_2O$ W/O microemulsion is a little higher than that in *n*-$C_5H_{11}OH$ without TS, which indicates that pyrene can be located in microemulsion droplet and the polarity of the microenvironment where pyrene is located is larger than that in *n*-$C_5H_{11}OH$[8]. In the presence of TS, the value of I_1/I_3 in the microemulsion is higher than that without TS (**Table 2**), which shows that TS can make pyrene molecules to move to the inner part of the membrane phase. Thus, it can be concluded that TS can be located in the membrane phase of this microemulsion.

Here, it should be theoretically noted that, once a fluorescence active molecule exists in the micellar drop, the I_f of this molecule will increase obviously due to the increase of

Table 2 The value of I_1/I_3 of pyrene with and without TS in the two different media

TS (mol/L)	I_1 / I_3	
	n-$C_5H_{11}OH$	W/O microemulsion*
0	0.98	1.00
1.0×10^{-5}	0.99	1.05

*weight ratio of SDS/*n*-$C_5H_{11}OH/H_2O$ is 15/68/17 the rigidity of its microenvironment[9]. However, **Table 1** shows that I_f of TS in SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion is smaller than that in *n*-$C_5H_{11}OH$. To explain this result, let us consider the currently accepted mechanism for photoisomerization of TS:

$$TS \xrightarrow{h\nu} TS^* \tag{4}$$

$$TS^* \rightarrow TS + h\nu \tag{5}$$

$$TS^* \rightarrow [P] \rightarrow CS \tag{6}$$

$$TS^* \xrightarrow{nonradiative-physical-decay} TS \tag{7}$$

where TS* indicate the excited TS molecule, [P] is the transition state formed by internal rotation of the double-bond in TS* molecule. Eq. 6, nonradiative chemical decay process for TS*, and Eq. 7, nonradiative physical decay processes can decrease the I_f of TS*. If the lower I_f of TS in SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion were caused by energy change between SDS and TS* (eq. 7), the photoisomerization rate of TS would not be higher than that in *n*-$C_5H_{11}OH$. So it can be concluded that Eq. 6 leads to the lower I_f in W/O microemulsion, *i.e.*, SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion can catalyze the photoisomerization of TS by facilitate the internal rotation of the double-bond in TS* molecule.

In conclusion, compared with *n*-$C_5H_{11}OH$, SDS/*n*-$C_5H_{11}OH/H_2O$ W/O microemulsion possesses catalysis effect on the photoisomerization of TS.

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