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ORIGINAL CONTRIBUTION

# The photoisomerization of *trans*-stilbene in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions

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**Abstract** Different from organic solvent, self-assemblies are environment friendly media, and moreover, if they are used as micro-reactor, many meaningful and exciting results may be obtained. In this paper, we investigated the photoisomerization of *trans*-stilbene in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions (a kind of self-assemblies) with different compositions and structures to establish the relationship between the reaction yields and the compositions and structures of microemulsions. The results show that the yield of *cis*-stilbene is increased with the increase of water content or with the decrease of Triton X-100 content, and oil in water (O/W) structure is the best structure for this reaction, which makes it possible to decrease the pollution of environment by organic solvent always used in organic reactions.

**Keywords** Photoisomerization · *trans*-stilbene · Microemulsion

## Introduction

Self-assemblies are usually composed of surfactants, cosurfactants, and water [1, 2], and their physical properties, for example, the droplet size, viscosity, structure, and microenvironmental polarity, can easily be adjusted by changing their compositions. Thus, many researchers [3–6] are interested in using self-assemblies rather than homogeneous solvent (such as alcohols, benzenes, nitriles, and so on) as micro-reactor to carry out reactions and prepare nanoparticles, medicines, etc. On the one hand, the application of this kind of micro-reactor can reduce the pollution of environment caused by organic solvents; on the other hand, reaction rate and yield may be increased in micro-reactor.

*cis-trans* Photoisomerization is an important reaction in photochemistry. However, the low transition yield and (or) the slow reaction rate for many photoisomerization reactions limit their applications [7–11]. Thus, how to improve the sensitivity of these reactions to light is both of interest and technically importance. As the rate and yield for *cis-trans* photoisomerization are closely related to the properties of the medium, such as the polarity, viscosity, and so on [12], selecting a new and efficient medium or adjusting the microenvironment of the reactant(s) may be one way to solve the above problems.

Microemulsion is a kind of self-assembly, and it is clear, thermodynamically stable, and optically transparent [2]. In the present paper, we use Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions with different structures and different compositions as micro-reactor for photoisomerization of *trans*-stilbene (TS), with the intention of finding information on how to optimize the reaction condition for photoisomerization and decrease the pollution by organic solvents. *trans*-Stilbene is chosen as reactant because its photoisomerization reaction is often used as a model for the dynamic study of photoisomerization reactions [12].

## Experimental

### Materials

*trans*-Stilbene (TS, Fluka, 97%), Triton X-100 (Sigma, >98%), *n*-$C_5H_{11}OH$ (Fluka, >98%), and pyrene (Sigma,

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99%) were used as obtained. Water used was deionized and distilled twice.

### Photoisomerization of TS

A 125-W high-pressure mercury lamp (Shanghai Yaming lamp factory, China) was used as the excitation source. The photoisomerization reaction of TS ($1.2\times10^{-4}$ mol/l) was carried out in a quartz tube with a diameter of 1.0 cm at 25 °C. The distance between the mercury lamp and the quartz tube was 5.0 cm.

### Measurement of the UV-Vis absorption spectra

UV-Vis absorption spectra of TS in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ systems were measured by using a Shimadzu MPS-2000 ultraviolet spectrophotometer at room temperature. Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system in which the photoisomerization reaction of TS was carried out was used as reference solution.

### Measurement of the fluorescence intensity

The emission spectra for TS ($5.0\times10^{-5}$ mol/l) in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions before UV-irradiation were measured by a Shimadzu RF-540 fluorescence spectrophotometer at 30.0±0.1 °C with excitation and emission slits of 1.5 nm. The excitation wavelength and emission wavelength were 320 and 350 nm, respectively.

### Determination of microenvironmental polarity

Pyrene was used as the probe to determine the microenvironmental polarity of the system by observing its fluorescence fine structure [13]. The fluorescence spectrum of pyrene was formed by five peaks, which are marked 1 through 5 from the shortest wavelength peak. By the intensity ratio $I_1/I_3$ of the first peak (at about 373 nm) to the third peak (at about 384 nm), which is sensitive to pyrene environment, the microenvironmental polarity of the micelles or microemulsions could be measured. Pyrene's concentration was $1.0\times10^{-6}$ mol/l and the experimental temperature 30.0±0.1 °C.

### Determination of the viscosity

The viscosities of the samples were determined with a capillary viscometer (NXS-11 type, Chengdu instrument factory) at 25.0±0.1 °C. By comparing the flow times required for the samples (i.e., Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions) level and water level in the capillary viscometer to drop from one line to the other as the fluid drains through the capillary, the relative viscosity of the samples could be obtained.

## Results and discussion

Figure 1, redrawn from [14], is the partial phase diagram for Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system and the symbols circle and cross in Fig. 1 represent the microemulsions used in this study. According to this figure, the structure of Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system can be controlled by changing the contents of Triton X-100 and/or $H_2O$. The line connecting the symbols circle and cross both pass through oil in water microemulsion (O/W) region, bicontinuous structure (BI) region, and water in oil microemulsion (W/O) region (Fig. 1). And the Triton X-100/*n*-$C_5H_{11}OH/H_2O$ systems symbolized by cross have a same weight ratio (4/3) of Triton X-100/*n*-$C_5H_{11}OH$ and different water content while those marked with circle are composed of a same weight ratio (1/10) of *n*-$C_5H_{11}OH/H_2O$ and different Triton X-100 content. Thus, by studying the photoisomerization of TS in all the above Triton X-100/*n*-$C_5H_{11}OH/H_2O$ systems, both of the effects of composition and structure of the Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system on the photoisomerization of *trans*-stilbene can be elucidated.

### Effect of water content on the photoisomerization of TS

Figure 2 exemplifies the UV-Vis spectra of TS ($1.2\times10^{-4}$ mol/l) in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsion before

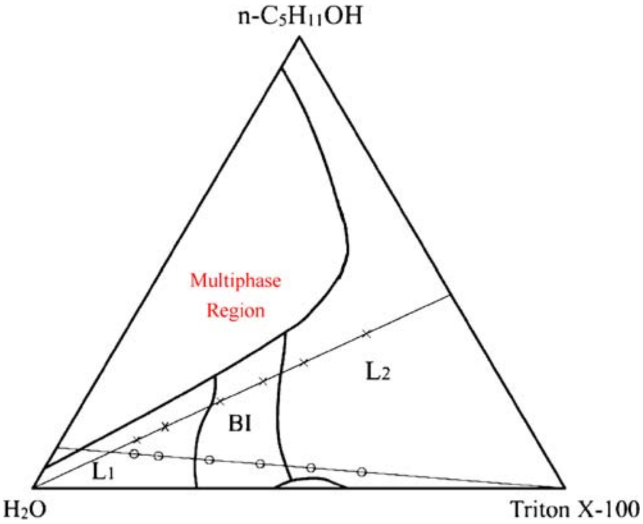

**Fig. 1** Partial phase diagram of Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system at 25.0±0.1 °C. $L_1$, BI, and $L_2$ show the Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions with O/W structure, bicontinuous structure, and W/O structure, respectively. Symbols, *circle* and *cross*, represent the microemulsions used in this study

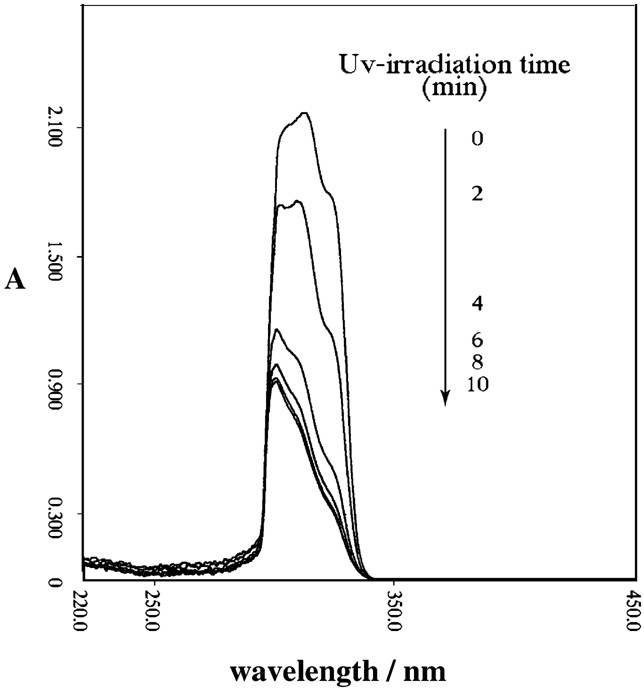

**Fig. 2** UV-Vis absorption spectra of TS ($1.2 \times 10^{-4}$ mol/l) with UV-irradiation time in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsion at the weight ratio of Triton X-100/$H_2O$/n-$C_5H_{11}OH$ being 15.7:82.3:2.0

UV-irradiation (the top curve) and at different UV-irradiation time (curves other than the top one). The maximum wavelength for TS is at about 310 nm [15]. From Fig. 2, it can be seen that the absorbance at 310 nm ($A_{310}$) is gradually reduced with the increase of the UV-irradiation time. The facts that *cis*-stilbene (CS) has no obvious absorption peak in this system and the absorbance at 220 nm remains constant indicate that there is no product other than *cis*-stilbene for this reaction [15]. Before UV-irradiation, the plot of $A_{310}$ vs the concentration of TS ($C_{\mathrm{TS}}$) in all the microemulsions used in this study obeys Lambert–Beer's Law when $C_{\mathrm{TS}}$ is less than $1.5 \times 10^{-4}$ mol/l (data not shown). As the concentration of TS before UV-irradiation is $1.2 \times 10^{-4}$ mol/l (the top curve in Fig. 2), the absorbance after UV-irradiation at 310 nm (curves other than the top one in Fig. 2) can be used to calculate the concentration of TS at different UV-irradiation times [$C_{\mathrm{TS}}(t)$], and then CS yield (%CS) can be obtained Eq. 1.

$$\%\mathrm{CS} = \frac{C_{\mathrm{CS}}(t)}{C_{\mathrm{TS}}(0)} = \frac{C_{\mathrm{TS}}(0) - C_{\mathrm{TS}}(t)}{C_{\mathrm{TS}}(0)} = \frac{A_{310}(0) - A_{310}(t)}{A_{310}(0)} \tag{1}$$

Here, $C_{\mathrm{TS}}(0)$ is the concentration of TS before UV-irradiation, $A_{310}(0)$ shows the absorbance of TS at 310 nm before UV-irradiation, and $A_{310}(t)$ and $C_{\mathrm{CS}}(t)$ are the absorbance of TS at 310 nm and the concentration of CS after *t*-minute UV-irradiation, respectively.

Figure 3 shows the relationship between the water content and the value of %CS after 2-min UV-irradiation in the Triton X-100/*n*-$C_5H_{11}OH/H_2O$ systems at the weight ratio of Triton X-100/*n*-$C_5H_{11}OH$ being 4:3. It can be seen from Fig. 3 that %CS is increased generally with the increase of the weight of water. Moreover, when water content is changed from 55 to 75%, %CS is increased much more obviously compared with the case when water content is increased from 20 to 55%. When the weight ratio of Triton X-100/*n*-$C_5H_{11}OH$ is fixed as 4:3, Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system shows O/W structure with water content larger than 57%, BI structure with water content between 57 and 40% and W/O structure with water content smaller than 40% (Fig. 1). Thus, it can be concluded from Fig. 3 that increasing water content in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system is favorable to the photoisomerization of TS, and O/W microemulsion is the best medium for this reaction. This result is very exciting because it can decrease the pollution of the environment by organic solvents, which are generally used.

The following shows the currently accepted mechanism for photoisomerization of TS [11, 12, 15–17]:

$$TS \xrightarrow{hv} TS^* \tag{2}$$

$$\mathrm{TS}^* \rightarrow \mathrm{TS} + \mathrm{hv} \tag{3}$$

$$\mathrm{TS}^* \rightarrow [P] \rightarrow \mathrm{CS} \tag{4}$$

$$TS^* \xrightarrow{nonradiative-physical-decay} TS \tag{5}$$

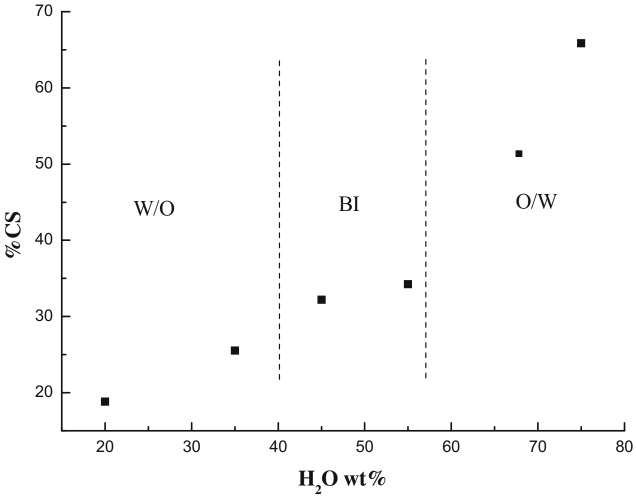

**Fig. 3** CS yield (%CS) after 2-min UV-irradiation in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions with water content (the weight ratio of Triton X-100/*n*-$C_5H_{11}OH$ is 4:3)

where TS* indicates the excited TS molecule and [*P*] is the transition state formed by the internal rotation of the double-bond in TS* molecule. Equations 3 and 5 show the radiative physical decay (fluorescence emission process in this case) and the possible nonradiative physical decay (such as energy change between TS* and other molecules, "self-quenching" reaction and so on) for TS*, respectively. Equation 4 shows the photoisomerization reaction of TS, which can also be called the chemical decay for TS*. Thus, the processes shown by Eqs. 3, 4, and 5 compete with each other. Fig. 4 shows the fluorescence intensity ($I_f$) of TS before irradiation is increased gradually with the increase of the water content. As %CS and $I_f$ of TS are both increased with water weight (Figs. 3 and 4), they are not caused by the competition between Eqs. 3 and 4 but by the competition of Eq. 5 with Eqs. 3 and 4, implying that the increase of water content could depress the process shown by Eq. 5. Table 1 shows that the addition of TS can make the fluorescence intensity ratio $I_1/I_3$ of the first peak to the third peak for pyrene decreased, implying that the addition of TS could make the microenvironmental polarity for pyrene decreased. Because pyrene molecules are located in the membrane phase of microemulsion droplet [13], TS should be located in the membrane phase, too (if TS molecules were not in the membrane phase, they could not change the microenvironmental polarity for pyrene and then, $I_1/I_3$ value must remain unchanged). The fluorescence intensity of TS in pure $n$-$C_5H_{11}OH$ is 106, much smaller than that in microemulsion (Fig. 4), indicating again that TS molecules should not be located in the oil continuous phase but located in the membrane phase of microemulsion droplet. The membrane phase of microemulsion droplet is formed by the interaction among the hydrophobic chains of surfactant molecules. According to the previous studies [12], the chain length of alkane has little effect on the photoisomerization of TS when liquid alkane is used as solvent. Then, why is CS yield different in different microemulsions?

**Table 1** The $I_1/I_3$ values of pyrene in Triton X-100/$n$-$C_5H_{11}OH/H_2O$ microemulsions

| Triton X-100/$n$-$C_5H_{11}OH$ | 4/3 | | | |
|---|---|---|---|---|
| $H_2O\%$ | 35 | 45 | 55 | 75 |
| $I_1/I_3$[a] | 1.323 | 1.305 | 1.289 | 1.258 |
| $I_1/I_3$[b] | 1.287 | 1.273 | 1.250 | 1.204 |
| Structure[c] | W/O | BI | BI | O/W |

[a] [TS]=0 mol/L

[b] [TS]=$1.0\times10^{-5}$ mol/l

[c] See Fig. 1

Microemulsion, a kind of self-assembly, is different from homogenous solvent; the size and properties of microemulsion droplet are closely related to the composition of microemulsion. With the increase of water content, the size of Triton X-100/$n$-$C_5H_{11}OH/H_2O$ microemulsion droplet is decreased, and hence, the movement of TS molecules could be restricted, which may depress the nonradiative decay process (Eq. 5). Moreover, with the increase of water, the viscosity of Triton X-100/$n$-$C_5H_{11}OH/H_2O$ system is decreased (Fig. 5), which could make the rotation of the double bond in TS molecule easier [12, 17]. The depression of the nonradiative decay process for TS and the enhancement of the rotation of the double bond in TS are both beneficial to the photoisomerization of TS. Thus, %CS is increased with water.

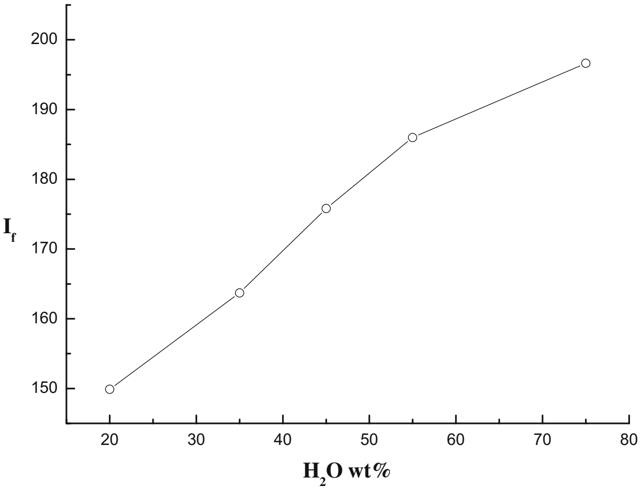

**Fig. 4** The fluorescence intensity $I_f$ of TS in Triton X-100/$n$-$C_5H_{11}OH/H_2O$ microemulsions with water content before UV-irradiation (the weight ratio of Triton X-100/$n$-$C_5H_{11}OH$ is 4:3)

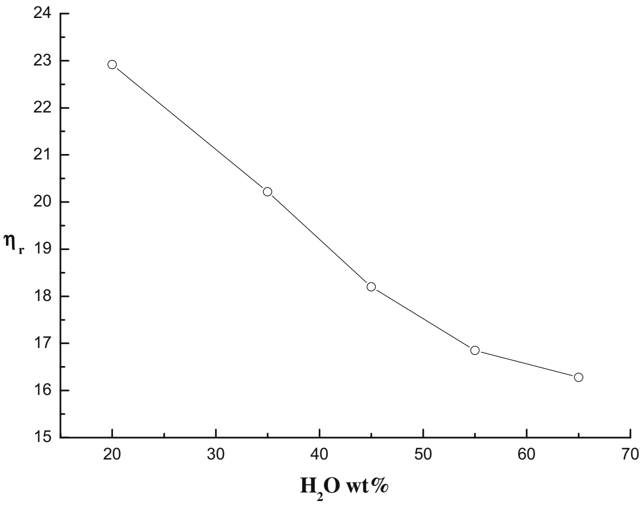

**Fig. 5** The relative viscosity of Triton X-100/$n$-$C_5H_{11}OH/H_2O$ microemulsions with water content (the weight ratio of Triton X-100/$n$-$C_5H_{11}OH$ is 4:3)

## Effect of Triton X-100 content on the photoisomerization of TS

Figure 6 shows after 2-min UV irradiation, %CS in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ systems with a constant weight ratio (1:10) of *n*-$C_5H_{11}OH/H_2O$ is decreased with Triton X-100. Figure 7 shows that the fluorescence intensity of TS is decreased with Triton X-100 before UV-irradiation. The size of microemulsion droplet is increased with the increase of Triton X-100 content, and hence, the nonradiative decay process for excited TS molecules (Eq. 5) should be enhanced due to a larger freedom for the movement of TS molecules with the addition of Triton X-100. As a result, the photoisomerization of TS could be depressed. Moreover, the viscosity for Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system is increased with Triton X-100 (Fig. 8), which may make the rotation of the double bond in TS more difficult [12, 17] and hence decrease %CS.

When the weight ratio of *n*-$C_5H_{11}OH/H_2O$ is 1:10, the Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system shows O/W structure with Triton X-100 content smaller than 27%, BI structure with Triton X-100 content between 27 and 46%, W/O structure with Triton X-100 content larger than 46% (Fig. 1). Thus, Fig. 6 also indicates that O/W microemulsion is the best microemulsion's structure for photoisomerization of TS.

Moreover, we also determined %CS in Triton X-100 micelle (i.e., Triton X-100/$H_2O$ system) with the weight ratio of Triton X-100 to water being 16:84. It is 21. According to Fig. 1, from left to right, both of the first Triton X-100/*n*-$C_5H_{11}OH/H_2O$ systems marked with cross and circle have a weight ratio of Triton X-100 to water of 16:84. According to Figs. 3 and 6, %CS in them are 66 (when *n*-$C_5H_{11}OH$ content is 11%, Fig. 3) and 33 (when *n*-$C_5H_{11}OH$ content is 7%, Fig. 6), respectively. Thus, the addition of *n*-$C_5H_{11}OH$ is favorable to the formation of CS. However, if we just use *n*-$C_5H_{11}OH$ as solvent, %CS is 30. Thus, by modulating the composition of Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system, we can get higher yield for CS in microemulsion than in organic solvent (*n*-$C_5H_{11}OH$ in this case), which is not only helpful in protecting environments but also useful to wide the application of photoisomerization reaction.

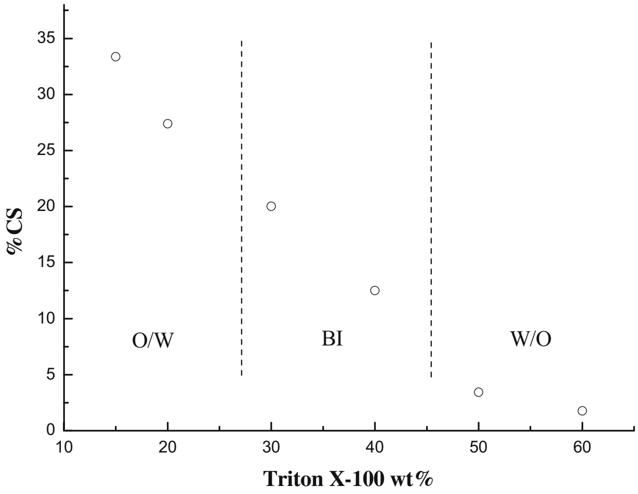

**Fig. 6** CS yield (%CS) after 2-min UV-irradiation in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions with Triton X-100 content (the weight ratio of *n*-$C_5H_{11}OH/H_2O$ is 1:10)

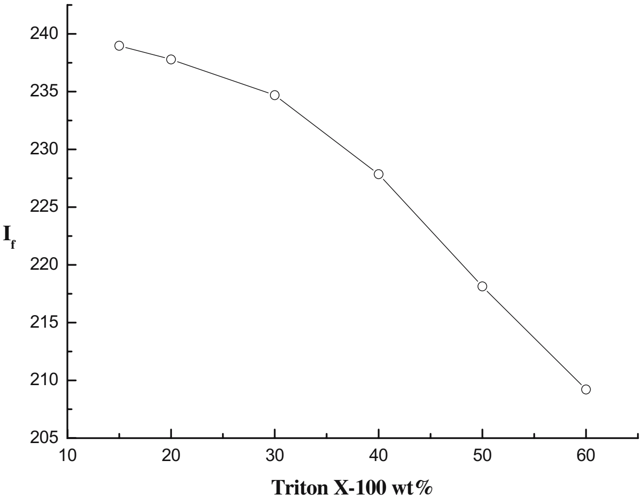

**Fig. 7** The fluorescence intensity $I_f$ of TS in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions with Triton X-100 content before UV-irradiation (the weight ratio of *n*-$C_5H_{11}OH/H_2O$ is 1:10)

## Conclusion

The photoisomerization yield of TS in Triton X-100/*n*-$C_5H_{11}OH/H_2O$ system is increased with the increase of

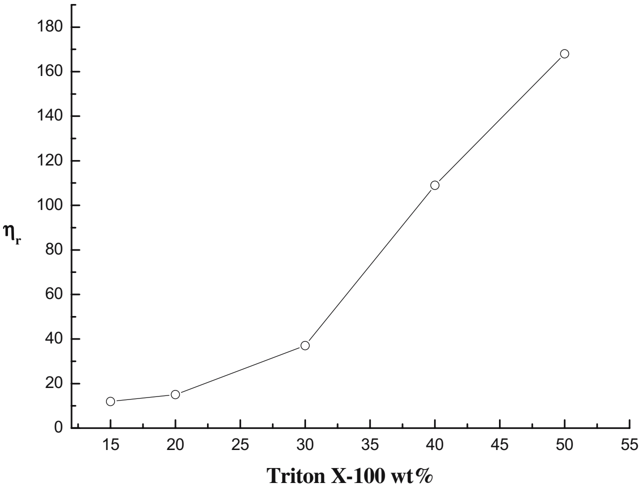

**Fig. 8** The relative viscosity of Triton X-100/*n*-$C_5H_{11}OH/H_2O$ microemulsions with Triton X-100 content (the weight ratio of *n*-$C_5H_{11}OH/H_2O$ is 1:10)

$H_2O$ content or with the decrease of Triton X-100 content. Compared with the W/O structure and BI structure, O/W structure is a better medium. Moreover, compared with Triton X-100 micelle (without $n$-$C_5H_{11}OH$), the addition of $n$-$C_5H_{11}OH$ in Triton X-100/$H_2O$ system is more helpful for the formation of CS. However, by modulating the composition of O/W microemulsion, %CS in O/W microemulsion can be higher than in pure $n$-$C_5H_{11}OH$.

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