

## 수용성 미셀용액에서 몇 가지 안트라센 유도체의 가용화 및 감광화 성질

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## Solubilization and Photosensitizing Properties of Some Anthracene Derivatives in Aqueous Micellar Solutions

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**요 약.** 메탄올-물 혼합용매 및 수용성 CTAB, SDS 용액에서 2-에틸안트라센[2-EA]과 9-페닐안트라센[9-PA]에 빛을 조사하는 동안 1,3-디페닐이소벤조푸란[DPBF]이 감소되는 것으로부터 이 반응에 단일항 산소(<sup>1</sup>O<sub>2</sub>)가 관여된다는 화학적 증거를 얻었다. 용매의 극성에 민감한 UV 분광학적 특성을 이용하여 2-EA와 9-PA의 평균미세환경의 극성을 조사하였다. 2-EA와 9-PA가 수용성 CTAB, SDS 및 Brij 35 용액에 가용화될 때 그들의 평균 미세환경은 극성이었으며, 미세환경의 극성 파라미터는 미셀의 이온성에 영향을 받지 않았다. 2-EA의 평균 미세환경의 극성은 40%(w/w) 에탄올 수용액의 극성과 비슷했으며, 9-PA의 경우는 30%(w/w)와 40%(w/w) 사이의 에탄올 수용액의 극성과 비슷했다. 이들 화학종들이 수용성 미셀용액에 가용화될 때 대부분 미셀의 표면에 분포할 것이라는 것을 알았다. 여러 용매에서 2-EA와 9-PA의 광증감능을 검토하였다. 메탄올-물 혼합용매가 수용성 미셀용액보다 광산화반응에 유리한 것으로 나타났다.

**ABSTRACT.** The chemical evidence for involvement of singlet oxygen during photoirradiation for 2-ethylanthracene [2-EA] and 9-phenylanthracene [9-PA] was based on the rapid decomposition of 1,3-diphenylisobenzofuran [DPBF] in methanol-water mixture and aqueous CTAB, and SDS micellar solutions. The average microenvironmental polarities of 2-EA and 9-PA were estimated by UV spectroscopic characteristics sensitive to the polarity of solvent. When 2-EA and 9-PA were solubilized in aqueous CTAB, SDS and Brij 35 solutions, their average microenvironmental polarities were polar, and their microenvironmental polarity parameter showed little dependence on the ionic properties of the micelles. The average microenvironmental polarity of 2-EA was similar to the polarity of 40% (w/w) aqueous ethanol, and that of 9-PA was similar to the polarity between 30 and 40% (w/w) aqueous ethanol. It was found that the greater part of these species might be distributed at the surface of micelles when they were solubilized in aqueous micellar solutions. The methanol-water mixture solution appeared to have characteristics more favorable for photooxidation reaction than aqueous micellar solutions.

### INTRODUCTION

Most of the sensitized oxidations proceed via the triplet state sensitizer and there are two major classes of reaction open to the triplet sensitizer<sup>1</sup>. In the first, the sensitizer interacts with another

molecule directly, usually with hydrogen atom or electron transfer<sup>2</sup>. The radicals thus formed react further with oxygen or other organic molecules. In the second class of reaction, the triplet sensitizer interacts with oxygen. This interaction is ene-

rgy transfer to give singlet molecular oxygen, which reacts further with various acceptors<sup>3</sup>. DPBF is a popular substrate for photooxidation studies in the liquid phase because of the rapidity with which it reacts with singlet oxygen<sup>4</sup>.

The solubilization of many normally insoluble substances by aqueous micellar solutions is a well known phenomenon. When any species is solubilized in micellar system, information about location, distribution, and orientation of their species acquires a fundamental importance in understanding of the equilibrium or the kinetic aspects of the solubilization process itself and the physical and chemical behavior of the solubilized species. Solubilization in aqueous micellar solutions has been studied extensively<sup>5,6</sup> and it has been noted that micelles serve as good models for membranes and other interfacial systems for investigating such problems<sup>7,8</sup>.

Many investigators have attempted to define the location of molecules solubilized by micelles. A number of techniques have been employed including UV spectroscopy<sup>9-13</sup>, NMR<sup>14,15</sup>, ultrasonic spectroscopy<sup>16</sup>, and fluorescence<sup>17</sup>. Cardinal and Mukerjee<sup>10</sup> identified UV spectral parameters sensitive to solvent polarity. Certain features of the UV absorption spectra of benzene, naphthalene, and some alkylbenzenes have been used to determine the polarity of the microenvironment in solution<sup>9,10,18</sup>. Cardinal Mukerjee have found the three types of polarities sensitive spectral characteristics to test it quantitatively. One of these is  $\epsilon_s/\epsilon_p$  representing the ratio of the absorbance at the position of a solvent-induced band and the adjacent vibronic peak at the lower wavelength. The second is  $R_c$  representing the ratio of the absorbances at two fixed wavelengths, one near a peak and the other near the adjacent valley as in the following equation.

$$R_c = R_{c,m} - \frac{\epsilon_{s,a} (R_c - R_{c,a})}{\epsilon_{c,m} K_m} \frac{\phi_a}{\phi_m} \quad (1)$$

Where  $\epsilon$  is the molar absorptivity,  $\phi$  is the volume fraction, and subscripts  $m$  and  $a$  mean micellar phase and aqueous phase, respectively.  $K_m$  is the

ratio of the concentrations of solubilize in the micellar phase and the corresponding concentration in the aqueous phase. Subscripts  $s$  and  $t$  correspond to the wavelengths. The third is  $R_p$  representing the ratio of the absorbances at the peak and valley obtained from the complete spectrum. These characteristics for benzene, naphthalene, and their derivatives showed the desired continuous variation over the whole polarity scale.

To obtain useful information about the environment of a solute in a micelle from the solvent sensitivity of the UV spectrum of aromatics, a spectroscopic parameter must be found, that can be related to some measurable properties of the solvents chosen. The solvent series chosen for reference purposes essentially represents a dilution of the -OH dipole with hydrocarbon. A new parameter,  $H$ , was defined<sup>10</sup> as the volume concentration of -OH dipoles in a relative of that in water. It was found to be related to the dielectric constant and could also provide a covalent polarity parameter<sup>10</sup>.

The fluorescence studies of 9-PA were performed in other groups<sup>19,22</sup>. It has been shown experimentally and theoretically that many of the aromatic hydrocarbons<sup>23</sup> including 9-PA<sup>24</sup> are effective singlet oxygen ( $^1O_2$ ) sensitizers. And most of the studies have been performed in organic media than micellar solutions. As far as we know, the photosensitizing properties of 2-EA have not been investigated. In this work, UV absorption spectroscopy was used to examine the photosensitizing properties of 2-EA and 9-PA and to estimate the average microenvironmental polarities of these species in some aqueous micellar solutions. The chemical evidence for intermediacy of singlet oxygen during photoirradiations for these species in some micellar solutions was based on the rapid decomposition of DPBF. Cetyltrimethylammonium bromide [CTAB], sodium dodecyl sulfate [SDS], and polyoxyethylene (23) lauryl ether [Brij 35] were taken as surfactants.

## EXPERIMENTS

**Materials.** Methanol and ethanol were obtai-

ned from Merck Chemicals Co. n-Propanol and n-butanol from Wako Chemicals Co. were purified by simple distillation. DPBF from Fluka Chemicals Co. was purified by recrystallization. CTAB, SDS, and Brij 35 from Sigma Chemicals Co. were used as received except for drying over calcium oxide. Deionized double distilled water with a conductivity of  $1.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  was used for preparing solutions.

**Preparing solutions.** For the experiments of solubilization, mixture solvents such as 20, 30, 40, 50 and 80% (w/w) methanol-water mixture and ethanol-water mixture were prepared by simple mixing. The ranges of concentration of the surfactants were 0.1~0.25 mol/l for CTAB, 0.15~0.30 mol/l for SDS, and 0.046~0.25 mol/l for Brij 35, respectively. The concentration of the solubilizes used in this study was in the order of  $10^{-4}$  mol/l so that the mutual interactions between the solubilizes are avoided.

For the experiments of photosensitization, the stock solutions of DPBF were prepared in concentration of  $6.8 \times 10^{-5}$  mol/l. The stock solutions of 2-EA and 9-PA were prepared in concentration of  $5.0 \times 10^{-5}$  mol/l. The range of concentration of the surfactants were  $6 \times 10^{-3}$ ~ $5.0 \times 10^{-2}$  mol/l for CTAB and  $1.0 \times 10^{-2}$ ~ $3.0 \times 10^{-2}$  mol/l for SDS, respectively. All kinds of stock solutions, methanol and water were saturated with oxygen or nitrogen according to circumstances. Nitrogen was purified by using the oxygen trap equipped with  $\text{Cr}_2(\text{SO}_3)_3$ ,  $\text{Zn}(\text{Hg})/2 \text{ M H}_2\text{SO}_4$ .

**Apparatus.** The Giford (Response model) UV-VIS spectrophotometer was used for this study. This spectrophotometer was equipped with units to regulate the cell compartment temperature to within  $\pm 0.1^\circ\text{C}$ . The temperature was controlled to  $26^\circ\text{C}$  during the measurement of the UV spectra. A spectral band width of 0.1 nm was used in all cases.

The UV lamp (UVP Inc. Model UVGL-25) was used for the light source, and the light (366 nm) was reflected into the reaction vessel (quartz semimicro UV cell).

## RESULTS AND DISCUSSION

Following others<sup>4</sup>, we have used DPBF as the monitor species to find the chemical evidence for intermediacy of  $^1\text{O}_2$  during photoirradiation for 2-EA and 9-PA in methanol. DPBF is very reactive toward singlet molecular oxygen and transparent for the light of 366 nm which absorbed by 2-EA and 9-PA. During the irradiation with the light of 366 nm, the absorption intensity of DPBF at 410 nm was monitored by UV-VIS spectrophotometer. At this wavelength region, absorption intensities of 2-EA and 9-PA are negligible. The absorption coefficient of DPBF at 410 nm was taken to be  $2.34 \times 10^4$  l/mol cm in methanol. Both possibilities of forming charge transfer complex and excimer of 2-EA with DPBF were eliminated by examination of the absorption spectra before and after mixing DPBF in the solution of 2-EA. There was no significant change of absorption intensity and wavelength of both species. As shown in Fig. 1, the absorption intensity of DPBF was not changed in the course of the irradiation without any sensitizer or without oxygen. But with 2-EA, the absorbance of DPBF was reduced remarkably. There was a regular change in the absorbance of DPBF for the irradiation time, as expected for increasing in the rate of photodecomposition of DPBF with increasing the concentration of 2-EA.

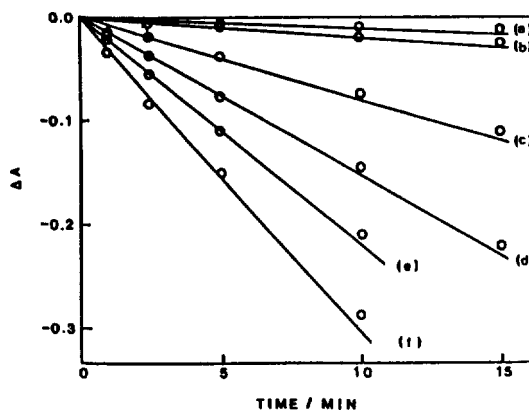


Fig. 1. 2-EA sensitized photodecomposition of DPBF ( $1.46 \times 10^{-5}$  mol/l) irradiated with the light of 366 nm in methanol. The concentrations of 2-EA in methanol are (a) 0, (b)  $3.94 \times 10^{-5}$  (without  $\text{O}_2$ ), (c)  $9.90 \times 10^{-5}$ , (d)  $1.97 \times 10^{-5}$ , (e)  $2.96 \times 10^{-5}$ , and (f)  $3.94 \times 10^{-5}$  mol/l, respectively.

Table 1. The values of  $H$  parameter for pure solvents and alcohol-water mixtures

Solvents		$H$ values
Pure solvent	Heptane	0.00
	n-Butanol	0.20
	n-Propanol	0.24
	Ethanol	0.31
	Methanol	0.44
	Water	1.00
Ethanol-water mixture	80%(w/w) Ethanol	0.42
	50%(w/w) Ethanol	0.61
	40%(w/w) Ethanol	0.68
	30%(w/w) Ethanol	0.76
	20%(w/w) Ethanol	0.83
Methanol-water mixture	80%(w/w) Methanol	0.54
	50%(w/w) Methanol	0.69
	40%(w/w) Methanol	0.75
	30%(w/w) Methanol	0.81
	20%(w/w) Methanol	0.87

The photosensitizing decomposition of DPBF with 9-PA, which has been known as a singlet oxygen sensitizer, was analogous to the case of 2-EA. From this result, it can be estimated that 2-EA is effective singlet oxygen sensitizer like 9-PA.

It is necessary to get the solvent parameter,  $H$ , of the solvents used in this work in order to examine the solubilization of these species in the aqueous micellar solutions by adopting Cardinal and Mukerjee's method. The solvent parameter,  $H$ , can be represented by the following equation through its definition<sup>10</sup>.

$$H = \frac{V_s \rho_s / M_s + V_w \rho_w / M_w}{(V_s + V_w) \rho_w / M_w} \quad (2)$$

Where  $V$  is volume,  $\rho$  is density,  $M$  is molecular weight, and subscripts  $s$  and  $w$  mean pure solvent and water, respectively. The calculated values of parameter  $H$  for various solvents are listed in Table 1. The plot of the dielectric constants versus  $H$  values is shown in Fig. 2. Fig. 2 also shows that an effective dielectric constant value can be assigned to an estimated  $H$ -value. Before quantitative treatment of the data is attempted, it is necessary to compare the wavelengths of the absorption peak in reference solvents. The UV spec-

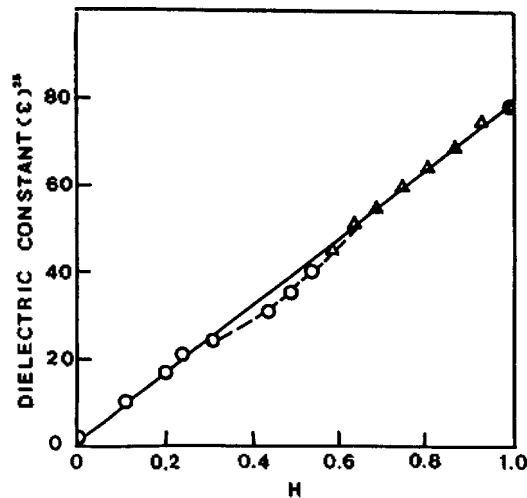


Fig. 2. Relation between the dielectric constants and  $H$  values.

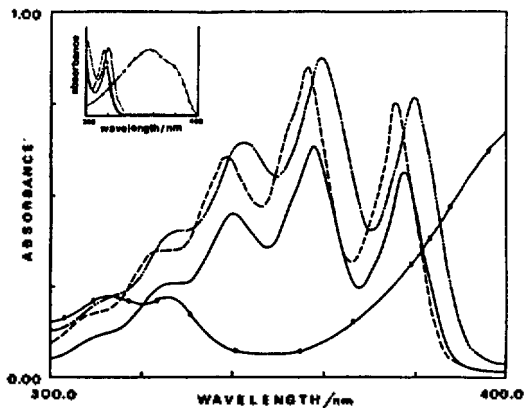


Fig. 3. The absorption spectra of 2-EA in heptane (----), n-butanol (—), 0.10 mol/l aqueous CTAB solution (-·-·-), and those of DPBF in 0.05 mol/l aqueous CTAB solution (-·-·-).

tra of 2-EA and 9-PA in two pure solvents and CTAB micellar solution are shown in Figs. 3 and 4, respectively. Here we found on inspection of the spectra that the average microenvironment of the solubilizates in this work in the aqueous micellar solution is similar to that in a polar solvent. The spectral characteristics of these substances are summarized in Table 2. As shown in Table 2, any relationship between the wavelengths of the major peak for our systems and the solvent polarities is not found. Table 2 also shows that

the band half-width fails to be a sensitive indicator of the changes in the solvent polarity as it remains essentially constant within the experimental error from n-butanol to 50% (w/w) ethanol. The results of  $R_c$  and  $R_{pv}$  which Cardinal and Mukerjee have suggested are not good. Although we tried to get a relationship between  $R_c$  in our systems and the solvent polarity by using equation (1), we did not find any pair of absorbances that showed the relationship.

However, to relate these spectral changes with the change in solvent polarity, several different

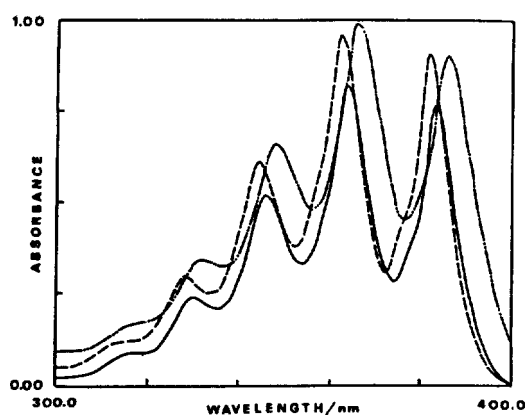


Fig. 4. The absorption spectra of 9-PA in heptane (-----), n-butanol (—), and 0.10 mol/l aqueous CTAB solution (— · —).

absorbance ratios were tested. It was found that the ratio of the absorbance at the major peak of higher wavelength and that at the wavelength that was separated by the same distance toward the lower wavelength from the major peak, could be successfully correlated with the solvent polarity. This ratio is defined as  $R_{pf}$ . This correlation is shown in the last column of Table 2 and in Fig. 5. The distances separated from the major peak are 5.3 nm for 2-EA, and 5.5 nm for 9-PA, respectively. These values are determined through the first derivative spectra of the solubilizates. The curves in Fig. 5 are so called the calibration curve to predict the microenvironment in micellar solutions, and show the S-shape for our systems. The dashed lines in Fig. 5 are not obvious, due to the low solubility of our systems.

The plots of  $R_{pf}$  against  $\phi_a/\phi_m$  for 2-EA and 9-PA are shown in Figs. 6 and 7, respectively. Figs. 6 and 7 both show that there are linear relationships between  $R_{pf}$  and  $\phi_a/\phi_m$  in CTAB, SDS and Brij 35 aqueous solutions. The value of  $R_{pf}$  in the micellar part is obtained by extrapolation of the plots in Figs. 6 and 7. The  $R_{pf}$  value leads to an estimate of the average polarity of solubilized 2-EA and 9-PA using the corresponding calibration curves in Fig. 5. We have expressed the microenvironmental polarity as an effective  $H$  value ( $H_{eff}$ )

Table 2. Spectral characteristics of 2-EA and 9-PA in various solvents  
2a). 2-EA

Solvents	$\lambda_{max}$ (nm)	Half-width (nm) at 90% absorbance	$R_{c1}(376.7/376.2)$	$R_{c2}(376.7/374.7)$	$R_{pv}$	$R_{pf}(5.3)^*$
Heptane	375.8	3.0	0.970	1.027	2.406	1.685
n-Butanol	377.1	3.3	1.027	1.206	2.226	1.631
n-Propanol	376.9	3.4	1.023	1.190	2.201	1.629
Ethanol	376.8	3.3	1.010	1.149	2.213	1.608
Methanol	376.5	3.4	1.000	1.110	2.178	1.592
80% Methanol	376.7	3.4	1.007	1.126	2.106	1.572
50% Ethanol	376.9	3.6	1.020	1.160	1.002	1.558
40% Ethanol	377.3	3.8	1.022	1.172	1.983	1.525
50% Methanol	377.1	3.7	1.023	1.163	1.972	1.526
40% Methanol	377.5	4.7	1.024	1.134	1.602	1.344
30% Ethanol	378.0	4.5	1.031	1.147	1.650	1.340

\* $R_{pf}(5.3)$  means the ratio of the absorbance at the major peak and that at the wavelength separated 5.3 nm toward lower wavelength from the peak.

## 2b). 9-PA

Solvents	$\lambda_{\max}$ (nm)	Half-width (nm) at 90% absorbance	$R_{r1}(383.7/382.7)$	$R_{r2}(383.7/381.7)$	$R_p$	$R_p(5.5)^*$
Heptane	382.1	2.8	0.962	0.985	2.969	1.988
n-Butanol	383.5	3.2	1.027	1.247	2.641	1.890
n-Propanol	383.2	3.1	1.014	1.196	2.655	1.884
Ethanol	382.9	3.1	0.991	1.111	2.701	1.868
Methanol	382.3	3.1	0.973	1.017	2.606	1.849
80% Methanol	383.2	3.3	1.010	1.177	2.559	1.838
50% Ethanol	383.8	3.3	1.031	1.253	2.486	1.798
40% Ethanol	383.8	3.4	1.051	1.186	2.362	1.780
50% Methanol	383.9	3.4	1.004	1.216	2.455	1.774
40% Methanol	383.9	3.5	1.033	1.143	2.285	1.685
30% Ethanol	384.7	3.8	1.089	1.235	2.000	1.606

\* $R_p(5.5)$  means the ratio of the absorbance at the major peak and that at the wavelength separated 5.5 nm toward lower wavelength from the peak.

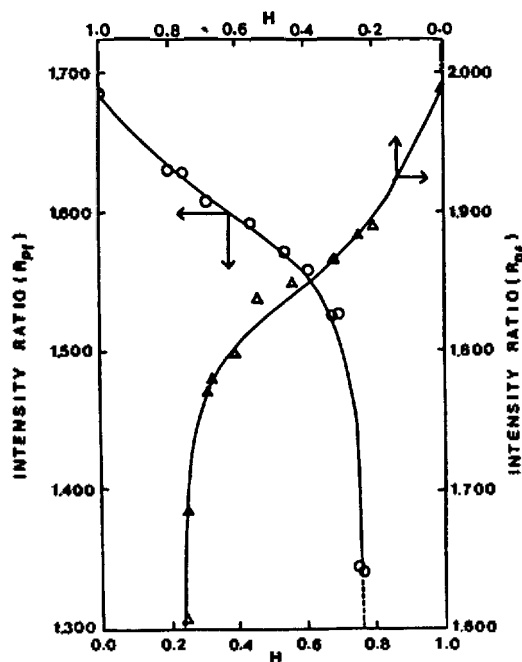


Fig. 5. The calibration curve of 2-EA (—○—) and 9-PA (—△—).

and the corresponding effective dielectric constant ( $D_{eff}$ ). The result of extrapolation is tabulated in Table 3.

As shown in Table 3, the average microenvironmental polarity 2-EA in CTAB micellar solution is similar to those in SDS and Brij 35, and may be independent of the ionic properties of surfactants.

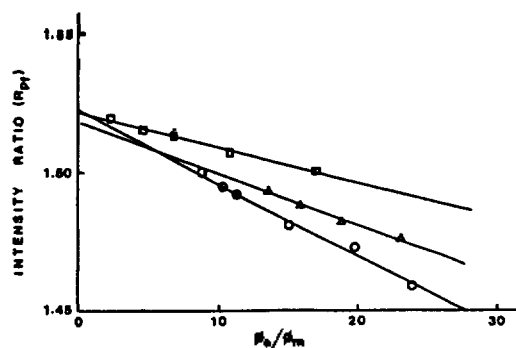


Fig. 6. Intensity ratios plotted against  $\phi_a/\phi_m$  for 2-EA in aqueous CTAB (—○—), (—△—), and Brij 35 (—□—) solutions.

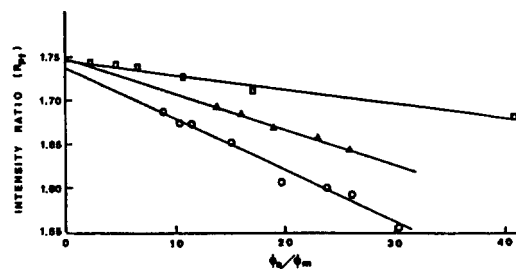


Fig. 7. Intensity ratios plotted against  $\phi_a/\phi_m$  for 9-PA in aqueous CTAB (—○—), SDS (—△—), and Brij 35 (—□—) solutions.

The results of 9-PA are similar to that of 2-EA, but the average microenvironment of 2-EA in aqueous micellar solutions is more polar than

Table 3. Effective polarities of the microenvironments of 2-EA and 9-PA in aqueous micellar solutions

Solubilizates	Micelles	$H_{eff}$	$D_{eff}$
2-EA	CTAB	0.67	53
	SDS	0.68	55
	Brij 35	0.67	53
9-PA	CTAB	0.72	58
	SDS	0.71	57
	Brij 35	0.71	57

that of 9-PA. In aqueous micellar solutions of CTAB, SDS and Brij 35, 2-EA and 9-PA may be distributed between a nonpolar dissolved state and a polar adsorbed state. Therefore we found that they are distributed in greater quantities at a polar adsorbed state. This result is agreed to the previous qualitative result. In addition to this we found that 9-PA is distributed in greater quantities at a polar adsorbed state.

The photosensitizing properties of 2-EA and 9-PA was examined in the aqueous CTAB and SDS micellar solutions. During the irradiation with light of 366 nm, the absorption intensity of 2-EA was negligible as shown in Fig. 3. The absorption coefficient of DPBF at this wavelength was taken to be  $2.20 \times 10^4$  l/mol cm in all surfactant solutions. The same experiments were performed in methanol-water mixture solutions by monitoring the absorption intensity of DPBF at 410 nm. At this wavelength the absorption coefficient of DPBF was taken to be  $2.34 \times 10^4$  l/mol cm in methanol-water mixture solutions. There was a regular change in concentration of DPBF for the irradiation time, as expected for increasing in the rate of photodecomposition with increasing the concentration of 2-EA in aqueous CTAB micellar solution as shown in Fig. 8. 2-EA and 9-PA sensitized photodecomposition rates of DPBF in aqueous micellar solutions are shown in Fig. 9. The molar absorptivity of 9-PA at 366 nm is larger than that of 2-EA. But the decomposition rate of DPBF with 2-EA as a sensitizer is faster than that with 9-PA. As shown in Table 4, in methanol-water mixture solutions, the decomposition rate of DPBF is slightly decreased with increasing the polarity of the

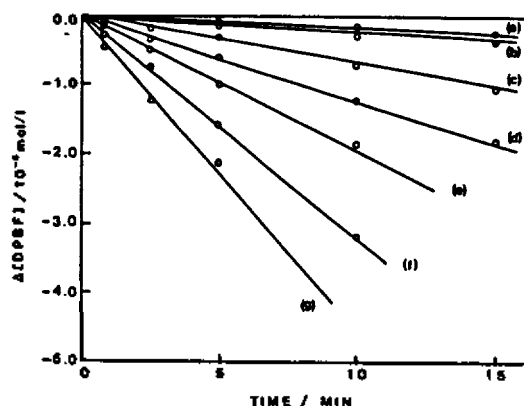


Fig. 8. 2-EA sensitized photodecomposition of DPBF ( $1.46 \times 10^{-5}$  mol/l) irradiated with the light of 366 nm in aqueous CTAB (0.01 mol/l) solutions. The concentrations of 2-EA in CTAB solutions are (a) 0, (b)  $3.94 \times 10^{-5}$  (without  $O_2$ ), (c)  $4.90 \times 10^{-6}$ , (d)  $9.90 \times 10^{-6}$ , (e)  $1.97 \times 10^{-5}$ , (f)  $2.96 \times 10^{-5}$ , and (g)  $3.94 \times 10^{-5}$  mol/l, respectively.

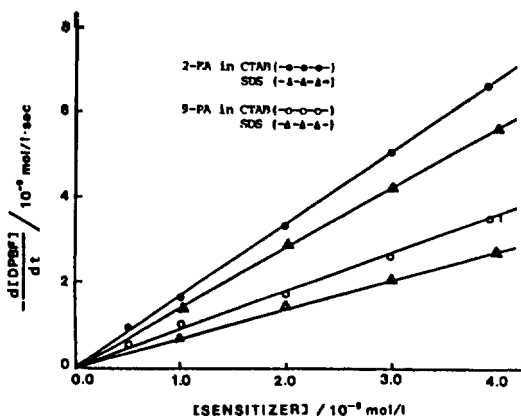


Fig. 9. 2-EA and 9-PA sensitized decomposition rate of DPBF in aqueous CTAB (0.01 mol/l) and SDS (0.03 mol/l) solutions.

medium. This result is coincident with the well known fact that an organic medium of low polarity is more suitable for photosensitized oxidation<sup>26</sup>. And DPBF was decomposed more slowly in aqueous micellar solution than in methanol-water mixture. The micelle concentration in 0.05 mol/l CTAB is ca.  $8.2 \times 10^{-4}$  mol/l<sup>8</sup>, and with  $1.97 \times 10^{-5}$  mol/l 2-EA, only one micelle will contain a 2-EA molecule. In addition, with less than  $1.46 \times 10^{-5}$  mol/l DPBF, only one in 56 micelles will have

Table 4. 2-EA and 9-PA ( $1.97 \times 10^{-5}$  mol/l) sensitized photodecomposition rate of DPBF ( $1.46 \times 10^{-5}$  mol/l) at various solutions

Solvents		$-d[\text{DPBF}]/dt/10^{-8}$ mol l <sup>-1</sup> sec <sup>-1</sup>	
		2-EA	9-PA
Methanol-water mixture	100% Methanol	17.2	16.8
	90% Methanol	15.0	15.5
	80% Methanol	13.7	12.9
	70% Methanol	13.3	12.4
CTAB	60% Methanol	13.5	11.8
	$5 \times 10^{-2}$ mol/l	3.27	1.76
	$3 \times 10^{-2}$ mol/l	3.21	1.72
	$1 \times 10^{-2}$ mol/l	3.36	1.78
	$8 \times 10^{-3}$ mol/l	3.49	1.84
SDS	$6 \times 10^{-3}$ mol/l	3.24	1.70
	$3 \times 10^{-2}$ mol/l	1.80	1.44
	$1 \times 10^{-2}$ mol/l	1.78	1.46

a DPBF molecule associated with it, hence the probability that any given micelle have both 2-EA and DPBF molecule will be low. These experiments demonstrate that singlet oxygen can diffuse out of one micelle system (its formation site) through the aqueous phase and into another micelle associated with DPBF, and that the life time of singlet oxygen in aqueous micellar solution has a value far lower than in methanol-water mixture. The life time of singlet oxygen is highly dependent on the type of solvent, with values ranging for 2  $\mu$ s in water, 5.5  $\mu$ s in methanol to 24  $\mu$ s in nonpolar solvent such as benzene<sup>26</sup>. In methanol-water mixture solutions, there was not so much difference in the sensitizing ability between 2-EA and 9-PA. But in micellar solutions, the sensitizing ability of 2-EA was greater than that of 9-PA. From these results, it can be estimated that 9-PA is distributed in greater quantities at a polar environment of the micelle than 2-EA.

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