

Articles

Microenvironmental Control of Photochemical Reactions. 3. Additive Effects on Micellar Structure and Properties of TX-100

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The cage effects of radical pairs produced by photolysis of *p*-methyl dibenzyl ketone, 1, as well as the fluorescence spectra of pyrene, 2, and 1,3-di- α -naphthylpropane, 3, in aqueous solutions containing TX-100 (TX) have been determined as a function of the concentration of TX and of the concentration of added ionic surfactants [sodium dodecylbenzene sulfate (SDBS) and cetyl trimethylammonium bromide (CTAB)] and neutral electrolytes. The results indicate that both the aggregation and micellar properties of TX are significantly influenced by the molecules of 1 solubilized in TX micelles. The results also show that comicelles are formed between TX and ionic surfactants and that the interior polarity of TX micelle is lowered by the addition of ionic surfactants. Neutral electrolytes are found to have at least two effects upon the aggregation of TX and its micellar properties: increasing ionic strength increases the dissimilarity between the TX micelle and the water phase and thus decreases the critical micelle concentration (cmc) and simultaneously enhances the interior micellar microviscosity. In addition, at a high concentration of electrolytes, the micellar volume changes. It is suggested that only the ions bonded onto the surface of the micelles significantly influence micellar parameters such as microviscosity and cage effects.

Introduction

Over the past decade, investigations of photochemical and photophysical processes in ionic micelles have provided very useful information about the structure and dynamic properties of aqueous solutions of micellar aggregates.^{1,2} An outstanding property of aqueous solutions of micelles is their ability to solubilize organic substrates and to respond in their solubilizing properties to the addition of electrolytes and other additives.³ In a previous paper,¹ we reported the effects of additives on the recombination efficiency and exit rate of micellized benzyl radicals produced by photolysis of unsymmetrical dibenzyl ketones in ionic micelles. These probes have not been extensively investigated for nonionic surfactants.^{4,5} Since the head groups of nonionic surfactants are uncharged, it is expected that nonionic micelles would show different responses to the additives from those of the ionic micelles.

Unsymmetrical dibenzyl ketones, such as *p*-methyl dibenzyl ketone, 1, have been used extensively as photochemical probes in investigating the properties of various microheterogeneous systems including ionic micelles.² The great advantages of these probes are based on their well-

established photochemistry and the sensitive environmental dependence of the products distribution.^{6,7} The cage effect (CE), which describes the product distribution,¹ is defined by eq 1. Homolytic cleavage (type I reaction)

$$\% \text{ CE} = \frac{\text{AB} - (\text{AA} + \text{BB})}{\text{AA} + \text{AB} + \text{BB}} \times 100 \quad (1)$$

reactions of dibenzyl ketone occur from its triplet state to generate a triplet radical pair. The latter undergoes intersystem crossing to form a singlet radical pair that undergoes cage recombination reactions in competition with diffusional separation and escape from the solvent cage or micelles.⁸ The recombination of the geminate radical pair gives only AB, while the products formed from the escaped radicals include AA, AB, and BB. In nonviscous homogeneous solution irreversible diffusional separation to form random radicals is usually much faster than intersystem crossing and geminate pair recombination of single pairs; as a result, free radical formation dominates and the measured CE is close to zero. However, due to the *restricted* space of the micelles, the efficiency of irreversible diffusional separation to form random radicals is reduced considerably;² the efficiency of geminate recombination increases. The product distribution and hence the CE will depend on the competition between intersystem crossing and the efficiency of irreversible diffusional separation and escape from the micelle into the bulk phase. The CE can be used thus as a qualitative

(1) Turro, N. J.; Zimmt, M. B.; Lei, X.-G.; Gould, I. R.; Nitsche, K. S.; Cha, Y. *J. Phys. Chem.* 1987, 91, 4544.

(2) Turro, N. J.; Cox, G. S.; Paczkowski, M. A. *Photochemistry in Micelles*. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: New York, 1985.

(3) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1985.

(4) Mandal, A. B.; Ray, S.; Biwas, M.; Moulik, S. P. *J. Phys. Chem.* 1984, 84, 856.

(5) (a) Kalayanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press, Inc.: Orlando, FL, 1987; (b) Thomas, J. K. *Chemistry of Photoexcitation at Interfaces*; ACS Monograph 181, American Chemical Society: Washington, DC, 1984.

(6) Turro, N. J.; Graetzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 675.

(7) Turro, N. J.; Kraeutler, B. *J. Am. Chem. Soc.* 1978, 100, 7432.

(8) Engel, P. S. *J. Am. Chem. Soc.* 1970, 92, 6047. Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* 1970, 92, 6076.

probe of the dynamics microenvironmental properties related to mobility within the micelle and the escape rate of radicals from the micelle, in addition to the effective volume of the micelle.

Pyrene, **2**, is a useful fluorescence probe for measuring environmental effects especially for the polarity of various heterogeneous systems as well as the internal fluidity of micelles.^{5,9} The basis for pyrene as a polarity probe results from the sensitivity of its monomer fluorescence vibronic bands (I_1/I_3) to the polarity of the medium. The basis for pyrene as a fluidity (microviscosity) probe⁹ results from the sensitivity of the ratio of pyrene's intermolecular excimer to monomer fluorescence intensity, I_e/I_m , to the internal viscosity of micellar aggregates. Similarly, the fluorescence intramolecular excimer to monomer intensity ratio of 1,3-di- α -naphthylpropane (**3**) has been used to measure the microviscosity of micellar systems.¹⁰

In the present paper, we investigated the CE of radical pairs produced by photolysis of *p*-methyl dibenzyl ketone, **1**, and by measurement of the fluorescence spectra of **2** and **3** as probes for the structure of micelles formed at different concentrations of nonionic surfactant TX and different additives in aqueous solution. The formation of micelles from TX and ionic surfactants, the additive effects on the micelle formation ability, the micellar structure, micellar size, and other micellar properties were examined experimentally with these probes.

Experimental Section

Chemicals. *p*-Methyl dibenzyl ketone (**1**) and 1,3-di- α -naphthylpropane (**3**) were prepared by the methods described in a previous paper.¹¹ Pyrene (**2**) (Fluka) was recrystallized twice from ethanol-cyclohexane (v:v = 1:1). Other chemicals were analytically pure and were used as supplied.

Photolysis of 1. The samples were prepared by ultrasonating an aqueous surfactant solution of **1** for 2 h and then allowing it to stand overnight. The photolysis of the samples was carried out by irradiating an Ar-purged 2 mM ketone aqueous solution containing surfactant in quartz equipment with a 500-W high-pressure Hg lamp. After the sample was extracted with ether or *n*-pentane, the products were analyzed on a Hitachi GC-9A chromatograph, using a SE-30 packing column. The injector, column, and the detector temperature were monitored at 300 °C, 180 °C, and 300 °C, respectively.

Fluorescence Measurements. All the fluorescence spectra were recorded on a Hitachi M850 fluorescence spectrophotometer. For **2**, the excitation wavelength was monitored at 335 nm. The I_1 (372.5 nm) to I_3 (383.2 nm) ratios were used to measure the cmc of TX and binary systems, while the maximum excimer emission I_e (ca. 488 nm) to the maximum monomer emission I_m (373 nm) ratios were used as criteria of the probability for pyrene molecules diffusing together and thereby probing the micellar viscosity. For **3** the excitation wavelength was monitored at 295 nm, while its monomer and excimer emission wavelengths were monitored at 337 and 420 nm, respectively, and, as for pyrene, the I_e/I_m ratio is used as a measurement of interior micellar microviscosity.

The cloud points were determined by heating and stirring a 1 mM TX aqueous solution (2 mL) in a test tube equipped with a thermometer in a water bath; the temperature at which the solutions suddenly turned turbid was recorded as the cloud point.

Results and Discussions

Cage Effect and Fluorescence Spectra as a Function of Concentration of TX in Water. Figure 1 shows the CE versus surfactant concentration relationships for

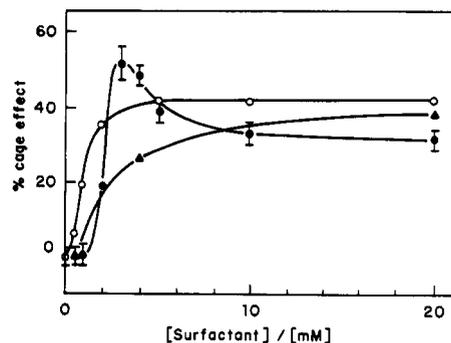


Figure 1. Concentration dependences of % CE on (●) [TX], (○) [CTAB], and (▲) [SDBS].

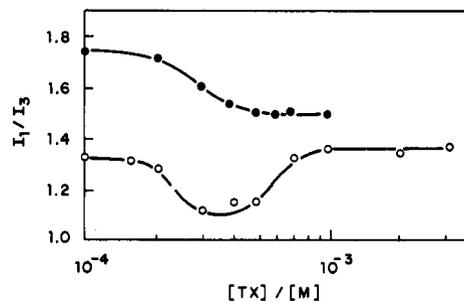


Figure 2. Fluorescence I_1/I_3 ratio vs the [TX] (●) in the absence and (○) in the presence of 1 mM of **1**.

photolysis of **1** in the nonionic surfactant TX, the anionic surfactant sodium dodecylbenzene sulfate (SDBS), and in the cationic surfactant cetyl trimethylammonium bromide (CTAB). The differences between the plot for TX and the plots for the two ionic surfactants are striking. The plots show breaks in relative narrow concentration ranges for CTAB and SDBS, and the shape and breaks in the curves coincide with their critical micelle concentration (cmc) reported in the literature.⁵ Above the cmc the CE values for the ionic surfactants remain relatively constant or increase slightly with increasing concentration of the surfactants. For TX, however, the concentration at the break is about 10 times as large as the cmc (2.6×10^{-4} mM/L) reported in the literature⁵ (this result is confirmed by the results with the pyrene fluorescence probe, vide infra, Figure 2). In addition, the CE reaches a maximum (at low concentrations of TX) and then decreases with increasing concentration of TX, and thus has a shape completely different from the ionic surfactants. These results indicate that both the aggregation and the micellar structure of ionic surfactants are minimally influenced but that of TX is significantly disturbed by solubilized **1**. The above difference can be attributed to the higher cmc of ionic surfactants (9.2×10^{-4} and 1.2×10^{-3} M for CTAB and SDBS, respectively) and stronger interaction between TX and molecules of **1**.

The [substrate]/[surfactant] ratios in ionic surfactants and TX aqueous solutions at the cmc (without **1**) are ca. 1 and 4, respectively. Thus the aggregation of ionic surfactants should be less affected by molecule **1**. In addition, ionic surfactants possess counterionic head groups which form a Stern layer in water, and the latter should be less disturbed by the nonionic molecules of **1**. Both the TX and **1** molecules possess benzene rings. Such a structural similarity should produce a strong hydrophobic interaction between the micelles and the solubilate.

The plot for TX in Figure 1 can thus be rationalized in the following manner: When the concentration of TX is lower than that at the break, instead of forming micelles, a surfactant-in-substrate aggregate may be formed. As

(9) Kalayanasundaram, K.; Thomas, J. H. K. *J. Am. Chem. Soc.* 1977, 99, 2039.

(10) Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* 1983, 105, 6347.

(11) Lei, X.-G.; Liu, Y.-C. *Acta Chim. Sin. (Engl. Ed.)* 1990, 3, 65.

(12) Breslow, R.; Guo, T. *J. Am. Chem. Soc.* 1988, 110, 5613.

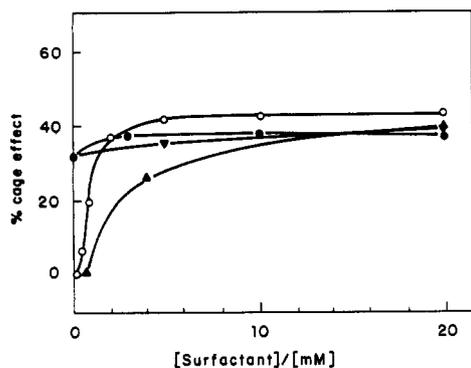


Figure 3. Concentration dependences of CE on (○) [CTAB], (●) [CTAB], (▲) [SDBS] in CTAB-TX (50 mM), and (▼) [SDBS] in SDBS-TX (50 mM) systems.

the [surfactant]/[substrate] ratio increases, TX micelles form, but the cmc is increased above that for TX alone for the mixed micelles of TX and 1. The observation that the cmc of TX for the mixed micelle is apparently increased above that for TX alone is perhaps surprising. However, it was found that addition of ethanol or propanol also causes an increase in the cmc of TX or a decrease in the slope of the I_3/I_1 plot. Addition of electrolytes decreases the cmc of TX slightly. The fact that CE decreases with increasing concentration of TX at the concentration above that of the maximum CE may result from two sources. As a first possibility, TX is not a single molecular species but is a disperse mixture of polyethers of different molecular weights. It may first form micelles that consist of surfactant possessing a longer polyether chain and which form larger, more hydrophobic micelles. The larger micellar volume results in a larger CE at relatively low [TX]. As the [TX] increases, more hydrophilic micelles composed of the smaller TX surfactant molecules begin to form, and 1 is redistributed between the larger and smaller micelles. The smaller micelles, being more hydrophilic, may produce smaller values of CE. A second possibility is that the ketone molecules perturb the TX micelles and the effect decreases with increasing the [surfactant]/[substrate] ratio, although it is not clear whether the volume and/or structure of the TX micelle is altered by addition of the ketone.

The results of pyrene monomer fluorescence probing of the polarity (as monitored by the I_1/I_3 of pyrene monomer fluorescence) of TX micelles as a function of [TX], in the absence and presence of 1, is shown in Figure 2. The results show that in the presence of 1 mM of 1, the pyrene molecules feel a less polar environment (lower values of I_1/I_3) for the entire concentration range of TX. The I_1/I_3 values at the concentration of TX below that of the cmc (unperturbed) and at the minimum are 1.32 and 1.12 corresponding to polarities of methanol and benzene, respectively.⁹ Thus, it is reasonable to suggest that the pyrene molecules are located in the surfactant-in-ketone aggregates below the cmc (unperturbed), while in the minimum I_1/I_3 , the molecules in the aggregates arrange so that the pyrene molecules are situated in the hydrophobic benzene atmosphere. When the TX micelle is formed, the pyrene molecules move close to the aqueous interface, thereby sensing a more polar, aqueous environment and reporting a higher value of I_1/I_3 .

Formation of Comicelles. Addition of ionic surfactants to a fixed concentration of TX results in an increase and leveling of the CE with increasing concentration of ionic surfactants (Figure 3). As the concentration of ionic surfactants in a 50 mM aqueous solution of TX increases progressively, the CE values show an initial sharp increase

Table I. Dependence of the Parameters on the [SDBS]/[TX] Ratio

[SDBS]:[TX]	cmc, ^a mM	X_1	β	f_1	f_2	I_1/I_3	ϵ
1:5	2.0×10^{-4}	0.223	-3.92	0.094	0.823	1.42	34.7
1:1	3.0×10^{-4}	0.295	-2.31	0.318	0.818	1.39	32.1
5:1	3.5×10^{-4}	0.481	-3.60	0.379	0.434	1.36	29.5

^a Measured by the pyrene I_1/I_3 method.

and then a leveling off (Figure 3). Interestingly, the CE in the bisurfactant systems are not the average of those in the individual surfactants especially when the concentration of the ionic component is low. Formation of comicelles is evidenced by the following observations: When the concentration of CTAB in the TX-CTAB system is lower than 3 mM or the concentration of SDBS in the TX-SDBS system is lower than 15 mM, the CE's are greater than those in each of the individually constituted surfactants in the same concentrations. This suggests that the structures of the mixed micelles involve ionic surfactants inserted into the TX micelles.

Table I shows that the cmc (measured by the pyrene I_1/I_3 method) of the TX-SDBS system increases with increasing the fraction of SDBS. When the fraction of SDBS is low, the cmc is lower than the cmc of TX alone, indicating that the addition of an ionic surfactant facilitates the micelle-forming ability of TX. That the cmc of the mixed system is larger than that of TX is further evidence for the formation of comicelles. Figure 3 also shows that the shape of the curves for bisurfactant systems are dominated by properties of the ionic surfactants, especially when the fraction of the ionic surfactant is high. This suggests a gradual transformation from essentially nonionic micelles to essentially ionic micelles.

It was demonstrated¹ that the value of the CE for benzyl radical pairs in micelles is mainly controlled by the exit rate of the benzyl radicals. For instance, the CTAB micelles have a larger CE than the TX micelles, although the former have a smaller volume and the polarities at the micelle-water interface for both are similar. We attribute the difference in the two micelles to the polar counterions of the Stern layer of CTAB micelles, which strongly inhibits the hydrophobic benzyl radicals from escaping to the water phase. The TX micelle, however, does not possess charged head groups and its micelle-water boundary is less binding or "looser" and does not inhibit the exit of benzyl radicals into the aqueous phase as strongly as the boundary of the charged micelles. As an ionic surfactant was added to the TX micelles, the micelle-water boundary becomes charged and the exit rate of the benzyl radical will be slowed down resulting in an increase in CE.

Quantitative relationships among the cmc of the mixed surfactant system (C^*), the mole fraction of SDBS in the micelles (x_1), and cmc of the individual surfactants (C_1 for SDBS and C_2 for TX) are related in eq 2,¹³ where α is the

$$1 = \frac{X_1 \ln(C^*/C_1 X_1)}{(1 - X_1)^2 \ln[C^*(1 - \alpha)/C_2(1 - X_1)]} \quad (2)$$

mole fraction of SDBS in the total mixed surfactant solution. On the basis of the calculated x_1 values, the interaction parameter β may be evaluated by eq 3 and the activity coefficients f_1 and f_2 of surfactants SDBS and TX from eqs 4 and 5, respectively. The environmental polarity

Table II. Salt Effect on the CE of Photolysis of 1 (1 mM) TX (61 mM) Micelle Solution (in the Absence of Salt, % CE is 32)

concn of additive, M	% CE (M) in addition of			
	NaCl	KCl	MgCl ₂	BaCl ₂
0.1	33 (0.5)	34 (1)	35 (1)	34 (1)
0.3			38 (0.5)	37 (1)
0.5	37 (1)	37 (0.5)	41 (1)	41 (1)

$$\beta = \ln(C^*/C_1 X_1)/(1 - X_1)^2 \quad (3)$$

$$f_1 = \exp(1 - X_1)^2 \quad (4)$$

$$f_2 = \exp(X_1^2) \quad (5)$$

$$\epsilon = 86.2(I_1/I_3 - 1.25) + 20 \quad (6)$$

(ϵ) which pyrene experienced can be calculated from the measured I_1/I_3 ratio (eq 6).¹⁴ The parameters obtained are listed in Table I. It is seen that the fraction of SDBS in comicelles is different from and in most cases smaller than those in the total solution. The interior micellar polarity of the comicelles decreases with increasing the fraction of SDBS. The decrease in polarity enhances the hydrophobicity of the comicelle and thus makes the diffusion separation of benzyl radicals more difficult; as a result, the CE increases.

Effects of Electrolyte Additives. Addition of neutral electrolytes to solutions containing TX micelles causes a much smaller increase in the CE (Table II) compared to that observed for the ionic micelles (ca. 1/10 of that in SDS).¹ In addition, in ionic micelles and crown ether micelles,¹⁵ the effects of electrolytes are quite dependent on the nature of the cations; in TX micelles however, these effects are independent of the ionic strength or the strength of binding of the cations but are dependent on the charge density. For electrolytes, the observed effect decreases in the order trivalent > bivalent > univalent cations. It was demonstrated^{1,15} that the influence of electrolytes on both ionic and crown ether systems parallels the strength of binding of the cations to the surfactants; e.g., for anionic surfactants, their binding ability is proportional to the ionic strength of the cations: the stronger the ionic strength of the cation, the stronger the binding. On the other hand, for crown ether surfactants, the binding is dependent on both the size of the crown ring and the ionic diameter of the cations.¹⁵ The small additive effects of electrolytes reflect their poor binding ability to TX micelles so that the ions are effective only in the bulk solution.

It is well-known that the properties of micellar systems may be significantly altered by additives that serve to modify either the micelle structure and/or the dynamics of the solubilized substrates.³ An enhanced efficiency of geminate radical pair recombination (increasing CE) could result from any of the following (interrelated) factors: an increased micellar size, an increased interior micellar microviscosity, or an increased hydrophobicity of the micelles. All of these factors would cause the decrease in the exit rate of the benzyl radicals and lead to an increase in CE.

It has been demonstrated that addition of electrolytes to the ionic micelles causes an increase in the aggregation number and thus an increase in the micelle size.^{1,16-18} The

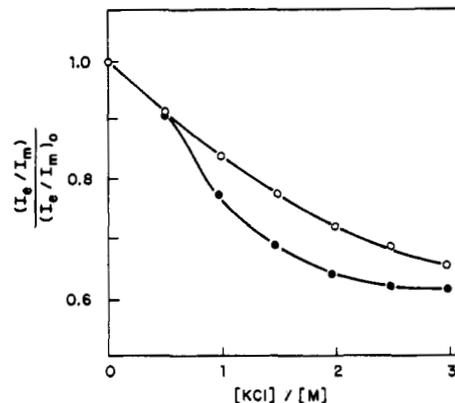


Figure 4. Fluorescence $(I_e/I_m)/(I_e/I_m)_0$ of (●) 2 and (○) 3 in TX micelle (1 mM) with [KCl].

controlling factor for micelle size and hence the micellar aggregation number of ionic surfactants is the surface area available per charged head group or, inversely, the surface density.^{19,20} The electrolytes interact mainly with the ionic atmosphere of the hydrophilic surface of ionic micelles; they also increase the dielectric constant of the solution and thus increase the dissociation of the surfactants. Thus, in the presence of strong electrolytes, the ionic micelle responds by growing until the number of ionic heads per surface area is about the same as in the original micelle. The effects of electrolytes on the nonionic micelles, however, are quite different. For example, it was reported²¹ that electrolytes cause a decrease in the aggregation number of crown ether micelles. TX has no charged head group and, unlike crown ethers, it cannot effectively coordinate with cations. It was reported²² recently that the addition of NaCl to an aqueous solution of TX has no effect on the micelle radii when the concentration of NaCl is lower than 0.5 M, while NaCl causes a small increase in the micellar radii when the concentration is above 0.5 M.

The effect of electrolytes on TX micelles was probed by measuring intermolecular excimer formation of 2 and intramolecular excimer formation of 3. Figure 4 shows the results. The concentration of added KCl is plotted against the relative excimer to monomer intensity ratio $(I_e/I_m)/(I_e/I_m)_0$, where the $(I_e/I_m)_0$ is the ratio without KCl. The concentrations of 2 and 3 were fixed at 1×10^{-4} and 1×10^{-5} M, respectively. It is seen that both the intermolecular excimer to monomer intensity ratio of 2 and intramolecular excimer to monomer intensity ratio of 3 decrease with increasing the [KCl], but the change for the intermolecular case is slightly larger when [KCl] is above 0.5 M. The decrease in intermolecular excimer to monomer intensity ratio may result from (1) an increased interior micellar microviscosity, which will slow down the efficiency of excimer formation by slowing down the rate of diffusion of pyrene molecules within a micelle, or (2) a decreased occupancy number of pyrene in micelles, which reduces the efficiency of excimer formation by reducing the statistical probability of an excited pyrene molecule finding a ground state pyrene molecule in a micelle. It should be pointed out that the lifetime of excited pyrene in a micelle is too short (ca. 100 ns) to allow escape of the excited state from the original micelle in which it is created.

(18) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978.

(19) Almgren, M.; Swarup, S. *J. Phys. Chem.* 1982, 86, 4212.

(20) Yamaguchi, T.; Yamaguchi, A.; Kimoto, E.; Kimizuka, H. *Bull. Chem. Soc. Jpn.* 1986, 59, 3029.

(21) Turro, N. J.; Kuo, P.-L. *J. Phys. Chem.* 1987, 91, 3321.

(22) Dubin, P. L.; Principi, J. M.; Smith, B. A.; Fallon, M. A. *J. Colloid Interface Sci.* 1989, 127, 558.

(14) Turro, N. J.; Kuo, P.-L.; Somasundaran, P.; Wong, K. *J. Phys. Chem.* 1986, 90, 288.

(15) Turro, N. J.; Kuo, P.-L. *J. Phys. Chem.* 1986, 90, 837.

(16) Chem, J.-M.; Su, Y.-M.; Mou, C.-Y. *J. Phys. Chem.* 1986, 90, 2418.

(17) Almgren, M.; Swarup, S. *J. Phys. Chem.* 1983, 87, 876.

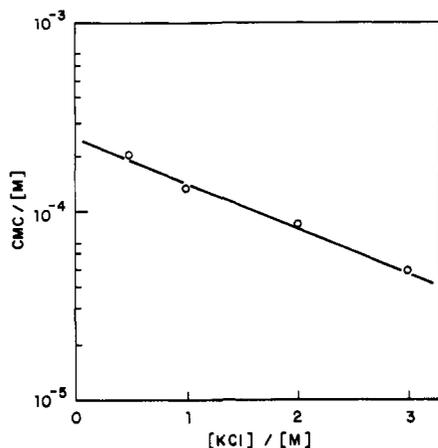


Figure 5. Relationship of $\log(\text{cmc})$ vs $[\text{KCl}]$.

According to eq 7

$$N = \frac{n(C - \text{cmc})}{C_P} \quad (7)$$

(where n and N express the average occupancy number and the aggregation number, respectively), as the concentration C and cmc of TX as well as the concentration of 2 (C_P) are all fixed the value of N should be proportional to the value of n . Thus, the decrease in $(I_e/I_m)/(I_e/I_m)_0$ for pyrene implies a decrease in the aggregation number and micelle volume. The decrease in intramolecular $(I_e/I_m)/(I_e/I_m)_0$ for **3** cannot be due to statistical factors and therefore probably reflects an increase in the interior micellar microviscosity. When the $[\text{KCl}]$ is lower than 0.5 M, the two curves in Figure 4 have the same slope. This means that the increase in CE responds to the increased interior microviscosity, and this result coincides with the result of radii measurement of TX micelle.²² However, the larger decrease in $(I_e/I_m)/(I_e/I_m)_0$ for **2** than that for **3** as the concentration increases above 0.5 M implies that either the micelle size decreases or the hydrophobicity of the micelle increases. The former is contrary to the radii measurement but coincides with the result in the crown ether micelles. A more detailed interpretation of these results requires further investigation.

Figure 5 shows the cmc of TX as a function of concentration of added KCl. It is seen that the cmc decreases with the increasing concentration of KCl. The relationship between the value of the cmc and $[\text{KCl}]$ can be expressed as eq 8, where the $k < 0$ and $C = \log(\text{cmc})_0$ is the cmc in the absence of electrolytes. These results are consistent with those reported²³⁻²⁵ for ionic surfactants.

$$\log(\text{cmc}) = k[\text{KCl}] + C \quad (8)$$

The influence of electrolytes on the aggregation of surfactants has been studied extensively by measuring the cloud point as a function of the concentration of electrolytes.^{15,26} The increase or decrease in cloud points is defined as "salting-in" (chaotropic or promoting deaggregation)¹² and "salting-out" (antichaotropic or promoting aggregation) effects, respectively.²⁷ Addition of KCl to the aqueous solution of TX causes a decrease in the cloud

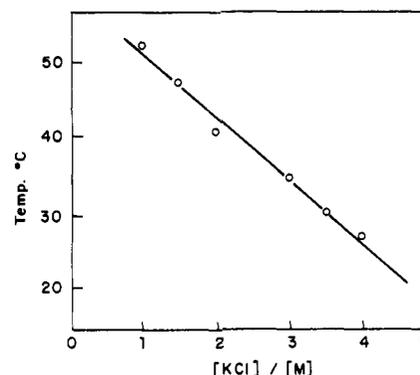


Figure 6. Cloud point of TX (1 mM) solution vs $[\text{KCl}]$.

point (Figure 6). This result is contrary to that for the crown ether surfactants, which show a "salting-in" or aggregating effect,¹³ but is consistent with results for most ionic surfactants. The "salting-in" effect for the crown ether has been explained as the special contribution of alkali-metal ion complexing to the hydrophilic head group of the crown ring; while in the case of TX, the "salting-out" effect can be attributed to the decrease in the solubility of the hydrophobic molecules of TX caused by the electrolytes. Thus, added electrolytes enhance the aggregation of TX and decrease the cloud point.

Conclusion

The aggregation of the nonionic surfactant TX is significantly altered by the addition of molecule **1** because of strong interactions between the benzene moieties of the aromatic portion of the TX structure and solubilized **1**. These interactions are not significant in ionic micelles. The effects of ionic surfactants on the recombination of benzyl radical pairs and the fluorescence spectra of molecule **2** in aqueous solutions of TX are consistent with the formation of comicelles of TX and ionic surfactants. The interior comicellar polarity decreases with increasing the fraction of ionic surfactants. The CE measurement, the cloud points, and the fluorescence spectra of **2** and **3** all show that added electrolytes enhance the aggregation of TX. The results show that the additive effects of electrolytes depend mainly on the binding ability of the ions to the surfactants. This conclusion is also supported by recent results on the lanthanide ion effect on the cage recombination of benzyl radical pairs in micelles in the presence of a laboratory applied magnetic field. In a 1.2-kG field, we find that addition of Gd^{3+} shows only a normal salt effect upon the recombination of benzyl radical in TX micelle. Electrolytes have little effect on the structure of nonionic micelles compared to that of ionic micelles, but they can affect certain properties, i.e., the interior microviscosity and the hydrophobicity of these micelles.

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(23) Miyamoto, S. *Bull. Chem. Soc. Jpn.* 1960, 33, 375.
 (24) Korshuk, E. F.; Danilov, N. I.; Aleksandrovich, Kh. M. *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk* 1977, 3, 89.
 (25) Singh, H. N.; Swarup, S.; Singh, R. P. *Indian J. Chem., Sect. A* 1984, 23A, 175.
 (26) Gu, T.-R.; Qin, S.-F.; Ma, C.-M. *J. Colloid Interface Sci.* 1989, 27, 586.
 (27) Schott, H. J.; Han, S.-K. *J. Pharm. Sci.* 1975, 64, 658.

Registry No. 1, 35730-02-0; 2, 129-00-0; 3, 14564-86-4; CTAB, 57-09-0; SDBS, 25155-30-0; TX, 9002-93-1.