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Interaction between TCNQ and Surfactant. III. The Effect of Light on the Spectra of TCNQ Solubilized in Surfactant Solutions

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The absorption spectra of 7,7,8,8-tetracyanoquinodimethane (TCNQ) solubilized in surfactant solutions were found to be influenced by day light (hereafter referred to as light). The formation of the monomer band of TCNQ anion radical in the aqueous solution of DPCl (dodecylpyridinium chloride), DPBr (dodecylpyridinium bromide) and $C_{12}E_8$ (homogeneous octaethylene glycol dodecylether) were enhanced by light. On the other hand, the spectra of TCNQ solubilized in surfactant micelle in the dark suggested that TCNQ exists as dimer anion radical form $(TCNQ)_2^{\dot{-}}$. Thus, in solubilized state of TCNQ in micelle there is an equilibrium between monomer $TCNQ^{\dot{-}}$ and dimer $(TCNQ)_2^{\dot{-}}$, which seems to be easily influenced by light and surfactant. Appearance of a monomer radical band was remarkable in DPCl, DPBr, and $C_{12}E_8$ but only the dimer band was found in SDS even in the light.

In a previous paper,[1] we reported that when TCNQ was solubilized into surfactant solutions above critical micelle concentration (CMC), a remarkable coloration took place in the surfactant solutions, and charge transfer complex bands were found in the spectra. The bands were considered to be due to the formation of the charge transfer complex between solubilized TCNQ and surfactant molecule, where the electron donor is surfactant and the acceptor is TCNQ. This suggests a new phenomenon concerning the solubilization of TCNQ with a different mechanism of the color change at CMC.

In this paper, the results of the study of the effect of light irradiation on spectra of TCNQ solubilized in surfactant solution are given.

Experimental

Preparation of Reagents. TCNQ was synthesized by the usual method.[2] Purification of TCNQ was carried out by recrystallization 5 times in acetonitrile. The crystals obtained had a rust-colored flaky form. Its purity was confirmed by elementary analysis:

Found: C, 70.2; H, 1.99; N, 27.7%. Calcd for $C_{12}H_4N_4$: C, 70.6; H, 1.97; N, 27.4%. Melting point of the TCNQ was 293.5—296°C.

Dodecylpyridinium chloride (DPCl) was prepared as follows. A mixture of chlorododecane and dry pyridine was refluxed for about 15 hr at 115°C.[3] The product was recrystallized three times from acetone, then dissolved in warm methanol, mixed with charcoal, and filtered. The filtrate obtained was extracted with petroleum ether for about 100 hr. The product was recrystallized five times from acetone.

Dodecylpyridinium bromide (DPBr) was prepared in the same manner as DPCl, taking bromododecane and dry pyridine.

Sodium dodecyl sulfate (SDS) was prepared by the reaction of dodecanol with chlorosulphonic acid in gracial acetic acid and by neutralization of the resulting acid with sodium carbonate.[4] The product was extracted with petroleum ether for about 200 hr and recrystallized five times from water-isopropanol mixture.

Homogeneous octaethylene grycol dodecyl ether ($C_{12}E_8$), supplied from Nikko Chemical Co. Ltd., was used as nonionic surfactant. Homogenity of polyethylene chain length was confirmed by means of IR spectra, elementary analysis, NMR, thin layer chromatography, and gas-liquid chromatograpy.

The water used was purified by passing tap water through a mixed-bed of ion-exchange resin. It was then distilled from alkaline potassium permanganate in the presence of sodium hydroxide in a pyrex still. The specific conductance of the water was 1 to 1.9×10^{-6} ohm^{-1} cm^{-1} at 25°C.

Solubilization Measurement. Solubilization of TCNQ was carried out as follows. A small amount of TCNQ was added to 15 m*l* of surfactant solutions of different concentrations, and the mixture was shaken in a thermostat at 25°C for about 72 hr. The small amount of TCNQ used was due to the fact that TCNQ is almost insoluble in water. The period of shaking (72 hr) was determined from the study of equilibrium time of solubilization. Shaking was carried out in the daylight and in the dark.

The absorption spectra of TCNQ solubilized in surfactant solutions were measured with a Hitachi Spectrophotometer (Model EPS-2).

Results

When TCNQ was solubilized in surfactant solutions above CMC, a remarkable coloration characteristic of the surfactant was observed. In solubilization equilibrium, the color of TCNQ solubilized was green in DPCl solution, blueish green in DPBr solution, pink in SDS solution and pink to greenish yellow in $C_{12}E_8$ solution. The spectra of TCNQ solubilized in these surfactant solutions change their shapes by the action of light. The absorption spectra of TCNQ solubilized in DPCl are shown in Figs. 1 and 2. Figure 1 shows the spectra measured in daylight. The spectra obtained below CMC had a slight absorption from 550 to 900 mμ, and its intensities were very broad. The forms of absorption spectra change with the increase of surfactant concentration, and new

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[1] a) S. Muto, K. Deguchi, K. Kobayashi, E. Kaneko, and K. Meguro, *J. Coll. and Interface Sci.*, **33**, 475 (1970); b) S. Muto, K. Deguchi Y. Shimazaki, Y. Aono, and K. Meguro, *J. Coll. and Interface Sci.*, in press.

[2] a) D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962); b) J. R. Vincent and L. I. Smith, *J. Org. Chem.*, **3**, 603 (1939).

[3] W. P. J. Ford, R. H. Ottewill, and H. C. Parreira, *J. Coll. and Interface Sci.*, **21**, 522 (1966).

[4] E. E. Dreger, G. I. Keim, G. A. Miles, L. Shedlovsky, and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).

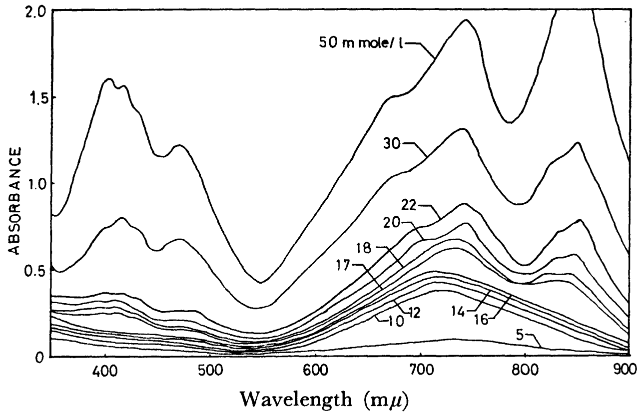

Fig. 1. Visible absorption spectra of TCNQ solubilized in DPCl solutions in the presence of the light.
Figures show concentration of surfactant solutions.

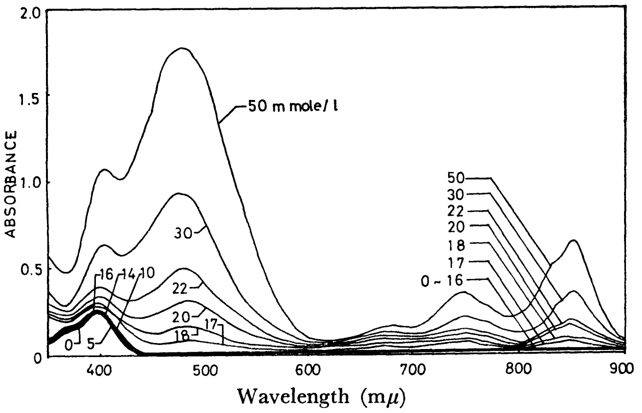

Fig. 2. Visible absorption spectra of TCNQ solubilized in DPCl solutions in the absence of the light. Figures show concentration of surfactant solutions.

TABLE 1. COMPARISON OF OPTICAL DENSITIES OF TCNQ SOLUBILIZED IN SURFACTANT SOLUTIONS AT DIFFERENT WAVELENGTH IN THE PRESENCE AND ABSENCE OF LIGHT AT 25°C

		Optical densities at different wavelength (mμ)			
		420	480	750	850
Concentration of DPCl solution is 30 mmol/l (above CMC)	Light condition	0.76	0.64	1.23	1.26
	Dark condition	0.63	0.94	0.20	0.35
Concentration of DPCl solution is 10 mmol/l (below CMC)	Light condition	0.22	0.12	0.34	0.22
	Dark condition	0.05	0.03	0.00	0.00

bands appeared at 420, 750, and 850 mμ (major) and 480 and 680 mμ (minor) above CMC.

Figure 2 shows the spectra obtained in the dark. In this case, a remarkable absorption cannot be found in the spectra below CMC, but new bands were observed at 420, 480, and 850 mμ (major) and 680 and 750 mμ (minor) above CMC. Comparison of optical densities of TCNQ solubilized in surfactant solutions at different wavelengths in the presence and absence of light is given in Table 1. As can be seen in Table 1, the ratio of the intensity at 420 mμ to that at 850 mμ in the presence of light was smaller than 1, but ratio was reversed in the absence of light.

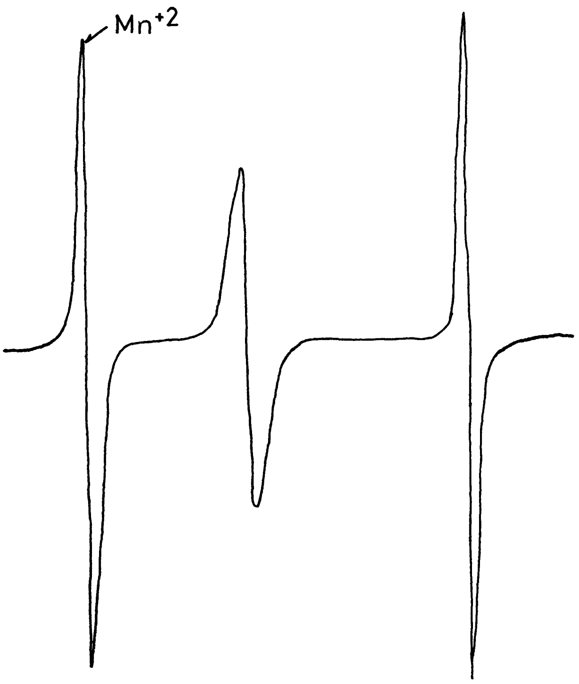

Fig. 3. Electron spin resonance spectra of TCNQ solubilized in 30 mmol/l DPCl solution in the presence of the light.

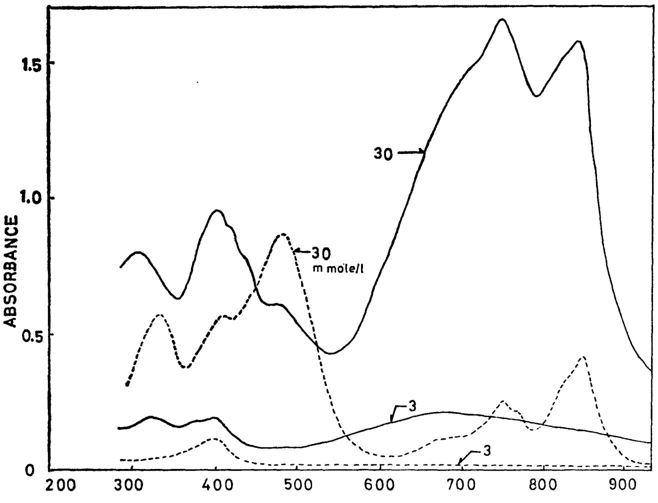

Fig. 4. Visible absorption spectra of TCNQ solubilized in DPBr solutions in the presence of the light and in the absence of the light. Figures show concentration of surfactant solutions.
The solid-line: in the presence of the light
The dashed portions: in the absence of the light

Figure 3 shows the ESR spectrum of TCNQ solubilized in DPCl solution above CMC. This is an evidence of the formation of charge transfer complex between TCNQ and surfactant.

Figure 4 shows the spectra of TCNQ solubilized in DPBr solution in the presence and absence of light. The results were almost the same as those obtained in DPCl solution.

The absorption spectra of TCNQ solubilized in anionic surfactant (SDS) are shown in Figs. 5 and 6. The shape of the absorption spectra of TCNQ solubilized in anionic surfactant solution was quite different. Figure 5 shows the spectra obtained in the presence of light, showing new bands at 400 and 600 mμ above, but no remarkable absorption below CMC. The spectra obtained in the dark are shown in Fig. 6, in which some change was found as compared with those obtained in the light, such as the increase at 400 mμ and decrease at 600 mμ with a slight shift of maximum absorption from 600 to 620 mμ.

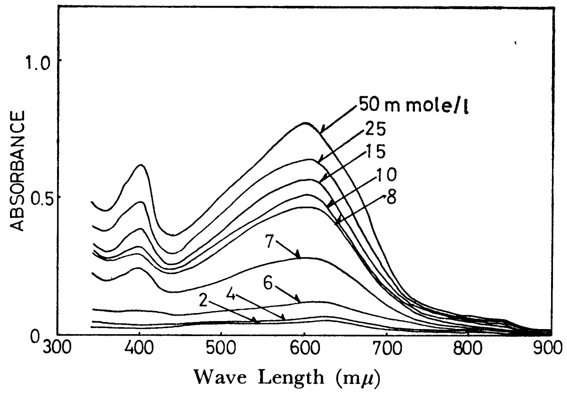

Fig. 5. Visible absorption spectra of TCNQ solubilized in SDS solutions (under light condition).

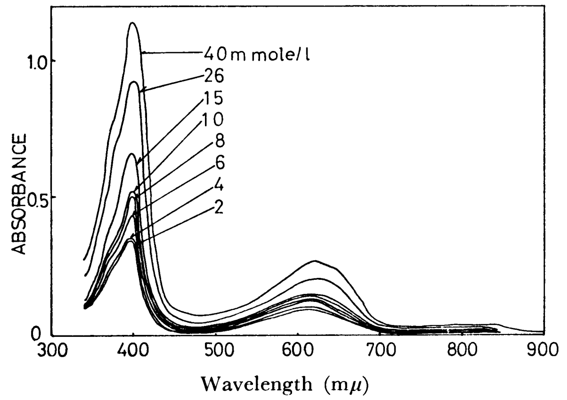

Fig. 6. Visible absorption spectra of TCNQ solubilized in SDS solutions (under dark condition).

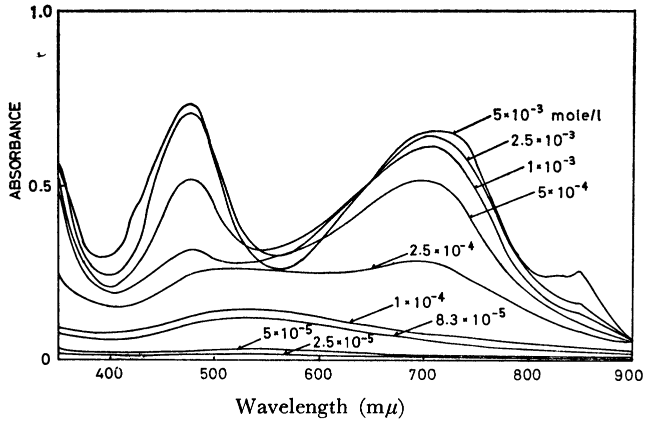

Fig. 7. Visible absorption spectra of TCNQ solubilized in octaethylene glycol dodecylether solutions in the presence of the light. Figures show concentration of surfactant solutions.

Figure 7 shows the spectra of TCNQ solubilized in aqueous solution of homogeneous octaethyleneglycol dodecyl ether in the presence of light, giving the characteristic bands of charge transfer at 480, 750, and 850 mμ above CMC (the CMC value of $C_{12}E_8$ obtained by the surface tension method: 8.2×10^{-5} mol/l). Figure 8 shows the spectra measured in the dark. They are quite different from those in the light, with a decrease of intensities at 480, 750, and 850 mμ bands and the appearance of a new band at 400 mμ.

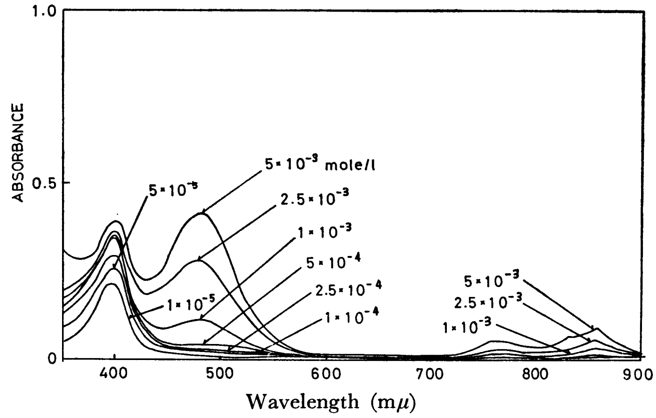

Fig. 8. Visible absorption spectra of TCNQ solubilized in octaethylene glycol dodecylether solutions in the absence of the light.

Figures show concentration of surfactant solutions.

Discussion

Scheibe[5] reported in his study of light effect on the color of acridine orange that the dimer of acridine orange dissociates into monomer by irradiation of the light. Boyd[6] studied the visible spectrum of aqueous $Li^+TCNQ^{\overline{\cdot}}$ solution and found the existence of equilibrium between the dimer and monomer of the TCNQ anion radical, and concluded that the bands of about 380 mμ and 643 mμ are characterized with the dimer of TCNQ and 420, 750, and 850 mμ bands were caused by the monomer anion radical.

Melby and *et al.*[7] reported that charge transfer complex of TCNQ has characteristic absorption at 420, 750 and 850 mμ in acetonitrile. They suggested that these TCNQ complexes are represented by the general formula $D^+(TCNQ^{\overline{\cdot}})$ where D is an electron donor molecule generally containing a nitrogen atom and an oxygen atom. The coloration accompanied by the solubilization of TCNQ in cationic surfactant solution was characterized by major maxima at 420 and 850 mμ in the light. The absorption seems to be due to the formation of charge transfer complex and formation of TCNQ monomer anion radical ion.

On the other hand, the spectra of TCNQ solubilized in cationic surfactant in the dark show a decrease of

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[5] G. Scheibe, *Z. Electrochem.*, **56**, 723 (1952).

[6] R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

[7] S. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

the absorbance at 420, 750, and 850 mμ, but a 400 mμ band due to the dimer anion radical solubilized in micelle.

In the study of the spectra of TCNQ solubilized in anionic surfactant SDS solution, a typical dimer band of $(\mathrm{TCNQ})_2^{\overline{\cdot}}$ was found in the light. This does not differ with light irradiation, except for some increase of the absorbance at 620 mμ with no shift in wave length of the absorbed bands. The cause of the production of the anion radical dimer of TCNQ will be the interaction between the counter ion Na^+ ion and solubilized TCNQ in surfactant micelle.

In the light, the spectra of TCNQ solubilized in nonionic surfactant were characterized by major bands at 480, 750, and 850 mμ of monomer band of TCNQ anion radical. In the dark, the spectra of monomer bands at 480, 750, and 850 mμ decreased and a new band appeared at 400 mμ.

Solubilization can be classified into sandwich and palisade types. Non-polar substances are solubilized in the sandwich type, and polar substances in the palisade type. As TCNQ is a non-polar substance, we might expect that the solubilization of TCNQ is of the sandwich type. However, from our results, the solubilization of TCNQ seems to be closer to the palisade type. If the charge transfer band of TCNQ was due to charge transfer between TCNQ and the nitrogen of cationic surfactant, or the oxygen atom of ethyleneoxide or hydroxyl group in nonionic surfactant, its appearance could be explained by assuming a palisade type of solubilization of TCNQ, even though TCNQ molecule is non-polar. However, there still remain questions as to why TCNQ, a non-polar substance, solubilizes in a palisade type solubilization, and also as to the theoretical mechanism for the formation of charge transfer complex between TCNQ and quaternary ammonium salts, such as cationic surfactant in the dark.