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An Electric-Field-Pulse Relaxation Study of the Electron-Donor-Acceptor Complex Formation Involving 7,7,8,8-Tetracyanoquinodimethane Solubilized at the Surfactant Bilayer/Magnetite Particle Interface

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Ultrafine magnetite particle (Fe_3O_4) which adsorbed the 7,7,8,8-tetracyanoquinodimethane (TCNQ)-dioctadecyldimethylammonium bromide (DODAB) bilayer on the surface were prepared in an aqueous solution by sonication. A single relaxation was found by using the electric-field-pulse method and was attributed to the association-dissociation process of the electron-donor-acceptor complexes involving TCNQ solubilized at the DODAB bilayer/magnetite particle interface.

In a previous paper,1) we have shown that tungstic acid particles incorporated with a dioctadecyldimethylammonium bromide (DODAB) bilayer exhibit unique properties. Surfactants can solubilize various organic materials in the lamellar layer.2) The kinetic studies of various reactions in the lamellar layer of the vesicles have made a significant contribution to various research fields, e.g., colloid chemistry and photochemistry.2—5) The surfactants sonicated with the ultrafine particles form a rigid lamellar layer on the dispersed particle surface. In order to understand the dynamic behavior of solubilized molecules and electrons in the lamellar layer of the surfactant, one must study the kinetics of various reactions in the lamellar layer around the ultrafine particles. The ultrafine magnetite particle we chose for such a study is a suitable material, for it has monodispersity and easily adsorbs the surfactant bilayer onto the particle surface.

In this paper, we present our findings on the electric-field-pulse relaxation kinetics of the electron-donor-acceptor complex formation involving TCNQ solubilized at the DODAB bilayer/magnetite particle interface.

Experimental

The 7,7,8,8-tetracyanoquinodimethane (TCNQ) and dioctadecyldimethylammonium bromide (DODAB) were purchased from the Kodak Co.

The ultrafine magnetite particles (Fe_3O_4) were prepared from an aqueous solution containing 1.51 g $FeCl_3$ and 0.64 g $FeCl_2$.6) During stirring, the pH of the solution was kept in the range of 10—11 by the drop-by-drop addition of 7.5% NH_4OH; the solution was then heated to about 60 °C in a water bath for 15 min. The precipitate was washed several times with distilled water by using the centrifugation of 10000 g for 10 min and was then dispersed in an aqueous solution. The large particles which aggregated were removed by using a membrane filter (pore size, 0.2 μm).

The magnetite particles which adsorbed TCNQ-containing DODAB were prepared as follows. DODAB of 10 mg and the required amount of TCNQ were dispersed in chloroform. After the evaporation of the chloroform, the residue was dispersed in distilled water (10 ml). The turbid suspension was added to the magnetite suspension and was sonicated by a horn-type ultrasonic homogenizer (28 kHz, Choonpa Co.) for 20 min at a temperature of about 60 °C. The magnetite particles are stabilized for a few days by the adsorption of the surfactant bilayer onto the solid surface. The size of the ultrafine magnetite particle studied here is less than 0.2 μm. The values of the pH after the preparation were in the range of 6.5—7. The details of the electric-field-pulse apparatus have been described elsewhere.7) The transient optical-transmittance change caused by the applied electric field was recorded with a transient recorder. The strength and the length of the electric-square pulse were 20 kV/cm and 25 μs respectively.

The ζ-potential of the magnetite particles incorporating the DODAB bilayer was measured by means of microelectrophoresis method.

The temperature of all the kinetic and spectral experiments was controlled at 25 °C.

Results and Discussion

To make clear the surface character of the present materials, microelectrophoretic measurements were carried out. It was found that the DODAB/magnetite particles which appeared in the microscope field moved toward the negative electrode in the pH range of 3—11. The values of the ζ-potential of the DODAB/magnetite particle system solubilized TCNQ were determined to be 70±3 mV in this pH range. This experimental result shows that no negatively charged particles exist in the basic region. Taking into account the fact that the pH_{zpc} value of the magnetite particle in an aqueous solution is nearly 7, one can see that the negative charge due to the surface functional groups of the magnetite particle is counteracted by the positive DODAB molecule of the bilayer under the present experimental conditions. Furthermore, it is seen that the surface charge may originate from only the DODAB molecule of the bilayer adsorbed on the particle surface or entrapping the particle in the vesicle.

Figure 1 shows the absorption spectrum of the TCNQ-DODAB system incorporating the magnetite particles. In this figure, three absorption bands appear at the wavelengths of 680, 750, and 850 nm, in agreement with those of the anion radical of TCNQ

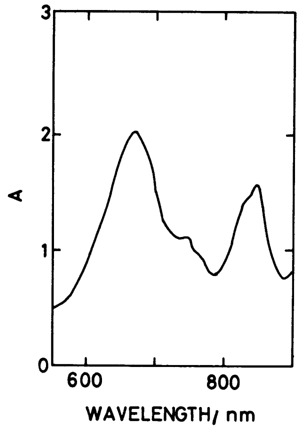

Fig. 1. Electronic absorption spectrum of the DODAB bilayer/magnetite particle system solubilized TCNQ. [TCNQ]=2.95×10^{-5} mol dm^{-3}, [DODAB]=2.54×10^{-3} mol dm^{-3}, particle concentration=0.36 g dm^{-3}, path length=1 cm.

Table 1. Kinetic Data of the Electric-Field Pulse Experiment in the TCNQ-DODAB/Magnetite System at 25 °C[a)]

[TCNQ]	[DODAB]	C_p	τ^{-1}
10^{-5} mol dm^{-3}	10^{-3} mol dm^{-3}	g dm^{-3}	10^4 s^{-1}
0.74	0.63	0.91	9.5±0.5
1.23	0.63	0.91	9.8±0.4
1.23	1.59	2.28	9.2±0.4
1.72	0.63	0.91	10.8±0.1
1.85	1.59	2.28	10.7±0.7
1.97	2.54	3.64	10.2±0.2
2.95	2.54	3.64	9.5±0.7
3.08	1.59	2.28	9.8±0.5
4.31	1.59	2.28	11.0±0.5
4.92	2.54	3.64	9.9±0.3
6.89	2.54	3.64	11.1±0.1

a) Each point is the mean value of the five lowest individual determinations. The experimental error stands for the standard deviation.

which have been reported by Melby et al.[8)] However, the TCNQ-DODAB system without particles and the TCNQ/magnetite particle system in chloroform do not show the absorption peak at 850 nm. Since TCNQ is insoluble in an aqueous solution, and since the steric hindrance of the DODAB molecule is too large to form an electron-donor-acceptor complex of DODAB with TCNQ in the DODAB bilayer solubilized TCNQ, an electron donor in this system may be the magnetite particles. Thus, one can see that an electron transfer from the magnetite particle to the solubilized TCNQ molecule takes place in the DODAB bilayer adsorbed on the magnetite-particle surface. In this reaction, the DODAB bilayer is not related to the complex formation, but provides only the reaction field.

A single relaxation was observed in the TCNQ-DODAB/magnetite system at the wavelength of 630—650 nm by using the electric-field-pulse method, in which the relaxation signal indicates an increase in the transmittance of the sample solution during the application of the electric field. No relaxation was observed in the aqueous solutions of DODAB-solubilized TCNQ or in the aqueous suspensions of only the DODAB/magnetite system. The value of the relaxation time, τ, in the presence of the electric field is equal to that in the absence of the electric field. The dependences of τ^{-1} on the concentrations of TCNQ and DODAB are given in Table 1. As can be seen from this table, the value of τ^{-1} increases slightly with an increase in concentration of TCNQ. In view of the lack of relaxation in both the DODAB/magnetite and the TCNQ-DODAB systems, it may be suggested that the single relaxation observed relates to an interfacial process at the DODAB bilayer/magnetite particle interface.

The formation of the electron-donor-acceptor complex at the bilayer/particle interface can be written schematically as:

$$(\mathrm{TCNQ})_{\mathrm{bilayer}} + \mathrm{Fe_3O_4} \overset{K}{\rightleftharpoons} (\mathrm{TCNQ}^{\overline{\cdot}}\cdots\mathrm{Fe_3O_4}^{\dagger})_{\mathrm{bilayer}}, \qquad [\mathrm{I}]$$

with:

$$K = \frac{[(\mathrm{TCNQ}^{\overline{\cdot}}\cdots\mathrm{Fe_3O_4}^{\dagger})_{\mathrm{bilayer}}]}{[\mathrm{Fe_3O_4}][(\mathrm{TCNQ})_{\mathrm{bilayer}}]}, \qquad (1)$$

where ( )$_{\mathrm{bilayer}}$ stands for "in the bilayer." TCNQ$^{\overline{\cdot}}$ is the anion radical of TCNQ, and K is the equilibrium constant. For the condition $C_{\mathrm{P}} \gg C_{\mathrm{TCNQ}}$, one can obtain the following equation:

$$\frac{C_{\mathrm{TCNQ}}}{A_{850}} = \frac{1}{\varepsilon_{850}}\left\{\frac{1}{KC_{\mathrm{p}}}+1\right\}, \qquad (2)$$

where C_{TCNQ}, C_{P}, A_{850}, and ε_{850} are the total concentration of TCNQ, the total concentration of the magnetite particle, the absorbance, and the molar extinction coefficient of the anion radical of TCNQ at the wavelength of 850 nm respectively. The plot of $C_{\mathrm{TCNQ}}/A_{850}$ vs. $1/C_{\mathrm{P}}$ yields a straight line, as is shown in Fig. 2a. From the intercept of the straight line, the value of ε_{850} was obtained as 44000. This value is in good agreement with that of 43300 reported by Melby et al.[8)] The value of the slope in this plot is close to zero, indicating a very high value for K. Thus, all of the TCNQ molecules form an electron-donor-acceptor complex with magnetite at the interface of the DODAB bilayer.

For the reaction at the interface (Mechanism II),

$$2(\mathrm{TCNQ}^{\overline{\cdot}}\cdots\mathrm{Fe_3O_4}^{\dagger})_{\mathrm{bilayer}} \underset{k_{\mathrm{b}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} (\mathrm{TCNQ}^{\overline{\cdot}}\cdots\mathrm{Fe_3O_4}^{\dagger})_{\mathrm{bilayer},2} \qquad [\mathrm{II}]$$

the reciprocal relaxation time is written as:

$$(\tau^{-1})^2 = 8k_{\mathrm{f}}k_{\mathrm{b}}C_{\mathrm{TCNQ}} + (k_{\mathrm{b}})^2. \qquad (3)$$

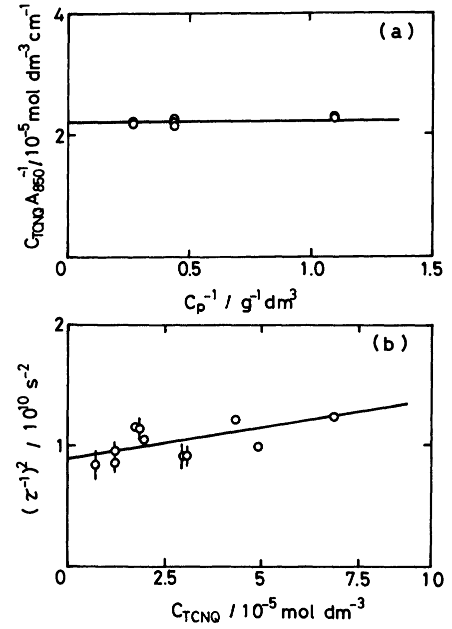

Fig. 2. (a) Plot of $C_{\mathrm{TCNQ}}/A_{850}$ vs. $1/C_p$ in Eq. 2. (b) Plot of $(\tau^{-1})^2$ vs. C_{TCNQ} in Eq. 3.

The plot of $(\tau^{-1})^2$ vs. C_{TCNQ}, shown in Fig. 2b, yields a straight line. This linearity leads to the conclusion that the single relaxation phenomenon observed may be attributed to Mechanism II. The values of the rate constants, k_f and k_b, obtained from the values of the slope and the intercept of the straight line in Fig. 2b are as follows: $k_f=6.6\times10^7$ mol^{-1} dm^3 s^{-1}; $k_b=9.5\times10^4$ s^{-1}. The anion radical of the TCNQ molecule, which has the absorption peak at 850 nm, could not be found in the TCNQ–DODAB system. This fact indicates that it is too hard to form an electron-donor-acceptor complex in the bilayer because of the lack of an electron donor. Since the DODAB bilayer/magnetite particle interface was made by incorporating the particle, we are led to the conclusion that the interface may act as a reaction field for the electron-donor-acceptor complex formation between the magnetite particle and the TCNQ molecule.

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