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Thermodynamic Study of the Reaction between N-Methylphenothiazine and Iron(III) Ion in SDS-Hexanol Mixed Micellar Solutions

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Abstract

N-methylphenothiazine reacts with Fe(III) ion and reaches equilibrium in the anionic SDS micellar solution as reported by Minero et al. However, the reaction did not take place in the cationic DTAB, non-ionic Brij 35 micellar and water-ethanol (1:1) solutions. In order to obtain more information about the effect of surface negative charge of micelle on the reaction, thermodynamic study of the reaction was carried out in SDS-hexanol mixed micellar solutions. The equilibrium constant decreases with increasing the concentration of hexanol in the mixed micellar solutions. Both free energy and enthalpy changes of the reaction shift in the positive direction with increasing the concentration of hexanol, reflecting the fact that the reaction becomes more difficult with increasing the concentration of hexanol. The entropy change seems independent of the concentration of hexnol.

Introduction

We previously reported that both redox reactions of N-benzoylleucomethylene blue (BLMB) with hexacyanoferrate(III) ion and of tetramethylbenzidine (TMB) with hexacyanoferrate(III) ion proceeded only in the anionic sodium dodecylsulfate (SDS) micellar solutions.[1] The reaction did not take place in the cationic dodecytrimethylammonium bromide (DTAB), non-ionic polyoxyethylenedodecyl ether (Brij 35) micellar and water-ethanol (1:1) solutions. In order to obtain more informations about the reason, we attempted to obtain micellar effect on the thermodynamic properties of the reactions. However, we could not obtain the thermodynamic properties because these reactions are irreversible.

Minero et al. had reported that N-methylphenothiazine (MPTZ) reacted with iron(III) ion and reached equilibrium in the presence of various micellar-forming surfactants (CTAN, Triton, SDS).[2] Our preliminary study on the reaction, however, indicated that the reaction proceeded only in the anionic SDS solution. In the present study, we reinvestigated micellar efects on the reaction. Further, we carried out the investigation of the thermo-dynamic properties of the reaction in SDS-hexanol mixed micellar solutions to obtain more

informations about the role of the negative surface charge of the micelle on the reaction.

Experimental Section

Materials. Biochemical grade SDS supplied by Wako Chemicals Co. was recrystallized from methanol-isopropanol (1:1) and dried in vacuo for 8 hours at 70 - 75℃.[3] The reagent grade DTAB was purchased from Tokyo Kasei Co. and recrystallized from acetone containing small amount of ethanol.[4] Brij 35 was GR grade from Kanto Chemicals Co., and triply crystallized from isopropanol.[5] Then the crystal was dried in vacuo for 8 hours at room temperature. Pyrene (Nakarai Chemicals Co., reagent grade) was recrystallized from ethanol and submitted to the vacuum sublimation (1 mm Hg, 90 - 110℃).[6] N, N -dimethyl-aniline (DMA) was reagent grade from Wako, and distilled under nitrogen atmosphere with reduced pressure (8 mm Hg, 67-68℃) after being refluxed together with acetic anhydride, washed with water and dried with potassium hydroxide.[7] N-Methylphenothiazine (MPTZ) was purchased from Acros and recrystallized from ethanol saturated with Ar.[2] The melting point of purified material was in agreement with the literature value (99℃). Both hexanol and iron(III) chloride hexahydrate were reagent grade from Kanto Chemicals Co., and used as received. All other chemicals were of reagent grade and used without further purification. The solutions were prepared with triply distilled water.

Apparatus. Absorbance was measured with a Hitachi MPS-3T spectrophotometer. Fluorescence spectra were recorded on a Hitachi 204 spectrofluorometer equipped with a Watanabe Sokki WX4421 X-Y recorder. An Union Giken MX-7 sample mixer was employed to initiate the reaction. The temperature was controlled by a Komatsu-Yamato CTE-240 Coolnics Circulator when it was needed.

Methods. The reaction was initiated by mixing micellar solutions containing MPTZ and those containing iron(III) chloride using a sample mixer, and monitored by measuring absorbance of $MPTZ^+$ cation radical produced by the reaction at 516 nm with a cell of 1-cm pathlength. A typical initial concentration of MPTZ was 1×10^{-4} M and that of iron(III) chloride 4×10^{-4} M.

The aggregation numbers of SDS in the SDS-hexanol mixed micelles were determined by the method proposed by Turro and Yekta[8] using pyrene as the fluorescence substance and DMA as the quencher instead of tris- (bipyridine) ruthenium ion and 9-methylanthracene, respectively.[9] Those of hexanol were determined according to the method described by Almgren and Swarup[10] assuming that all hexanol added to the solution reside in the micellar phase.

Results and Discussion

Micellar Effect. First, we reinvestigated the micellar effect on the redox reaction

between MPTZ and iron(III) ion. The reaction proceeded in the anionic SDS micellar solution and reached equilibrium as reported by Minero et al.[3] Fig. 1 shows the absorption spectrum of the reaction mixture of MPTZ and iron(III) chloride in the SDS solution. No spectrum was, however, observed in this wavelength region when the reactants were mixed in DTAB, Brij 35 micellar and water-ethanol (1:1) solutions.
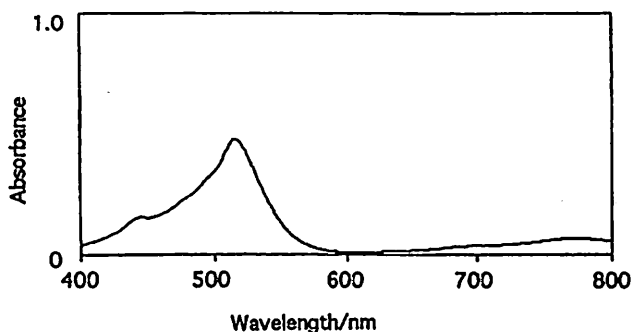

Fig. 1. Spectrum for the reaction mixture between MPTZ and Fe(III) ion in the SDS micellar solution. [SDS]: 0.05, [H₂SO₄]: 0.005, [Na₂SO₄]: 0.05, [MPTZ]: 1×10^{-4}, [FeCl₃]: 4×10^{-4}M.

According to Minero et al., the spectrum observed in SDS solution is ascribed to $MPTZ^+$ cation radical produced by the reaction. $MPTZ^+$ is produced instantaneously when the reactants are mixed, and the absorbance due to $MPTZ^+$ remains constant for long time, suggesting that the reaction reaches equilibrium as shown by equation (1). Fig. 2 shows

$$MPTZ + Fe^{3+} \rightleftharpoons MPTZ^+ + Fe^{2+} \qquad (1)$$
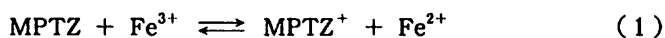
the time profile of absorbance of $MPTZ^+$ at 516 nm.
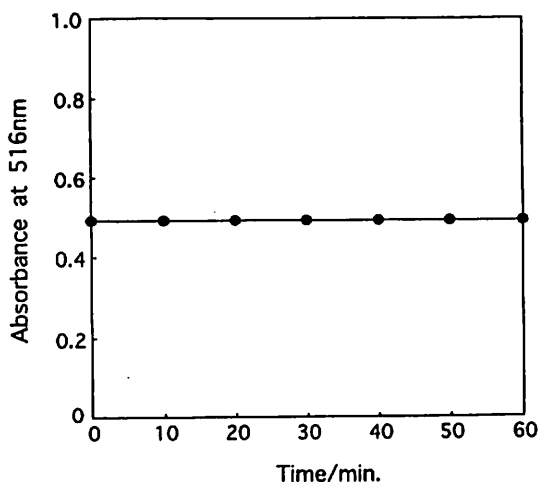

Fig. 2. Relationship between absorbance of the reaction mixture of MPTZ with Fe (III) ion and the reaction time. [SDS]: 0.05, [H₂SO₄]: 0.005, [Na₂SO₄]: 0.05, [MPTZ]: 7.5×10^{-5}, [FeCl₃]: 6×10^{-3}M.

In order to obtain absorption coefficient of MPTZ$^+$ cation radical, absorbance of MPTZ$^+$ was measured while the concentration of MPTZ was kept constant at 4×10^{-5} M and that of iron(III) ion was varied in the SDS micellar solution. The results are shown in Fig. 3. As seen from the figure, the absorbance of MPTZ$^+$ at 516 nm increased with
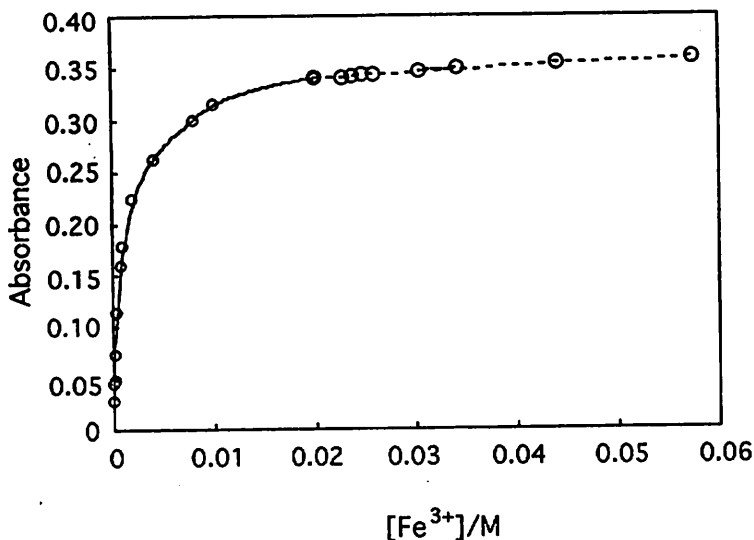

Fig. 3. Relationship between absorbance (516 nm) of MPTZ$^+$ produced by the reaction of MPTZ with Fe(III) ion and the latter concentration in SDS micellar solutions. Broken line was extended by a curve fitting method. [SDS]: 0.05, [H$_2$SO$_4$]: 0.005, [Na$_2$SO$_4$]: 0.05, [MPTZ]: 4×10^{-5}M.

increasing the concentration of iron(III) ion, but did not reach a constant value even at the concentration of 0.02 M (concentration beyond 0.02 M produced precipitate). In the figure, the broken line was extended by a curve fitting method using the ninth order polynomial. The absorption coefficient of MPTZ$^+$ at 516 nm was determined to be 8.6 $\times 10^3$ M^{-1} cm^{-1} from the absorbance of plateau region on the broken line assuming that the original MPTZ was completely changed to MPTZ$^+$ in this region. Minero et al.[2] obtained 9.3×10^3 M^{-1} cm^{-1} as the absorption coefficient by using the more stronger oxidant Ce(IV) ion. However, we could not obtain stable absorbance when Ce(IV) ion was employed instead of Fe(III) ion. It seemed that MPTZ$^+$ was further oxidized by the stronger oxidant Ce(IV) ion.

SDS-Hexanol Mixed Micellar Solutions. SDS-hexanol mixed micellar solutions were prepared by keeping the concentration of SDS at 0.05 M and changing the concentration of hexanol from 0 to 0.05 M. Then the aggregation numbers of SDS and hexanol of the mixed micelle were determined by the method described in the experimental section. The results are shown in Fig. 4. As seen from the figure, the aggregation number of SDS remained constant but that of hexanol increased with increasing its concentration.
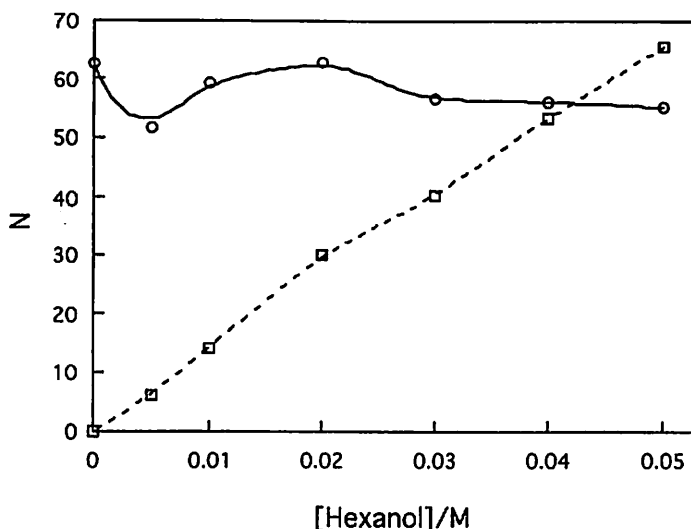
Fig. 4. Aggregation number of SDS (○) and hexanol (□) as a function of hexanol concentration in SDS-hexanol mixed micellar solutions. [SDS]: 0.05 M.

Thermodynamic Properties. Since the reaction between MPTZ and iron(III) ion proceeded only in the anionic SDS micellar solution, we carried out the experiment in SDS-hexanol mixed micellar solutions and investigated the effect of the composition of the mixed micelle on the thermodynamic properties of the reaction between MPTZ and Fe(III) ion to obtain more information about the role of negative surface charge of the micelle on the reaction.

The concentration of MPTZ$^+$ was determined using the absorption coefficient of 8.6 $\times 10^3$ M^{-1} cm^{-1} obtained in this study by measuring the absorbance at 516 nm promptly after the reactants were mixed with a sample mixer. The equilibrium constant was calculated by putting the concentration of each species to mass action law for the reaction described by equation (1). The results are shown in Table 1. The equilibrium constant

Table 1. Equilibrium constant K for the reaction between MPTZ and Fe(III) ion in SDS-hexanol mixed micellar solutions. [SDS]: 0.05, [H$_2$SO$_4$]: 0.005, [Na$_2$SO$_4$]: 0.05, [MPTZ]: 1×10^{-4}, [FeCl$_3$]: 4×10^{-4}M.

[Hexanol]/ M	N$_{SDS}$	N$_{Hexanol}$	K			
			20℃	25℃	30℃	35℃
0	63	0	6.62×10^{-2}	8.61×10^{-2}	9.58×10^{-2}	9.84×10^{-2}
0.005	52	6	1.40×10^{-1}	1.69×10^{-1}	1.97×10^{-1}	2.26×10^{-1}
0.01	59	14	7.05×10^{-2}	7.84×10^{-2}	9.14×10^{-2}	1.02×10^{-1}
0.02	63	30	3.22×10^{-2}	3.87×10^{-2}	4.46×10^{-2}	5.09×10^{-2}
0.03	57	40	1.84×10^{-2}	2.27×10^{-2}	2.56×10^{-2}	2.78×10^{-2}
0.04	56	53	1.14×10^{-2}	1.64×10^{-2}	1.92×10^{-2}	2.12×10^{-2}
0.05	55	66	4.53×10^{-3}	8.39×10^{-3}	1.02×10^{-2}	1.14×10^{-2}

has a tendency to decrease with increasing the concentration of hexanol of the mixed micellar solutions, that is, with decreasing the negative surface charge density of micelle.

Fig. 5 is a typical example of the plots of equation (2). From the plots thermodynamic

$$-R \ln K = \Delta H^0 / T - \Delta S^0 \qquad (2)$$

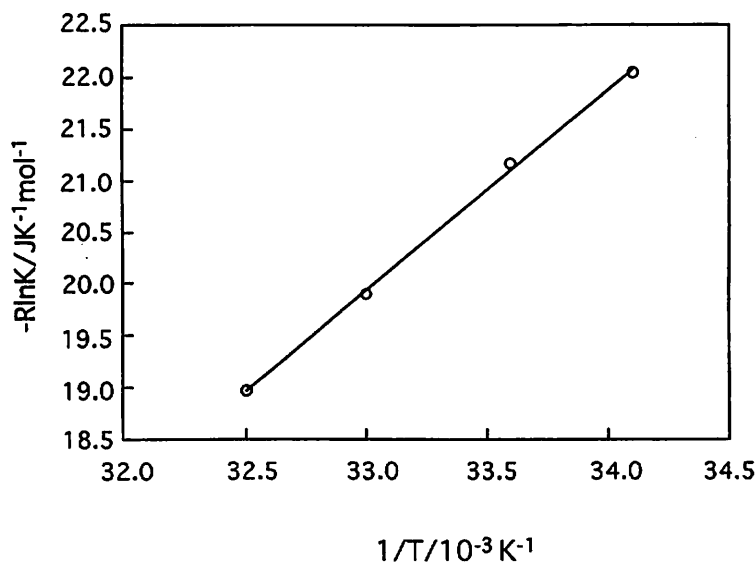properties such as enthalpy and entropy changes were evaluated. The results are shown

Fig. 5. Plot of $-R \ln K$ vs $1/T$. [SDS]: 0.05, [hexanol]: 0.01, [H$_2$SO$_4$]: 0.005, [Na$_2$SO$_4$]: 0.05, [MPTZ]: 1×10^{-4}, [FeCl$_3$]: 4×10^{-4}M.

in Table 2. As seen from the table, both free energy and enthalpy changes for the reaction between MPTZ and Fe(III) ion increase in the positive direction with increasing the

Table 2. Free energy, enthalpy and entropy change for the reaction between MPTZ and Fe(III) ion in SDS-hexanol mixed micellar solutions. [SDS]: 0.05, [H$_2$SO$_4$]: 0.005, [Na$_2$SO$_4$]: 0.05, [MPTZ]: 1×10^{-4}, [FeCl$_3$]: 4×10^{-4}M.

[Hexanol]/ M	N_{SDS}	$N_{Hexanol}$	ΔG^0/KJmol^{-1}	ΔH^0/KJmol^{-1}	ΔS^0/JK^{-1}mol^{-1}
0	63	0	6.24	19.9	45.8
0.005	52	6	4.43	24.4	67.1
0.010	59	14	6.26	19.4	44.2
0.020	63	30	8.09	23.3	51.0
0.030	57	40	9.47	20.9	38.2
0.040	56	53	10.4	31.0	69.0
0.050	55	66	12.3	45.4	111

concentration of hexanol, reflecting the fact that the reaction becomes more difficult with increasing the concentration of hexanol maybe because of the decrease in the negative surface charge density of the mixed micelle. The entropy change of the reaction seems to be independent of the concentration of hexanol except the value of the last row in the table.

The results may be explained in the following way. The energy level of the highest occupied molecular orbital of MPTZ may be enhanced by the repulsive interaction of the orbital electron and the negative surface charge of the micelle, and MPTZ may become more difficult to transfer electron to Fe(III) ion with increasing the concentration of hexanol in the mixed micellar solution because the negative surface charge density of the micelle is lowered. In our previous electrochemical study of N-benzoylleucomethylene blue (BLMB) in Brij 35-SDS mixed micellar solutions, the redox potential of BLMB was shifted toward nagative direction with increasing the concentration of SDS, that is, inreasing the negative surface charge density of micellte. [1] MPTZ is supposed to behave in the same way as BLMB.

Conclusions

MPTZ and Fe(III) ion undergo redox reaction, and reach equilibrium in the anionic SDS micellar solution as reported by Minero et al.[2] However, the reaction did not take place in the cationic DTAB, non-ionic Brij 35, and water-ethanol (1:1) solutions.

The equilibrium constant of the reaction decreases with increasing the concentration of hexanol in SDS-hexanol mixed micellar solutions. Both free energy and enthalpy changes of the reaction shift in the positive direction with increasing the concentration of hexanol in the SDS-hexanol mixed micellar solutions, reflecting the fact that the reaction becomes more difficult with increasing the concentration of hexanol maybe because of the decrease in the negative surface charge density of the mixed micelle. The entropy change of the reaction seems to be independent of the concentration of hexanol.

The results may be explained by the assumption that the energy level of the highest occupied molecular orbital of MPTZ is enhanced by the repulsive interaction between the orbital electron and negative surface charge of micelles and MPTZ becomes to be able to transfer an electron to Fe(III) ion.

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