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Kinetic and Electrochemical Studies of N-Benzoylleucomethylene Blue and Hexacyanoferrate(Ⅲ) Ion in Brij 35-SDS Mixed Micellar Solutions

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Abstract

The Kinetic study was carried out for the redox reaction between N-benzoylleucomethylene blue(BLMB) and hexacyanoferrate(Ⅲ) ion in polyoxyethylenedodecyl ether(Brij35)-sodium dodecyl sulfate(SDS) mixed micellar solutions. No reaction proceeded in the solution containing only Brij 35 micelles. The reaction, however, took place when SDS was added to the Brij 35 micellar solutions, and the rate was increased with increasing the concentration of SDS. The redox potentials of hexacyanoferrate(Ⅲ) ion and BLMB were measured in the mixed micellar solutions by means of cyclic voltammetry. The oxidation potential of BLMB was suddenly decreased by the addition of SDS to the Brij 35 micellar solutions, while the reduction potential of hexacyanoferrate(Ⅲ) ion remains almost constant irrespective of the concentration of SDS.

Introduction

The micellar effects on the reaction kinetics have been extensively studied[1]. The results showed that the rate was acceleratad for the reaction between ion in the bulk water phase and organic molecule in the micellar phase with the surface charge opposite to the ion, and retarded in the reverse case because of the electrostatic interactions between the ion and the surface charge of the micelle. In the previous study[2], however, we reported that BLMB and hexacyanoferrate(Ⅲ) ion did not react in cationic dodecyltrimethylammonium bromide (DTAB) and nonionic Brij 35 micellar solutions. Further, no reaction proceeded in water-ethanol(1:1) solutions either. On the other hand, the reaction took place fairly fast in the anionic SDS micellar solutions in spite of the electrostatic repulsion between hexacyanoferrate(Ⅲ) anion and SDS micelle with negative surface charge. The results were ascribed to the interpretation that methylene blue(MB) cation produced by the reaction was stabilized by the negative surface charge of the SDS micelle or BLMB became more easily oxidizable when it was surrounded by the negative surface charge of the micelle.

In the present study, we carried out the kinetic study of the redox reaction between BLMB and hexacyanoferrate(Ⅲ) ion in Brij 35-SDS mixed micellar solutions, and also the electrochemical study of both reactants in the same solutions in order to obtain more information about our previous result that the redox reaction between BLMB and hexacyanoferrate(Ⅲ) ion proceeded only in the micellar solutions with negative surface charge.

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Experimental

Materials. EP grade BLMB was purchased from Nakalai Tesque, Inc.and recrystallaized from ethanol[3]. Brij 35(Tokyo Chemicals, Co.,GR grade) and SDS(Wako Chemicals Co., biochemical grade) were also recrystallized from isopropanol and metanol-isopropanol(1:1), respectively[3]. Sodium bis(2-ethylhexyl)sulfosuccinate(AOT)was supplied by Tokyo Chemicals Co.and dried according to the method described dy Joselevich and Willner [4]. Sodium hexacyanoferrate(Ⅲ) was synthesized dy oxidizing sodium hexacyanoferrate(Ⅱ) according to the method used for the sythesis potassium hexacyanoferrate(Ⅲ)[5], and recrystallized from water. Water was distilled from potassium permanganate solution containing sodium hydroxide, then submitted to twice distillation by use of pyrex glassware. All the other chemicals were of reagent grade obtained from Kanto Chemicals Co.and used without further purification.

Apparatus. The absorption spectra were recorded on Hitachi U-2000 double beam spectrophotometer. A Uniongiken MX-7 sample mixer was used to mix the reactants. The redox potentials were measured by a BAS 100B/W & CV-50W cyclic voltammograph equipped with a glassy carbon electrode.

Measurements. The reaction was monitored by measuring the absorbance of methylene blue produced from the reaction at around 664 nm using a stopped-flow photometric technique. The redox potentials of BLMB and hexacyanoferrate(Ⅲ) ion were measured by the cyclic voltammetry. The surface tension of the sample solutions was measured with a drop-weight method. Sodium salt of hexacyanoferrate(Ⅲ) was used as a source of hexacyanoferrate(Ⅲ) ion because potassium cation produced precipitation with SDS anion. The typical initial concentrations of the reactants were 1.0×10^{-5}M for BLMB and 5.0×10^{-4}M for hexacyanoferrate(Ⅲ) ion.

Results and Discussion

Brij 35-SDS Mixed Micelle. In order to obtain knowledge about whether Brij 35 and SDS surfactants form mixed micelle or not, we measured the surface tension of the solutions containing SDS alone and both SDS and Brij 35. The surface tension is plotted against the concentration of SDS in Figure I. In the case of the solution containing SDS alone,the bending point on the surface tension curve appears at the SDS concentration of about 8×10^{-3}M consistent with the literature value of cmc for SDS. On the other hand,the bending point was at about 10×10^{-3}M when the solution contains 0.01M Brij 35 and various amount of SDS. The difference of 2×10^{-3}M in SDS concentration is supposed to be dissolved into already existing Brij 35 micelles,forming mixed micelles.

The Rate Constant in Brij 35 - SDS Mixed Micellar Solutions. The second-order rate constants were measured for the redox reaction between BLMB and hexacyanoferrate(Ⅲ) ion in Brij 35 - SDS mixed micellar solutions where the concentration of Brij 35 was kept constant and that of SDS was varied. The results are plotted against the concentration of SDS in Figure 2. As seen from the figure,the rate constant is almost zero in the solution

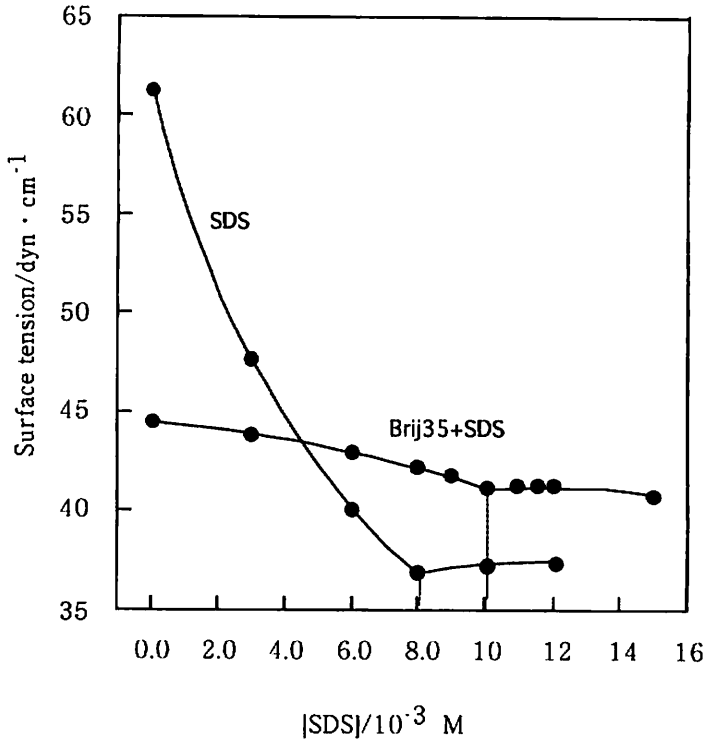

Figure 1. Surface tension of SDS and Brij35+SDS solutions as a function of the SDS concentrations. Concn. of Brij35 : 0.010 M.

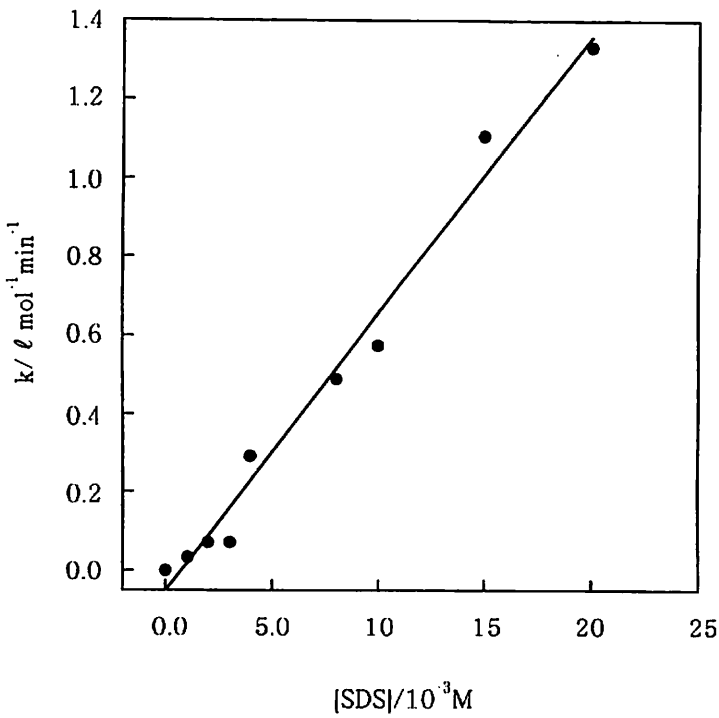

Figure 2. Relationship between the rate constant(k) and concentration of SDS for the reaction of BLMB with $Fe(CN)_6^{3-}$ in Brij35-SDS mixed micellar solutions. Concn. of Brij35 : 0.01 M, concn. of BLMB : 1.0×10^{-5} M, conc. of $Fe(CN)_6^{3}$: 5.0×10^{-4} M.

containing only nonionic Brij 35 micelle, but it increases with increasing the concentration of SDS in spite of electrostatic repulsion between negative charge of hexacyanoferrate(Ⅲ) anion and that of SDS in the mixed micelle in which BLMB resides. The reason may be as follows; the reaction rate becomes larger when SDS concentration increases because the reaction product methylene blue cation is stabilized by the negative charge of SDS, or BLMB becomes more easily oxidizable when it is surrounded by the negative charge of the mixed micelle.

Effect of the Ionic Strength on the Reaction. We investigated effect of the ionic strength on the reaction between BLMB and hexacyanoferrate(Ⅲ) ion in Brij 35 -SDS mixed micellar solutions to obtain the knowledge about the position of BLMB in the mixed micellar solutions during the reaction with hexacyanoferrate(Ⅲ) ion. The ionic strength of the solution was varied by adding sodium sulfate. The logarithm of the second order rate constant is plotted against square root of the ionic strength in Figure 3. It increases linearly

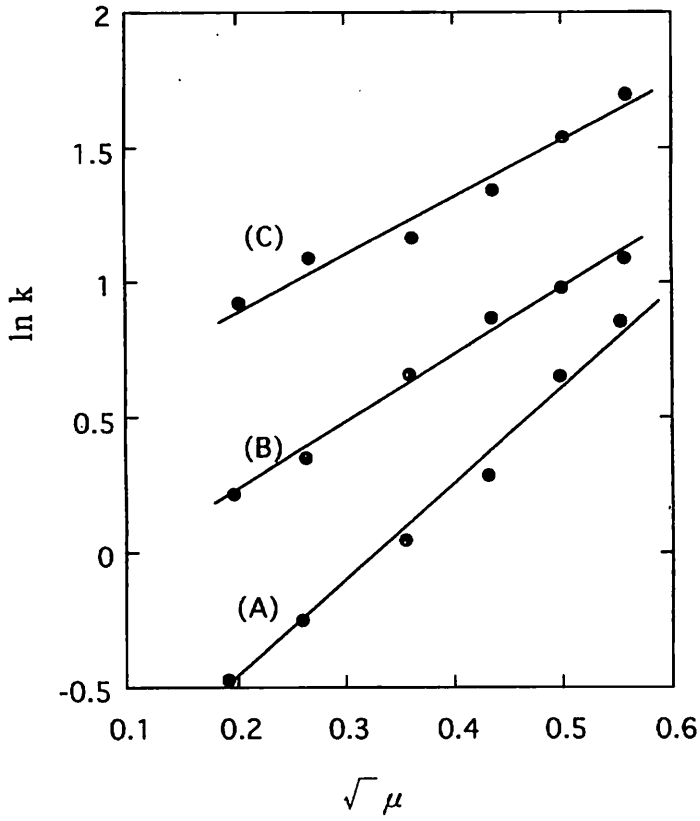

Figure 3. Effects of ionic strength(μ) on the rate constant(k) of the reaction between BLMB and $Fe(CN)_6^{3-}$ in Brij35-SDS mixed micellar solutions containing various amount of Na_2SO_4. Concn. of Brij35 : 0.010 M, concn. of BLMB : 1.0×10^{-5} M, concn. of $Fe(CN)_6^{3-}$:5.0×10^{-4} M, conc. of SDS : (A)0.004 M, (B)0.006 M, (C)0.008 M.

with increasing square root of the ionic strength of the mixed micellar solutions. The result suggests that BLMB behaves as if it were on anion, indicating that BLMB is surrounded by the negative surface charge of SDS in Brij 35-SDS mixed micellar solutions.

The Reaction in the Other Solutions. In the previous section, we indicated that BLMB can react with hexacyanoferrate(Ⅲ) ion when the former is surrounded with negative surface charge due to SDS in the Brij 35-SDS mixed micelle. In this section, we investigated more about the role of SDS in the reaction. We studied the kinetics of the reaction between BLMB and hexacyanoferrate(Ⅲ) ion in water ethanol (1:1) solutions containing SDS from 0 to 0.02 M. No reaction was observed in these solutions. It is known that SDS does not form micelles in the existence of ethanol. The present results indicate again that BLMB can react with hexacyanoferrate(Ⅲ) ion when the former is surrounded with negative charge.

Further, we investigated whether BLMB react with hexcyanoferate(Ⅲ) ion in reverse micellar solutions where BLMB is not surrounded by negative charge. We employed anionic AOT as reverse micelle forming surfactant because it is well known to form reverse micelle in heptane. In addition, it is observed that BLMB and hexacyanoferrate(Ⅲ) ion react in the ordinary AOT micellar solutions as in the case of SDS. AOT reverse micellar solutions were prepared according to the method described by Joselevich and Willner. The typical reverse micelle solution contained 0.01 M AOT, 1×10^{-5} M BLMB, 5×10^{-4} M $K_3Fe(CN)_6$ and 0.75 M water in heptane. The reaction of BLMB and hexacyanoferrate(Ⅲ) ion did not proceed in this solution. The reaction did not take place either even when SDS was added to the solutions up to 6.0×10^{-3} M. However, oxidation of BLMB occured in the AOT reverse micellar solution when the more stronger oxidant iron(Ⅲ) ion was employed instead of hexacyanoferrate(Ⅲ) ion. The present study also suggests that BLMB is oxidizd by hexacyanoferrate(Ⅲ) ion only when the former is surrounded with negative charge of micelles as we mentioned before.

Cyclic Voltammetry of BLMB and Hexacyanoferrate(Ⅲ) Ion in Brij 35 SDS Mixed Micellar Solutions. The results in the previous sections suggested that BLMB became more easily oxidizable when it was surrounded by the surface negative charge of micelle. In order to obtain more informations, we carried out the cyclic voltammetry of BLMB and hexacyanoferrate(Ⅲ) ion in the Brij 35-SDS mixed micellar solutions in which the concentration of Brij 35 was kept constant at 0.01M and that of SDS was varied from 0 to 0.008 M. The working electrode was glassy carbon, reference electrode Ag/AgCl, and counter electrode Pt wire. The solutions contained 0.10 M Na_2SO_4 as supporting electrolyte. The typical examples of voltammograms are shown for hexacyanoferrate(Ⅲ) ion and BLMB in Figure 4(A) and(B), respectively. Oxidation potentials of BLMB and the reduction potentials of hexacyanoferrate(Ⅲ) ion are plotted against the concentration of SDS in Figure 5. As seen from the plots, the oxidation potential of BLMB decreases with increasing

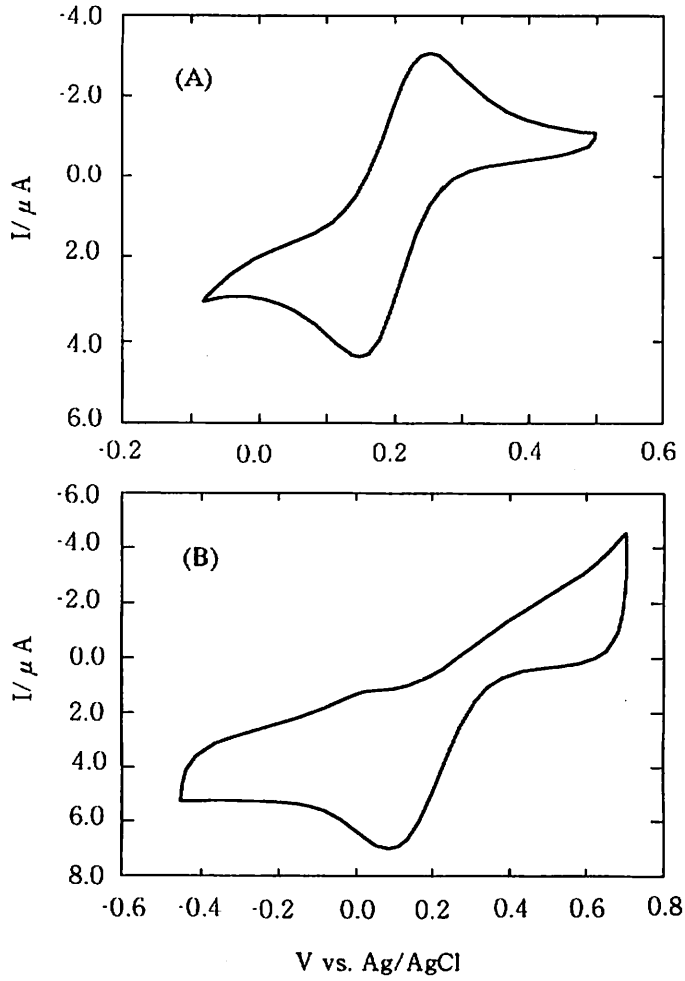

Figure 4. Cyclic voltammograms of $Fe(CN)_6^{3-}$ (A) and BLMB (B) in Brij35-SDS mixed micellar solutions. Concn. of Brij35 : 0.010 M, concn. of SDS : 0.003 M, concn. of $Fe(CN)_6^{3-}$:1.0×10^{-3} M, concn. of BLMB : 2.0×10^{-5} M.

the concentration of SDS in the mixed micellar solutions and levels off, while the reduction potential of hexacyanoferrate(Ⅲ) ion remains almost constant regardless of the concentration of SDS. The results are consistent with the observations in the previous sections.

Conclusions

The redox reaction between BLMB and hexacyanoferrate(Ⅲ) ion was studied in the various solutions. No reaction took place in Brij 35 micellar solutions. The reaction, however, proceeded in the Brij 35-SDS mixed micellar solutions, and the second-order rate constant increased with increasing the concentration of SDS. Furthermore, the rate was also increased with increasing the ionic strength of the mixed micellar solutions, indicating

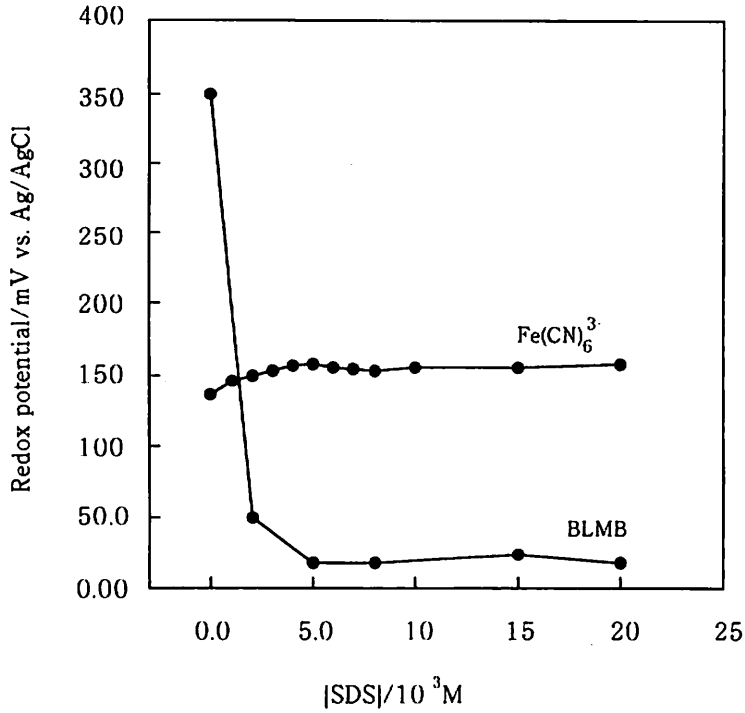

Figure 5. Reduction potentials of $Fe(CN)_6^{3-}$ and oxidation potentials of BLMB in Brij35-SDS mixed micellar solutions as a function of SDS concentrations. Concn. of Brij35 : 0.010 M, concn. of $Fe(CN)_6^{3-}$: 1.0×10^{-3} M, concn. of BLMB : 2.0×10^{-5} M.

that BLMB behaves like an anion surrounded by the negative surface charge due to SDS in the mixed micelle. In the water-ethanol(1:1) solutions, the reaction did not occur even when SDS was added. The reaction did not take place either in the AOT reverse micellar solutions with and without SDS.

Oxidation potential of BLMB decreased with increasing the concentration of SDS in the mixed micelles, while the reduction potential of hexacyanoferrate(Ⅲ) ion remains almost constant regardless of the concentration of SDS. These results seem to suggest that BLMB becomes more easily oxidizable when it is surrounded by negative charge. This may be the reason for the observation that the reaction between BLMB and hexacyanoferrate(Ⅲ) ion takes place only in the micellar solutions with negative surface charge.

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References

1) (a)J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York, 1975. (b)C. A. Bunton, F. Nome F. H. Quina, and L. S. Romsted, *Account of Chemical Research*, *24*, 357(1991).
2) T. Uchihara, A. Abe, and A. Kinjo, *Bull. Coll. Sci., Univ. Ryukyus*, No.44 : 119(1987).
3) T. Uchihara, A. Abe, and A. Kinjo, *Ibid.*, No. 36 : 81(1983).
4) E. Joselevich and I. Willner, *J. Phys. Chem.*, *99*, 6903(1995).
5) The Chemical Society of Japan ed., "Shinjikkenkagakukoza;Synthesis of Inorganic Compound(Ⅲ)", 8, Maruzen, Tokyo, 1977, p. 1197.