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Kinetic Studies of the Redox Reaction between N-Benzoylleucomethylene Blue and Hexacyanoferrate (III) Ions in SDS-Hydrocarbon Mixed Micellar Solutions

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Abstract

The second-order rate constant was measured for the reaction between N-benzoylleucomethylene blue (BLMB) and hexacyanoferrate (III) ions by using the stopped flow spectrophotometric technique in sodium dodecylsulfate (SDS)-hexane, SDS-heptane and SDS-octane mixed micellar solutions. The rate constant increased with increasing the molecular fraction of SDS in the mixed micelles for all the hydrocarbons used, despite electrostatic repulsion between the negative surface charge of the micelles and hexacyanoferrate (III) anions. The results seem to support the conclusion that electrostatic stabilization of methylene blue (MB) cations (reaction product) by the negative surface charge of the micelles is the driving force for the reaction.

Introduction

Micellar effects on the reaction kinetics have been extensively studied.¹⁻³⁾ For the reaction between organic compound compartmentalized in micelles and ions in the aqueous phase, the rate is accelerated in the case of micelles with surface charge opposite to that of ions and retarded in the micelles with the same charge as the ions because of the electrostatic interaction between the micelles and ions.

However, Uchihara et al.⁴⁾ reported the unusual results for the reaction between BLMB and hexacyanoferrate (III) ion. The largest reaction rate was observed in the SDS micellar solutions in spite of the electrostatic repulsion between negatively charged SDS micelles containing BLMB and hexacyanoferrate (III) anions in the aqueous phase. In the nonionic Brij 35 micellar solutions, the reaction proceeded very slowly. No reaction took place both in the positively charged dodecyltrimethylammonium bromide micelle and water-ethanol solutions. Their observations seem to suggest that the negative surface charge of the micelle plays an essential role on the reaction.

In the present study, we investigated kinetics of the redox reaction between BLMB and hexacyanoferrate (III) ion in SDS-hydrocarbon mixed micellar solutions with different hydrocarbon contents using the stopped flow spectrophotometric technique to obtain more information on the relationship between the reaction rate and negative surface charge of the mixed micelles. n-Hexane, n-heptane and n-octane were used to prepare the SDS-hydrocarbon mixed micellar solutions.

Experimental

Materials. BLMB (Nakarai Chem. Co., reagent grade) and SDS (Wako Pure Chemicals Industries, Ltd., biochem. grade) were recrystallized from ethanol and methanol-isopropanol (1:1) mixed solvent, respectively, and dried in vacuo before use⁵⁾.

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Sodium hexacyanoferrate (III) was synthesized by oxidizing commercially available sodium hexacyanoferrate (II) in accordance with the method for the synthesis of potassium hexacyanoferrate (III)⁶. The purity was checked spectrophotometrically against reagent grade potassium hexacyanoferrate (III). Sodium salt was used as the source of hexacyanoferrate (III) ions, because potassium ions give rise to precipitation with SDS anions. Pyrene (Nakarai Chem. Co., reagent grade) was recrystallized from ethanol and submitted to the vacuum sublimation (1mm Hg, 90–110°C)⁷. N, N-dimethylani-line (DMA) was reagent grade from Wako, and distilled under the nitrogen atmosphere with reduced pressure (8mm Hg, 67–68°C) after being refluxed together with acetic anhydride, washed with water and dried with potassium hydroxide⁸. n-Hexane (Wako Pure Chemicals Industries Ltd., spectroscopic grade), n-Heptane (Nakarai Chem. Co., spectroscopic grade) and n-octane (Kishida Chemical Co., reagent grade) were used without further purification. All the solutions were prepared with triply distilled water.

Apparatus. Absorbance was measured with a Hitachi Model EPS-3T spectrophotometer. Fluorescence spectra were recorded on a Hitachi Model 850 spectrofluorometer. An Union Giken Model MX-7 sample mixer was employed to initiate the reaction.

Kinetic Measurement. The reaction was initiated by mixing micellar solutions containing BLMB with those containing sodium hexacyanoferrate (III) using a sample mixer and the reaction was monitored by measuring absorbance of methylene blue produced by the reaction at 662 nm with a 1cm-cell. The concentration of MB was calculated from the absorbance using the molar extinction coefficient of $8.86 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. A typical initial concentration of BLMB was $1.00 \times 10^{-5} \text{ M}$ and that of hexacyanoferrate (III) ions was $6.06 \times 10^{-3} \text{ M}$.

Results and Discussion

Aggregation Numbers of SDS-Hydrocarbon Mixed Micelles. The aggregation numbers of SDS (N_{SDS}) in the mixed micelles were determined in accordance with the method proposed by Turro and Yekta⁹ using pyrene as the fluorescence substance and DMA as the quencher instead of tris-(bipyridine) ruthenium ions and 9-methylanthracene, respectively.¹⁰ Their method is expressed by equation(1), where I_0 and I are the fluorescence intensities of pyrene without and with DMA, respectively.

$$\ln (I_0/I) = N_{\text{SDS}} [\text{DMA}] / ([\text{SDS}] - [\text{free monomer}]) \quad (1)$$

The cmc of SDS, $8.1 \times 10^{-3} \text{ M}$, was used as the concentration of free monomer. The reciprocal micelle concentration, $1/[\text{micelle}]$, was obtained as the slope of plots of $\ln (I_0/I)$ vs. $[\text{DMA}]$. Typical plots for SDS-heptane mixed micellar solutions are shown in Fig. 1. The plots for the other hydrocarbons are similar to Fig. 1. N_{SDS} was calculated using equation (2) and the results are presented in Table 1.

$$N_{\text{SDS}} = ([\text{SDS}] - [\text{free monomer}]) / [\text{micelle}] \quad (2)$$

The aggregation numbers of hydrocarbon (N_{RH}) in the mixed micelles were determined by using equation (3) assuming that all the hydrocarbons added to the solutions exist in the micellar phase.¹¹

$$N_{\text{RH}} = [\text{hydrocarbon}] / [\text{micelle}] \quad (3)$$

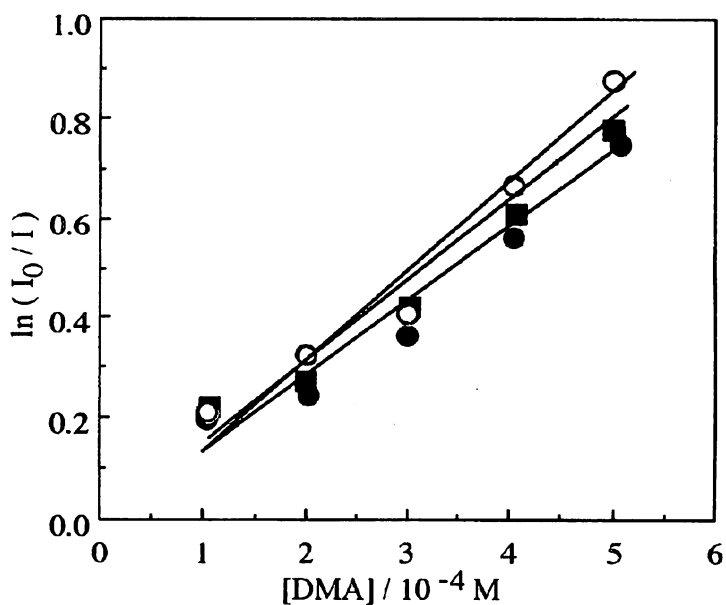


Fig. 1. Plots of $\ln(I_0/I)$ vs. $[DMA]$ for quenching of pyrene fluorescence by DMA in SDS–heptane mixed micellar solutions. Concentration of heptane: (●) 0.001M, (■) 0.003M, (○) 0.007M.

Table 1. The aggregation numbers of the compositions, molecular fractions of SDS in the SDS–hydrocarbon mixed micelles, and the rate constants in the corresponding micellar solutions. Concentration of SDS : 0.05M

Hydrocarbon/M	N_{SDS}	N_{RH}	$N_{SDS}/(N_{SDS}+N_{RH})$	$k/M^{-1}s^{-1}$
[Hexane]				
0	52.8	0.0	1.00	0.490
0.001	52.9	1.3	0.98	0.201
0.003	52.4	3.8	0.93	0.210
0.005	51.5	6.1	0.89	0.095
0.007	49.9	8.3	0.86	0.089
[Heptane]				
0.001	58.5	1.4	0.98	0.400
0.003	62.2	4.5	0.93	0.226
0.005	65.9	8.0	0.89	0.111
0.007	69.9	11.4	0.86	0.089
[Octane]				
0.001	74.4	1.8	0.98	0.385
0.003	59.9	4.3	0.93	0.245
0.005	60.0	7.2	0.89	0.099

The values of N_{RH} are also listed in Table 1.

As seen from Table 1, the aggregation number of SDS decreases slightly with increasing the concentration of hexane added. On the contrary, the aggregation number of SDS increases slightly with increasing the concentration of hydrocarbon in the case of heptane. These conflicting results may be ascribed to the difference in the size of both hydrocarbons, but we can not find the reasonable explanation for the result at present. In the SDS-octane solutions, the regular tendency was not obtained for the aggregation numbers of SDS. The difficulty of solubilization of octane by SDS micelle seems to give irregular results for the determination of the aggregation number of SDS.

The rate constant. The redox reaction between BLMB and hexacyanoferrate (III) ions proceeds bimolecularly and produces MB and benzoic acid as described by equation (4).⁴⁾



The kinetic data were plotted in accordance with the second-order rate equation (5), to obtain the rate constants, where $[\text{BLMB}]_0$ and $[\text{Fe}(\text{CN})_6^{3-}]_0$ are the initial concentrations of BLMB and hexacyanoferrate (III) ions, respectively.

$$\frac{1}{[\text{Fe}(\text{CN})_6^{3-}] - [\text{BLMB}]_0} \ln \frac{[\text{Fe}(\text{CN})_6^{3-}] [\text{BLMB}]_0}{[\text{Fe}(\text{CN})_6^{3-}]_0 [\text{BLMB}]} = kt \quad (5)$$

Typical plots are shown in Fig. 2 for SDS-heptane solutions. The plots for the other hydrocarbons are almost similar to Fig. 2. The second-order rate constants were obtained from the slopes of the plots. The values are presented in Table 1 together with the aggregation numbers.

Relationship between the rate constant and the relative surface charge density. Our previous work of micellar effect on the reaction suggests that the negative charge of micelle has an essential role on the redox reaction between BLMB and hexacyanoferrate (III) ions.⁴⁾ In order to get more information about the role of negative surface charge of micelle, we tried to obtain the relationship between rate constants and relative surface charge densities of SDS-hydrocarbon mixed micelles.

In the beginning, we estimated the relative surface charge densities of the mixed micelles in accordance with the method described by Almgren and Swarup¹¹⁾. The surface charge densities are supposed to be proportional to the number of SDS molecules per unit surface area of the mixed micelles. So we took the number of SDS molecules per unit surface area of the mixed micelles as the relative surface charge densities, and calculated it in the following way. The volume of a SDS molecule was obtained from equation (6), wherer is the hydrophobic radius of the SDS micelle and its value is 18.1 \AA ¹¹⁾.

$$(4/3) \cdot \pi r^3 / N_{\text{SDS}} \quad (6)$$

The volume of SDS (V_{SDS}) in the mixed micelles was determined as the product of the volume of a SDS molecule given by equation (6) and the aggregation number of SDS. The volume of a hydrocarbon molecule in the mixed micelles was taken as the sum of

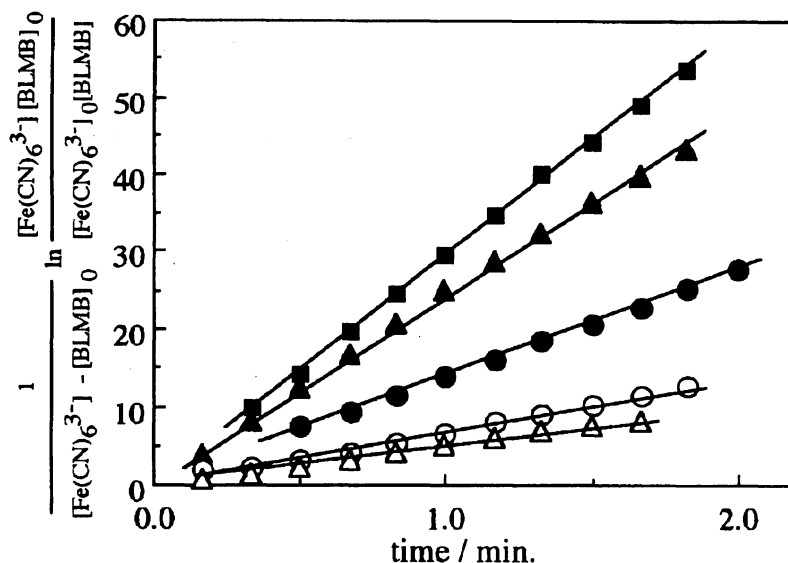


Fig. 2. Plots of the second-order rate equation for the reaction between BLMB and $\text{Fe}(\text{CN})_6^{3-}$ in SDS–heptane mixed micellar solutions. Concentration of heptane: (■) 0M, (▲) 0.001M, (●) 0.003M, (○) 0.005M, (△) 0.007M.

contributions from the components; these contributions were calculated from group contributions (49 \AA^3 per CH_3 , 28 \AA^3 per CH_2)¹¹. The hydrocarbon volume (V_{RH}) in the mixed micelles was obtained by multiplying the volume of a hydrocarbon molecule and the aggregation number of hydrocarbons. The sum of V_{SDS} and V_{RH} is the volume of SDS–hydrocarbon mixed micelle. The radius of the mixed micelle is calculated by equation (7) assuming a spherical shape for the micelle.

$$V_{\text{SDS}} + V_{\text{RH}} = (4/3) \cdot \pi r^3 \quad (7)$$

The total surface area of mixed micelle (S) was obtained from the radius given by equation (7). Therefore, the number of SDS molecules per unit surface area of the mixed micelle is obtained as N_{SDS}/S , which are presented in Table 2. The plots of the rate constants vs. N_{SDS}/S are shown in Fig. 3. As seen from the plots, N_{SDS}/S shows almost constant value, independent of the concentration of hydrocarbon added. So we could not obtain the relationship between the rate constant and the relative surface charge density of the mixed micelles from these plots. We think that N_{SDS}/S thus calculated may not be appropriate to represent the relative surface charge density in the concentration range we used.

Next, we assumed that the relative surface charge densities were proportional to the molecular fraction of SDS in the mixed micelles, $N_{\text{SDS}}/(N_{\text{SDS}} + N_{\text{RH}})$, because the aggregation numbers of SDS did not differ so much each another over the concentration range of hydrocarbon suggesting that the packing conditions of the mixed micelles were same. The values of the molecular fraction are also given in Table 1. The rate constants are plotted against the molecular fraction of SDS in Fig.4. As seen from

Table 2. The volumes of the compositions, total volume, surface area, number of SDS per unit surface area of the mixed micelles, and the rate constant in the corresponding micellar solutions

Hydrocarbon/M	$V_{\text{ms}} \times 10^4 / \text{\AA}^3$	$V_{\text{RH}} \times 10^4 / \text{\AA}^3$	$(V_{\text{ms}} + V_{\text{RH}}) \times 10^4 / \text{\AA}^3$	$r / \text{\AA}$	$S(4\pi r^2) \times 10^4 / \text{t}\text{\AA}^2$	N_{ms} / S	$k / \text{M}^{-1} \text{s}^{-1}$
[Hexane]							
0	1.88	0.00	1.88	16.5	3.42	0.015	0.490
0.001	1.89	0.27	1.92	16.6	3.46	0.015	0.201
0.003	1.87	0.79	1.95	16.7	6.50	0.015	0.210
0.005	1.84	1.29	1.97	16.7	3.52	0.014	0.089
0.007	1.78	1.75	1.96	16.7	3.51	0.014	0.089
[Heptane]							
0.001	2.09	0.33	2.12	17.2	3.70	0.016	0.400
0.003	2.22	1.06	2.32	17.7	3.94	0.016	0.226
0.005	2.35	1.88	2.54	18.2	4.18	0.016	0.111
0.007	2.49	1.77	1.76	18.8	4.42	0.016	0.089
[Octane]							
0.001	2.66	0.43	2.70	18.6	4.36	0.017	0.385
0.003	2.14	1.14	2.25	17.5	3.86	0.016	0.245
0.005	2.14	0.91	2.33	17.9	3.95	0.015	0.099

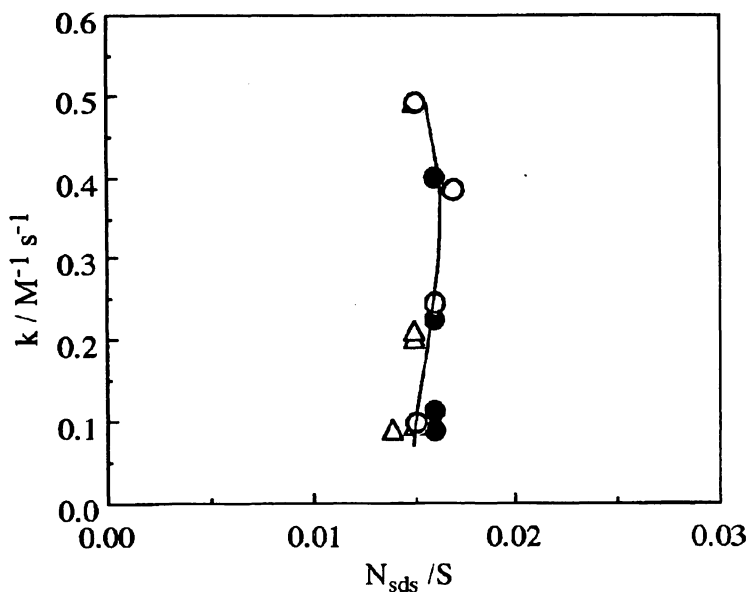


Fig. 3. Relationship between the rate constant and N_{sds}/S of SDS-hydrocarbon mixed micelles. Hydrocarbon: (○) Hexane, (●) Heptane, (△) Octane.

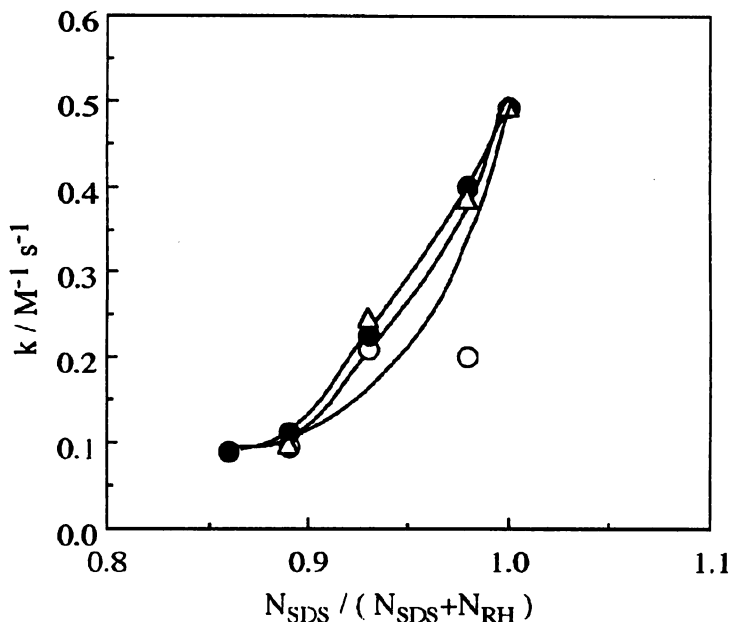


Fig 4. Relationship between the rate constant and $N_{\text{SDS}} / (N_{\text{SDS}} + N_{\text{RH}})$ of SDS-hydrocarbon mixed micelles. Hydrocarbon: (○) Hexane, (●) Heptane, (△) Octane.

the plots, the rate constant is very sensitive to the molecular fraction of SDS and steeply increases with increasing the molecular fraction, that is, the relative negative surface charge density for all hydrocarbons used. The result supports the conclusion that electrostatic stabilization of MB cations by the negative surface charge of the micelles is the driving force for the reaction. Furthermore, we think that the molecular fraction of SDS may be more appropriate to represent the relative surface charge density of the SDS-hydrocarbon mixed micelle in the concentration range we used.

Conclusions

The rate constants for the redox reaction between BLMB and hexacyanoferrate (III) ions in the SDS-hexane, SDS-heptane and SDS-octane mixed micellar solutions increase with increasing the molecular fraction of SDS in the mixed micelles, despite electrostatic repulsion between the negative surface charge of the micelles and hexacyanoferrate (III) anions. The results seem to support the conclusion that electrostatic stabilization of MB cations by the negative surface charge of the micelles is the driving force for the reaction. Furthermore, the molecular fraction of SDS appears to be more appropriate to represent the relative surface charge density of the SDS-hydrocarbon mixed micelle in some concentration range.

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