Bull. Chem. Soc. Jpn. Vol. 80, No. 7, 1383–1390 (2007)

Effects of Ionic Surfactants and Cyclodextrins on Hydride-Transfer Reaction of 1-Benzyl-1,4-dihydronicotinamide with Methylene Blue

Takeshi Matsumoto, Yingjin Liu, Yoshimi Sueishi, and Shunzo Yamamoto*

The Graduate School of Natural Science and Technology, Okayama University,
3-1-1 Tsushimanaka, Okayama 700-8530

Received December 13, 2006; E-mail: yamashun@cc.okayama-u.ac.jp

The kinetics of the hydride-transfer reaction between methylene blue (MB^+) and 1-benzyl-1,4-dihydronictinamide (BNAH) were studied in media containing cyclodextrins (β- and γ-CD) and surfactants (sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, and hexadecyltrimethylammonium bromide). Cationic surfactants decreased the apparent first-order rate constant (k_{obsd}) above the cmc, while SDS increased k_{obsd} just above the cmc and then decreased k_{obsd} with increasing surfactant concentration. This behavior for cationic surfactants was typical of micellar effects due to a separation of the reactants by the micelles. BNAH associated with micelles, whereas MB^+ ions were repelled from the cationic interface of the micelles. Binding of BNAH and MB^+ to the same SDS micelle enhanced the reaction, but dilution of reagents within the micellar interface with the increase in [SDS] caused a decrease in k_{obsd}. In β-CD–cationic surfactant mixtures, the results were interpreted in terms of the model which takes into account the formation of CD–BNAH, CD–MB^+, and CD–surfactant complexes and the association of BNAH with micelles. The decrease in k_{obsd} with increasing surfactant concentration observed in γ-CD–cationic surfactant mixtures can be explained by the decrease in the concentration of free γ-CD by the formation of 1:1 and 2:1 complexes of surfactant monomer with γ-CD.

Aqueous micellar solutions appear to be homogeneous since these aggregates are of colloidal size, but in reality they are highly anisotropic solvents whose properties change gradually from those of pure water to those of hydrocarbon-like liquids upon going from the bulk water phase to the interior of the micellar core.[1–3] Micelles can cause acceleration or inhibition of a given reaction relative to the equivalent reaction in aqueous solutions. The influence of micellar systems on chemical reactivity is often analyzed in terms of the pseudo-phase model.[4–9]

Extensive research has been carried out to investigate the effects of surfactants on the electron absorption spectra of many dyes.[10–17] Recently, we observed that the absorbance of methylene blue (MB^+) at 655 nm decreases rapidly at first with increasing SDS concentration but increases gradually near the cmc.[18] On the other hand, the absorbance of MB^+ is almost independent of the hexadecyltrimethylammonium bromide (HTAB) concentration. At low SDS concentrations, formation of an MB^+–SDS aggregate occurs starting with the ion pair (MB^+–SDS^-) and continues to a aggregate represented by $(MB^+SDS^-)_n$. Near and just below the cmc $(MB^+SDS^-)_n$ aggregates reorganize into premicelles with a monomeric MB^+ content, resulting in an increase in the absorbance of MB^+. With further increases in SDS concentration, all MB^+ molecules are accommodated into normal micelles as monomeric molecules.[18]

Cyclodextrins (CDs) possess cavities with a truncated cone shape with a nonpolar and hydrophobic interior and two hydrophilic rims formed by primary and secondary alcohol groups. The CD cavity is capable of encapsulating (in whole or in part) a variety of guest molecules of the appropriate size, shape, and polarity and forming noncovalent host–guest inclusion complexes.[19] Changes in the reactivities of the guest molecules results from such host–guest interactions. The effects of inclusion complexes on reactivities vary widely and depend on the guest, the CD, and the reaction.[20,21]

The inclusion of MB^+ with β- and γ-CD in aqueous solutions was studied using absorption and fluorescence spectroscopy. It was found that the position of the monomer/dimer equilibrium of MB^+ was suppressed by the addition of β-CD and enhanced by addition of γ-CD. These findings were explained by the inclusion of a monomer by β-CD and a dimer by γ-CD.[22–24]

The properties of surfactant solutions are changed by the addition of a CD because of the formation of inclusion complexes of surfactant molecules.[25–31] In general, complex formation increases the cmc of surfactants. There have been several studies of the effects of CD–surfactant systems on reaction rate constants.[21,32–36]

Micellar effects on bimolecular reaction rates are due mainly to the increase or decrease of reactant concentrations in the micellar pseudophase and the changes in the reaction rate with surfactant concentration often can be explained in these terms.[37] Generally, it is easier to evaluate the partition of hydrophobic reactants between the aqueous phase and micellar pseudophase. In the case of ionic reactants, the Coulombic interaction between the ions and the charge of the micellar surface takes an important role.

There has been little research either on how cyclodextrins affect the effects of the micelles on the reaction rate or how the presence of surfactants affects the behavior of cyclodextrins. It seems generally to have been assumed that micelles are only formed once all the cyclodextrin present has been

Published on the web July 11, 2007; doi:10.1246/bcsj.80.1383

rendered inactive by complexation with surfactant monomers. The experimental investigation of this assumption could be made using the reactions which are influenced by micelles as well as cyclodextrins.

The kinetics of the hydride-transfer reaction between Methylene Blue (MB^+) and 1-benzyl-1,4-dihydronicotinamide (BNAH) were studied in 10% ethanol–90% water mixed solvents containing β- and γ-CD. The reaction was found to be suppressed by the addition of β-CD but enhanced by the addition of γ-CD.[38] Since the reaction between BNAH and MB^+ involves neutral and cationic species, the different effects of the cationic and anionic surfactants on the reaction rate are expected.

In this manner, MB^+ shows various interactions with CDs and surfactants. Furthermore, in the mixed system of CD–surfactant, CD can change the properties of surfactant solutions. It is interesting to know how surfactants alone or in combination with CDs affect the kinetics of the reaction of MB^+. In this paper, we study the effects anionic and cationic surfactants on the reaction of MB^+ with BNAH in the absence and presence of CDs.

Experimental

Materials. MB^+, β- and γ-cyclodextrins (β- and γ-CD), and surfactants (sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (HTAB)) were of the highest commercially available purity (Wako Pure Chemical Industries) and were used without further purification. BNAH was purchased from Tokyo Kasei Kogyo Chemical Industry and was used as supplied. Because of the low solubility of BNAH in water and in order to reduce the spontaneous decomposition of BNAH, 10 vol % ethanol aqueous basic buffer solutions (0.2 mol dm^{-3} NaOH–sodium tetraborate buffer; pH 9.4) were used for kinetic measurements.[38]

Measurements. In a previous study, the reactions of MB^+ with BNAH were followed by recording the decrease in absorbance of MB^+ at 665 nm under deaerated conditions where the initial concentrations of BNAH were 10-fold or greater in excess over MB^+. In this study, however, the reactions were followed by recording the decrease in absorbance of BNAH at 360 nm in the presence of O_2 using a Hitachi spectrophotometer, model 2001, at 25.0 °C, because the absorption spectra of MB^+ significantly depended on the concentrations of MB^+, CDs, and surfactants. In the presence of O_2 (oxygen-saturated condition), the absorbance of BNAH at 360 nm decreased smoothly, while the absorbance of MB^+ at 665 nm decreased a little at first, then became almost constant, even under conditions of excess concentration of BNAH over that of MB^+ (Fig. 1). Figure 1 shows that the leuco methylene blue (MBH) produced by reduction with BNAH was re-oxidized by dissolved oxygen and the steady-state was attained for MB^+. This suggests that the reaction obeys pseudo-first-order kinetics after the steady-state was reached and the absorbance at 360 nm could be used to obtain the apparent first-order rate constants.[39] All runs gave good first-order plots over three or 4 half-lives. The steady-state concentration of MB^+ was assumed to be equal to the initial concentration.

Surface tensions of the surfactant solutions in 10% ethanol aqueous buffer solutions in the absence and presence of β- and γ-CD were measured by the drop-weight method.[40,41] The cmcs of the surfactant solutions were determined by plots of surface tension versus surfactant concentration.[41] To ensure that the instruments properly worked and that the method of determination of the cmc was appropriate, the cmcs of SDS and HTAB in aqueous solutions were determined. The results were 8.2×10^{-3} and 9.0×10^{-4} mol dm^{-3} for SDS and HTAB, respectively, and were in good agreement with literature values (8.26×10^{-3} and 9.02×10^{-4} mol dm^{-3} for SDS and HTAB, respectively).[41]

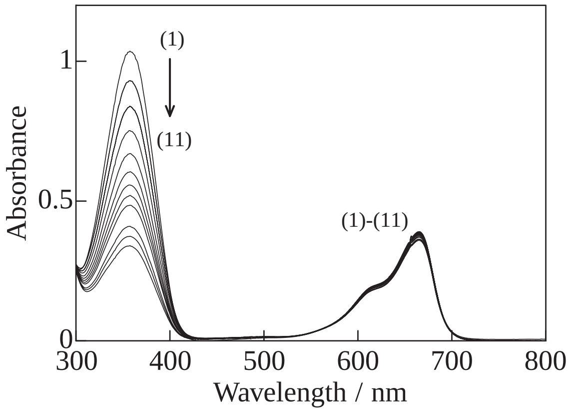
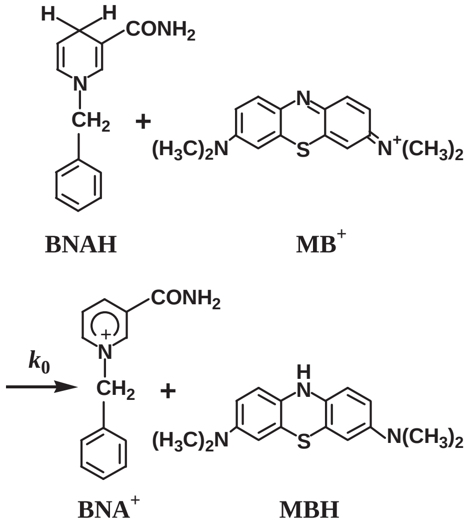


Fig. 1. Repetitive scan of absorption spectrum for the hydride-transfer reaction of BNAH with MB^+ in 0.2 mol dm^{-3} NaOH–sodium tetraborate buffer (10 vol % ethanol–90 vol % water) at pH 9.4 and 25 °C in the presence of O_2. $[\mathrm{BNAH}]_0 = 1.41 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{MB^+}]_0 = 4.27 \times 10^{-6}$ mol dm^{-3}. (1) Taken immediately after mixing: (2)–(11) taken at subsequent 5 min intervals.

Results and Discussion

Kinetics of the Oxidation of BNAH by MB^+ in the Presence of O_2. The reaction of BNAH with MB^+ was studied in 10 vol % ethanol aqueous buffer solutions in the presence of O_2.



(1)

Figure 1 shows the time dependence of the absorption spectrum for the reaction of BNAH with MB^+. The absorption of BNAH at 360 nm gradually decreased after mixing a BNAH solution with an MB^+ solution ($[\mathrm{BNAH}]_0 = 1.41 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{MB^+}]_0 = 4.27 \times 10^{-6}$ mol dm^{-3}), while that of MB^+ at 665 nm showed only slight decrease. Under the conditions that the initial concentrations of MB^+ were less than that

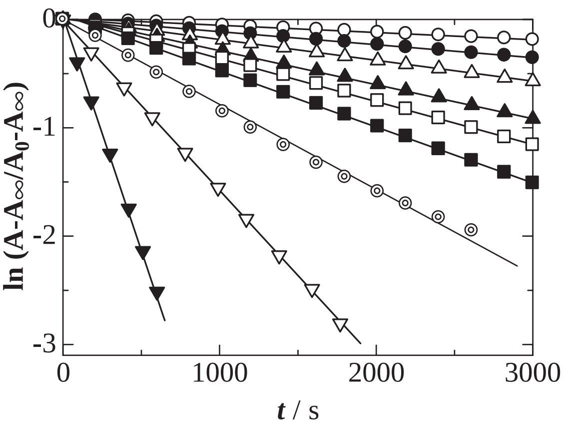


Fig. 2. Pseudo-first-order plots of the reaction of BNAH with MB^+ at pH 9.4 in the presence of O_2. $[BNAH]_0 = 1.40 \times 10^{-5}\,mol\,dm^{-3}$; $[MB]_0 = 0.57$ (○), 1.18 (●), 2.36 (△), 3.53 (▲), 4.27 (□), 5.70 (■), 11.8 (◎), 23.6 (▽), $34.2 \times 10^{-6}\,mol\,dm^{-3}$ (▼).

of BNAH, the absorbance of MB^+ was kept nearly constant while the absorbance of BNAH decreased. As mentioned above, the leuco methylene blue (MBH) produced by the reaction with BNAH was rapidly re-oxidized by dissolved O_2 and the steady-state for MB^+ was attained. All the runs gave good first-order plots (Fig. 2). The apparent first-order rate constants (k_{obsd}) were obtained at some initial concentrations of MB^+. A saturation curve was obtained by plotting the k_{obsd}-values against $[MB^+]_0$. The saturation curve shows the existence of a 1:1 complex between reactants in this reaction. As mentioned in a previous study, the reaction of BNAH with MB^+ resulted in a 1:1 complex between BNAH and MB^+, and this complex is the real intermediate. However, the plots between k_{obsd} and $[MB^+]_0$ at concentrations below 5.72×10^{-6} $mol\,dm^{-3}$ approximately gave a straight line with a small intercept. This intercept showed the rate constant for the spontaneous decomposition of BNAH. The equation for k_{obsd} in these regions of MB^+ concentration is expressed as

$$k_{obsd} = k_0[MB^+]_0 + k_{SD}, \qquad (2)$$

where k_0 is the rate constant for the reaction (3) shown later and k_{SD} is the first-order rate constant for the spontaneous decomposition of BNAH ($k_0 = 54.7\,dm^3\,mol^{-1}\,s^{-1}$ and $k_{SD} = 2.1 \times 10^{-6}\,s^{-1}$). This indicates that at the low concentrations of MB^+ and BNAH, the concentration of the complex could be neglected. All measurements of the effects of CD and surfactants on the reaction rate were done in these concentration regions.

Effects of CD on the Reaction of BNAH with MB^+. Figure 3 shows the changes in k_{obsd} with β-CD concentration. As shown in Fig. 2, k_{obsd} decreased with increasing β-CD concentrations. As mentioned in a previous paper, the decrease in k_{obsd} with the addition of β-CD is due to separate inclusions of BNAH and MB^+ in the cavity of β-CD.[25] Taking into account the formation of the complexes of NMAH and MB^+ with β-CD and assuming that these inclusion complexes did not react with each other, nor with free reactants, Eq. 6 was obtained from the following reactions:

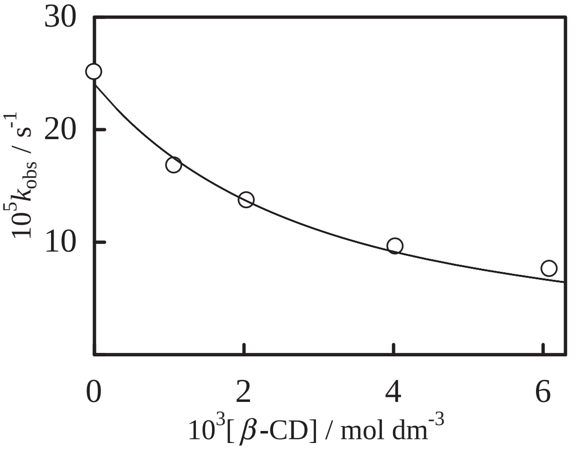


Fig. 3. Effect of β-CD on the observed first-order rate constant (k_{obsd}) for the hydride-transfer reaction of BNAH with MB^+ in $0.2\,mol\,dm^{-3}$ NaOH–sodium tetraborate buffer (10 vol % ethanol–90 vol % water) at pH 9.4 and 25 °C.

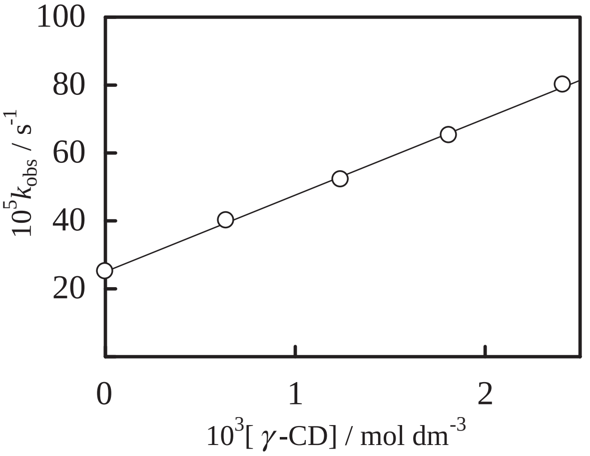


Fig. 4. Effect of γ-CD on the observed first-order rate constant (k_{obsd}) for the hydride-transfer reaction of BNAH with MB^+ in $0.2\,mol\,dm^{-3}$ NaOH–sodium tetraborate buffer (10 vol % ethanol–90 vol % water) at pH 9.4 and 25 °C.

$$\mathrm{BNAH} + \mathrm{MB}^+ \xrightarrow{k_0} \mathrm{BNA}^+ + \mathrm{MBH}, \qquad (3)$$

$$\mathrm{BNAH} + \beta\text{-CD} \overset{K_1}{\rightleftharpoons} \mathrm{BNAH\text{–}CD}, \qquad (4)$$

$$\mathrm{MB}^+ + \beta\text{-CD} \overset{K_2}{\rightleftharpoons} \mathrm{MB\text{–}CD}, \qquad (5)$$

$$k_{obsd}(\beta\text{-CD}) = \frac{k_0[\mathrm{MB}]_0}{(1 + K_1[\beta\text{-CD}])(1 + K_2[\beta\text{-CD}])} + k_{SD}, \qquad (6)$$

where k_{obsd}(β-CD) was the observed rate constant in the presence of β-CD. The solid line in Fig. 3 shows the values calculated by Eq. 6 using $K_1 = 220\,dm^3\,mol^{-1}$ and $K_2 = 130$ $dm^3\,mol^{-1}$, which are values obtained in a previous study.[38] The observed and calculated values were in good agreement.

As shown in Fig. 4, the k_{obsd}-value increased with increasing γ-CD concentration. In a previous study, this increase in k_{obsd} was explained by the inclusion of the complex between BNAH and MB^+ in the cavity of γ-CD. To explain the effect of γ-CD, the following reactions were considered:

$$\mathrm{MB^+ + BNAH} \overset{K_C}{\rightleftharpoons} \mathrm{C}, \tag{7}$$

$$\mathrm{C} + \gamma\text{-CD} \overset{K_3}{\rightleftharpoons} \text{C–CD}, \tag{8}$$

$$\mathrm{C} \xrightarrow{k_1} \mathrm{MBH + BNA^+}, \tag{9}$$

$$\text{C–CD} \xrightarrow{k_2} \mathrm{MBH + BNA^+} + \gamma\text{-CD}. \tag{10}$$

In the low γ-CD concentration region, the following approximate equation can be obtained:

$$k_{\mathrm{obsd}}(\gamma\text{-CD}) = k_0[\mathrm{MB}]_0\left(1 + \frac{k_2}{k_1}K_3[\gamma\text{-CD}]_0\right) + k_{\mathrm{SD}}, \tag{11}$$

where $k_{\mathrm{obsd}}(\gamma\text{-CD})$ was the observed rate constant in the presence of γ-CD. The value of $(k_2/k_1)K_3$ was determined from the slope of the straight line shown in Fig. 4. Using the values of k_1 and k_2 (0.13 and 0.11 $\mathrm{s^{-1}}$) shown in a previous paper, the value of 1100 $\mathrm{dm^3\,mol^{-1}}$ for K_3 was obtained. This value is about a half of the value obtained in a previous study. Since the experimental conditions in both studies were similar (the buffer solutions differed in both studies and the present and previous studies were carried out in the presence and absence of $\mathrm{O_2}$, respectively), the reason for the discrepancy in K_3-value was not clear.

The equilibrium constants for the dimerization of $\mathrm{MB^+}$ and the formation of the inclusion complex of the dimer with γ-CD were obtained by the dependences of the absorption intensity of $\mathrm{MB^+}$ on the concentrations of $\mathrm{MB^+}$ and γ-CD in 10% ethanol–90% water mixed solvent (4300 and 910 $\mathrm{dm^3\,mol^{-1}}$ for the dimerization and the inclusion). From these equilibrium constants the value of $([\mathrm{D}] + [\text{D–CD}])/[\mathrm{MB^+}]_0 = 0.035$ was obtained for $[\mathrm{MB^+}]_0 = 4.27 \times 10^{-6}\ \mathrm{mol\,dm^{-3}}$ (the initial concentration of $\mathrm{MB^+}$ in Fig. 4) and $[\gamma\text{-CD}]_0 = 2.56 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$ (the highest concentration of γ-CD in Fig. 4). This shows that the existence of the dimer species was negligible under the conditions shown in Fig. 4.

Effects of Surfactants on the Reaction of BNAH with $\mathrm{MB^+}$. Figure 5 shows the plots of k_{obsd} against [SUR] for HTAB, TTAB, and DTAB. As shown in Fig. 5, the k_{obsd}-values were almost constant below cmc and they decreased with increasing the concentrations of surfactants above cmc. This behavior was typical of micellar effects due to a separation of the reactants by the micelles. BNAH associated with micelles, whereas $\mathrm{MB^+}$ ions were repelled from the interface of the micelles due to electrostatic effects.

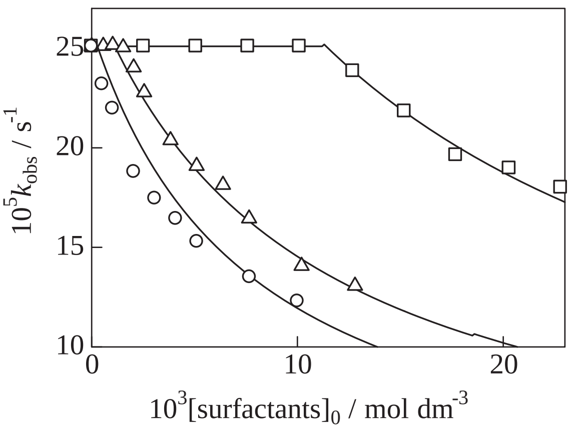


Fig. 5. Variations of k_{obsd} in the hydride-transfer reaction of BNAH with $\mathrm{MB^+}$ in micellar solutions of HTAB, TTAB, and DTAB as functions of the surfactant concentration. Solid lines show the calculated values (see text).

Taking into account that the overall reaction rate was the sum of the rate in solution and in the micellar phase (in the present case, since $\mathrm{MB^+}$ could not approach BNAH in the micelle due to the electrostatic interaction between $\mathrm{MB^+}$ and the cationic surface of micelles, the latter rate was neglected), the expression of k_{obsd} was obtained from reactions (1) and (12) and given in Eq. 13:

$$\mathrm{BNAH} + \mathrm{D_n} \overset{K_S}{\rightleftharpoons} \text{BNAH–D}_\mathrm{n}, \tag{12}$$

where $\mathrm{D_n}$ shows the micelle.

$$k_{\mathrm{obsd}}(\mathrm{SUR}) = \frac{k_0[\mathrm{MB}]_0}{1 + K_S[\mathrm{D_n}]} + k_{\mathrm{SD}}, \tag{13}$$

where $k_{\mathrm{obsd}}(\mathrm{SUR})$ is the apparent rate constant in the presence of surfactant, K_S is the associate constant of BNAH to micelles and $[\mathrm{D_n}]$ is the concentration of micellized surfactants ($[\mathrm{D_n}] = [\mathrm{SUR}]_{\mathrm{total}} - \mathrm{cmc}$).

Herzfeld et al. measured the cmc of dodecylammonium chloride in the presence of alcohols and salts and found that the cmc depended on alcohol and salt concentrations.[42] It is also known that the cmc increased with the addition of β-CD.[30,35] Since in the present study we measured the reaction rates in 10% ethanol–90% water solutions with buffer and examined the effects of β- and γ-CD, we obtained the cmc of surfactants under several conditions mentioned above and show the results in Table 1.

The solid lines in Fig. 5 show the values calculated by Eq. 13 using $K_S = 120$, 80, and 40 $\mathrm{dm^3\,mol^{-1}}$ for HTAB, TTAB, and DTAB, respectively (cmc for HTAB, TTAB, and DTAB obtained in 10 vol % ethanol–90 vol % water mixed solvent were 0.65, 1.41, and $11.1 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$, respectively). The observed and calculated values were in good agreement. BNAH was more easily associated with the micelles in the order: DTAB < TTAB < HTAB.

Figure 6 shows the k_{obsd}–[SDS] profile. The k_{obsd} value was constant in the low [SDS] region (below the cmc), sharply increased at higher [SDS] than the cmc, passed through a maximum value, then decreased at higher surfactant concentrations. These findings were typical for micellar effects of anionic micelles in reactions between a hydrophobic neutral substrate and a cationic substrate.

As mentioned in a previous paper, the absorption spectrum of $\mathrm{MB^+}$ depended on the SDS concentration.[35] Figure 7 shows the change in the absorbance of $\mathrm{MB^+}$ at 655 nm with increas-

Table 1. The cmc of HTAB, TTAB, and DTAB in 10 vol % ethanol–90 vol % water Buffer Solutions (0.2 mol dm^{-3} NaOH–$\mathrm{Na_4B_4O_8}$ Buffer; pH 9.4) in the Presence of β-CD

	10^3 cmc/mol dm^{-3}		
10^3[β-CD]/mol dm^{-3}	HTAB	TTAB	DTAB
0	0.65	1.41	11.1
1.0	1.32	1.98	—
2.0	1.90	2.54	14.1
4.0	3.31	5.06	—

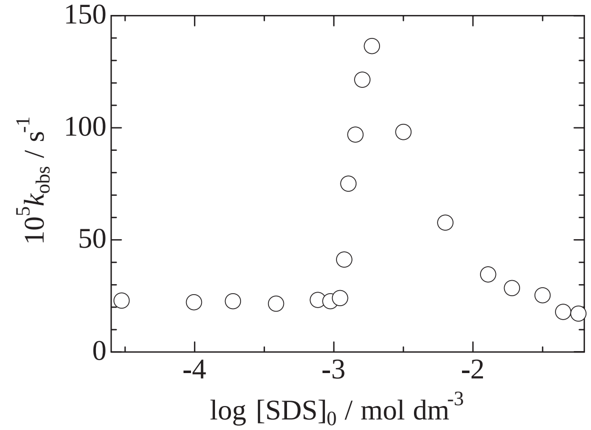


Fig. 6. Variations of k_{obsd} in the hydride-transfer reaction of BNAH with MB^+ in micellar solutions of SDS as a function of the SDS concentration.

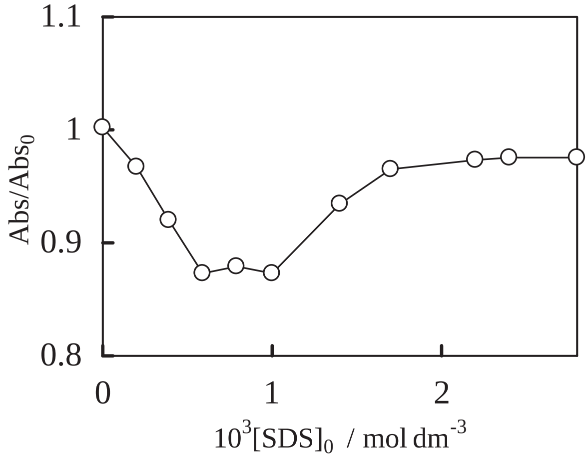


Fig. 7. Effect of SDS on the absorbance of MB^+ at 664 nm in 0.2 mol dm^{-3} NaOH–sodium tetraborate buffer (10 vol % ethanol–90 vol % water) at pH 9.4.

ing [SDS]. The change observed in this study was somewhat different from that shown in a previous paper. This difference was due to the differences in the cmc of SDS in water and ethanol–water mixture (and also the presence of buffer reagents). As shown in Fig. 7, initially, the absorbance of MB^+ at 655 nm decreased with increasing SDS concentration, but increased gradually above the cmc. At low SDS concentrations, formation of MB^+–SDS aggregates started with the ion-pair (MB^+SDS^-). Above the cmc, aggregates reorganized at the surface of micelles with a monomeric MB^+ form, resulting in an increase in the absorbance of MB^+. With further increases in [SDS], the absorbance of MB^+ reached its limiting value and all MB^+ molecules were accommodated at the surface of micelles as monomeric molecules.

As shown in Figs. 6 and 7, the change in k_{obsd} with increasing SDS concentration was not consistent with that in the absorbance of MB^+, except for the part of the increase in k_{obsd} above the cmc. The formation of the ion pair (MB^+SDS^-) and its aggregates ($(MB^+SDS^-)_n$) at low SDS concentrations did not affect the k_{obsd} value. The formation of the monomeric MB^+ molecules at the surface of the micelles increased k_{obsd} above the cmc.

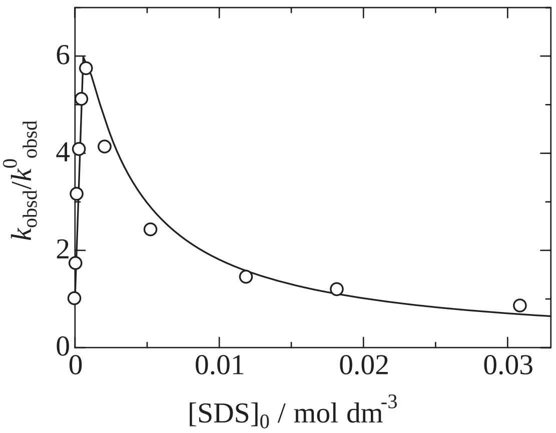


Fig. 8. Effects of SDS concentration on k_{obsd}/k^0_{obsd} for the reaction of BNAH with MB^+. $[BNAH]_0 = 1.40 \times 10^{-5}$ mol dm^{-3}; $[MB]_0 = 4.27 \times 10^{-6}$ mol dm^{-3}. The solid line shows the calculated values (see text).

The tendencies of k_{obsd} shown in Fig. 6 were consistent with previous observations for other reactions between neutral and cationic reactants. Binding of BNAH and MB^+ to SDS micelles began at the cmc, hence the concentration of both reagents in the small volume of the micelle explained the sharp increase in k_{obsd}, but the continuous dilution of reagents within the micellar interface with the increase in [SDS] caused a decrease in k_{obsd} (the fraction of BNAH accommodated into the micelles which were not associated with MB^+ at their surfaces increased with increasing micelle concentration).

As mentioned above, the overall reaction rate was the sum of the rate in solution and in the micellar phase (in the present case, since MB^+ was associated at the surface of SDS micelle and BNAH was accommodated into the micelle, it was assumed that the reaction occurred at the micelle which associated both of MB^+ and BNAH). The expression of k_{obsd} was obtained from reactions (1) and (14)–(16) and given in Eq. 17.

$$MB^+ + Dn \overset{K_{S1}}{\rightleftharpoons} MB\text{–}Dn, \tag{14}$$

$$BNAH + Dn \overset{K_{S2}}{\rightleftharpoons} BNAH\text{–}Dn, \tag{15}$$

$$(MB\text{–}BNAH)_m\text{–}Dn \xrightarrow{k_m} MBH + BNA^+ + Dn, \tag{16}$$

where Dn shows the SDS micelle and $(MB\text{–}BNAH)_m$ denotes the micelle which have MB^+ and BNAH.

$$k_{obsd} = \frac{(k_0 + k_m K_{S1} K_{S2}[D_n])[MB^+]_0}{(1 + K_{S1}[D_n])(1 + K_{S2}[D_n])} + k_{SD}. \tag{17}$$

The following equation could be obtained by neglecting k_{SD}

$$\frac{k_{obsd}}{k^0_{obsd}} = \frac{(1 + (k_m/k_0)K_{S1}K_{S2}[D_n])}{(1 + K_{S1}[D_n])(1 + K_{S2}[D_n])}, \tag{18}$$

where k^0_{obsd} shows the k_{obsd}-value in the absence of SDS micelle.

Figure 8 shows the plots of k_{obsd}/k^0_{obsd} against $[D_n]$. The solid line shown in Fig. 8 was obtained from Eq. 18 using $k_m/k_0 = 0.023$ mol dm^{-3}, $K_{S1} = 6000$ dm^{-3} mol and $K_{S2} = 400$ dm^{-3} mol estimated by trial and error method (K_{S1} and K_{S2} are symmetrical in Eq. 18 and they are not distinguishable.

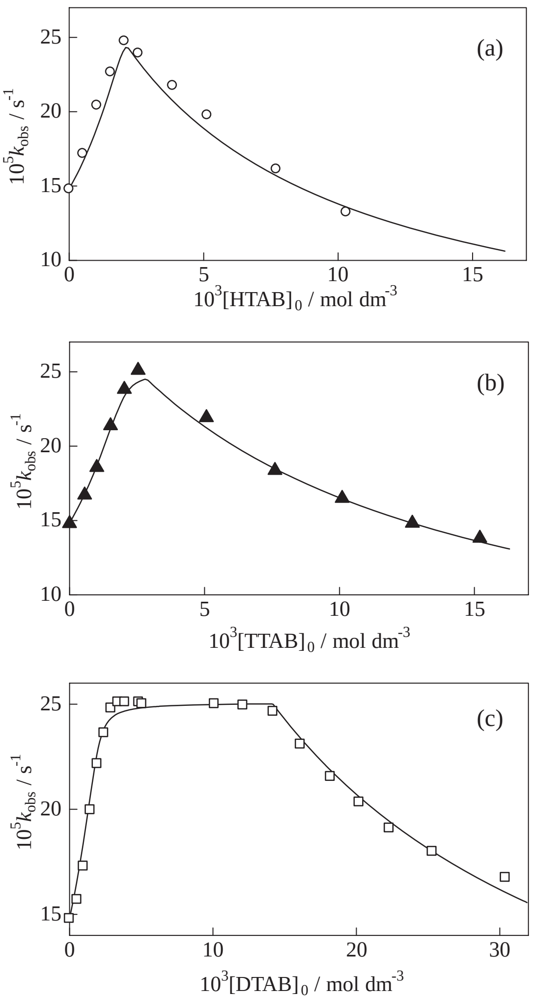


Fig. 9. Effects of (a) [HTAB], (b) [TTAB], and (c) [DTAB] on k_{obsd} in the hydride-transfer reaction of BNAH with MB^+ in the presence of β-CD ([β-CD] $= 2.0 \times 10^{-3}$ mol dm^{-3}. Solid lines show the calculated values (see text).

We assigned the value shown above for K_{S1} and K_{S2}, because K_{S1} reflected the spectral change of MB^+ in the presence of SDS (Fig. 7), and K_{S2} must be the similar values to the association constant s for BNAH–cationic surfactants systems). As shown in Fig. 8, the observed and calculated values were in good agreement.

Effects of Cyclodextrins and Cationic Surfactants on the Reaction of BNAH with MB$^+$. Figure 9 shows the effects of HTAB, TTAB, and DTAB on k_{obsd} in the presence of β-CD. In each series, k_{obsd} increased with surfactant concentration up to a maximum and then decreased in the absence of β-CD. The surfactant concentration required to begin decreasing k_{obsd} increased with a decrease in the chain length of the surfactant (with increases in the cmc). The experimental behavior shown in Fig. 9 was explained qualitatively by considering the overlap of the effects of β-CD and surfactants.

$$\mathrm{SUR} + \beta\text{-CD} \overset{K_{SUR}}{\rightleftharpoons} \text{SUR–CD}. \tag{19}$$

According to reactions (2)–(4) and (19), the following equation for k_{obsd} was obtained:

$$k_{obsd} = \frac{k_0[\mathrm{MB}^+]}{(1 + K_1[\mathrm{CD_f}] + K_{SUR}[\mathrm{SUR_f}])(1 + K_2[\mathrm{CD_f}])} + k_{SD}. \tag{20}$$

In the surfactant concentration region below the cmc, a complex of surfactant monomers with β-CD was formed, and the decrease in the concentration of free β-CD induced the displacement of BNAH and MB^+ from the cavity of β-CD to the aqueous medium. The increase in the concentration of free BNAH and MB^+ increased k_{obsd} until the effect of β-CD on k_{obsd} became negligible.

In this region of surfactant concentration, the total β-CD and surfactant concentrations were expressed as

$$\begin{aligned}[\mathrm{CD_{total}}] &= [\mathrm{CD_f}] + [\text{BANH–CD}] \\ &\quad + [\text{MB–CD}] + [\text{SUR–CD}] \\ &= [\mathrm{CD_f}] + K_1[\mathrm{BNAH}][\mathrm{CD_f}] + K_2[\mathrm{MB}^+][\mathrm{CD}] \\ &\quad + K_{SUR}[\mathrm{SUR_f}][\mathrm{CD_f}], \end{aligned} \tag{21}$$

$$\begin{aligned}[\mathrm{SUR_{total}}] &= [\mathrm{SUR_f}] + [\text{SUR–CD}] \\ &= [\mathrm{SUR_f}] + K_{SUR}[\mathrm{SUR_f}][\mathrm{CD_f}]. \end{aligned} \tag{22}$$

As mentioned above, $K_{BNAH} = 220$ dm^3 mol^{-1}, $K_{MB} = 130$ dm^3 mol^{-1}, and K_{SUR} reported were about two orders larger than these values in aqueous solution.[31–33] Since the concentration of surfactants were higher than those of BNAH and MB^+ in this study, the concentrations of BANH–CD and MB–CD in determining the concentration of free CD was negligible. From the above equations, the following equation was obtained by neglecting the concentrations of BANH–CD and MB–CD:

$$\begin{aligned} K_{SUR}[\mathrm{CD_f}]^2 + (1 + K_{SUR}[\mathrm{SUR_{total}}] \\ - [\mathrm{CD_{total}}])[\mathrm{CD_f}] - [\mathrm{CD_{total}}] = 0. \end{aligned} \tag{23}$$

By assuming the K_{SUR}-values for HTAB, TTAB, and DTAB, and using $[\mathrm{CD_{total}}] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{CD_f}]$ was calculated as a function of $[\mathrm{SUR_{total}}]$.

Using the values of $[\mathrm{CD_f}]$ obtained (the values of 10000, 30000, and 100000 dm^3 mol^{-1} for K_{SUR} of DTAB, TTAB, and HTAB were used), k_{obsd} was calculated from Eq. 20. The solid lines in Fig. 9 show the calculated values of k_{obsd}. As shown in Fig. 9, the calculated and observed values for k_{obsd} were in good agreement at low concentrations of surfactants.

As shown in Fig. 9, the roles of surfactants in the effect of β-CD on k_{obsd} were almost saturated near or below the cmc. Therefore, above the cmc, the concentration of free β-CD was almost zero, and the change in k_{obsd} was exclusively caused by the increasing association of BNAH with micelles. By setting $[\mathrm{CD_f}] = 0$, Eq. 20 was rewritten as

$$k_{obsd} = \frac{k_0[\mathrm{MB}^+]}{1 + K_S[\mathrm{D_n}]} + k_{SD} \tag{12}$$

As mentioned above, the cmc increased with increasing β-CD concentration. At the concentration of β-CD used in this study, the cmcs of HTAB, TTAB, and DTAB were 1.90, 2.54, and 14.1×10^{-3} mol dm^{-3}, respectively (see Table 1).

The solid lines above the cmc in Fig. 9 were obtained from Eq. 12 by using the K_S-value given above for the effects of surfactants on k_{obsd} in the absence of β-CD and by using the cmc shown in Table 1. As shown in Fig. 9, the calculated and observed values were in good agreement. Since the cmc

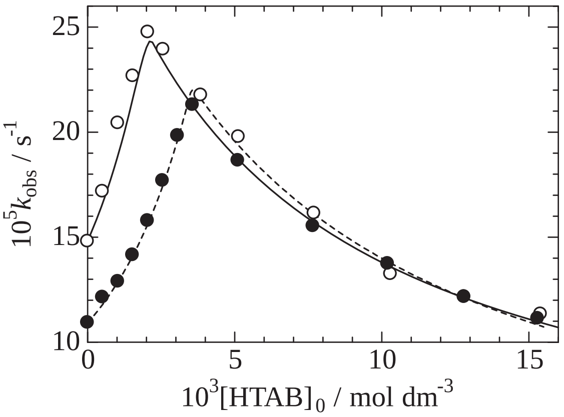


Fig. 10. Effects of [HTAB] on k_{obsd} in the hydride-transfer reaction of BNAH with MB^+ in the presence of β-CD (○: [β-CD] $= 2.0 \times 10^{-3}$ mol dm^{-3} and ●: [β-CD] $= 4.0 \times 10^{-3}$ mol dm^{-3}). Solid and dashed lines show the calculated values (see text).

of DTAB in the presence of β-CD is large, the influence of DTAB in the effect of β-CD on k_{obsd} was saturated considerably below the cmc. Therefore, as shown in Fig. 9, k_{obsd} is constant from the saturation point to the cmc for DTAB.

Figure 10 shows the effect of HTAB concentration on k_{obsd} in the presence of [β-CD] $= 2.0$ and 4.0×10^{-3} mol dm^{-3}. An increase in β-CD concentration decreased the peak value of k_{obsd} and increased the HTAB concentration at which the peak appears. In the case of [β-CD] $= 4.0 \times 10^{-3}$ mol dm^{-3}, the peak value of k_{obsd} was smaller than that in the absence of β-CD and HTAB. This indicated that some amount of free β-CD existed at the cmc at which the peak of k_{obsd} appeared. Above the cmc, however, the effect of the association of BNAH with micelles seemed to be predominant. For both β-CD concentrations, the observed and calculated values were in good agreement (the dashed lines were obtained by the similar method mentioned above). This indicated that the decrease in k_{obsd} above the cmc was explained by the effect of the association of BNAH with micelles. An increase in the surfactant concentration at which the maximum value of k_{obsd} appeared with increasing β-CD concentrations was also observed for TTAB. For TTAB, the peak value of k_{obsd} was similar to that in the absence of β-CD and TTAB. The increase of TTAB concentration at the peak was explained again by the increase in the cmc with increasing β-CD concentration.

Figure 11 shows the effects of TTAB concentration on k_{obsd} in the presence of γ-CD ([γ-CD] $= 2.56 \times 10^{-3}$ mol dm^{-3}). As mentioned above, the addition of γ-CD increased k_{obsd} (shown by Eq. 11). As shown in Fig. 11, k_{obsd} decreased with increasing TTAB concentration. The effects of TTAB on k_{obsd} were thought to be due to two factors (the formation of an inclusion complex of TTAB monomer and the association of BNAH with micelles) in the presence of γ-CD, as in the presence of β-CD. These factors decreased k_{obsd} for the case of γ-CD.

It was reported that γ-CD forms 1:1 and 2:1 TTAB/CD complexes.[26] The formation of these complexes decreased the concentration of free γ-CD and decreased k_{obsd} by suppressing the enhancing effect of γ-CD.

$$\mathrm{TTAB} + \gamma\text{-CD} \overset{K_T}{\rightleftharpoons} \mathrm{T–CD}, \tag{24}$$

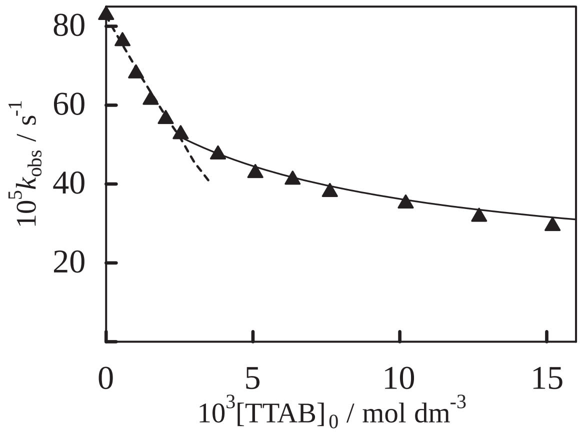


Fig. 11. Effects of [HTAB] on k_{obsd} in the hydride-transfer reaction of BNAH with MB^+ in the presence of γ-CD ([γ-CD] $= 2.56 \times 10^{-3}$ mol dm^{-3}). Solid and dashed lines show the calculated values (see text).

$$\mathrm{T–CD} + \mathrm{TTAB} \overset{K_{2T}}{\rightleftharpoons} \mathrm{T_2–CD}, \tag{25}$$

where T–CD and T_2–CD are the 1:1 and 2:1 complexes between TTAB and γ-CD.

Below the cmc, only the inclusion complex formation affects k_{obsd}. From reactions (24) and (25), the concentrations of γ-CD and TTAB were expressed as follows:

$$[\mathrm{CD_{total}}] = [\mathrm{CD_f}](1 + K_T[\mathrm{T_f}] + K_TK_{2T}[\mathrm{T_f}]^2), \tag{26}$$

$$[\mathrm{T_{total}}] = [\mathrm{T_f}](1 + K_T[\mathrm{CD_f}] + 2K_TK_{2T}[\mathrm{T_f}][\mathrm{CD_f}]), \tag{27}$$

where [CD_{total}] and [T_{total}] are total concentrations of γ-CD and TTAB, and [CD_f] and [T_f] are concentrations of free γ-CD and TTAB. By assuming the values of K_T and K_{2T}, [CD_f] were calculated for various total concentrations of TTAB at [CD_{total}] $= 2.56 \times 10^{-3}$ mol dm^{-3} by using successive approximations. The values of k_{obsd} were determined by putting the [CD_f] obtained into Eq. 11. The solid line shown in Fig. 9 at the low concentration region of TTAB were obtained using $K_T = 600$ and $K_{2T} = 6700$ dm^3 mol^{-1}. These values are similar to those reported for TTAB–γ-CD system in aqueous solution by Tominaga et al.[26]

As shown in Fig. 11, the dashed line fit the k_{obsd} below [TTAB]$_0$ $= 2.5 \times 10^{-3}$ mol dm^{-3}. Though the cmc of TTAB in the presence of γ-CD could not be determined in the present study, the cmc of TTAB under the present experimental conditions was thought to be about 2.5×10^{-3} mol dm^{-3} from the result shown in Fig. 11 (somewhat higher than that in the absence of γ-CD). The effect of the complex formation must have been constant above the cmc, because the concentration of free TTAB became constant above the cmc.

As mentioned above, the change in k_{obsd} above the cmc was caused by increasing association of BNAH with micelles. In this case, k_{obsd} was expressed by the following equation:

$$k_{obsd} = \frac{k_{obsd}^{cmc}}{1 + K_S[\mathrm{D_n}]} + k_{BO}, \tag{28}$$

where k_{obsd}^{cmc} is k_{obsd} at the cmc and was assumed to be 52.6×10^{-5} s^{-1}. The solid line above the cmc in Fig. 11 was obtained from Eq. 28 by using $K_S = 80$ dm^3 mol^{-1} obtained above for the effect of TTAB on k_{obsd} in the absence of CD. As shown in Fig. 11, the calculated and observed values were in good agreement.

Conclusion

The rate of hydride-transfer reaction of BNAH with MB^+ was suppressed by β-CD and enhanced by γ-CD. These effects of CD were explained by the formation of inclusion complexes of BNAH and MB^+ with β-CD and by the formation of a 1:1:1 BNAH–MB^+–γ-CD complex. Cationic surfactants (DTAB, TTAB, and HTAB) also suppressed the rate above the cmc, while anionic surfactant (SDS) showed a complex k_{obsd}–[SDS] profile. These effects of surfactants were due to the association of BNAH with micelles for cationic surfactants and due to the association of BNAH and the attachment of MB^+ on the surface of SDS micelle for SDS. The change in k_{obsd} observed in CD and cationic surfactant mixtures was explained by the model which involves the formation of inclusion complexes of BNAH, MB^+, and surfactant with CD and the association of BNAH with micelles.

References

1 F. H. Quina, H. Chaimovich, *J. Phys. Chem.* **1979**, *83*, 1844.

2 C. A. Bunton, F. J. Nome, F. H. Quina, L. S. Romsted, *Acc. Chem. Res.* **1991**, *24*, 357.

3 T. Dwars, E. Paetzold, G. Oehme, *Angew. Chem., Int. Ed.* **2005**, *44*, 7174.

4 C. Ebert, L. Lassiani, P. Linda, M. Lovrecich, C. Nisi, F. Rubessa, *J. Pharm. Sci.* **1984**, *73*, 1691.

5 A. Cipiciani, C. Ebert, R. Germani, P. Linda, M. Lovrecich, F. Rubessa, G. Savelli, *J. Pharm. Sci.* **1985**, *74*, 1184.

6 C. Bravo, P. Herves, J. R. Leis, M. E. Pena, *J. Colloid Interface Sci.* **1992**, *153*, 529.

7 E. Abuin, E. Lissi, R. Duarto, *J. Colloid Interface Sci.* **2005**, *283*, 593.

8 E. Iglesias, *New J. Chem.* **2005**, *29*, 457.

9 E. Iglesias, *New J. Chem.* **2005**, *29*, 625.

10 M. E. Diaz Garcia, A. Sanz-Medel, *Talanta* **1986**, *33*, 255.

11 D. Pramanick, D. Mukherjee, *J. Colloid Interface Sci.* **1993**, *157*, 131.

12 S. S. Shah, M. S. Kahn, H. Ullah, M. A. Awan, *J. Colloid Interface Sci.* **1997**, *186*, 382.

13 M. A. Awan, S. S. Shah, *Colloids Surf., A* **1997**, *12*, 97.

14 A. K. Mandal, M. K. Pal, *Spectrochim. Acta, Part A* **1999**, *55*, 1347.

15 S. Gokturk, M. Tuncay, *Spectrochim. Acta, Part A* **2003**, *59*, 1347.

16 R. Sabate, J. Kstelrich, *J. Phys. Chem. B* **2003**, *107*, 4137.

17 J. Yang, *J. Colloid Interface Sci.* **2004**, *63*, 181.

18 S. Yamamoto, S. Kobashi, K. Tsutsui, Y. Sueishi, *Spectrochim. Acta, Part A* in press.

19 A. Connors, *Chem. Rew.* **1997**, *97*, 1325.

20 E. Iglesias, A. Fernández, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1691.

21 L. Garcia-Rio, J. R. Leis, J. C. Mejuto, J. Perez-Juste, *J. Phys. Chem.* **1997**, *101*, 7383.

22 C. Lee, Y. W. Sung, J. W. Park, *J. Phys. Chem. B* **1999**, *103*, 893.

23 S. Hamai, H. Satou, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2207.

24 X. Guo, H. Xu, R. Guo, *Colloid Polym. Sci.* **2003**, *281*, 777.

25 T. Okubo, Y. Maeda, H. Kitano, *J. Phys. Chem.* **1989**, *93*, 3721.

26 T. Tominaga, D. Hachisu, M. Kamada, *Langumuir* **1994**, *10*, 4676.

27 I. Topchieva, K. Karezin, *J. Colloid Interface Sci.* **1999**, *213*, 29.

28 B. Dorrego, L. Garcia-Rio, P. Herves, J. R. Leis, J. C. Mejuto, J. Perez-Juste, *Angew. Chem., Int. Ed.* **2000**, *39*, 2945.

29 B. Dorrego, L. Garcia-Rio, P. Herves, J. R. Leis, J. C. Mejuto, J. Perez-Juste, *J. Phys. Chem. B* **2001**, *105*, 4912.

30 B.-Y. Jiang, J. Du, S.-Q. Cheng, J.-W. Pan, X. C. Zeng, Y.-J. Liu, S. Yamamoto, Y. Sueishi, *J. Dispersion Sci. Technol.* **2003**, *24*, 63.

31 L. Garcia-Rio, J. R. Leis, J. C. Mejuto, J. Perez-Juste, *J. Phys. Chem. B* **1997**, *101*, 7383.

32 L. Garcia-Rio, J. R. Leis, J. C. Mejuto, J. Perez-Juste, *J. Phys. Chem. B* **1998**, *102*, 4581.

33 I. Fernández, L. García-Río, P. Hervés, J. Perez-Juste, P. Rodrigez-Dafonte, *J. Phys. Org. Chem.* **2000**, *13*, 664.

34 L. Garcia-Rio, J. R. Leis, J. C. Mejuto, A. Navarro-Vazguez, J. Perez-Juste, P. Rodriguez-Dafonte, *Langumuir* **2004**, *20*, 606.

35 C. Bravo-Diaz, E. Gonzalez-Romero, *Langumuir* **2005**, *21*, 4888.

36 J. Xie, Y. Zhang, J. Du, X.-C. Zeng, Y.-J. Liu, S. Yamamoto, Y. Sueishi, *J. Dispersion Sci. Technol.* **2003**, *24*, 97.

37 C. A. Bunton, G. Savelli, *Adv. Phys. Org. Chem.* **1986**, *22*, 213.

38 Y. Liu, N. Horiuchi, Y. Sueishi, S. Yamamoto, *J. Inclusion Phenom. Macrocyclic. Chem.* **2006**, *54*, 233.

39 P. Sevcík, H. B. Dunford, *J. Phys. Chem.* **1991**, *95*, 2411.

40 M. C. Wilkinson, *J. Colloid Interface Sci.* **1972**, *40*, 14.

41 V. Nunez-Tolin, H. Hoebregs, J. Leonis, S. Parades, *J. Colloid Interface Sci.* **1982**, *85*, 597.

42 S. H. Herzfeld, M. L. Corrin, W. D. Harkins, *J. Phys. Colloid Chem.* **1950**, *54*, 271.