

Micellar Effects on the Reduction of Tris(acetylacetonato)cobalt(III) by 1-Benzyl-1,4-dihydronicotinamide with Ionic Surfactants

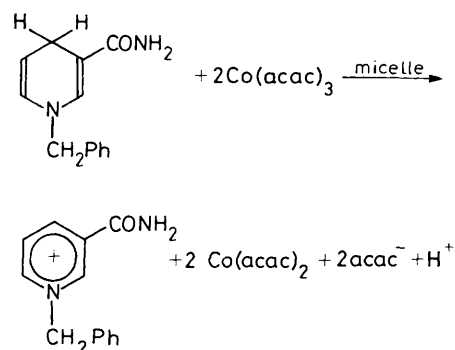
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The reduction of tris(acetylacetonato)cobalt(III) [Co(acac)₃] by 1-benzyl-1,4-dihydronicotinamide (BNAH) has been studied in 4–100% (v/v) methanol–borate buffer with or without surfactants of anionic sodium dodecylsulphate (SDS) or cationic dodecyltrimethylammonium chloride (DTAC) micelles. The second-order reaction rate decreases on increased methanol content of the solvent system and in the presence of the surfactant micelles in the reaction system; it is retarded in the order of DTAC > SDS > none, and the rate constants of the electron transfer in the micellar pseudophase are 15–70 times smaller than that in the bulk aqueous phase. The binding constants of BNAH to SDS and DTAC micelles were determined to be 236 and 102 mol⁻¹ dm³, respectively, at 30 °C by fluorescence measurements. It was also well reflected, by the estimated values of the activation parameters, that the micellar reaction of both the incorporated reactants [BNAH and Co(acac)₃] proceeded at the water–micelle interface, in which low polar environments suppress the reaction through the unfavourable orientation of the reactants and the destabilization of the transition state of the reaction.

The oxidation of reduced nicotinamide adenine dinucleotide (NADH) and/or NADH model compounds by one-electron oxidants such as a transition-metal complex has received much attention with a particular view to the three-step mechanism of sequential electron–proton–electron transfer.^{1–9} Since the neutral 1,4-dihydropyridine moiety of an NADH model compound is transformed into a pyridinium cation *via* a radical-cation intermediate during the redox process, the electron-transfer reaction of NADH model compounds seems to be sensitive to reaction circumstances. However, environmental influences such as micellar effects on the reaction of NADH model compounds have remained uncertain,¹⁰ even though a large number of discussions have hitherto been developed on the mechanism of the reaction involving the NADH model compound.¹ Micellar systems have been known to offer characteristic microenvironments which are composed of an aqueous phase, a lipophilic phase, and a charged interface.^{11,12} Surfactant micelles are able to incorporate such hydrophobic reactants as NADH model compounds and the polar head group of a surfactant molecule might affect the reaction in the following way. An anionic micelle promotes the reaction through the stabilization of the dihydropyridine radical cation intermediate and the pyridinium cation, while a cationic micelle retards the reaction by depressing the formation of the above cationic species. Accordingly, it is of interest to study the micellar effect on the electron-transfer reaction from the NADH model compound to the transition-metal complex. Although several studies on the reaction of NADH model compounds in micellar systems have hitherto been reported,^{10,13,14} there is no report dealing with the electron-transfer reaction between NADH model compounds and transition-metal complexes in the micellar system.

In this paper, we describe the first example for the micellar effect on thermal electron transfer from an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH), to a hydrophobic transition-metal complex, tris(acetylacetonato)cobalt(III) [Co(acac)₃], with ionic surfactants of anionic sodium dodecylsulphate (SDS) or cationic dodecyltrimethylammonium chloride (DTAC) (Scheme 1).



Scheme 1.

Experimental

Materials.—BNAH was prepared in accordance with the previous method.¹⁵ Commercially available Co(acac)₃ was used after recrystallization with benzene and light petroleum, and commercially available surfactants (SDS and DTAC) were used without further purification. Methanol and water used as solvents were distilled and deoxygenated before use by being purged with gaseous nitrogen.

Reaction Procedure.—The reduction of Co(acac)₃ (1.0 × 10⁻³ mol dm⁻³) by BNAH (5.0 × 10⁻⁴ mol dm⁻³) was carried out with or without surfactants (0–4.0 × 10⁻² mol dm⁻³) at 30 ± 0.1 °C in 4–100% (v/v) methanol–0.02 mol dm⁻³ H₃BO₃–NaOH buffer (pH 9.0, μ = 0.02 mol dm⁻³ with KCl) under a nitrogen atmosphere. All reactions were performed with exclusion of light in 3 cm³ vials which were placed in a thermostatted shaker. The amount of Co(acac)₃ which had reacted was determined spectrophotometrically at 595 nm using JASCO UVIDEC-220A spectrophotometer. The rate constant was calculated according to second-order rate laws.

Fluorescence Measurement.—The fluorescence intensity was measured by using JASCO FP-550A fluorescence spectro-

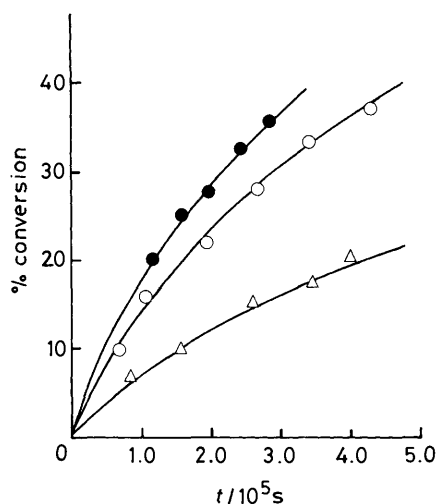


Figure 1. Time-conversion plots for the reduction of $\text{Co}(\text{acac})_3$ by BNAH in 4% (v/v) methanol-borate buffer (pH 9.0) under N_2 at 30 °C; SDS = $1.6 \times 10^{-2} \text{ mol dm}^{-3}$ (○). DTAC = $4.0 \times 10^{-2} \text{ mol dm}^{-3}$ (△), and none (●).

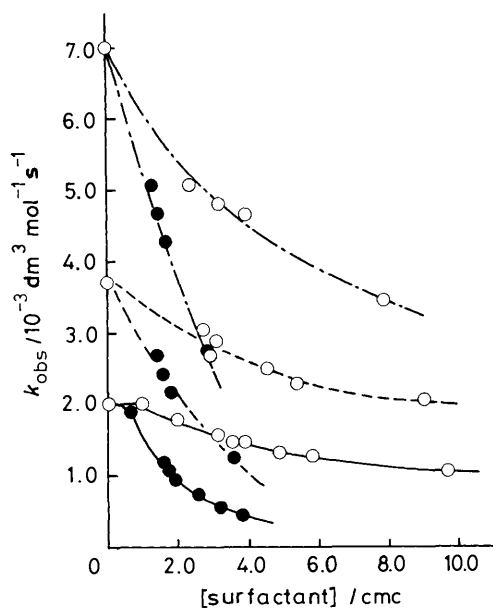


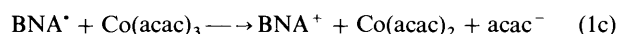
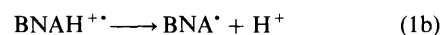
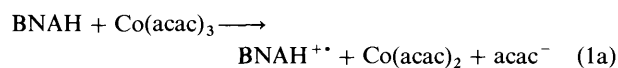
Figure 2. Micellar effects on the second-order rate constants of the reduction of $\text{Co}(\text{acac})_3$ by BNAH with SDS (○) or DTAC (●) in 4% (v/v) methanol-borate buffer (pH 9.0) under N_2 at 30 °C: (—), 35 °C: (---); and 40 °C: (- · - · -).

photometer and the temperature was kept to within 0.1 °C of the required value by a thermostatted cell holder. The critical micelle concentrations (cmc) of the surfactants were determined by measuring the fluorescence intensity of pyrene at various surfactant concentrations according to the literature.¹⁶ When the solution containing pyrene ($2.0 \times 10^{-6} \text{ mol dm}^{-3}$) and surfactants ($0\text{--}4.0 \times 10^{-2} \text{ mol dm}^{-3}$) was excited at 320 nm, the fluorescence intensities of the two vibronic bands were measured at 373 and 383 nm. The cmc values were obtained from plots of the surfactant concentration *versus* the ratio of fluorescence intensity at 373 nm to that at 383 nm. The binding constants of BNAH to micelles (K_{BAH}) were determined by the fluorescence intensity measurement according to equation (6) (see later). The relative emission intensity was measured for 4%

(v/v) methanol-0.02 mol dm^{-3} borate buffer (pH 9.0) solution containing BNAH ($4.0 \times 10^{-6} \text{ mol dm}^{-3}$) and surfactants ($0\text{--}6.0 \times 10^{-2} \text{ mol dm}^{-3}$). The excitation and the monitoring wavelength were 360 nm and 455 nm, respectively.

Results and Discussion

Reduction of $\text{Co}(\text{acac})_3$ by BNAH with or without Surfactants.—When the reduction of $\text{Co}(\text{acac})_3$ by BNAH was carried out with or without surfactants at 30 °C in 4% (v/v) methanol-borate buffer (pH 9.0), the amount of the substrate, $\text{Co}(\text{acac})_3$, decreased as the reaction proceeded (Figure 1). The electron-transfer reaction from BNAH to $\text{Co}(\text{acac})_3$ seems to proceed *via* equation (1a)–(c) (analogous to the electron transfer from



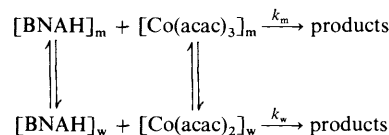
1-propyl-1,4-dihydronicotinamide to hexacyanoferrate(II) in aqueous methanol)² where BNA^+ and $\text{Co}(\text{acac})_2$ were detected experimentally. In practice, all the present reactions obeyed good second-order kinetics derived from equation (1a)–(c), and the second-order rate constant (k_{obs}) obtained by stationary-state assumptions of concentrations of BNAH^{++} and BNA^+ was not dependent on the initial concentrations of BNAH and $\text{Co}(\text{acac})_3$ [equation (2)].

$$-\frac{d[\text{Co}(\text{acac})_3]}{dt} = 2k_{\text{obs}}[\text{BNAH}][\text{Co}(\text{acac})_3] \quad (2)$$

Among the reactions of (1a)–(c), the first electron-transfer reaction [equation (1a)] might be a rate-determining step because the $\text{p}K_{\text{a}}$ value of BNAH^{++} was 3.6^{3a} and the redox potentials (*vs.* SCE) of BNAH, BNA^+ , and $\text{Co}(\text{acac})_3$ were 0.89,^{1a} -1.08 ,¹⁷ and *ca.* -0.3 V ,¹⁸ respectively.

With regard to the effect of the surfactant on the k_{obs} value, Figure 2 shows the plot of k_{obs} *versus* the concentration of the surfactants for the $\text{Co}(\text{acac})_3$ reductions at various reaction temperatures. The k_{obs} value decreased with increased concentration of the surfactants; the extent of the rate decrease by the micelles followed the order DTAC > SDS over the whole temperature range of the reaction.

Since the reaction of BNAH and $\text{Co}(\text{acac})_3$ proceeds not only in the micelles but in the bulk solution, the following reaction scheme can be given for the present reaction systems in the presence of surfactant micelles, where the subscripts m and w



Scheme 2.

stand for micellar and aqueous phases, respectively. According to Scheme 2, the Berezin expression (3) for a second-order rate constant can be given quantitatively for the micellar effect on the present bimolecular reaction,^{12,19} where P_{BNAH} and P_{Co}

$$k_{\text{obs}} = \frac{k_m P_{\text{BNAH}} P_{\text{Co}} C_m v + k_w (1 - C_m v)}{[1 + (P_{\text{BNAH}} - 1) C_m v][1 + (P_{\text{Co}} - 1) C_m v]} \quad (3)$$

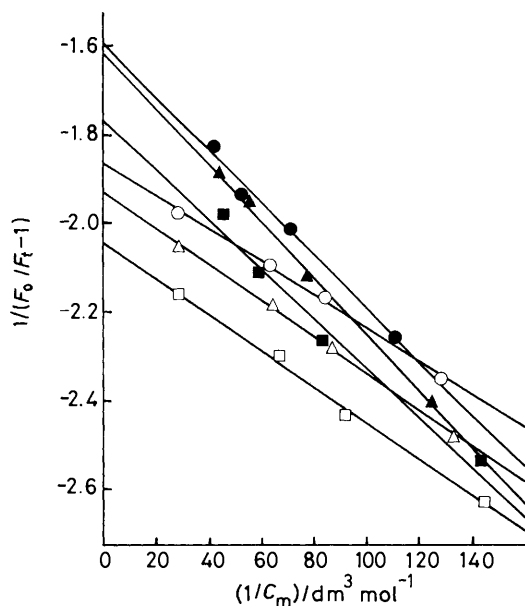


Figure 3. Plots of $1/(F_0/F_t - 1)$ vs. $1/C_m$ for BNAH in the surfactant micelles at various temperatures; SDS at 30 °C (○), 35 °C (△), and 40 °C (□); DTAC at 30 °C (●), 35 °C (▲), and 40 °C (■).

represent the partition coefficients between micelles and water of BNAH and $\text{Co}(\text{acac})_3$, respectively, v is the partial molar volume of the micelles, and C_m is the concentration of the micelles ($C_m = [\text{surfactant}] - \text{cmc}$). The volume fraction of the micelles, $C_m v$ is small at all surfactant concentrations under the present conditions. The partition coefficients P_{BNAH} and P_{Co} are also much larger than unity because of considerably large hydrophobicity of BNAH and $\text{Co}(\text{acac})_3$, therefore equation (3) can be simplified to equation (4).

$$k_{\text{obs}} = \frac{k'_m K_{\text{BNAH}} K_{\text{Co}} C_m + k_w}{(1 + K_{\text{BNAH}} C_m)(1 + K_{\text{Co}} C_m)} \quad (4)$$

The binding constants (K_{BNAH} and K_{Co}) and a rate constant (k'_m) are defined by equation (5)–(7).

$$K_{\text{BNAH}} = v(P_{\text{BNAH}} - 1) \quad (5)$$

$$K_{\text{Co}} = v(P_{\text{Co}} - 1) \quad (6)$$

$$k'_m = k_m/v \quad (7)$$

The following equation is then derived from equation (4), where

$$\frac{1}{k_{\text{obs}}(1 + K_{\text{BNAH}} C_m) - k_w} = \frac{1}{k'_m K_{\text{BNAH}} - k_w} \left(\frac{1}{K_{\text{Co}} C_m} + 1 \right) \quad (8)$$

k_w is given as the rate constant obtained for the reaction without the surfactants in 4% (v/v) methanol–borate buffer solution. The rate constant, k'_m , in the micellar pseudophase and/or the binding constant, K_{Co} , can be evaluated from equation (8), if the value of K_{BNAH} is known (this will be discussed in the later part of this text).

The fluorescence intensity of photoexcited BNAH in aqueous solution is increased by the addition of surfactants, so that the binding constant of BNAH to micelles, K_{BNAH} , can be determined by the following fluorescence intensity measurement

using modified literature treatments for micellar systems.²⁰ The partition coefficient of BNAH between the aqueous phase and the micellar pseudophase can be represented by equation (9),

$$P_{\text{BNAH}} = \frac{[\text{BNAH}]_m}{[\text{BNAH}]_w} = \frac{f}{(1-f)} \cdot \frac{[\text{BNAH}]_t/C_m v}{[\text{BNAH}]_t/(1-C_m v)} = \frac{f(1-C_m v)}{(1-f)C_m v} \quad (9)$$

where $[\text{BNAH}]_t$ = total concentration of BNAH and f = concentration fraction of BNAH in micelles to $[\text{BNAH}]_t$. The volume fraction of the micellar pseudophase is small ($C_m v \ll 1$) for dilute surfactant solutions. Therefore, K_{BNAH} can be given as equation (10) under the conditions of $P_{\text{BNAH}} \gg 1$ and $C_m \ll 1$.

$$K_{\text{BNAH}} = \frac{f}{(1-f)C_m} \quad (10)$$

The fluorescence intensity of BNAH is proportional to the concentration of BNAH when the concentration is low ($[\text{BNAH}] \leq 1 \times 10^{-5} \text{ mol dm}^{-3}$). The fluorescence intensity (F) of BNAH can be represented by equations (11)–(13) under

$$F_m = \Phi_m f I_t \quad (11)$$

$$F_w = \Phi_w (1-f) I_t \quad (12)$$

$$F_t = F_m + F_w = [\Phi_w + (\Phi_m - \Phi_w)f] I_t \quad (13)$$

the present conditions, where Φ is the quantum yield of the fluorescence and I is the number of photons absorbed by BNAH. From equation (10) and (13), the fluorescence intensity of the solution containing BNAH and the micelles is expressed as follows:

$$F_t = \frac{\Phi_m K_{\text{BNAH}} C_m + \Phi_w}{1 + K_{\text{BNAH}} C_m} I_t \quad (14)$$

Equation (14) is rewritten as equation (15) in the absence of

$$F_o = \Phi_w I_t \quad (15)$$

the micelles. Consequently, the relationship between the relative fluorescence intensity F_o/F_t and the concentration of the micelles is given by equation (16).

$$\frac{1}{F_o/F_t - 1} = \frac{1}{(1 - \Phi_m/\Phi_w)} \left(\frac{1}{K_{\text{BNAH}} C_m} + \frac{\Phi_m}{\Phi_w} \right) \quad (16)$$

As shown in Figure 3, the linear relationships between $1/(F_o/F_t - 1)$ and $1/C_m$ were obtained for the micellar solutions of SDS and DTAC containing BNAH at various temperatures. The binding constants, K_{BNAH} , obtained from the slopes and the intercepts of the lines are summarized in Table 1 in addition to the cmc values.

The binding constant, K_{Co} , and the rate constant, k'_m in micellar pseudophases were then estimated from equation (8) by means of K_{BNAH} values obtained. As expected from equation (8), the plots of $1/[k_{\text{obs}}(1 + K_{\text{BNAH}} C_m) - k_w]$ vs. $1/C_m$ were linear in both of the SDS and DTAC systems (Figures 4 and 5), and the evaluated values of K_{Co} and k'_m are listed in Table 1. The binding of BNAH to SDS micelles was twice as strong as that to DTAC micelles, but the binding constant of $\text{Co}(\text{acac})_3$ to SDS micelles was half that of DTAC micelles. Moreover, the

Table 1. Binding constants of BNAH and $\text{Co}(\text{acac})_3$ to SDS or DTAC (K_{BNAH} and K_{Co}) and second-order rate constants (k'_m for the micellar pseudophase and k_w for the bulk aqueous phase) in 4% (v/v) methanol-borate buffer (pH 9.0) at 30, 35, and 40 °C.

Surfactant	T °C	cmc $10^{-3} \text{ mol dm}^{-3}$	K_{BNAH} $\text{dm}^3 \text{ mol}^{-1}$	K_{Co} $\text{dm}^3 \text{ mol}^{-1}$	k'_m or k_w $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
SDS	30	4.2	236	11	1.4
	35	4.5	229	10	2.6
	40	5.1	257	7.7	5.8
DTAC	30	16	102	27	0.28
	35	17	97	23	0.94
	40	18	139	20	2.0
None	30				20.0
	35				37.1
	40				70.2

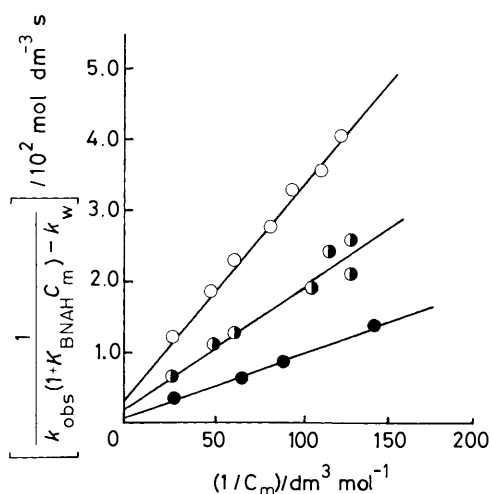


Figure 4. Plots of $1/[k_{\text{obs}}(1 + K_{\text{BNAH}}C_m) - k_w]$ vs. $1/C_m$ for the reduction of $\text{Co}(\text{acac})_3$ by BNAH in the presence of SDS at 30 °C (○), 35 °C (●), and 40 °C (●).

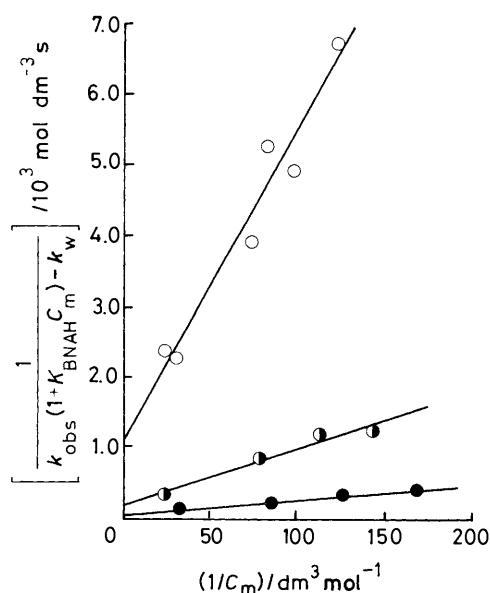


Figure 5. Plots of $1/[k_{\text{obs}}(1 + K_{\text{BNAH}}C_m) - k_w]$ vs. $1/C_m$ for the reduction of $\text{Co}(\text{acac})_3$ by BNAH in the presence of DTAC at 30 °C (○), 35 °C (●), and 40 °C (●).

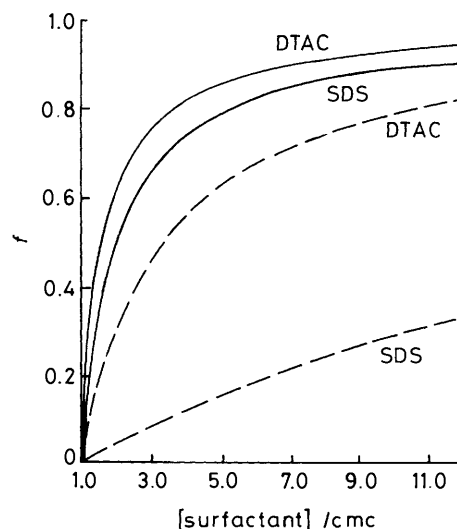


Figure 6. Calculated fractions of the concentrations for BNAH (—) and $\text{Co}(\text{acac})_3$ (---) in the micellar phase at 30 °C.

values of K_{BNAH} is much larger than those of K_{Co} in both surfactant systems. The present K_{BNAH} values, 236–257 $\text{dm}^3 \text{ mol}^{-1}$, for SDS solution with 4% (v/v) methanol coincide with the previously reported K_{BNAH} values for the binding of BNAH to SDS micelles, 285 in H_2O ¹⁰ and 190 $\text{dm}^3 \text{ mol}^{-1}$ in 10% (v/v) methanol- H_2O .¹⁴

It is noteworthy from Table 1 that the second-order rate constants, k'_m , of the present reaction in the lower polar pseudophase of the micelles are much smaller than those in the polar aqueous phase of 4% (v/v) methanol-borate buffer solution. This is related to the fact that the rate of the present reaction without the surfactants is retarded with increasing methanol contents in the range of 4–100% (v/v) MeOH- H_2O (Table 2).

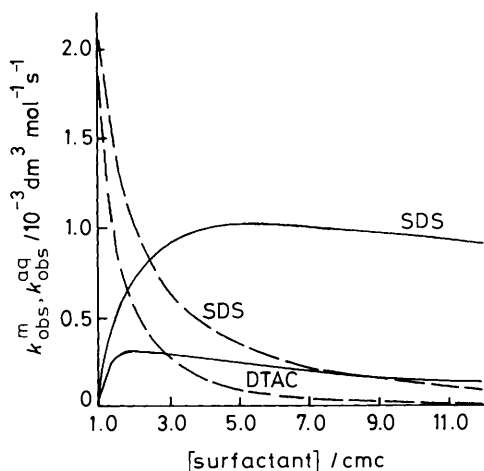
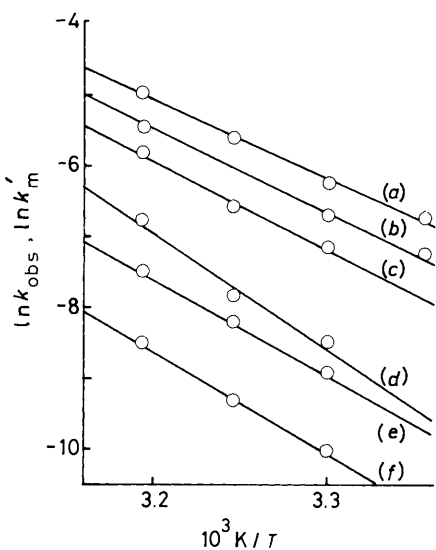
The micellar effects on the second-order rate constants is also reflected in the difference in reactant distributions and reaction rates between in the micellar pseudophase and in the aqueous phase. The concentration fraction of the reactants [BNAH and $\text{Co}(\text{acac})_3$] incorporated by the micelles can be estimated from equation (17) by use of K_{BNAH} and K_{Co} values,

$$f = \frac{KC_m}{1 + KC_m} \quad (17)$$

and the change in f values by the surfactant concentrations are shown in Figure 6. The increase in the concentration of the surfactants promotes the incorporation of the reactants by the

Table 2. Second-order rate constants for the reduction of Co(acac)₃ by BNAH in 4–100% (v/v) methanol–borate buffer solution at 30 °C.

$\frac{k_{\text{obs}}}{10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$	% Methanol content (v/v)				
	4	20	30	50	100
	2.00	1.25	0.80	0.21	0

**Figure 7.** Calculated reaction rate constants of BNAH and Co(acac)₃ in the micellar pseudophase (—) and in the aqueous phase (---) at 30 °C.**Figure 8.** Arrhenius relationships for reduction of Co(acac)₃ by BNAH in (a) 4%, (b) 20%, (c) 30%, (d) 50% (v/v) methanol–borate buffer, (e) SDS, and (f) DTAC.

micelles, accompanying the retardation of the reaction rate (Figures 2 and 6).

The observed second-order rate constant given by equation

$$k_{\text{obs}} = k_{\text{obs}}^{\text{m}} + k_{\text{obs}}^{\text{aq}} \quad (18)$$

$$k_{\text{obs}}^{\text{m}} = \frac{k_{\text{m}}^{\text{m}} K_{\text{BNAH}} K_{\text{Co}} C_{\text{m}}}{(1 + K_{\text{BNAH}} C_{\text{m}})(1 + K_{\text{Co}} C_{\text{m}})} \quad (19)$$

$$k_{\text{obs}}^{\text{aq}} = \frac{k_{\text{w}}}{(1 + K_{\text{BNAH}} C_{\text{m}})(1 + K_{\text{Co}} C_{\text{m}})} \quad (20)$$

Table 3. Activation parameters (ΔH^{\ddagger} and ΔS^{\ddagger}) estimated for the reduction of Co(acac)₃ by BNAH in the micellar systems or 4–50% (v/v) methanol–borate buffer solutions.

Medium		ΔH^{\ddagger}	ΔS^{\ddagger}
		J mol ⁻¹	J mol ⁻¹ K ⁻¹
Micelle	SDS	110	35
	DTAC	120	51
Methanol–borate buffer	4%	87	–8.5
	20%	89	–8.0
	30%	100	18
	50%	131	115

(6) can be divided into the reaction rate constant for the micellar pseudophase ($k_{\text{obs}}^{\text{m}}$) and that for the aqueous phase ($k_{\text{obs}}^{\text{aq}}$).

The $k_{\text{obs}}^{\text{m}}$ and $k_{\text{obs}}^{\text{aq}}$ values in various concentrations of SDS and DTAC are then estimated from equation (19) and (20), and the values obtained are shown in Figure 7. As Figure 7 indicates, the $k_{\text{obs}}^{\text{m}}$ values are comparable to the $k_{\text{obs}}^{\text{aq}}$ values at 2.5 times cmc of the surfactants, even though the k_{m}^{m} values are 15–70 times smaller than the k_{w} values. Furthermore, both the surfactant micelles of SDS and DTAC drastically depressed the reaction in the aqueous phase while promoting the reaction in the micellar pseudophase in the range of $1 < [\text{surfactant}] < 2.5 \text{ cmc}$. This fact is probably due to condensation of the reactants by the SDS or DTAC micelles, and the actual concentrations of the reactants in the micelles are considerably large compared with those in the bulk water phase. In any case, the total rate constant was reduced by the presence of the surfactant micelles.

Notice also from Figure 7 that the $k_{\text{obs}}^{\text{m}}$ value increases with increased surfactant concentration with its maximum at [SDS] = 5 cmc or [DTAC] = 2 cmc, and in the higher concentration of SDS and DTAC it suffered from a gradual decrease through the decrease of the reactant concentration in a micelle.

Thermodynamic Parameters of the Reaction with or without the Surfactants.—Both the rate constants of k_{obs} (for the reaction in methanolic solutions) and k_{m}^{m} (for the reaction in the micellar pseudophase) were appreciably changed by the reaction temperature (25–40 °C). Arrhenius plots for the reaction in the temperature range 25–40 °C with and/or without the surfactants are depicted in Figure 8, where the cmc values of SDS and DTAC micelles are almost constant (see Table 1). The estimated activation parameters, ΔH^{\ddagger} and ΔS^{\ddagger} , are listed in Table 3; these values increase with increased methanol content in the methanol–borate buffer solution. The activation parameters evaluated in the micellar systems are almost the same as those obtained in the 30–50% (v/v) methanol–borate buffer solution. This is coincident with the fact that the micropolarity of Stern layer of micelles corresponds to that in methanol,²¹ and the reaction circumstances of the present reaction in the micellar pseudophase is akin to those in the solution of 30–50% (v/v) methanol–borate buffer.

The value of activation enthalpy (ΔH^{\ddagger}) decreased with decreasing methanol content in the solvent system; *i.e.*, the present reaction is energetically favourable in a polar medium. Since the main elementary steps of the present reaction for the reduction of Co(acac)₃ [equations (1a) and (1c)] proceed *via* the generation of the ionic species of BNAH⁺⁺ and BNA⁺ through the transition state of the electron-transfer reaction from BNAH (or BNA⁺) to Co(acac)₃, the positive charge formation on the nicotinamide ring of BNAH or BNA⁺ during the activation process of the elementary reaction [equations (1a) and (1c)] might be promoted by the polar solvent (*viz.*, low methanol

content solution). The remarkable increase of the ΔS^\ddagger value on increase of the methanol content from 4 to 50% (v/v) in the solvents suggests difficulty in formation of the activated complex *via* the rigid interaction of the reactants in the low-polarity solution (*viz.* high methanol-content solution). At high methanol content, the reaction rate is therefore decreased by the destabilization of the transition state.

With regard to the micellar reaction, the relatively large ΔH^\ddagger values for the reaction in the micellar pseudophase, as compared with those for the reaction in 4–30% (v/v) methanol-borate buffer (Table 3), suggest that the activation of the reactants in the micellar pseudophase is unfavourable such that the micellar reaction is slow compared with the methanolic reaction (see Figure 2). The fact that the micellar reaction proceeds more easily in SDS than in DTAC (see Figure 2 and k'_m value in Table 1) is also reflected in the small ΔH^\ddagger value for the reaction in the former compared with that for the reaction in the latter; the formation of the cationic species (BNAH⁺⁺ and BNA⁺) and/or the charge separation of the generated anionic acac⁻ from the micellar surface occur in preference to the anionic SDS micelles rather than in the cationic DTAC ones.

Thus, the reduction of Co(acac)₃ by BNAH in the presence of micelles proceeds both in the aqueous phase and in the micellar pseudophase, and the low polarity at the water-micelle interface, especially in cationic micellar pseudophase, suppresses the reaction rate through the destabilization of the transition state of the electron transfer from BNAH (or BNA⁺) to Co(acac)₃.

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