Micellar Promoted Photoreduction of Ethylenediaminetetraacetato-cobaltate(III) by 1-Benzyl-1,4-dihydronicotinamide

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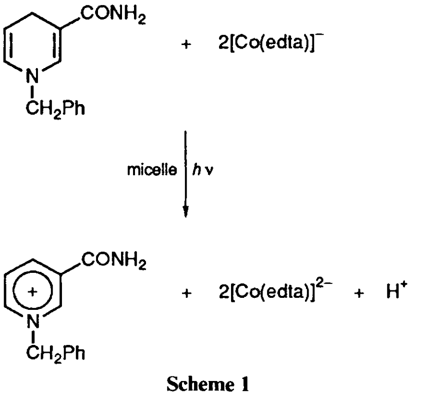
The photoreduction of ethylenediaminetetraacetato cobaltate(III) ($[Co(edta)]^-$) by 1-benzyl-1,4-dihydronicotinamide (BNAH) has been studied in the presence of the surfactants cationic dodecyltrimethylammonium chloride (DTAC) and anionic sodium dodecylsulphate (SDS). Cationic DTAC accelerates the photoreduction of $[Co(edta)]^-$, while anionic SDS suppresses the reaction. The micellar effects on the reaction rates have been analysed by distribution of the reactants between an aqueous phase and a micellar phase and monitoring the difference in rate. In the DTAC micellar system, cationic micelles promote the reaction significantly by concentrating the photoexcited BNAH and $[Co(edta)]^-$ through hydrophobic and electrostatic interactions in spite of the smaller rate constant in the micellar phase compared with that in the aqueous phase. On the other hand, anionic SDS hinders approach of the anionic $[Co(edta)]^-$ to the photoexcited BNAH in the SDS micelles, so as to retard the reaction rate.

The 1,4-dihydronicotinamide derivatives capable of acting as two-electron reductants, related to the reduced nicotinamide adenine dinucleotide [NAD(P)H], have already been extensively investigated.[1,2] The photoreactions of such NAD(P)H model compounds as the 1,4-dihydropyridines have also received increasing attention because their reducing ability is substantially enhanced by photoexcitation.[3–21] Since micellar systems have the advantage of promoting photoinduced electron transfer and charge separation in photoreactions,[22,23] the study of micellar effects on the photoreaction of NADH model compounds is of interest.

Previously, we found that the reduction rates of a nonionic, hydrophobic transition-metal complex [tris(acetylacetonato)-cobalt(III)] with 1-benzyl-1,4-dihydronicotinamide (BNAH) or photoexcited BNAH were strongly affected by such properties of the micelles as polarity, or the charge on the micellar surface, rather than the concentration of reactants in the micellar phase.[21,24]

The electrostatic interactions of ionic micelles may also play an important role in electron-transfer reactions between ionic reactants and NADH model compounds. When both the substrate and the micellar surface have the same charge, electron transfer from the NADH model compounds in the micelles to the ionic substrate is depressed by the electrostatic repulsion, but is promoted by the electrostatic attraction when they have opposite charges.

In this paper, we wish to describe the micellar effects of cationic dodecyltrimethylammonium chloride (DTAC) and anionic sodium dodecylsulphate (SDS) on the photoreduction of anionic ethylenediaminetetraacetato cobaltate(III) ($[Co(edta)]^-$) with BNAH, Scheme 1.



Scheme 1

Experimental

The materials were the same as those used in the previous work,[24] except that potassium ethylenediaminetetraacetato cobaltate(III) ($K[Co(edta)]\cdot 2H_2O$) was prepared according to the literature.[25]

Solutions of BNAH (5.0×10^{-4} mol dm^{-3}), $[Co(edta)]^-$ (1.0×10^{-3} mol dm^{-3}), and surfactants (0–6.0×10^{-2} mol dm^{-3}) in Pyrex cells were placed in a thermostatted cell holder (30 ± 0.1 °C) equipped with a magnetic stirring device and irradiated using a 400 W mercury lamp in the wavelength range λ = 340–410 nm using Toshiba glass filters UV-35 and UV-D35. The quantity of BNAH and $[Co(edta)]^-$ consumed was determined spectrophotometrically at 360 and 540 nm using quartz cells with path lengths of 1 mm and 1 cm, respectively.

The quantum yields of the reductions were evaluated for the solutions with sufficiently high absorbance ($A > 2.0$) at λ = 340–410 nm to ensure complete absorption of light entering the samples during the experiment. The quantity (I) of photons absorbed by BNAH was estimated by eqn. (1) from the light

$$I = \frac{-\int_{\lambda_2}^{\lambda_1} T(\lambda)\frac{A_{\mathrm{BNAH}}(\lambda)}{A_{\mathrm{BNAH}}(\lambda) + A_{\mathrm{Co}}(\lambda)}\,\mathrm{d}\lambda}{\int_{\lambda_2}^{\lambda_1} T(\lambda)\,\mathrm{d}\lambda}\, I_{\mathrm{tot}} \qquad (1)$$

intensity (I_{tot}), as measured by Reineck's salt actinometry.[26] In eqn. (1), λ_1 = 410 nm, λ_2 = 340 nm and T = transmittance of cutfilters, and A_{BNAH} and A_{Co} = absorbance of BNAH and $[Co(edta)]^-$, respectively.

The lifetime (τ) of photoexcited BNAH was estimated by measuring the ratio of the theoretical lifetime of BNAH (calculated from the Strickler–Berg equation)[27] to the fluorescence intensity, relative to the same ratio obtained in methanol,[28] assuming that τ = 0.93 ns in the latter case.[18]

The binding constants of $[Co(edta)]^-$ to SDS and DTAC micelles were determined using gel-filtration chromatography

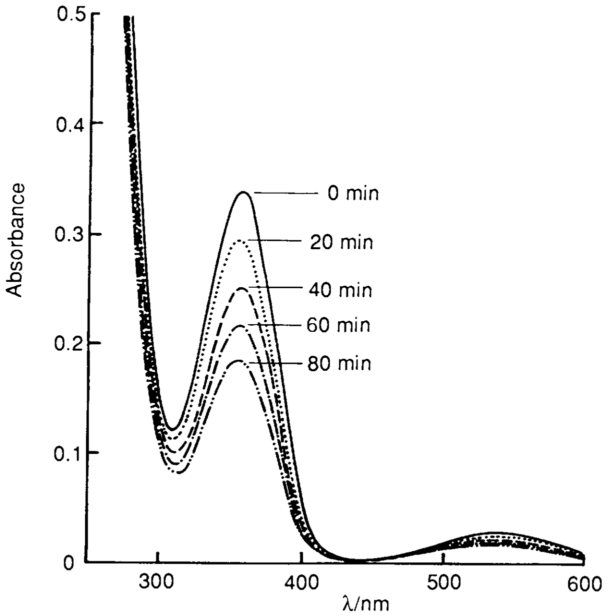


Fig. 1 Absorption spectral change measured using quartz cell with light-path length of 1 mm during photoreaction of $[Co(edta)]^-$ and BNAH in the presence of 3.0×10^{-2} mol dm^{-3} DTAC under N_2 at 30 °C

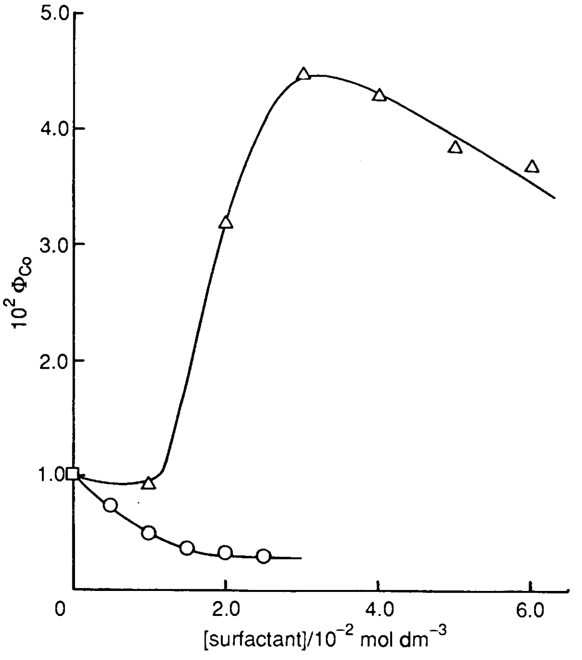


Fig. 2 Micellar effects on quantum yields for photoreduction of $[Co(edta)]^-$ by BNAH with SDS (○) or DTAC (△)

on Sephadex G-15.[29] A column (diameter = 3 cm and length = 30 cm) with an outer jacket for circulating water from a thermostat (30 ± 0.1 °C) was used. The void volume (V_0) of the packed column was estimated to be 29.0 cm^3 by using Blue Dextran 2000. Before each run the column was equilibrated with 1000 cm^3 of 4% (v/v) methanol–borate buffer (pH = 9.0, $\mu = 0.02$ mol dm^{-3}) containing the surfactants (0–9.0 × 10^{-2} mol dm^{-3}). Each run was started by the addition of 1.0 cm^3 of $K[Co(edta)]\cdot 2H_2O$ (2×10^{-3} mol dm^{-3}). Elution with the appropriate eluent was followed at a rate of 1.0 cm^3 min^{-1}. Fractions (0.5–1.0 cm^3) were collected using an automatic fraction collector and were monitored spectrophotometrically at 275 nm. The elution volume was calculated corresponding to the fraction of maximum absorbance.

Results and Discussions

The reduction of $[Co(edta)]^-$ (1.0×10^{-3} mol dm^{-3}) by BNAH (5.0×10^{-4} mol dm^{-3}) with or without the surfactants (0–6.0 × 10^{-2} mol dm^{-3}) was accelerated remarkably by photoirradiation at λ = 340–410 nm, as shown in Fig. 1. In the absence of photoirradiation, similar spectral changes to those in Fig. 1 were observed, but over a much longer period (48 h). The absorbance change of BNAH at 360 nm and that of $[Co(edta)]^-$ at 540 nm during the photoreaction indicated that 1 mol of BNAH reduced 2 mol of $[Co(edta)]^-$.

Fig. 2 indicates the quantum yields (Φ_{Co}) of the present photoreaction evaluated on the basis of the quantity of $[Co(edta)]^-$ consumed by photoexcited BNAH at various surfactant concentrations. Cationic DTAC enhanced the Φ_{Co} value remarkably and the maximum Φ_{Co} value was obtained at [DTAC] = 3.0×10^{-2} mol dm^{-3}. Anionic SDS, however, retarded the photoreduction.

According to the three-step mechanism, involving sequential electron–proton–electron transfer for oxidation of NADH model compounds,[17,18,30,31] the present photoreduction seems to proceed *via* the reactions in Scheme 2. Since the oxidation

$$\mathrm{BNAH} \xrightarrow{I} \mathrm{BNAH^*} \qquad (a)$$

$$\mathrm{BNAH^*} \xrightarrow{k_{ic}} \mathrm{BNAH} \qquad (b)$$

$$\mathrm{BNAH^*} \xrightarrow{k_f} \mathrm{BNAH} + h\nu \qquad (c)$$

$$\mathrm{BNAH^*} + [\mathrm{Co(edta)}]^- \xrightarrow{k_1} [\mathrm{BNAH^{\cdot +}Co(edta)^{2-}}] \qquad (d)$$

$$[\mathrm{BNAH^{\cdot +}Co(edta)^{2-}}] \xrightarrow{k_2} \mathrm{BNAH^{\cdot +}} + [\mathrm{Co(edta)}]^{2-} \qquad (e)$$

$$[\mathrm{BNAH^{\cdot +}Co(edta)^{2-}}] \xrightarrow{k_3} \mathrm{BNAH} + [\mathrm{Co(edta)}]^- \qquad (f)$$

$$\mathrm{BNAH^{\cdot +}} \xrightarrow{k_{H^+}} \mathrm{BNA^{\cdot}} + \mathrm{H^+} \qquad (g)$$

$$\mathrm{BNA^{\cdot}} + [\mathrm{Co(edta)}]^- \xrightarrow{k_{e2}} \mathrm{BNA^+} + [\mathrm{Co(edta)}]^{2-} \qquad (h)$$

Scheme 2

potentials of photoexcited BNAH (BNAH*) and $BNA^{\cdot}$ (*ca.* −2.6 V and −1.08 V *vs.* SCE)[3,31] are more negative than the reduction potential of $[Co(edta)]^-$ (0.14 V *vs.* SCE),[32] the formation of an encounter complex $[BNAH^{\cdot +}Co(edta)^{2-}]$ [Scheme 2, reaction (*d*)] and the second electron transfer reaction [Scheme 2, reaction (*h*)] are diffusion-controlled processes. The deprotonation of $BNAH^{\cdot +}$ takes place immediately after the first electron transfer under the present reaction conditions (pH = 9.0) because the pK_a value of $BNAH^{\cdot +}$ has been reported to be 3.6.[31] The oxidation potential of BNAH in a ground state is 0.57 V *vs.* SCE,[31] so that the heterolytic dissociation of the encounter complex [Scheme 2, reaction (*e*)] competes with the back electron transfer reaction [Scheme 2, reaction (*f*)]. Therefore, the dissociation of the encounter complex to $BNAH^{\cdot +}$ and $[Co(edta)]^{2-}$ might be a rate-determining step in the present reaction.

The following relation between Φ_{Co}^{-1} and $[[Co(edta)]^-]^{-1}$ is then derived by stationary-state assumption of the concentration of BNAH*, $[BNAH^{\cdot +}Co(edta)^{2-}]$, $BNAH^{\cdot +}$ and $BNA^{\cdot}$,

$$\frac{1}{\Phi_{Co}} = \frac{1}{2k_{el}\tau}\,\frac{1}{[[\mathrm{Co(edta)}]^-]} + \frac{k_2 + k_3}{2k_2} \qquad (2)$$

where $k_{el} = k_1k_2/(k_2 + k_3)$ and τ = lifetime of BNAH* in the absence of substrates.

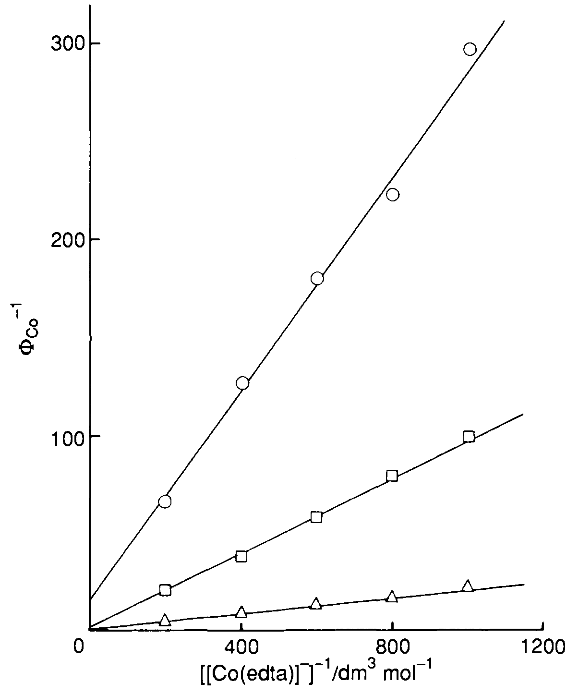


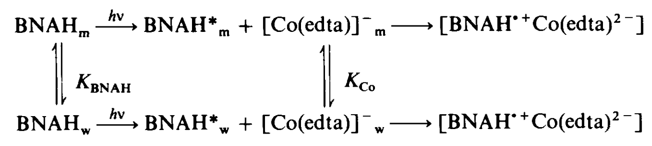
Fig. 3 Typical plots of Φ_{Co}^{-1} *vs.* $[[Co(edta)]^-]^{-1}$ for photoreduction of $[Co(edta)]^-$ by BNAH; [SDS] = 2.0×10^{-2} mol dm^{-3} (○), [DTAC] = 3.0×10^{-2} mol dm^{-3} (△), and no surfactant (□)

Table 1 Concentration effects of DTAC and SDS on the lifetime (τ) of BNAH* and on the rate constants (k_{el}) of the electron transfer reaction between BNAH* and $[Co(edta)]^-$

Surfactant	[Surfactant]/ 10^{-2} mol dm^{-3}	τ/ns	$k_{el}/10^{10}$ dm^3 mol^{-1} s^{-1}
None	0	0.38 ± 0.02	1.37 ± 0.10
DTAC	1.0	0.38 ± 0.02	1.23 ± 0.10
	2.0	0.53 ± 0.02	3.11 ± 0.20
	3.0	0.68 ± 0.03	3.88 ± 0.18
	4.0	0.74 ± 0.02	2.85 ± 0.17
	5.0	0.77 ± 0.02	2.66 ± 0.12
	6.0	0.79 ± 0.02	2.46 ± 0.11
SDS	0.5	0.44 ± 0.03	0.84 ± 0.07
	1.0	0.60 ± 0.02	0.47 ± 0.05
	1.5	0.66 ± 0.02	0.33 ± 0.03
	2.0	0.69 ± 0.02	0.27 ± 0.02
	2.5	0.71 ± 0.02	0.22 ± 0.01

As shown in Fig. 3, the plots of Φ_{Co}^{-1} *vs.* $[[Co(edta)]^-]^{-1}$ gave fairly good straight lines for all reactions studied (correlation coefficients $r > 0.995$). The k_{el} values are calculated from the slope of eqn. (2) using the lifetimes (τ) of BNAH* obtained at various surfactant concentrations.[27,28] Table 1 shows the micellar effects of DTAC and SDS on the τ and k_{el} values. The lifetime of BNAH* increased with increasing concentration of both SDS and DTAC. The electron-transfer reaction between BNAH* and $[Co(edta)]^-$ was accelerated considerably by the cationic DTAC micelles, while the anionic SDS micelles retarded the reaction. The similarity of the micellar effects on the k_{el} values to those on the Φ_{Co} values suggests that the DTAC micelles promotes the present photoreaction by accelerating the electron transfer from BNAH* to $[Co(edta)]^-$.

The micellar effects of DTAC and SDS on the photoreduction can be analysed by Scheme 3 in which the redistribution of BNAH* between the micellar phase and the aqueous phase is neglected because of its short lifetime (*ca.* 10^{-10} s). In Scheme 3 the subscripts w and m refer to an aqueous phase and a micellar phase, respectively. Since the micellar effects could result from distribution of the reactants between a micellar phase and an aqueous phase,[33,34] the kinetic data in the presence of the micelles can be treated by Berezin's approach,[34,35] and by the ion-exchange model.[34,36]


$$\begin{tikzcd}
BNAH_m \arrow[r, "h\nu"] \arrow[d, shift left] & BNAH^*_m + [Co(edta)]^-_m \arrow[r] \arrow[d, shift left] & {[BNAH^{\cdot+}Co(edta)^{2-}]} \\
BNAH_w \arrow[u, shift left, "K_{BNAH}"'] \arrow[r, "h\nu"] & BNAH^*_w + [Co(edta)]^-_w \arrow[u, shift left, "K_{Co}"'] \arrow[r] & {[BNAH^{\cdot+}Co(edta)^{2-}]}
\end{tikzcd}$$

Scheme 3

According to Berezin's approach, the concentrations of BNAH and $[Co(edta)]^-$ in the micelles were evaluated as their binding constants. The apparent binding constants (K_{BNAH^*}) of BNAH* to SDS and DTAC in 4% (v/v) methanol–borate buffer (pH = 9.0, μ = 0.02 mol dm^{-3}) at 30 °C were determined to be 447 ± 16 and 243 ± 16 dm^3 mol^{-1}, respectively, from micellar effects on the lifetime of BNAH*.[21]

For the evaluation of the binding constant (K_{Co}) of $[Co(edta)]^-$, gel-filtration chromatography was used.[29] The elution volume (V_e) and the binding constant of $[Co(edta)]^-$ are related by eqn. (3),

$$\frac{1}{V_e - V_o} = \frac{K_{Co}}{V_i k' K_D} C_m + \frac{1}{V_i k' K_D} \tag{3}$$

$$k' = (kV_g + V_i)/V_i$$

where V_o and V_i are a void volume and an imbibed (stationary) volume, respectively; V_g is the total volume of a gel matrix; K_D is a molecular sieving constant; C_m (C_m = [surfactant] − CMC) is the concentration of micelles; and k is the proportionality constant between $[Co(edta)]^-$ absorbed per unit volume of a gel matrix and the equilibrium concentration of $[Co(edta)]^-$ in a liquid phase.

As shown in Fig. 4, the plot of $(V_e - V_o)^{-1}$ *vs.* C_m for the DTAC micellar system gave a straight line and the K_{Co} value was evaluated as 15.3 ± 2.8 dm^3 mol^{-1}. On the other hand, the elution volume (V_e) increased with increasing SDS micellar concentration because the electrostatic repulsion between $[Co(edta)]^-$ and anionic SDS suppressed the diffusion of $[Co(edta)]^-$ from an imbibed phase to a liquid phase. Thus, the plots of $(V_e - V_o)^{-1}$ *vs.* C_m did not satisfy eqn. (3) in the SDS micellar system (Fig. 4). These facts indicate that $[Co(edta)]^-$ is distributed between a DTAC micellar phase and an aqueous phase, while the SDS micelles localize $[Co(edta)]^-$ in an aqueous phase. Accordingly, the anionic SDS micelles retard the reaction rates by suppressing the approach of $[Co(edta)]^-$ in the aqueous phase to BNAH* in the micellar phase through electrostatic repulsion.

Berezin's approach gives the observed rate constant (k_{el}) for electron transfer from BNAH* to $[Co(edta)]^-$ in the DTAC micellar system,[34,35] eqn. (4), where k_{el}^m and k_{el}^w are the rate constants of electron transfer reactions between BNAH* and $[Co(edta)]^-$ in the micellar phase and in the aqueous phase, respectively. Eqn. (4) may be rewritten as eqn. (5).

$$k_{el} = \frac{(k_{el}^m/v)K_{BNAH^*}K_{Co}C_m + k_{el}^w}{(1 + K_{BNAH^*}C_m)(1 + K_{Co}C_m)} \tag{4}$$

$$k_{el}(1 + K_{BNAH^*}C_m)(1 + K_{Co}C_m) = (k_{el}^m/v)K_{BNAH^*}K_{Co}C_m + k_{el}^w \tag{5}$$

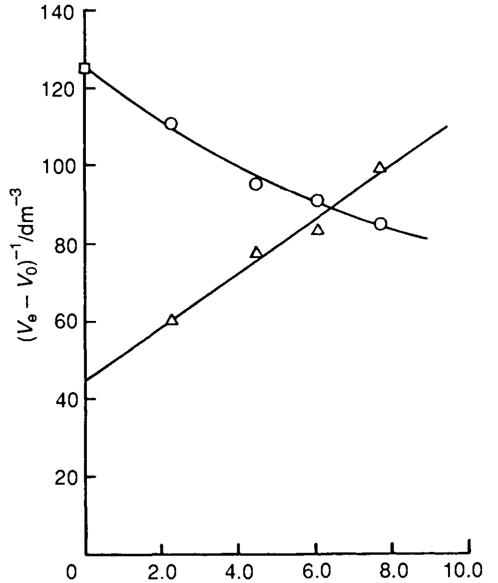


Fig. 4 Plots of $(V_e - V_0)^{-1}$ *vs.* C_m for elution of $[Co(edta)]^-$ on a column of Sephadex G-15 at 30 °C in the presence of SDS (○) or DTAC (△)

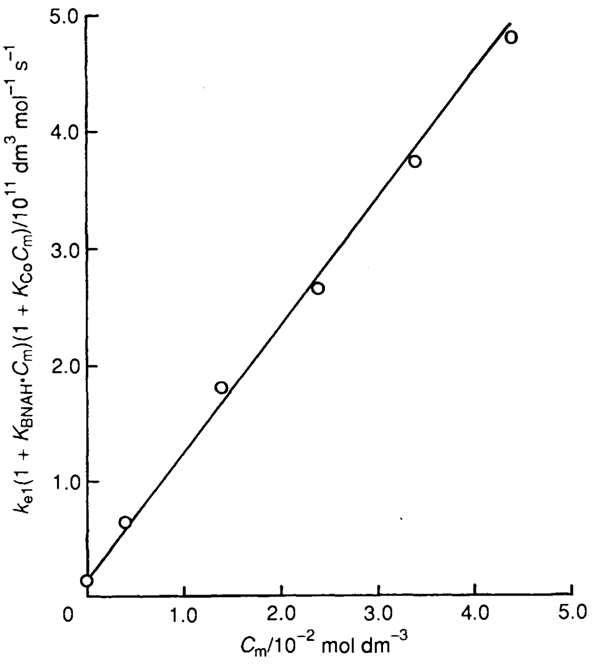


Fig. 5 Plots of $k_{el}(1 + K_{BNAH^{\bullet}}C_m)(1 + K_{Co}C_m)$ *vs.* C_m for photoinduced electron transfer from BNAH* to $[Co(edta)]^-$ in the presence of DTAC

A linear relationship was obtained by plotting $k_{el}(1 + K_{BNAH^{\bullet}}C_m)(1 + K_{Co}C_m)$ against C_m in accordance with eqn. (5) (see Fig. 5), and the k_{el}^{w} value [$(1.41 \pm 0.13) \times 10^{10}$ dm^3 mol^{-1} s^{-1}] estimated from the intercept was in good agreement with the k_{el} value [$(1.37 \pm 0.10) \times 10^{10}$ dm^3 mol^{-1} s^{-1}] determined experimentally in the absence of surfactants. The rate constant in the DTAC micellar phase was estimated to be $k_{el}^{m} = (7.54 \pm 0.25) \times 10^{8}$ dm^3 mol^{-1} s^{-1} from the slope of the linear plots by using the partial molar volume ($v = 0.256$ dm^3 mol^{-1}) of DTAC, estimated from the partial specific volume (0.97 cm^3 g^{-1}) of dodecyltrimethylammonium bromide.[37]

The micellar effects of DTAC on the present reaction were also treated by means of the ion-exchange model.[34,36] The distribution of $[Co(edta)]^-$ between the micellar phase and the aqueous phase can be evaluated in terms of the ion-exchange constants (K_1 and K_2), defined by eqns. (6) and (7).

$$K_1 = \frac{\overline{[[Co(edta)]^-]}_m \overline{[Cl^-]}_w}{\overline{[[Co(edta)]^-]}_w \overline{[Cl^-]}_m} \quad (6)$$

$$K_2 = \frac{\overline{[[Co(edta)]^-]}_m \overline{[H_2BO_3^-]}_w}{\overline{[[Co(edta)]^-]}_w \overline{[H_2BO_3^-]}_m} \quad (7)$$

where $\overline{[[Co(edta)]^-]}$, $\overline{[Cl^-]}$ and $\overline{[H_2BO_3^-]}$ are the stoichiometric (bulk) concentrations of $[Co(edta)]^-$, Cl^- and $H_2BO_3^-$, respectively. Then, eqns. (8) and (9) may be derived for the gel-filtration chromatography[29] and the observed rate constants,[34,36] respectively.

$$\frac{1}{V_e - V_0} = \frac{1}{V_i k' K_D}\left(1 + K_1 \frac{\overline{[Cl^-]}_m}{\overline{[Cl^-]}_w}\right)\left(1 - C_m v\right) \quad (8)$$

$$k_{el} = \frac{(k_{el}^{m}/v)K_{BNAH^{\bullet}}K_1 \dfrac{\overline{[Cl^-]}_m}{\overline{[Cl^-]}_w} + k_{el}^{w}}{(1 + K_{BNAH^{\bullet}}C_m)\left(1 + K_1 \dfrac{\overline{[Cl^-]}_m}{\overline{[Cl^-]}_w}\right)} \quad (9)$$

To make use of eqns. (8) and (9), the concentrations of Cl^- in the micellar phase and in the aqueous phase are calculated by eqns. (10)–(12),

$$\overline{[Cl^-]}_m = (1 - \alpha)C_m - \overline{[[Co(edta)]^-]}_m - \overline{[H_2BO_3^-]}_m \quad (10)$$

$$\overline{[Cl^-]}_w = \alpha C_m + \mathrm{cmc} + \overline{[[Co(edta)]^-]}_m + \overline{[H_2BO_3^-]}_m + \overline{[Cl^-]}_{add} \quad (11)$$

$$A[[Co(edta)]^-]_m^3 + B[[Co(edta)]^-]_m^2 + C[[Co(edta)]^-]_m + D = 0 \quad (12)$$

where

$$A = (1 - K_1)(1 - K_2)$$

$$B = E(1 - K_2) + (K_1[[Co(edta)]^-]_{tot} + [H_2BO_3^-]_{tot})(1 - K_1)$$

$$C = [EK_1 + K_1\{[[Co(edta)]^-]_{tot} - (1 - \alpha)C_m(1 - K_1)\}][[Co(edta)]^-]_{tot}$$

$$D = -(1 - \alpha)C_m K_1 K_2 [[Co(edta)]^-]_{tot}^2$$

$$E = \alpha C_m + \mathrm{cmc} + \overline{[Cl^-]}_{add} + K_1[[Co(edta)]^-]_{tot} + (1 - \alpha)C_m K_1$$

and α is the degree of ionization of the micelle, $\overline{[Cl^-]}_{add}$ is the concentration of Cl^- added as KCl, and the subscript 'tot' refers to the total concentration in the solution.

Thus the experimental data obtained by gel-filtration chromatography is satisfactorily explained by eqns. (8) and (10)–(12). In fact, the values of $K_1 = 1.2 \pm 0.1$ and $K_2 = 0.2 \pm 0.2$ were found to give the best fit with the data shown in Fig. 3 by using a value of $\alpha = 0.2$.[36] When the parameter values ($K_1 = 1.2 \pm 0.1$ and $K_2 = 0.2 \pm 0.2$) obtained were used, simulations were performed by varying the k_{el}^{m} value in eqn. (9). The best-fit value of $k_{el}^{m} = (7.2 \pm 0.5) \times 10^{8}$ dm^3 mol^{-1} s^{-1} gave simulation for the micellar effects of DTAC on the present

Table 2 Binding constants of BNAH* and $[\mathrm{Co(edta)}]^-$ to DTAC ($K_{\mathrm{BNAH^*}}$ and K_{Co}), ion-exchange constants for $[\mathrm{Co(edta)}]^-$ (K_1 and K_2), and second-order rate constants for the photoinduced electron transfer reaction between BNAH* and $[\mathrm{Co(edta)}]^-$ ($k_{\mathrm{el}}^{\mathrm{w}}$ for the aqueous phase and $k_{\mathrm{el}}^{\mathrm{m}}$ for the DTAC micellar phase) in 4% (v/v) methanol–borate buffer (pH = 9.0) at 30 °C

Surfactant	$K_{\mathrm{BNAH^*}}{}^a/\mathrm{dm^3\ mol^{-1}}$	$K_{\mathrm{Co}}{}^b/\mathrm{dm^3\ mol^{-1}}$	$K_1{}^c$	$K_2{}^c$	$k_{\mathrm{el}}^{\mathrm{w}}$ or $k_{\mathrm{el}}^{\mathrm{m}}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
None					$(1.37 \pm 0.10) \times 10^{10}$
DTAC	243 ± 16	15.3 ± 2.8	1.2 ± 0.1	0.2 ± 0.2	$(7.54 \pm 0.25) \times 10^{8b}$ $(7.2 \pm 0.5) \times 10^{8c}$

[a] Ref. 21. [b] Determined from plots of the data according to eqn. (5). [c] Determined by treating the data according to eqns. (8)–(12).

photoreduction. The rate constants obtained are listed in Table 2, in addition to $K_{\mathrm{BNAH^*}}$, K_{Co}, K_1 and K_2 values.

The $k_{\mathrm{el}}^{\mathrm{m}}$ value obtained by the ion-exchange model was in good agreement with that estimated by Berezin's approach (Table 2). Therefore, it appears that the rate constant, $k_{\mathrm{el}}^{\mathrm{m}}$, for the reaction in the DTAC micellar phase is 20 times smaller than $k_{\mathrm{el}}^{\mathrm{w}}$, for the reaction in the aqueous phase. The k_{el} values are affected by both the rate of encounter complex formation [Scheme 2, reaction (*d*)] and heterolytic dissociation [Scheme 2, reaction (*e*)] of the encounter complex, as reflected in the relation $k_{\mathrm{el}} = k_1k_2/(k_2 + k_3)$. Since the formation of the encounter complex is a diffusion-controlled process, the k_1 value in the aqueous phase can be estimated from eqn. (13) according to the diffusion-controlled reaction theory based on statistical nonequilibrium thermodynamics.[38] In eqns. (13)–(16), N_{A} is Avogadro's number, D is the sum of the diffusion

$$k_1/N_{\mathrm{A}} = 4\pi DRC(R) \qquad (13)$$

$$C(R) = \left[\frac{(D_{\mathrm{Co}} - D_{\mathrm{BNAH}})}{2D_{\mathrm{Co}}}\exp(-R\alpha^{\frac{1}{2}}) + \frac{(D_{\mathrm{Co}} + D_{\mathrm{BNAH}})}{2D_{\mathrm{Co}}}\exp(-R\beta^{\frac{1}{2}})\right]^{-1} \qquad (14)$$

$$\alpha = [(\tau^{-1} + k_1[[\mathrm{Co(edta)}]^-])/(D_{\mathrm{BNAH}} + D_{\mathrm{Co}})] \qquad (15)$$

$$\beta = [(\tau^{-1} + k_1[[\mathrm{Co(edta)}]^-])/D_{\mathrm{BNAH}}] \qquad (16)$$

coefficients of BNAH* (D_{BNAH}) and $[\mathrm{Co(edta)}]^-$ (D_{Co}), and R is the fictitious encounter radius. Since BNAH* and/or $[\mathrm{Co(edta)}]^-$ seem to diffuse in the surface of a micellar particle, the k_1 value in the micellar phase is given [eqn. (17)] which treats the motion of the reactants in two-dimensions.[38] In eqn.

$$k_1/N_{\mathrm{A}} = Ck_1{}^{(2)}/N_{\mathrm{A}} = C\frac{4\pi D_{\mathrm{BNAH}}k^0/K_0(R\beta^{\frac{1}{2}})}{k^0 + 4\pi D_{\mathrm{BNAH}}/K_0(R\beta^{\frac{1}{2}})} \qquad (17)$$

(17) k^0 is the intrinsic bimolecular rate constant, the superscript (2) refers to two-dimensions, the coefficient C is the ratio of the surface area to the volume of a micellar particle, K_0 is the McDonald function of zero order, and τ_{m} is the lifetime of BNAH* in the micellar phase (0.78 and 0.88 ns in SDS and DTAC, respectively).[21] The C value was estimated to be $5.2 \times 10^{-7}\ \mathrm{dm^3\ m^{-2}}$ by using the partial molar volume ($v = 0.256\ \mathrm{dm^3\ mol^{-1}}$),[37] the aggregation number ($AN = 62$),[39] and the radius (2 nm) of a micellar particle.

The k_1 value in the aqueous phase was evaluated as $2.7 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ from eqns. (13)–(16) by iteration with the typical diffusion coefficients ($D = 5 \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$) of small molecules in aqueous solution and the reaction radii ($R_{\mathrm{BNAH}} = 0.2$ nm and $R_{\mathrm{Co}} = 0.5$ nm) evaluated for BNAH* and $[\mathrm{Co(edta)}]^-$ on the basis of molecular models. Since the calculated k_1 value is close to the experimentally obtained $k_{\mathrm{el}}^{\mathrm{w}}$ value [$(1.37 \pm 0.10) \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$], the encounter complex dissociates into $\mathrm{BNAH^{\bullet +}}$ and $[\mathrm{Co(edta)}]^-$ efficiently in the aqueous phase. In the micellar phase, the D_{BNAH} and D_{Co} values were assumed to be $2.0 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$ because the internal microviscosity of the micelle is *ca.* 25 times as high as the aqueous solution.[40] Thus, the $K_0(R\beta^{\frac{1}{2}})$ value calculated was exponentially small [$K_0(x) = ca\ (\pi/2x)^{\frac{1}{2}}\exp(-x)$] under the present reaction conditions,[38] so that eqn. (17) reduces to $k_1/N_{\mathrm{A}} = Ck_0$. This fact suggests that photoexcited BNAH* in the micellar phase reacts immediately with $[\mathrm{Co(edta)}]^-$ in the vicinity of the micellar surface before diffusion occurs and that the rate of encounter complex formation in the micellar phase does not depend on the diffusion of BNAH* and $[\mathrm{Co(edta)}]^-$.

Accordingly, the smaller $k_{\mathrm{el}}^{\mathrm{m}}$ value (as compared to the $k_{\mathrm{el}}^{\mathrm{w}}$ value) is attributable to the low efficiency of heterolytic dissociation of the encounter complex in the micellar phase. That is, the high internal microviscosity of the micelles[40] depresses the diffusion of $\mathrm{BNAH^{\bullet +}}$ from the encounter complex since the hydrophobic substituent of $\mathrm{BNAH^{\bullet +}}$ is incorporated into the micellar phase. In addition, the cationic charge of the micellar surface suppresses the separation of $[\mathrm{Co(edta)}]^{2-}$ from the micellar phase. The low polarity of the micellar phase also retards the formation of ionic species such as $\mathrm{BNAH^{\bullet +}}$. However, the observed rate constant, k_{el}, was enhanced remarkably by the DTAC micelles even though the $k_{\mathrm{el}}^{\mathrm{m}}$ value was small.

To conclude, the micellar effects on the photoreduction of $[\mathrm{Co(edta)}]^-$ with BNAH were analysed by the kinetic treatment of Berezin, and by the ion-exchange model. Both treatments gave the same values for the rate constants for the photoreaction in the micellar phase. The estimated kinetic parameters demonstrate the following characteristic features of micellar photoreaction; cationic DTAC enhances the rate constants by concentrating BNAH* and $[\mathrm{Co(edta)}]^-$ at the micellar surface through hydrophobic and electrostatic interactions, while the electrostatic repulsion between anionic SDS and $[\mathrm{Co(edta)}]^-$ suppresses the approach of $[\mathrm{Co(edta)}]^-$ to BNAH* incorporated in the micellar phase.

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