J. CHEM. SOC. FARADAY TRANS., 1990, 86(3), 507–510

Micellar Effects upon the Reactions of Complex Ions in Solution

Part 4.[1,2]—Kinetics of Aquation and Base Hydrolysis of some *cis*-(Chloro)(amine)bis(ethylenediamine)cobalt(III) Complexes in the Presence of Neutral and Anionic Surfactants in an Aqueous Medium

Anadi C. Dash,* Jayashree Prusti, Jyotsnamayee Pradhan and Prafulla K. Das
Department of Chemistry, Utkal University, Bhubaneswar-751004, India

The binding of the substrates *cis*-$[Co(en)_2BCl]^{2+}$ (en = 1,2-diaminoethane, B = alkylamines, imidazole, *N*-methylimidazole) to the micellar surface of sodium dodecyl sulphate resulted in the retardation of their dissociative aquation rates, the effect being sensitive to the hydrophobicity of the nonlabile amine ligand B. A contrastingly small rate acceleration for the corresponding ethanolamine and propan-2-ol amine complexes was observed under similar conditions. Triton X-100 ($0.02 \leqslant [\text{Triton X}]_T/\text{mol dm}^{-3} \leqslant 0.1$) had virtually no effect on the aquation rates of such complexes except for *cis*-$[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$, in which case a small rate retardation was also observed. The rates of base hydrolysis of the cobalt(III) substrates were strongly retarded by the anionic micelles of SDS; the neutral micelles of Triton X-100 were effective in decelerating the rate of base hydrolysis of the cyclohexylamine complex *cis*-$[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$ only. The pseudo-phase ion-exchange equilibrium model satisfactorily explained the binding of the cationic substrates to the anionic micellar pseudophase of SDS. The values of the ion-exchange equilibrium constant and the relative base hydrolysis rates (k^W/k^M) indicated that both micellar binding and retardation of hydrolysis are governed by hydrophobic and electrostatic interactions.

Previous studies from this laboratory have indicated that the rates of base hydrolysis of suitable carboxylatoaminecobalt(III) complexes are significantly mediated by the micelles of cationic and anionic surfactants.[1–4] Both hydrophobic and electrostatic interactions of the micelles with the substrates appeared to control their reactivities. However, further work was necessary for the proper assessment of the relative importance of these effects. We believed that this could be possible through the investigation of the aquation and base hydrolysis of a series of cationic octahedral halogenoaminecobalt(III) complexes with non-labile ligands of varying hydrophobicity in the presence of neutral and anionic surfactants. The present study is an attempt in that direction, and reports the kinetics of aquation and base hydrolysis of a series of *cis*-(chloro)(amine)bis(ethylenediamine)cobalt(III) cations in the presence of Triton X-100 and sodium dodecyl sulphate in an aqueous medium.

Experimental

Materials

cis-(Chloro)(amine)bis(ethylenediamine)cobalt(III) chlorides, *cis*-$[Co(en)_2(B)Cl]Cl_2$ (B = amine ligand, see table 1) were prepared by the method of Bailar and Clapp[5] and converted into their diperchlorates or dinitrates by repeated crystallisation from aqueous perchloric acid or aqueous nitric acid under ice-cold conditions. The Co and Cl^- analysis data for the complexes agreed to better than 0.2% with the calculated values.

Sodium dodecyl sulphate (SDS) (E. Merck, F.R.G., >99% pure) and Triton X-100, $C_8H_{17}Ph(OC_2H_2)_{9.5}OH$, (B.D.H.) were used as received. The pH measurements were made with an Elico digital pH meter LI 120 using a combined glass Ag/AgCl, Cl^- (2 mol dm^{-3} NaCl) electrode Cl 51; NBS buffers of pH 4.01, 6.86 and 9.20 were used to celibrate the pH meter. Surface tension measurements were made at room temperature (30 °C) using a Du Nuoy surface tensiometer. The critical micelle concentration (CMC) of SDS agreed well with the reported value (0.008 mol dm^{-3}).[6] The spectral measurements were made with a Hitachi model H 200-20 UV–visible spectrophotometer.

Kinetic Procedure

Aliquots (5.00 cm^3) were withdrawn from the thermally equilibrated reaction mixture at known time intervals and delivered quickly to a dilute nitric acid–acetone mixture chilled in an ice bath. Rates of hydrolysis were followed by titrating the liberated chloride potentiometrically against 0.010 mol dm^{-3} $AgNO_3$. The titre value for complete hydrolysis (V_∞) was determined by subjecting the reaction mixture (5.00 cm^3) to base hydrolysis, acidifying the content with HNO_3 and then working up in the usual way. Preliminary experiments showed that NaCl [(2–4) × 10^{-3} mol dm^{-3}] in the presence of varying amounts of SDS, HNO_3 and acetone could be quantitatively titrated potentiometrically against 0.010 mol dm^{-3} $AgNO_3$. The pseudo-first-order rate constants (k_ψ) were calculated from the gradients of the plots of $\log(V_\infty - V_t)$ against time (t); values of k_ψ from replicate runs agreed to within *ca.* 5%.

Results and Discussion

Effect of SDS and Triton X-100 on the Rates of Aquation of *cis*-$[Co(en)_2(B)Cl]^{2+}$

Table 1 presents the rate constants of aquation of various *cis*(chloro)(amine)cobalt(III) substrates at varying $[SDS]_T$:

$$[Co(en)_2(B)Cl]^{2+} \xrightarrow[H_2O]{k_\psi} [Co(en)_2(B)OH_2]^{3+} + Cl^-. \quad (1)$$

k_ψ attained limiting value at $[SDS]_T \geqslant 0.020$ mol dm^{-3}. The value of the rate constant for the micelle-bound complex was

Table 1. Effect of SDS on the rates of aquation of *cis*-$[Co(en)_2(B)Cl]^{2+}$; $[HClO_4]_T = 0.01$, $[complex]_T = (2.20\text{–}2.30) \times 10^{-3}$ mol dm^{-3}

B	[SDS]$_T$/mol dm^{-3} 0.00	0.020	0.030	0.050	0.080	0.10	$k^M/10^{-5}$ s^{-1} [b]	k^M/k^W [c]
	$k_\psi/10^{-5}$ s^{-1} [a]							
CH_3NH_2	2.62	2.31	—	2.43	—	2.46	2.40 ± 0.10	0.92 ± 0.04
$CH_3CH_2NH_2$	2.49	2.11	—	2.22	—	2.24	2.19 ± 0.07	0.88 ± 0.03
$CH_3(CH_2)_2NH_2$	2.91	1.53	1.68	1.62 ± 0.05[d]	1.75	1.46	1.61 ± 0.11	0.55 ± 0.03
$CH_3CH(CH_3)CH_2NH_2$	2.75	1.72	1.57	1.50	1.47	1.67	1.59 ± 0.10	0.58 ± 0.03
$C_6H_5CH_2NH_2$	1.84	0.80	0.78	0.56	0.72	0.74	0.72 ± 0.09	0.39 ± 0.05
$C_6H_{11}NH_2$	6.71	3.26	3.01	3.10 ± 0.20[d]	3.42	3.08	3.17 ± 0.16	0.47 ± 0.02
$OH(CH_2)_2NH_2$	12.2	14.2	14.1	14.8 ± 0.5[d]	14.9	14.9	14.6 ± 0.4	1.20 ± 0.04
$OHCH(CH_3)CH_2NH_2$	9.30	12.1	—	12.0	—	11.5	11.9 ± 0.3	1.28 ± 0.03
imH[e]	3.67	2.47	2.28	2.02 ± 0.20[d]	2.20	2.39	2.29 ± 0.20	0.62 ± 0.05
imMe[e]	3.20	2.14	2.27	2.07	1.69	1.70	1.97 ± 0.26	0.61 ± 0.08

[a] $T = 55.0 \pm 0.01$ °C for B = $C_6H_{11}NH_2$ and 59.8 ± 0.1 °C for all other amines; all values of k_ψ are an average of at least two runs unless otherwise stated. [b] Average of k_ψ at $[SDS]_T = 0.02\text{–}0.10$ mol dm^{-3}. [c] Values calculated using $k^w = k_\psi$ at $[SDS]_T = 0$. [d] Average of k_ψ at $[HClO_4] = 0.005$, 0.010 and 0.050 mol dm^{-3}. [e] imH = imidazole, imMe = *N*-methylimidazole.

taken to be the mean of k_ψ at $[SDS]_T = 0.020\text{–}0.100$ mol dm^{-3} (see table 1). The calculated values of k^M/k^W, where k^M and k^W denote k_ψ in the micellar and aqueous pseudophases, respectively, indicate that micellar binding resulted in retardation of the aquation of most substrates (except for B = ethanolamine and propanolamine), and this effect increased with increasing hydrophobicity of the non-labile amine ligands (see table 1). On the other hand, multivalent anions are reported to accelerate the rate of aquation of acidoaminecobalt(III) complexes significantly *via* the formation of reactive ion pairs.[7] The present study demonstrates that the anionic micelles do not behave as multivalent anions as far as rate effects are concerned. The ligands imidazole, *N*-methylimidazole and alkanolamines are relatively more hydrophilic than the alkylamines; micellar retardation is less for B = imidazole and is replaced by small rate acceleration for B = alkanolamines. A small rate acceleration ($k^M/k^W = 1.3$ at 35 °C) for the aquation of $(NH_3)_5CoCl^{2+}$, a substrate with no hydrophobic carbon skeleton, by SDS micelles has been observed by Tachiyashiki and Yamatera.[8] These dipositive substrates are likely to be positioned in the water-rich region of the micelle–bulk aqueous interface. This is supported by the fact that their absorption spectra ($\lambda = 260\text{–}600$ nm) are virtually unperturbed by the SDS micelles. Since the electrostatic effects remain constant, the observed trend in reactivity may be attributed to the effect of a hydrophobic interaction of the substrates with the SDS micelles. The hydrophobic interaction is likely to be significant if the diffuse structure of SDS micelles, as proposed by Menger, is considered.[9] The activation enthalpies and entropies for the aquation of *cis*-$[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$ and *cis*-$[Co(en)_2(NH_2CH_2CH_2OH)Cl]^{2+}$ in the micellar pseudophase of SDS are very similar in magnitude to those for the aqueous phase (see below), a result which lends support to the belief that the micelles do not alter the intimate mechanism (Id)[10] of reaction.

complex	$\Delta H^{\neq}$/ kJ mol^{-1}	$\Delta S^{\neq}$/ J K^{-1} mol^{-1}
cis-$[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$	61.8 ± 1.9	−137 ± 6
	(64.6 ± 7.4)	(−136 ± 22)
cis-$[Co(en)_2(NH_2CH_2CH_2OH)Cl]^{2+}$	92.7 ± 4.1	−43 ± 12
	(88.3 ± 1.1)	(−53 ± 3)

(Values in parentheses are for $[SDS]_T = 0.08$, $[HClO_4]_T = 0.01$ mol dm^{-3}, other values are for $[SDS]_T = 0$ at the same acidity).

The neutral micelles exert virtually no effect on the rates of aquation of most complexes, except in the case of the most hydrophobic cyclohexylamine complex, for which a small $[\text{Triton X-100}]_T$-dependent rate retardation was observed (see table 2). This is consistent with scheme 1, for which the pseudo-first-order rate constant is given by

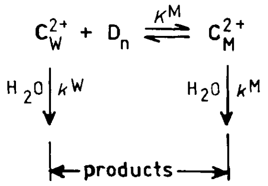
$$k_\psi = \frac{k^W + k^M K^M[D_n]}{1 + K^M[D_n]} \qquad (2)$$

where k^W and k^M are as defined earlier, K^M denotes the micellar binding constant and $[D_n] = [\text{Triton X-100}]_T - \text{CMC}$. Since the CMC of Triton X-100 is *ca.* 10^{-4} mol dm^{-3}, $[D_n] = [\text{Triton X-100}]_T$ was assumed. Taking $k^W = k_\psi$ at $[\text{Triton X-100}]_T = 0$, the rate data for the cyclohexylamine complex at $[\text{Triton X-100}]_T = 0.0050\text{–}0.100$ mol dm^{-3}

Table 2. Effect of Triton X-100 on the rates of aquation of *cis*-$[Co(en)_2(B)Cl]^{2+}$; $[HClO_4]_T = 0.010$, $[complex]_T = (2.20\text{–}2.30) \times 10^{-3}$ mol dm^{-3}

B	[Triton X-100]$_T$/mol dm^{-3} 0.000	0.0020	0.0050	0.010	0.020	0.050	0.100
	$k_\psi/10^{-5}$ s^{-1} [a]						
$C_6H_{11}NH_2$	5.81	5.65	5.35	5.14	4.98	4.89	4.75
$C_6H_5CH_2NH_2$	1.84	—	—	1.82	1.84	1.86	1.85
imH	3.67	3.61	3.62	3.57	3.62	3.58	3.57
$OH(CH_2)_2NH_2$	3.82	—	3.98	3.95	4.04	3.96	3.96
$OHCH(CH_3)CH_2NH_2$	3.28	3.39	3.48	3.50	3.49	3.55	3.65

[a] $T = 59.8 \pm 0.1$ °C for B = $C_6H_5CH_2NH_2$ and 50.0 ± 0.1 °C for other amines.



Scheme 1. C^{2+} = *cis*-$[Co(en)_2(C_6H_{11}NH_2)Cl]^{2+}$.

yielded $k^M = (4.71 \pm 0.10) \times 10^{-5}$ s^{-1} and $K^M = 152 \pm 23$ dm^3 mol^{-1} (50.0 ± 0.1 °C) from the intercept and gradient of the least-squares best-line plot of $(k^W - k_\psi)^{-1}$ *vs.* $[D_n]^{-1}$ [eqn (2)]. Relatively weaker micellar binding and a smaller rate retardation ($k^M/k^W = 0.8$ for Triton X-100) are observed for the neutral micelles as compared to the anionic micelles, thereby indicating that the electrostatic effect dominates over the hydrophobic effect. However, the combined effects of low polarity of the intermicellar zone (dielectric constant ≈ 40),[11] in which the reactants are positioned, as well as the less favourable solvation of the substrates by water molecules owing to their hydrophobic interactions with the micelles, resulted in only a small rate retardation.

For the substrates with a non-labile amine ligand (B) endowed with a hydrophilic group, the rate retardation by the neutral micelles is practically unobservable and is replaced by a small rate acceleration for ethanolamine and propan-2-ol–amine complexes (see table 2). However, the observed rate effects are too small to warrant further explanation.

Effect of SDS and Triton X-100 on the Rates of Base Hydrolysis of *cis*-$[Co(en)_2(B)Cl]^{2+}$

Rate data for the hydrolysis of a series of cobalt(III) substrates at *ca.* pH 8 (40.0 ± 0.1 °C), $0.00 \leqslant [SDS]_T/\text{mol dm}^{-3} \leqslant 0.10$ and $0.00 \leqslant [NaClO_4]/\text{mol dm}^{-3} \leqslant 0.20$ are presented in table 3. The reaction in the absence of SDS is essentially base-catalysed hydrolysis:[10]

$$cis\text{-}[Co(en)_2(B)Cl]^{2+} \xrightarrow[OH^-,H_2O]{k_\psi} (cis + trans)[Co(en)_2BOH]^{2+} + Cl^- \qquad (3)$$

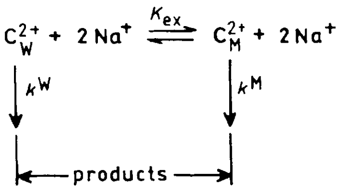
as the spontaneous aquation of all such substrates at the experimental temperature in a fully aqueous medium is negligible [k_{calcd} (40 °C)/10^{-5} s^{-1} = 0.20, 0.21, 1.8, 0.37, 0.17 and 0.10 for B = CH_3NH_2, $CH_3CH_2NH_2$, $C_6H_{11}NH_2$, imH, imMe and $C_6H_5CH_2NH_2$, respectively].[12] The retarding effect of ionic strength[13] on the base hydrolysis rate, as evident from the variation of k_ψ with $[NaClO_4]$, is small. However, a considerable rate retardation by SDS as a consequence of micellar binding of the substrates is evident. The micellar effect virtually attains the saturation limit at $[SDS]_T \geqslant 0.02$ mol dm^{-3} in the absence of added $NaClO_4$. However, adding a large excess of $NaClO_4$ at constant $[SDS]_T$ (0.05 mol dm^{-3}) resulted in a small but definite increase of k_ψ from its limiting value, which is not compatible with the expected ionic strength effect. This behaviour is consistent with the fact that both Na^+ and the dipositive complex ions compete for micellar binding, and the pseudophase ion-exchange equilibrium[1,14] (see scheme 2) is shifted in the direction favouring an increase in the number of reactive complex ions in the aqueous pseudophase with increasing $[Na^+]$.

For scheme 2, the observed pseudo-first-order rate constant (k_ψ) is given by

$$k_\psi = \frac{k^W + k^M K_{ex}/YF}{1 + K_{ex}/YF} \qquad (4)$$

where k^W and k^M are as defined earlier and K_{ex} is the pseudophase ion-exchange equilibrium constant:

$$K_{ex} = \frac{[C_M^{2+}]YF}{[C_W^{2+}]} \qquad (5)$$



Scheme 2.

Table 3. Effect of $[SDS]_T$ on the rate of base hydrolysis of *cis*-$[Co(en)_2(B)Cl]^{2+}$ at 40.0 ± 0.1 °C; $[\text{tris base}]_T = 0.100$, $[HClO_4]_T = 0.050$, $[\text{complex}]_T = 2.1 \times 10^{-3}$ mol dm^{-3}

B	$[NaClO_4]_T$/mol dm^{-3}	$[SDS]_T$/mol dm^{-3}					
		0.000	0.020	0.050	0.100		
		$k/10^{-5}$ s^{-1} (pH)[a]					
CH_3NH_2	0.000	25.2 (8.18)	1.51 (8.16)	0.88 (8.25)	0.87 (8.28)	28.8	
$C_6H_5CH_2NH_2$	0.000	40.7 (8.22)	—	1.24 (8.15)	1.26 (8.15)	32.6	
imMe	0.000	44.0 (8.20)	—	1.32 (8.15)	1.34 (8.28)	33.0	
imH	0.000	47.3 (8.20)	1.65 (8.24)	1.47 (8.23)	1.44 (8.22)	31.1	0.91 ± 0.33
	0.020	46.6 (8.19)	—	1.75 (8.08)	—		
	0.050	43.2 (8.20)	—	2.21 (8.07)	—		
	0.100	39.7 (8.21)	—	3.01 (8.07)	—		
	0.200	35.5 (8.22)	—	4.36 (8.09)	—		
$CH_3CH_2NH_2$	0.000	27.3 (8.22)	0.86 (8.23)	0.75 (8.25)	0.64 (8.23)	36.4	1.7 ± 0.4
	0.020	24.0 (8.12)	—	0.69 (8.09)	—		
	0.050	23.0 (8.10)	—	0.77 (8.08)	—		
	0.100	21.0 (8.09)	—	1.26 (8.10)	—		
	0.200	19.9 (8.10)	—	1.81 (8.11)	—		
$C_6H_{11}NH_2$	0.000	104.0 (8.24)	1.34 (8.24)	1.17 (8.23)	1.27 (8.22)	82.5	3.2 ± 0.1
	0.020	87.4 (8.22)	—	1.25 (8.18)	—		
	0.050	76.2 (8.19)	—	1.22 (8.15)	—		
	0.100	73.2 (8.18)	—	1.30 (8.18)	—		
	0.200	71.6 (8.19)	—	1.51 (8.18)	—		

[a] Values in parentheses are for pH.

$$Y = ([\mathrm{Na}_\mathrm{W}^+]/[\mathrm{Na}_\mathrm{M}^+])^2$$

and

$$F = \gamma_\mathrm{W}^2(\mathrm{Na}^+)/\gamma_\mathrm{W}(\mathrm{C}^{2+}).$$

The activity coefficient ratio, $\gamma_\mathrm{M}^2(\mathrm{Na}^+)/\gamma_\mathrm{M}(\mathrm{C}^{2+})$, for the micellar pseudophase was assumed to be constant and equal to unity. Note that the measured pH of the aqueous pseudophase maintained by tris-hydroxymethylaminomethane and $HClO_4$ is little perturbed by the added SDS, indicating that the tris base and its monoprotonated form predominantly prefer the aqueous pseudophase. Hence the overall micellar binding parameter (β), defined in terms of the net fraction of the micellar surface charge compensated by the bound ions under consideration (*i.e.* Na^+ and C^{2+}), is given by

$$\beta = \frac{[\mathrm{Na}_\mathrm{M}^+]}{[\mathrm{D_n}]} + \frac{2[\mathrm{C}_\mathrm{M}^{2+}]}{[\mathrm{D_n}]} = m_\mathrm{Na}^\mathrm{s} + 2m_\mathrm{c}^\mathrm{s}$$

where the analytical concentration of the micellised surfactant ion $[\mathrm{D_n}] = [\mathrm{SDS}]_\mathrm{T} - \mathrm{CMC}$; $[\mathrm{Na}_\mathrm{M}^+]$ and $[\mathrm{C}_\mathrm{M}^{2+}]$ denote the analytical concentration of the micelle-bound Na^+ and the complex ion (C^{2+}), respectively. It can be easily shown that

$$Y = ((\beta - 2m_\mathrm{c}^\mathrm{s})[\mathrm{D_n}]/\{[\mathrm{Na}^+]_\mathrm{T} - (\beta - 2m_\mathrm{c}^\mathrm{s})[\mathrm{D_n}]\})^2. \qquad (6)$$

For SDS added electrolytes reduce its CMC appreciably,[6] and the value of β is taken to be 0.7 ± 0.1.[15] With $\beta = 0.7$, CMC = 0.002 mol dm^{-3} and $m_\mathrm{c}^\mathrm{s} = [\mathrm{C}^{2+}]_\mathrm{T}/[\mathrm{D_n}]$ the values of Y were calculated. The activity coefficient factor, F, was calculated using the Davies equation[16] for the activity coefficient of the ions, the ionic strength of the aqueous pseudophase being computed from the relationship

$$I_\mathrm{w} = \tfrac{1}{2}\{\mathrm{CMC} + [\mathrm{SDS}]_\mathrm{T} - (\beta - 2m_\mathrm{c}^\mathrm{s})[\mathrm{D_n}]\} + [\mathrm{HClO_4}]_\mathrm{T} + [\mathrm{NaClO_4}]_\mathrm{T} + [\mathrm{complex}]_\mathrm{T}.$$

The value of k^M for any complex was taken to be the mean of k_ψ at $[\mathrm{SDS}]_\mathrm{T}$ = 0.020–0.10 mol dm^{-3} and $[\mathrm{NaClO_4}]_\mathrm{T} = 0$. k_ψ at $[\mathrm{SDS}]_\mathrm{T}$ = 0.05 mol dm^{-3} and $[\mathrm{NaClO_4}]_\mathrm{T}$ = 0.10 and 0.20 mol dm^{-3} was used to calculate K_ex from the knowledge of k^W (= k_ψ at the corresponding $[\mathrm{NaClO_4}]_\mathrm{T}$ and $[\mathrm{SDS}]_\mathrm{T}$ = 0). The high value of K_ex (10^3, see table 3) for the divalent cobalt(III) substrates is worth noting. The value of K_ex also increases with increasing hydrophobicity of the amine ligand B ($C_6H_{11}NH_2 > CH_3CH_2NH_2 >$ imH, table 3). The calculated values of $k^\mathrm{W}/k^\mathrm{M}$ (table 3) for different non-labile amine ligands (B) at virtually the same pH (*ca.* 8) follow the trend $CH_3NH_2 < C_6H_5CH_2NH_2 < CH_3CH_2NH_2 <$ imH $<$ imMe $< C_6H_{11}NH_2$, which also indicates that, since the electrostatic effect remains constant, the rate-retarding influence of the anionic micelles stems at least partly from the hydrophobic interaction effect. However, the remarkable inertia of the substrates in the anionic micellar pseudophase towards the base-catalysed hydrolysis must be attributed to the fact that the pH of the intermicellar region in which the reactants are positioned is significantly lower than the measured pH of the aqueous pseudophase.

Effect of $[\mathrm{Triton\ X\text{-}100}]_\mathrm{T}$ on the rate of Base Hydrolysis of *cis*-$[\mathrm{Co(en)_2(B)Cl}]^{2+}$, B = $C_6H_{11}NH_2$, $C_6H_5NH_2$, imH

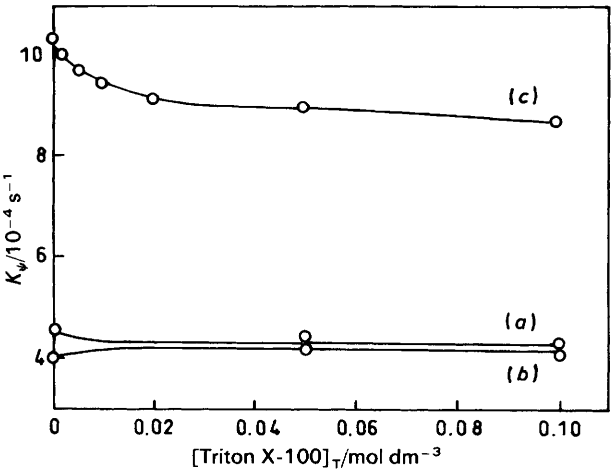


Fig. 1. Effect of $[\mathrm{Triton\ X\text{-}100}]_\mathrm{T}$ on the rate of base hydrolysis of *cis*-$[\mathrm{Co(en)_2BCl}]^{2+}$ [B = imH (*a*), $C_6H_5CH_2NH_2$ (*b*) and $C_6H_{11}NH_2$ (*c*)] at 40.0 ± 0.1 °C and pH 8.22 ± 0.02 (tris buffer). Plot of $k_\psi/10^{-4}\ \mathrm{s}^{-1}$ *vs.* $[\mathrm{Triton\ X\text{-}100}]_\mathrm{T}/\mathrm{mol\ dm}^{-3}$.

Fig. 1 depicts the effect of Triton X-100 on the rate of base hydrolysis of some complexes at 40 °C and pH 8. $[\mathrm{Triton\ X\text{-}100}]_\mathrm{T}$ has no effect on the base hydrolysis of the complexes with B = benzylamine and imidazole. A small but definite rate retardation was observed for the most hydrophobic cyclohexylamine complex. With an increase in $[\mathrm{Triton\ X\text{-}100}]_\mathrm{T}$ the rate retardation increased and tended to attain a limiting value at high surfactant concentrations, indicating appreciable micellar binding of this substrate and reduced reactivity of the micelle-bound complex. The rate data [curve (*a*) of fig. 1] were analysed in accordance with eqn (2) to yield K^M = 108 ± 20 and k^M = (8.20 ± 0.21) × $10^{-4}\ \mathrm{s}^{-1}$. Note that the value of $k^\mathrm{W}/k^\mathrm{M}$ (1.3) for Triton X-100 is considerably lower than the value for SDS. The results thus indicate that the hydrophobic interaction assists micellar binding of the substrates, and that the micellar environment has a rate-retarding effect which is governed by both electrostatic and non-electrostatic forces.

Support of this work by the University Grants Commission, New Delhi, India is gratefully acknowledged. J. P. and J. M. P. are grateful to the U.G.C., New Delhi for a fellowship grant. P. K. D. thanks the Education Department, Government of Orissa, India for study leave.

References

1 Part 2: A. C. Dash and R. C. Nayak, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1307.
2 Part 3: A. C. Dash and R. C. Nayak, *Ind. J. Chem., Sect. A*, 1987, **26**, 293.
3 A. C. Dash, *Ind. J. Chem., Sect. A*, 1984, **23**, 421.
4 A. C. Dash and R. C. Nayak, *Inorg. Chem.*, 1986, **25**, 2237.
5 J. C. Bailar and L. B. Clapp, *J. Am. Chem. Soc.*, 1945, **67**, 171.
6 E. H. Cordes and C. Gitler, *Progr. Bio-organic Chem.*, ed. E. T. Kaiser and F. J. Kezdy (Wiley, New York, 1973), vol. 1, p. 1.
7 A. C. Dash and R. K. Nanda, *J. Ind. Chem. Soc.*, 1975, **52**, 298 and references cited therein.
8 S. Tachiyashiki and H. Yamatera, *Inorg. Chem.*, 1986, **25**, 3043.
9 F. M. Menger, *Acc. Chem. Res.*, 1979, **12**, 111.
10 C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (Benjamin, New York, 1965).
11 P. Mukherjee and A. Roy, *J. Phys. Chem.*, 1966, **70**, 2144.
12 J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta Rev.*, 1974, **11**, 47; D. R. Fenemor and D. A. House, *Int. J. Chem. Kinet.*, 1976, **8**, 573; A. C. Dash and S. K. Mohapatra, *J. Chem. Soc., Dalton Trans.*, 1977, 246.
13 H. Eyring, S. H. Lin and S. M. Lin, *Basic Chemical Kinetics* (Wiley, New York, 1980), p. 415.
14 E. A. Lissi, E. B. Abuin, L. Sepulveda and F. H. Quina, *J. Phys. Chem.*, 1984, **88**, 81.
15 C. J. Garnett, A. J. Lambie, W. H. Beck and M. Liler, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 953.
16 C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

Paper 9/01936G; *Received* 9th *May*, 1989