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Effects of pure non-ionic and mixed non-ionic–cationic surfactants on the rates of hydrolysis of phenyl salicylate and phenyl benzoate in alkaline medium

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ABSTRACT: The pseudo-first-order rate constants (k_{obs}) for the alkaline hydrolysis of phenyl benzoate (PB) decrease monotonically from 72.0×10^{-4} to 7.4×10^{-4} s^{-1} with increase in the concentration of polyoxyethylene 23 lauryl ether ($[C_{12}E_{23}]_T$) from 0.0 to 0.01 M at 0.01 M NaOH and 35 °C. The results fit satisfactorily to a pseudophase model of micelles. The values of k_{obs} for the hydrolysis of ionized phenyl salicylate (PS^-) are almost independent of $[C_{12}E_{23}]_T$ within the range 0.0–0.02 M at 0.01 and 0.03 M NaOH and 35 °C. The rate of alkaline hydrolysis of PB appears to be negligible in the micellar pseudophase than in the aqueous pseudophase, which is ascribed to the extremely low concentration of HO^- in the micellar region of micellized PB molecules. The values of k_{obs} for hydrolysis of PB and PS^- at 0.01 M NaOH become almost zero at $\geq$0.02 and $\geq$0.03 M $C_{12}E_{23}$, respectively. The effects of mixed $C_{12}E_{23}$–CTABr on k_{obs} for the alkaline hydrolysis of PB reveal that mixed micelles behave like pure CTABr micelles within the $[C_{12}E_{23}]_T$ range 0.0–5×10^{-4} M whereas an increase in $[C_{12}E_{23}]_T$ from $\geq 7 \times 10^{-4}$ to 0.02 M decreases k_{obs} at 0.006, 0.01, 0.02 and 0.03 M CTABr. However, the values of k_{obs} are significantly higher at $[CTABr]_T = 0.006$, 0.01, 0.02 and 0.03 M than at $[CTABr]_T = 0$ in the presence of $[C_{12}E_{23}]_T$ in the range $>5 \times 10^{-4}$ – 0.02 M. An increase in $[C_{12}E_{23}]_T$ from 0.0 to 0.015 M causes nearly a twofold increase in k_{obs} at 0.01, 0.02 and 0.03 M CTABr and 0.01 M NaOH. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: phenyl salicylate; phenyl benzoate; hydrolysis; kinetics; non-ionic micelles; mixed non-ionic–cationic surfactants

INTRODUCTION

Studies on the effects of mixed surfactants or mixed micelles on reaction rates have been started only recently.[1–3] Systematic kinetic studies on the effects of mixed non-ionic –cationic micelles on the rates of organic reactions have shown that the kinetic data can be explained in terms of a pseudophase model of micelles.[2–4] The effects of mixed cationic–anionic surfactants on the rates of methanolysis of ionized phenyl salicylate (PS^-) and hydrolysis of phenyl benzoate (PB) have revealed the mixed micelles behaving as cationic in nature when $X \leq 0.3$ and anionic in nature when $X \geq 4$, where $X = [SDS]/[CTABr]$ (SDS = sodium dodecyl sulfate and CTABr = cetyltrimethylammonium bromide).[5] Most studies on the effects of mixed non-ionic–cationic surfactants on the rates of reactions involved $C_{10}H_{21}(OCH_2CH_2)_3OCH_2CH_2OH$ ($C_{10}E_4$) as the non-ionic surfactant.[2–4] The head groups of $C_{10}E_4$ micelles are not as voluminous as those of $C_{12}E_{23}$ (Brij 35) and the size of the head groups affects the characteristic properties of micellar and presumably mixed micellar systems. In a recent study on the effects of pure CTABr, $C_{12}E_{23}$ and mixed CTABr–$C_{12}E_{23}$ surfactants on the acid –base behavior of phenyl salicylate, an unusual result was obtained.[6] We became interested in finding out whether there are some unusual effects of pure $C_{12}E_{23}$ and mixed CTABr–$C_{12}E_{23}$ surfactants on the rates of alkaline hydrolysis of esters. The present study was aimed at determining the effects of pure $C_{12}E_{23}$ and mixed CTABr–$C_{12}E_{23}$ surfactants on the rates of hydrolysis of phenyl salicylate and PB under mild alkaline conditions and the results and their probable explanations are described in this paper.

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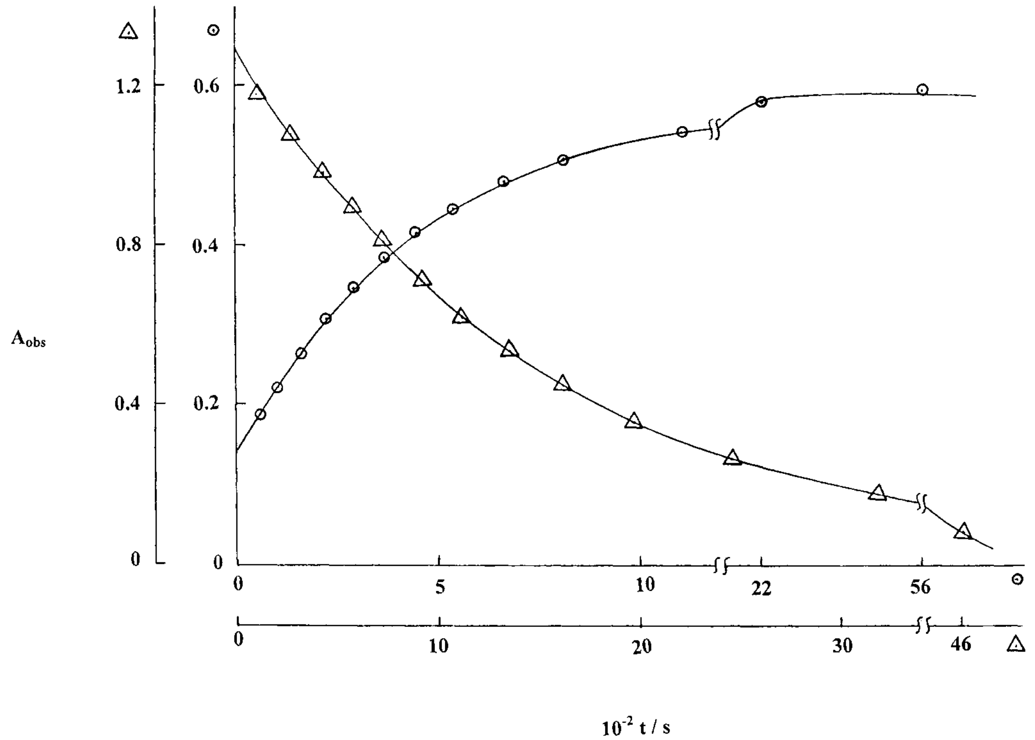


Figure 1. Plots showing the relationship between A_{obs} and reaction time, *t*, for the hydrolysis of PB (○) and PS^- (△) under alkaline conditions. (△) The solid line is drawn through the calculated data points using Eqn. (1) with $10^4\ k_{obs} = 6.51 \pm 0.18\ s^{-1}$, $E_{app} = 6284 \pm 61\ M^{-1}\ cm^{-1}$ and $A_\infty = 0.015 \pm 0.013$, obtained under the reaction conditions $[X]_0 = 2 \times 10^{-4}$ M, $[C_{12}E_{23}]_T = 0.01$ M, [NaOH] = 0.03 M, 35 °C and $\lambda = 350$ nm. (○) The solid line is drawn through the calculated data points using Eqn. (2) with $10^3\ k_{obs} = 2.16 \pm 0.04\ s^{-1}$, $E_{app} = 2248 \pm 18\ M^{-1}\ cm^{-1}$ and $A_0 = 0.137 \pm 0.003$, obtained under the reaction conditions $[X]_0 = 2 \times 10^{-4}$ M, $[C_{12}E_{23}]_T = 0.01$ M, $[CTABr]_T = 0.03$ M, [NaOH] = 0.01 M, 35 °C and $\lambda = 290$ nm

EXPERIMENTAL

Materials. Phenyl salicylate (PSL), phenyl benzoate (PB), cetyltrimethylammonium bromide (CTABr) and $C_{12}H_{25}(OCH_2CH_2)_{22}OCH_2CH_2OH$ ($C_{12}E_{23}$ or Brij 35) were obtained from Fluka, Sigma and Aldrich and were of the highest commercially available purity. All other chemicals used were of reagent grade. Stock solutions (0.01 M) of PSL and PB were prepared in acetonitrile.

Kinetic measurements. The rate of hydrolysis of ionized PSL (PS^-) was studied spectrophotometrically by monitoring the disappearance of PS^- as a function of time at 350 nm. Similarly, the rate of alkaline hydrolysis of PB was studied spectrophotometrically by monitoring the appearance of the product (phenolate ion) as a function of time at 290 nm. The absorbance values (A_{obs}), at different reaction times (*t*) were measured using a Shimadzu Model UV-1601 UV–visible spectrophotometer equipped with a thermoelectrically temperature-controlled cell positional Model CPS 240A. Two to four kinetic runs were carried out simultaneously under reaction conditions where the reaction rates were fairly slow. The reaction rates were monitored for a reaction period of 4–18 half-lives of the reactions. Pseudo-first-order rate constants (k_{obs}) were calculated from either Eqn. (1) [if disappearance of reactant (PS^-) was monitored periodically] or Eqn. (2) [if the appearance of product(s) was monitored periodically]

$$A_{obs} = E_{app}[X]_0 \exp(-k_{obs}t) + A_\infty \qquad (1)$$

$$A_{obs} = E_{app}[X]_0[1 - \exp(-k_{obs}t)] + A_0 \qquad (2)$$

where E_{app} is the apparent molar absorptivity of the reaction mixture, $[X]_0$ is the initial concentration of ester (PSL or PB), $A_\infty = A_{obs}$ at $t = \infty$ and $A_0 = A_{obs}$ at $t = 0$. The non-linear least-squares technique was used to calculate k_{obs}, E_{app} and A_∞ or A_0 from Eqn. (1) or (2). The fitting of the observed data to either Eqn. (1) or (2) was good, as is evident from the typical plots of A_{obs} versus *t* shown in Fig. 1, where solid lines are drawn through the calculated data points using either Eqn. (1) or (2) with the calculated values of unknown parameters k_{obs}, E_{app} and A_∞ or A_0 and from the standard deviations associated with the calculated parameters (Tables 1 and 2). The details of the kinetic procedure and data analysis have been described elsewhere.[7]

Table 1. Effect of $[C_{12}E_{23}]_T$ on k_{obs} for hydrolysis of PB at 0.01 M NaOH and 35 °C[a]

$10^4\ [C_{12}E_{23}]_T$ (M)	$10^4\ k_{obs}$ (s^{-1})	E_{app} ($M^{-1}\ cm^{-1}$)	A_0	$10^4\ k_{calcd}$[b] (s^{-1})	Q_{obs}[c]	Q_{calcd}[d]
0.0	69.7 ± 0.5^{e}	2420 ± 6^{e}	0.100 ± 0.001^{e}			
0.5	74.6 ± 0.8	2358 ± 9	0.106 ± 0.001			
1.0	72.3 ± 0.5	2363 ± 6	0.106 ± 0.001			
2.0	67.4 ± 0.5	2322 ± 5	0.098 ± 0.001	67.6	1.071	1.137
3.0	62.1 ± 0.6	2371 ± 6	0.098 ± 0.001	61.9	1.163	1.225
5.0	53.0 ± 0.5	2368 ± 8	0.113 ± 0.002	53.0	1.362	1.400
7.0	45.4 ± 0.4	2382 ± 7	0.089 ± 0.001	46.4	1.590	1.575
10.0	39.9 ± 0.3	2541 ± 7	0.094 ± 0.001	39.1	1.810	1.837
20.0	25.2 ± 0.2	2544 ± 8	0.102 ± 0.000	25.7	2.865	2.712
30.0	19.3 ± 0.1	2346 ± 3	0.093 ± 0.000	19.2	3.741	3.587
60.0	11.9 ± 0.3	2061 ± 22	0.099 ± 0.001	11.0	6.067	6.213
100.0	7.42 ± 0.15	1289 ± 16	0.098 ± 0.000	7.14	9.730	9.713
150.0	4.13 ± 0.17	1077 ± 14	0.099 ± 0.002	5.04		
200.0	[f]	[f]				

[a] $[PB]_0 = 2 \times 10^{-4}$ M, 0.01 M NaOH, 35 °C, $\lambda = 290$ nm, reaction mixture for each kinetic run contained 2% (v/v) CH_3CN.

[b] Calculated from Eqn. (3) with the parameters mentioned in the text.

[c] $Q_{obs} = k^h{}_W / k_{obs}$, where $10^4\ k^h{}_W = 72.2\ s^{-1}$.

[d] Calculated from Eqn. (4) as described in the text.

[e] Error limits are standard deviations.

[f] The rate of reaction was too slow to measure k_{obs} and E_{app} accurately (the value of A_{obs} changed from 0.10 to 0.15 with change in reaction time (t) from ~20 s to 3 h).

RESULTS AND DISCUSSION

Effect of $[C_{12}E_{23}]_T$ on k_{obs} for hydrolysis of PB

A series of kinetic runs were carried out within the total $C_{12}E_{23}$ concentration ($[C_{12}E_{23}]_T$) range 0.0–0.015 M at 0.01 M NaOH and 35 °C. First-order rate constants (k_{obs}), E_{app} and A_0, obtained under these experimental conditions, are shown in Table 1. An attempt to obtain k_{obs} at ≥0.02 M $C_{12}E_{23}$ failed because the absorbance at 290 nm remained almost unchanged within the reaction period of nearly 3 h.

The k_{obs} values decreased monotonically with increase in $[C_{12}E_{23}]_T$ until $[C_{12}E_{23}]_T \approx 0.01$ M at 0.01 M NaOH. The rate of alkaline hydrolysis of PB should involve uncatalyzed (k_{H_2O} [PB]) and hydroxide ion-catalyzed (k_{OH} $[HO^-]$ [PB]) kinetic steps, as shown in Scheme 1.

$$\underset{\text{(PB)}}{\text{phenyl benzoate}} \xrightarrow[2.\ k_{OH}[HO^-]]{1.\ k_{H_2O}} \underset{(PhO^-)}{\text{phenolate ion}} + \underset{\text{(BZ)}}{\text{benzoate ion}}$$

Scheme 1

However, the contribution of k_{H_2O} [PB] has been shown to be negligible compared with k_{OH} $[HO^-]$ [PB] in the rate law at pH >9.[8] Thus, $k_{obs} = k_{OH}\ [HO^-]$ under the present experimental conditions.

The non-linear decrease in k_{obs} with increase in $[C_{12}E_{23}]_T$ (Table 1) may be explained by the use of the pseudophase (PP) model of micelles.[9] The assumptions involved in this model and its usefulness and weaknesses were critically discussed by Bunton.[10] The reaction scheme for alkaline hydrolysis of PB, in terms of the PP model of micelles, may be expressed by Scheme 2.

$$\begin{aligned} S_W + D_n &\overset{K_S}{\rightleftharpoons} S_M \\ S_W + HO^-_W &\overset{k_{OH,W}}{\longrightarrow} \text{Products} \\ S_M + HO^-_M &\overset{k_{OH,M}}{\longrightarrow} \text{Products} \end{aligned}$$

Scheme 2

S stands for reactive substrate (PB), K_S is the micellar binding constant of S, D_n represents the micelle, $k_{OH,W}$ and $k_{OH,M}$ are second-order rate constants for the reactions occurring in the aqueous pseudophase and micellar pseudophase, respectively, and the subscripts W and M stand for the aqueous pseudophase and micellar pseudophase, respectively. The observed rate law (rate $= k_{obs}\ [S]_T$, where $[S]_T = [S_W] + [S_M]$) and the rate law for the reaction, based on the reaction steps in Scheme 2, can lead to

$$k_{obs} = \frac{k^h{}_W + k^h{}_M K_S [4oxD_n]}{1 + K_S [D_n]} \tag{3}$$

where $[D_n] = [C_{12}E_{23}]_T - \text{cmc}$, with cmc representing the critical micelle concentration of the micelle-forming surfactant $C_{12}E_{23}$, $k^h{}_W = k_{OH,W}\ [HO^-{}_W]$ and $k^h{}_M = k_{OH,M}\ m_{OH}/V_M$ (where $m_{OH} = [HO^-{}_M]/[D_n]$ and V_M represents the micellar molar volume[10]). The values of cmc, obtained by an iterative technique[11] and Broxton's graphical technique,[12] are 1.5×10^{-4} and 1.3×10^{-4} M, respectively.

The non-linear least-squares technique was used to

Table 2. Effect of $[C_{12}E_{23}]_T$ on k_{obs} and E_{app} for hydrolysis of PS^- at 35 °C[a]

	0.01 M NaOH			0.03 M NaOH		
10^4 $[C_{12}E_{23}]_T$ (M)	10^4 k_{obs} (s^{-1})	E_{app} (M^{-1} cm^{-1})	A_∞	10^4 k_{obs} (s^{-1})	E_{app} (M^{-1} cm^{-1})	A_∞
0.0	7.48 ± 0.12[b]	6339 ± 40[b]	−0.007 ± 0.008[b]	7.51 ± 0.14[b]	6290 ± 44[b]	−0.020 ± 0.009[b]
5.0	7.52 ± 0.13	6021 ± 46	−0.053 ± 0.010	7.85 ± 0.12	6100 ± 42	−0.019 ± 0.009
5.0	7.11 ± 0.14	5813 ± 44	−0.006 ± 0.010			
10.0	7.89 ± 0.04	5993 ± 12	0.001 ± 0.003			
10.0	7.13 ± 0.13	5780 ± 39	−0.011 ± 0.008	7.83 ± 0.09	6138 ± 28	0.005 ± 0.005
20.0	7.11 ± 0.21	6173 ± 64	−0.012 ± 0.013	8.26 ± 0.33	6205 ± 99	−0.005 ± 0.018
30.0	7.11 ± 0.19	6091 ± 59	−0.006 ± 0.012	7.50 ± 0.22	6199 ± 73	0.002 ± 0.014
50.0	7.18 ± 0.15	5944 ± 45	0.007 ± 0.009	6.94 ± 0.19	6330 ± 62	0.001 ± 0.013
60.0	7.37 ± 0.04	5866 ± 13	0.037 ± 0.003	8.07 ± 0.04	5822 ± 11	0.028 ± 0.002
60.0	6.95 ± 0.09	5792 ± 28	0.086 ± 0.006	7.30 ± 0.06	6249 ± 17	0.052 ± 0.003
100.0	7.54 ± 0.05	5838 ± 14	0.065 ± 0.003	6.51 ± 0.18	6284 ± 61	0.015 ± 0.013
100.0	7.27 ± 0.06	5482 ± 16	0.032 ± 0.003	7.43 ± 0.05	6154 ± 14	0.023 ± 0.003
200.0	5.89 ± 0.17	1804 ± 18	0.067 ± 0.004	6.40 ± 0.10	6211 ± 35	0.051 ± 0.008
300.0	[c]	[c]		6.41 ± 0.07	6078 ± 23	0.074 ± 0.005

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, 35 °C, $\lambda = 350$ nm, reaction mixture for each kinetic run contained 2% (v/v) CH_3CN.

[b] Error limits are standard deviations.

[c] The absorbance value ($A_{obs} = 0.012$) remained unchanged with change in the reaction time (t) from ~20 s to 3 h.

calculate $k^h{}_M$ and K_S from Eqn. (3) considering $k^h{}_W$ as a known parameter. The least-squares calculated values of $k^h{}_M$ and K_S are $(0.47 \pm 0.53) \times 10^{-4}$ s^{-1} and 987 ± 27 M^{-1}, respectively. The calculated value of $k^h{}_M$ is associated with a relative standard deviation of >100% and hence it is not statistically different from zero, and therefore K_S was also calculated from Eqn. (4), which is the rearranged form of Eqn. (3) with $k^h{}_M = 0$ and $\phi = 1 - \text{cmc}\ K_S$:

$$k^h{}_W/k_{obs} = \phi + K_S[C_{12}E_{23}]_T \tag{4}$$

The linear least-squares calculated values of ϕ and K_S are 0.962 ± 0.046 and 875 ± 11 M^{-1}, respectively. The value of K_S is only 11% lower than that (987 M^{-1}) obtained from Eqn. (3). It may be worth mentioning that the non-linear least-squares technique used in the calculation of $k^h{}_M$ and K_S from Eqn. (3) involves a simulation where it may be possible that large errors in both $k^h{}_M$ and K_S may compensate each other, producing a seemingly good fit of the observed data to Eqn. (3). However, the linear least-squares treatment gives an exact solution of Eqn. (4) and hence there is no possible compensatory errors in the calculated values of ϕ and K_S. The fitting of the observed data to Eqn. (4) is evident from the $(k^h{}_W/k_{obs})_{calcd}$ values listed in Table 1. The pseudo-first-order rate constants (k_{obs}) for the alkaline hydrolysis of securinine, in the presence of $C_{12}E_{10}$ micelles, were found to fit a kinetic equation similar to Eqn. (4).[13]

The insignificant value of $k^h{}_M$ shows that the rate of hydrolysis of PB is much slower in the micellar pseudophase than in the aqueous pseudophase. The micellar-mediated reactions are generally believed to occur at the micellar surface (i.e. palisade or Stern layer) where the microscopic hydrophilicity (i.e. microscopic dielectric constant) of the medium is considerably lower compared with the macroscopic hydrophilicity (i.e. dielectric constant) of the aqueous pseudophase. An increase in acetonitrile content from 2 to 70% (v/v) decreased k_{obs} for hydrolysis of PB from 14.9×10^{-3} to 1.41×10^{-3} s^{-1} at 0.02 M NaOH and 35 °C.[8] However, the value of $k^h{}_M \approx 0$ cannot be explained in terms of a medium effect only. The possible reason for the slower rate of hydrolysis in the micellar pseudophase is the presence of a kinetically insignificant amount of HO^- in the vicinity of micellized PB molecules. A similar proposal has been made to explain the inhibitory effects of non-ionic micelles on the rate of reaction of HO^- with *p*-nitrophenyl diphenylphosphate.[14] The evidence for the presence of different locations or the non-uniformity in the concentrations of two different reactants in the micellar pseudophase is no longer rare.[14–17] The PB molecules, being highly hydrophobic, are expected to be dragged deeper inside the micellar pseudophase whereas hydroxide ions, being highly hydrophilic, are expected to remain in the considerably polar and hydrophilic region of the micellar pseudophase.

The values of k_{obs} at ≥ 0.015 M $C_{12}E_{23}$ show a sharp decrease with increase in $[C_{12}E_{23}]_T$ (Table 1), which is largely due to depletion of HO^- ions in the micellar environment of micellized PB molecules, and these k_{obs} values fail to obey the PP model, i.e. Eqn. (3) or (4). This is a rather unusual observation in view of the theoretical micellar models, such as the PP model, used to explain such data quantitatively.

The molar absorptivities of non-ionized and ionized phenol at 290 nm and 1 M ionic strength are 0 and

2350 M^{-1} cm^{-1}, respectively.[18] In Eqn. (2), $E_{\text{app}} = E_{\text{P}} - E_{\text{PB}}$, where E_{P} and E_{PB} represent the molar absorptivities of products, phenolate and benzoate ions, and PB, respectively, and $A_0 = E_{\text{PB}}$ $[\text{X}]_0$. The value of E_{app} (= 2420 M^{-1} cm^{-1}, Table 1) at $[\text{C}_{12}\text{E}_{23}]_{\text{T}} = 0$ and the relationship $E_{\text{app}} = E_{\text{P}} - E_{\text{PB}}$ reveal that $E_{\text{P}} \approx E_{\text{BZ}}$ (where BZ represents benzoate ion) at 290 nm. The values of A_0 and E_{app} are almost independent of $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ within the range 0.0–0.02 and 0.0–0.003 M, respectively. An increase in $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ beyond 0.003 M decreased E_{app} and the value of E_{app} at 0.015 M $\text{C}_{12}\text{E}_{23}$ became almost half of that at $[\text{C}_{12}\text{E}_{23}]_{\text{T}} = 0$. Thus, the value of E_{app} at 0.015 M $\text{C}_{12}\text{E}_{23}$ indicates that the hydroxide ion concentration in the micellar environment of micellized product phenol molecules was insufficient to cause their complete ionization. It should be noted that phenol is apparently more hydrophilic than PB and hence the location in the micellar pseudophase for phenol should be more polar than that for PB.[18] Thus, the concentration of $\text{HO}^-{}_{\text{M}}$ in the vicinity of micellized PB molecules must be even lower than that of micellized phenol.

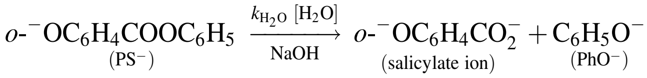
The possibility that the decrease in E_{app} with the increase in $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ at 0.006 M is due to the effect of the medium on E_{P} and E_{PB} may be ruled out because E_{P} and E_{PB} remained essentially unchanged with the change in the acetonitrile content from 2 to 70% (v/v) in mixed aqueous solvents.[8] The most obvious reason for the decrease in E_{app} with the increase in $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ at a constant [NaOH] is the depletion of hydroxide ions in the region of micellized PB molecules in the palisade layer through a mechanism (unknown to us at the moment) by which $\text{C}_{12}\text{E}_{23}$ micelles affect the pK_{a} or pK_{b} of phenyl salicylate.[6]

Effect of $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ on k_{obs} for the hydrolysis of PS^-

In order to find out the effect of $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ on the rate of hydrolysis of PS^-, a few kinetic runs were carried out at different $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ ranging from 0.0 to 0.02 M at 0.01 M NaOH, and 35 °C. Similar results were obtained at 0.03 M NaOH. First-order rate constants (k_{obs}), E_{app} and A_∞ obtained under these experimental conditions are summarized in Table 2. The values of k_{obs} could not be obtained at $[\text{C}_{12}\text{E}_{23}]_{\text{T}} \geq 0.03$ M within the [NaOH] range 0.01–0.03 M because, under such conditions, the absorbance (A_{obs}) at 350 nm became ~0.02 at reaction time $t \approx 15$ s and remained unchanged within the reaction period of nearly 3 h.

The values of the molar absorptivities for PS^- and PSH (non-ionized form of phenyl salicylate) at 350 nm are 5700–6000 and ~0 M^{-1} cm^{-1}, respectively.[18] The values of the initial absorbance ($A_0 = A_{\text{obs}}$ at $t = 0$) of the reaction mixtures at 0.01 and 0.03 M NaOH were found to be unchanged with change in $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ from 0.0 to 0.01 M and from 0.0 to 0.03 M, respectively {it is evident from Eqn. (1) that at $t = 0$, $A_{\text{obs}} = A_0 = E_{\text{app}}$ $[\text{X}]_0 + A_\infty$, which can be used to calculate the values of A_0 at different $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ with the values of E_{app} and A_∞ summarized in Table 2 where $[\text{X}]_0 = 2 \times 10^{-4}$ M}. If the change in the reaction conditions, such as an increase in $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$, increases $[\text{PSH}]_{\text{T}}$ (= $[\text{PSH}_{\text{M}}] + [\text{PSH}_{\text{W}}]$), then the values of A_0 should have been dependent upon $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$. The unchanged values of A_0 with the change in $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ show the presence of 100% ionized form (PS^-) of phenyl salicylate in the reaction mixtures under such experimental conditions. However, the value of A_0 (~0.012) at 0.01 M NaOH and 0.03 M $\text{C}_{12}\text{E}_{23}$ and also at 0.03 M NaOH and >0.03 M $\text{C}_{12}\text{E}_{23}$ remained unchanged within the reaction period of ~3 h, which shows that $[\text{PS}^-]_{\text{T}} = 0$ and the entire PSH molecules are fully bound by micelles, i.e. $[\text{PSH}_{\text{W}}] = 0$ under such conditions because the aqueous pK_{a} of PSH_{W} is 9.25.[7] Similar results were obtained in the study on the effect of $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ on the pK_{a} of PSH.[6]

The first-order rate constants (k_{obs}) for the hydrolysis of phenyl salicylate were found to be independent of $[\text{HO}^-]$ within the range 0.005–0.060 M in the absence of micelles.[18] Similarly, k_{obs} for the hydrolysis and methanolysis of phenyl salicylate turned out to be independent of $[\text{HO}^-]$ within the respective [NaOH] range 0.01–0.04 and 0.005–0.050 M in the presence of 0.0015 M[19] and 0.01 M CTABr.[20] It has been shown unequivocally that pH-independent hydrolysis of phenyl salicylate involves PS^- and H_2O as the reactants.[21] The brief reaction scheme for the cleavage of phenyl salicylate, under the present experimental conditions, may be as shown in Scheme 3.



$$\underset{(\text{PS}^-)}{o\text{-}^-\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_5} \xrightarrow[\text{NaOH}]{k_{\text{H}_2\text{O}}\,[\text{H}_2\text{O}]} \underset{(\text{salicylate ion})}{o\text{-}^-\text{OC}_6\text{H}_4\text{CO}_2^-} + \underset{(\text{PhO}^-)}{\text{C}_6\text{H}_5\text{O}^-}$$

Scheme 3

The observed data, summarized in Table 2, show that k_{obs} remained almost independent of $[\text{C}_{12}\text{E}_{23}]_{\text{T}}$ within the range 0.0–0.01 M at 0.01 M NaOH and 0.0–0.03 M at 0.03 M NaOH. These results may be explained in terms of either $K_{\text{S}} = 0$ (i.e. PS^- ions do not have a detectable binding affinity with $\text{C}_{12}\text{E}_{23}$ micelles) or $K_{\text{S}} \neq 0$, but the location of micellized PS^- in the micellar pseudophase is very similar to that in the aqueous pseudophase in terms of medium polarity and water concentration. The possibility that $K_{\text{S}} = 0$ can be ruled out for the following reason. If $K_{\text{S}} = 0$ {where $K_{\text{S}} = [\text{PS}^-{}_{\text{M}}]/([\text{PS}^-{}_{\text{W}}][\text{D}_{\text{n}}])$}, then $K_{\text{S}}{}^{\text{app}} = [\text{PSH}_{\text{M}}]/([\text{PS}^-{}_{\text{W}}][\text{D}_{\text{n}}]) \approx 100\ \text{M}^{-1}$.[†] Under

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[†] (By definition, $K_{\text{S}}{}^{\text{app}} = \{[\text{PS}^-{}_{\text{M}}] + [\text{PSH}_{\text{M}}]\}/\{([\text{PS}^-{}_{\text{W}}] + [\text{PSH}_{\text{W}}])[\text{D}_{\text{n}}] = [\text{PSH}_{\text{M}}]/([\text{PS}^-{}_{\text{W}}][\text{D}_{\text{n}}])\}$. Where $[\text{PS}^-{}_{\text{M}}] = 0$ because $K_{\text{S}} = 0$ and $[\text{PSH}_{\text{W}}] = 0$ because the K_{a} of PSH is 5.67×10^{-10} M[7] and, therefore, at 0.01 M NaOH, $[\text{PSH}_{\text{W}}] = 0$. The values of E_{app} (= molar absorptivity of PS^- at 350 nm because the molar absorptivities of PSH, non-ionized and ionized products, salicylic acid and phenol are nearly zero at 350 nm[18]) at 0.0 and 0.02 M $\text{C}_{12}\text{E}_{23}$ are 6300 and 1800 M^{-1} cm^{-1} (Table 2), respectively, in the presence of 0.01 M NaOH. Thus, $K_{\text{S}}{}^{\text{app}} = (6300 - 1800)/(1800 \times 0.02) = 125\ \text{M}^{-1}$.

such conditions, the PP model can lead to

$$k_{obs} = k^{h}{}_{W}/(1 + K_S{}^{app}[D_n]) \qquad (5)$$

which shows that $k_{obs} = k^{h}{}_{W}/3$ at 0.02 M $C_{12}E_{23}$. However, the observed value of k_{obs} (= 5.89×10^{-4} s^{-1}) at 0.02 M $C_{12}E_{23}$ is only 22% smaller than k_{obs} (= $k^{h}{}_{W} = 7.48 \times 10^{-4}$ s^{-1}) at $[C_{12}E_{23}]_T = 0$. The possibility that $K_S = 0$ may be also ruled out based on the observed effect of $C_{12}E_{23}$ and mixed $C_{12}E_{23}$–CTABr micelles on pK_a or pK_b of PSH.[6]

The kinetic data reveal that PS^- ions exist in the micellar interface or micellar pseudophase of CTABr[17] and sodium dodecyl sulfate[18] micelles of very low $[H_2O]$ compared with $[H_2O]$ of the aqueous pseudophase. Therefore, it seems surprising that the $C_{12}E_{23}$ micellar location of $PS^-{}_M$ does not differ from the aqueous pseudophase in terms of water concentration. However, it has been reported that in aqueous non-ionic micelles, such as $C_{12}E_{23}$, the ethylene oxide palisade layer is extensively hydrated[22,23] and hence the water concentration in the palisade layer of $C_{12}E_{23}$ micelles must be larger than in the interior of the Stern layer of ionic micelles. As mentioned earlier, the hydrolysis of PS^- involves PS^- and monomeric H_2O (i.e. H_2O_{free}) as the reactants. Ethers and monofunctional alcohols such as the head groups of $C_{12}E_{23}$ are known to cause disruption of the water structure at a high mole fraction of organic cosolvent in mixed aqueous solvents.[24] Such an interaction is bound to produce more monomeric water molecules (H_2O_{free}) and consequently increase the rate of hydrolysis of PS^-. If this argument is correct, then it is merely a coincidence that the effect of the decrease in $[H_2O_M]$ (compared with $[H_2O_W]$) in the vicinity of $PS^-{}_M$ ions is nearly counterbalanced by the effect of the increase in $[H_2O_{free,\ M}]$ (compared with $[H_2O_{free,\ W}]$), owing to disruption of the water structure by headgroups, on k_{obs}.

Effect of $C_{12}E_{23}$–CTABr mixed micelles on k_{obs} for the hydrolysis of PB

A series of kinetic runs were carried out within the $[C_{12}E_{23}]_T$ range 0.0–0.025 M at 0.01 M NaOH and 35 °C in the presence of 0.006 M CTABr. Similar results were obtained at 0.01 M, 0.02 and 0.03 M CTABr. These results are shown graphically in Fig. 2 as plots of k_{obs} versus $[C_{12}E_{23}]_T$. The value of k_{obs} for the hydrolysis of PB at 0.01 M NaOH is 6.77×10^{-3} s^{-1} at 0.01 M NaOH and $[CTABr]_T = [C_{12}E_{23}]_T = 0$. The effects of $[CTABr]_T$ on k_{obs} for alkaline hydrolysis of PB in the absence of $C_{12}E_{23}$ micelles have been explained in terms of the pseudophase ion-exchange (PIE) model and this data treatment resulted in a CTABr micellar binding constant of PB of 300 M^{-1}.[8]

It is evident from the plots of Fig. 2 that the values of k_{obs} are almost independent of $[C_{12}E_{23}]_T$ within the range 0.0–5×10^{-4} M at 0.006, 0.01, 0.02 and 0.03 M CTABr.

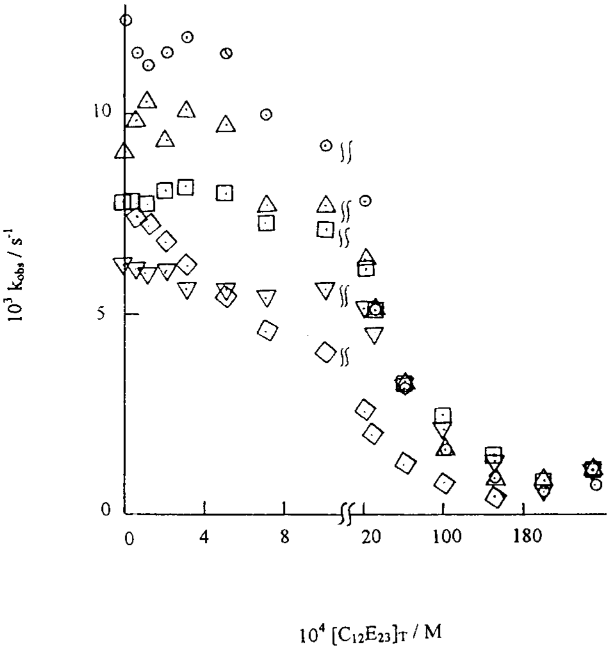

Figure 2. Plots showing the relationship between k_{obs} and $[C_{12}E_{23}]_T$ for the hydrolysis of PB at (◊) 0.0, (○) 0.006, (△) 0.01, (□) 0.02 and (▽) 0.03 M CTABr

An increase in $[C_{12}E_{23}]_T$ from $\geq 7 \times 10^{-4}$ M caused a decrease in k_{obs} and this decrease became nearly independent of $[CTABr]_T$ at $\geq 25 \times 10^{-4}$ M $C_{12}E_{23}$. The values of k_{obs} are significantly higher at $[CTABr]_T = 0.006$, 0.01, 0.02 and 0.03 M than at $[CTABr]_T = 0$ in the presence of $[C_{12}E_{23}]_T$ in the range $> 5 \times 10^{-4}$–200×10^{-4} M. These observations reveal that mixed CTABr–$C_{12}E_{23}$ micelles behave like pure CTABr micelles at $[C_{12}E_{23}]_T \leq 5 \times 10^{-4}$ M and the decrease in k_{obs} with increase in $[CTABr]_T$ from 0.006 to 0.03 M at a constant $[C_{12}E_{23}]_T$ is due to dilution effect on $[HO^-{}_M]$ as generally ascribed in the interpretation of the k_{obs} versus $[CTABr]_T$ profile by use of the PIE model.[8,10,25] It is clear from a number of reports that organic solutes and non-ionic surfactants increase both the fractional micellar ionization (α) and the volume of the micellar pseudophase.[4] These two effects on the concentration of $HO^-{}_M$ may be attributed to the decrease in k_{obs} with increase in $[C_{12}E_{23}]_T$ at a constant $[CTABr]_T$ (Fig. 2). A quantitative treatment of these observations is difficult to provide because of the lack of a perfect kinetic model and imperfect understanding of the structural features of mixed micelles at varying mole ratios of its surfactant components.

It is perhaps noteworthy that the values of k_{obs} became almost independent of $[CTABr]_T$ within the range 0.006–0.03 M at a constant $[C_{12}E_{23}]_T$ within the range 25×10^{-4}–250×10^{-4} M (Fig. 2). However, even under such conditions, the presence of CTABr increased the concentration of $HO^-{}_M$ compared with that of $HO^-{}_M$ at $[CTABr]_T = 0$. This is evident from the larger values of

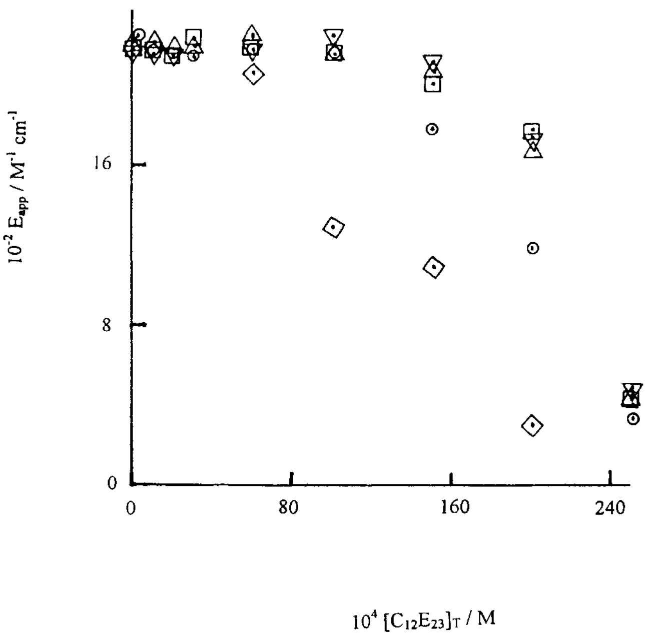

Figure 3. Effect of $[C_{12}E_{23}]_T$ on E_{app} for hydrolysis of PB at (◊) 0.0, (○) 0.006, (△) 0.01, (□) 0.02 and (▽) 0.03 M CTABr

k_{obs} (Fig. 2) and E_{app} (Fig. 3) in mixed CTABr–$C_{12}E_{23}$ micelles compared with those in pure $C_{12}E_{23}$ micelles. These observations reflect the fact that in the interface of a cationic micelle the hydroxide ion concentration will be higher than that in the interface of a non-ionic micelle and, therefore, the reaction will be faster in mixed cationic–non-ionic than in non-ionic micelles. However, the dilution effect on $[HO^-_M]$ due to the increase in $[CTABr]_T$ at a constant $[C_{12}E_{23}]_T$ and the decreasing effects of the increase in $[C_{12}E_{23}]_T$ on $[HO^-_M]$ and α at a constant $[CTABr]_T$ are no longer kinetically significant. It is interesting that the pK_a of phenyl salicylate (PSL) was unaffected by an increase in $[CTABr]_T$ from 0.0 to 0.03 M at $[C_{12}E_{23}]_T = 0.02$ M.[6] This shows that the presence of CTABr did not cause an increase in $[HO^-_M]$ (compared with $[HO^-_M]$ at $[CTABr]_T = 0$) sufficient enough to show an effect on the pK_a of PSL under such conditions.

The value of E_{app} at 0.006 M CTABr is nearly 30% smaller than those at 0.01, 0.02 and 0.03 M CTABr in the presence of 0.02 M $C_{12}E_{23}$ (Fig. 3), whereas the values of k_{obs} are independent of $[CTABr]_T$ under such conditions (Fig. 2). These observations may be explained with the assumptions that PB_M molecules are located deeper inside the micellar pseudophase compared with the relatively more hydrophilic product phenolate ions (PhO^-_M) and the rate of hydrolysis of PB is insignificant in the micellar pseudophase compared with that in the aqueous pseudophase. However, the product, phenolate ion, formed in the aqueous pseudophase is trapped by the cationic interface of mixed $C_{12}E_{23}$–CTABr micelles where $[HO^-_M]$ increases with increase in $[CTABr]_T$ at a constant $[C_{12}E_{23}]_T$. Mukerjee pointed out that for micelles, such as $C_{12}E_{23}$ micelles, containing bulky polyoxyethylene head groups, the voluminous outer mantle of the micelle can also serve as a locus of solubilization of some polar solubilizate.[26] The distribution ratios of the amounts in the mantle and the amounts associated with the hydrocarbon core, which includes the molecules in the interfacial region, increased in favor of the core location as the molecules became more hydrophobic.[26]

Effect of Mixed $C_{12}E_{23}$–CTABr micelles on k_{obs} for the hydrolysis of PS^-

A few kinetic runs were carried out within the $[C_{12}E_{23}]_T$ range 0.005–0.015 M at 0.01 M CTABr and 0.01 M NaOH. The first-order rate constants (k_{obs}) showed a linear increase with increase in $[C_{12}E_{23}]_T$, as is evident from the plot in Fig. 4. Similar results were obtained at 0.02 and 0.03 M CTABr (Fig. 4). It is apparent that mixed $C_{12}E_{23}$–CTABr micelles behave as pure CTABr micelles at $[C_{12}E_{23}]_T < 0.005$ M and $[CTABr]_T \geq 0.01$ M. As mentioned earlier, the increase in $[C_{12}E_{23}]_T$ at a constant $[CTABr]_T$ is expected to increase both α and the volume of micellar pseudophase.[4] These two effects are expected to increase the water concentration in the vicinity of micellized PS^- ions, which could be the cause of the increase in k_{obs} with increase in $[C_{12}E_{23}]_T$. The linear increase in k_{obs} with increase in $[C_{12}E_{23}]_T$ at constant $[CTABr]_T$ cannot be attributed to the probable reaction

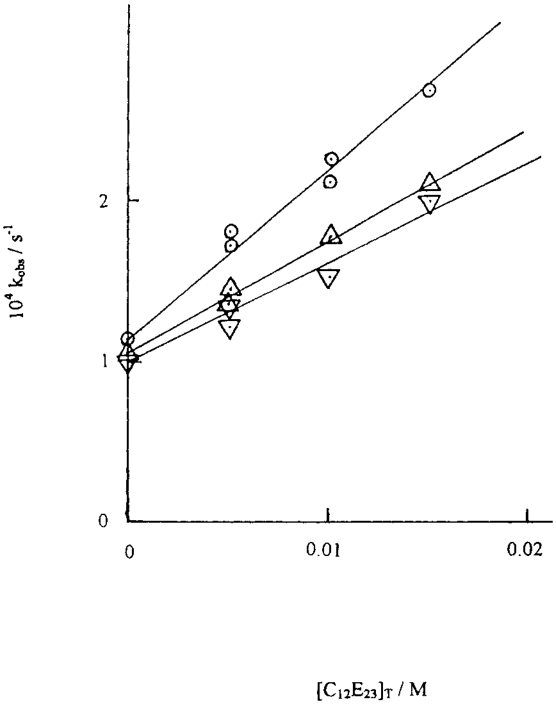

Figure 4. Effect of $[C_{12}E_{23}]_T$ on k_{obs} for hydrolysis of PS^- at (○) 0.01, (△) 0.02 and (▽) 0.03 M CTABr

between PS^- and ionized or non-ionized hydroxyl groups of $C_{12}E_{23}$ because the product (ionized alkyl salicylate) of such a reaction could not be detected spectrophotometrically[7] in the presence of either pure $C_{12}E_{23}$ micelles or mixed $C_{12}E_{23}$–CTABr micelles. Similarly, the reaction of *p*-nitrophenyl diphenylphosphate with terminal alkoxide groups of non-ionic micelles was found to be unimportant,[14,27] but the reaction of 2,4-dinitrochlorobenzene (DNCB) with HO^- in $C_{12}E_{10}$ and $C_{12}E_{23}$ gave considerable amounts of the ether formed by the reaction of alkoxide ion with DNCB.[14] The apparent linear variation of k_{obs} with $[C_{12}E_{23}]_T$ at a constant $[CTABr]_T$ (Fig. 4) could not be tested beyond 0.015 M at 0.01 M NaOH because under such conditions the rate of hydrolysis of PS^- became too slow to monitor conveniently owing to presence of an insignificant amount of PS^- in the reaction mixture.

CONCLUSION

The effect of $[C_{12}E_{23}]_T$ on k_{obs} for the hydrolysis of PB reveals an insignificant rate of hydrolysis in the micellar pseudophase compared with that in the aqueous pseudophase. This shows the presence of PB_M molecules in the micellar region where $[HO^-{}_M]$ is kinetically insignificant. These results also show that at 0.01 M NaOH, the observed data, obtained at <0.015 M $C_{12}E_{23}$, can be explained in terms of the PM model. However, the values of k_{obs} and E_{app} drop sharply and the k_{obs} values fail to obey the PM model at $[C_{12}E_{23}]_T > 0.015$ M owing to some unusual effect of $[C_{12}E_{23}]_T$ on the distribution of HO^- between the aqueous and micellar pseudophases under such conditions. The effect of $[C_{12}E_{23}]_T$ on k_{obs} for the hydrolysis of PS^- shows the presence of $PS^-{}_M$ ions in the micellar environment of a high concentration of H_2O_M and hence $PS^-{}_M$ ions most likely remain in the voluminous polyoxyethylene head groups of the micelles. The presence of mixed micelles of CTABr and $C_{12}E_{23}$ causes an increase in $[HO^-{}_M]$ at the interface of the cationic surfactant which makes k_{obs} larger than that at the corresponding $[C_{12}E_{23}]_T$ with $[CTABr]_T = 0$ for PB. The addition of CTABr micellar solution to $C_{12}E_{23}$ micellar solution causes the presence of $PS^-{}_M$ at the CTABr micellar interface where $[H_2O_M]$ is significantly lower than $[H_2O_W]$. However, an increase in $[C_{12}E_{23}]_T$ from 0.005 to 0.015 M at a constant $[CTABr]_T$ increases k_{obs}, which is due to the increase in $[H_2O_M]$ caused by the swelling of the mixed micelles.

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