JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15**: 374–384
DOI: 10.1002/poc.514

Effects of non-ionic and mixed cationic–non-ionic micelles on the rate of alkaline hydrolysis of phthalimide

M. Niyaz Khan* and Emran Ismail

Department of Chemistry, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Received 16 January 2002; revised 1 March 2002; accepted 13 March 2002

ABSTRACT: Pseudo-first-order rate constants (k_{obs}) for the alkaline hydrolysis of phthalimide (PTH) show a monotonic decrease with the increase in $[C_{16}E_{20}]_T$ (total concentration of Brij 58) at constant $[CH_3CN]$ and [NaOH]. This micellar effect is explained in terms of the pseudophase model of micelles. The rate of hydrolysis of PTH in $C_{16}E_{20}$ micellar pseudophase appears to be negligible compared with that in the aqueous pseudophase. The values of k_{obs} for $C_{12}E_{23}$ (Brij 35) show a sharp decrease at very low values of $[C_{12}E_{23}]_T$ followed by a very slow decrease with increase in $[C_{12}E_{23}]_T$ at relatively higher values of the latter. The rate of hydrolysis becomes too slow to monitor at $[C_{12}E_{23}]_T \geq 0.04$ M in the absence of cetyltrimethylammonium bromide (CTABr) and at $[C_{12}E_{23}]_T \geq 0.05$ M in the presence of 0.006–0.02 M CTABr at 0.02 M NaOH whereas such characteristic behavior is kinetically absent with $C_{16}E_{20}$. The values of k_{obs}, obtained at different $[NIS]_T$ (where NIS represents $C_{16}E_{20}$ and $C_{12}E_{23}$) in the presence of a constant amount of CTABr, follow the empirical relationship $k_{obs} = (k_0 + kK[NIS]_T)/(1 + K[NIS]_T)$ where k and K are empirical parameters. The values of k are only slightly affected whereas the values of K decrease with increase in $[CTABr]_T$ for the mixed $C_{16}E_{20}$–CTABr micellar system. The rate of hydrolysis of PTH at $\geq$0.01 M $C_{12}E_{23}$ and $\geq$0.01 M CTABr reveals the formation of phthalic anhydride whereas this was not observed in the mixed $C_{16}E_{20}$–CTABr micellar system under similar experimental conditions.

KEYWORDS: phthalimide; alkaline hydrolysis; micelles; mixed micelles; non-ionic surfactants; cationic surfactant

INTRODUCTION

Surface-active compounds play a major role in many applications. For example, they are used as coatings to improve wettability of surfaces, as emulsifiers to stabilize emulsions, as detergents to improve washing activity and as adjuvants to increase the biological activity of herbicides. It is known that mixed surfactants can show a very different behavior in comparison with their components. It is interesting to investigate the behavior of mixed surfactants, which have different head-groups with most likely synergistic interactions but also different chains with most likely antagonistic interactions. Kinetic studies on the effects of mixed surfactants on reaction rates are very limited. The effects of non-hydrolyzable surfactants on the rates of lipase-catalyzed hydrolysis of surfactant esters have been attributed to both competitive inhibition and exclusion of the lipase from the substrate by the presence of surfactant at the interface.[1] In a few systematic kinetic studies on the effects of mixed cationic–non-ionic micelles on the rates of S_N2 reactions, the observed data have been satisfactorily explained in terms of the pseudophase micellar (PM) model.[2] The rate-decreasing effect of mixed micelles has been attributed to increases in both the fractional micellar ionization (α) and the volume of the micellar pseudophase.[2]

Recently, it has been observed that an increase in the total concentration of cetyltrimethylammonium bromide ($[CTABr]_T$) from 0.0 to 0.03 M has no effect on the apparent pK_a of phenyl salicylate in the presence of 0.02 M polyoxyethylene (23) dodecyl ether [$C_{12}E_{23}$ or Brij35 = $C_{12}H_{25}(OCH_2CH_2)_{23}OH$], which is considered to be unusual in terms of our understanding of the occurrence of HO^-–Br^- ion-exchange on a CTABr micellar surface.[3] The present study was initiated with an aim of establishing whether there is any characteristic difference in the behavior of mixed $C_{12}E_{23}$–CTABr and $C_{16}E_{20}$–CTABr [where $C_{16}E_{20} = C_{16}H_{33}(OCH_2CH_2)_{20}OH$] in addition to pure $C_{12}E_{23}$ and $C_{16}E_{20}$ micelles on the rate of alkaline hydrolysis of phthalimide. The observed results and their probable explanation(s) are presented in this paper.

EXPERIMENTAL

Materials. Reagent-grade phthalimide (PTH), cetyltrimethylammonium bromide (CTABr), polyoxyethylene

---

*Correspondence to: M. N. Khan, Department of Chemistry, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia.
E-mail: niyaz@kimia.um.edu.my
Contract/grant sponsor: National Scientific Research Development Council of Malaysia; *Contract/grant number:* 09-02-03-0785.

Table 1. Values of k_{obs}, E_{app} and A_∞ calculated from Eqn. (1) for alkaline hydrolysis of PTH at different $[C_{16}E_{20}]_T$[a]

$[C_{16}E_{20}]_T$ (M)	$10^3 k_{obs}$ (s^{-1})	E_{app} ($M^{-1}\ cm^{-1}$)	A_∞	Y_{obs}[b]	Y_{calcd}[c]
0.0001	2.46 ± 0.03[d]	2100 ± 9[d]	0.001 ± 0.002[d]		
0.001	2.47 ± 0.02	2110 ± 5	0.005 ± 0.001		
0.003	2.46 ± 0.03	2107 ± 8	0.010 ± 0.001		
0.005	2.32 ± 0.03	2028 ± 9	0.016 ± 0.002	1.060	1.025
0.01	2.26 ± 0.03	2058 ± 9	0.027 ± 0.002	1.088	1.063
0.02	2.13 ± 0.02	1966 ± 7	0.053 ± 0.001	1.155	1.138
0.03	2.09 ± 0.05	2102 ± 17	0.082 ± 0.003	1.177	1.213
0.04	1.89 ± 0.02	1992 ± 7	0.095 ± 0.001	1.302	1.288
0.05	1.83 ± 0.01	2046 ± 4	0.119 ± 0.001	1.344	1.364
0.06	1.74 ± 0.01	2023 ± 5	0.141 ± 0.001	1.414	1.439
0.08	1.54 ± 0.01	2028 ± 5	0.175 ± 0.001	1.597	1.589
0.10	1.49 ± 0.02	2027 ± 10	0.210 ± 0.002	1.651	1.739
0.12	1.29 ± 0.02	1950 ± 10	0.245 ± 0.002	1.907	1.890
0.14	1.19 ± 0.02	2002 ± 10	0.287 ± 0.002	2.067	2.040
0.18	1.04 ± 0.02	1903 ± 10	0.363 ± 0.002	2.365	2.340

[a] Conditions: $[\text{phthalimide}]_0 = 2 \times 10^{-4}$ M, [NaOH] = 0.02 M, 35 °C, $\lambda = 300$ nm and aqueous reaction mixture for each kinetic run contained 2% (v/v) CH_3CN.

[b] $Y_{obs} = k^h w / k_{obs}$ with $10^4\ k^h w = 24.6\ s^{-1}$.

[c] Calculated from Eqn. (4) with $(1 - \text{c.m.c.}K_s) = 0.99$ and $K_s = 7.5\ M^{-1}$.

[d] Error limits are standard deviations.

(23) dodecyl ether [$C_{12}H_{25}(OCH_2CH_2)_{23}OH$ (Brij 35 or $C_{12}E_{23}$)] and polyoxyethylene (20) cetyl ether [$C_{16}H_{33}(OCH_2CH_2)_{20}OH$ (Brij 58 or $C_{16}E_{20}$)] were obtained from Fluka or Aldrich and were of the highest commercially available purity. All other chemicals were also of reagent grade. Stock solutions (0.01 M) of PTH were prepared in acetonitrile.

Kinetic measurements. The rate of hydrolysis of PTH, in an alkaline medium, was studied by monitoring the disappearance of reactant (PTH) spectrophotometrically at 300 nm. The details of the kinetic procedure are described elsewhere.[4] All the kinetic runs were carried out under pseudo-first-order kinetic conditions. Pseudo-first-order rate constants (k_{obs}) were calculated from the equation

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

with the non-linear least-squares technique considering E_{app} (apparent molar absorptivity of the reaction mixture) and A_∞ (the absorbance at reaction time $t = \infty$) also as unknown parameters. In Eqn. (1), Abs is the absorbance value at any time t and $[X]_0$ is the initial concentration of PTH. The reactions were carried out for up to 3–8 half-lives and the absorbance data fitted Eqn. (1) well. The molar absorptivities of ionized and non-ionized phthalamic and phthalic acids at 300 nm are very low ($\sim 40\ M^{-1}\ cm^{-1}$).[5] Therefore, $E_{app} \approx E_{PTH}$ at 300 nm because $E_{app} = E_{PTH} - E_P$, where E_{PTH} and E_P represent the molar absorptivity of PTH and products (phthalamic and phthalic acids), respectively. It should be noted that the rate of formation of phthalic acid would not affect the rate of disappearance of PTH (monitored in the present study).

RESULTS AND DISCUSSION

The rate of hydrolysis of PTH, at alkaline pH, obeys the following rate law:

$$\text{rate} = k_{H_2O}[H_2O][SH] + k_{OH}[HO^-][SH] + k'_{OH}[HO^-]S^-] \qquad (2)$$

where SH and S^- represent the non-ionized and ionized forms of PTH, respectively. The value of $k_{H_2O}[H_2O]$ is expected to be $\leq 10^{-7}\ s^{-1}$ and the values of k_{OH} and k'_{OH} are 39 and $38 \times 10^{-4}\ M^{-1}\ s^{-1}$, respectively.[6] The mechanistic details for the rate terms $k_{OH}[HO^-][SH]$ and $k'_{OH}[HO^-]S^-]$ have been discussed elsewhere.[7] The rate term $k_{OH}[HO^-][SH]$ is kinetically indistinguishable from the rate term $k_{H_2O}[H_2O][S^-]$. However, it has been concluded elsewhere[8] that $[HO^-]$-independent hydrolysis of PTH involved the rate law rate = $k_{OH}[HO^-][SH]$. The rate of hydrolysis of PTH was found to be independent of $[HO^-]$ within the $[HO^-]$ range ~0.0025–0.10 M in the absence of micelles.[7]

Effects of $[C_{16}E_{20}]_T$ on k_{obs} for hydrolysis of PTH at 0.02 M NaOH and 35 °C

The hydrolytic cleavage of PTH was studied within a total concentration of $C_{16}H_{33}(OCH_2CH_2)_{20}OH$ ($[C_{16}E_{20}]_T$) ranging from 0.0001 to 0.18 M. Pseudo-first-order rate constants (k_{obs}), E_{app} and A_∞, obtained under such conditions, are summarized in Table 1. The values of k_{obs} showed a monotonic decrease whereas E_{app} remained unchanged with increase in $[C_{16}E_{20}]_T$ from 0.0001 to 0.18 M. The significant increase in A_∞ with increase in $[C_{16}E_{20}]_T$ at ≥ 0.01 M showed the increase in

A_0 (= Abs at $t = 0$) with increase in $[C_{16}E_{20}]_T$ because E_{app} is independent of $[C_{16}E_{20}]_T$ (Table 1). Such an increase in A_0 may be attributed to the increase in the turbidity or microturbidity of micellar solutions with increase in $[C_{16}E_{20}]_T$. It should be noted that the microturbidity, even at 0.18 M $C_{16}E_{20}$ (the highest value of $[C_{16}E_{20}]_T$ attained in the study), was not strong enough to cause the observed data (Abs versus t) to deviate from the fit to Eqn. (1) within a reaction period of seven half-lives. This shows that the intensity of microturbidity (not visible to the naked eye) was not strong enough to cause the observed data (Abs versus t) to deviate from the satisfactory fit to Eqn. (1). The satisfactory fit of the observed data to Eqn. (1) also revealed that the intensity of the microturbidity remained essentially unchanged with progress of the reaction in a single kinetic run.

The rate of hydrolysis of PTH in the aqueous pseudophase should be independent of $[HO^-]$ at 0.02 M NaOH and hence under such conditions HO^- and SH should be reactants. Since the non-ionic micellar affinity of HO^- is very low and the mechanism of a reaction remains generally unchanged with change in the reaction medium from aqueous to micelles, the micellar-mediated hydrolysis of PTH may also be expected to involve HO^- and SH as reactants. The decrease in k_{obs} with increase in $[C_{16}E_{20}]_T$ may be explained in terms of simple Menger 'enzyme-kinetic' or pseudophase micellar (PM) model:[9]

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

where the subscripts W and M represent aqueous pseudophase and micellar pseudophase, respectively, $k^h{}_W$ and $k^h{}_M$ are pseudo-first-order rate constants for the hydrolysis of PTH in the respective aqueous pseudophase and micellar pseudophase, K_S is the apparent $C_{16}E_{20}$ micellar binding constant of PTH and $[D_n] = [C_{16}E_{20}]_T -$ c.m.c., with c.m.c. representing the critical micelle concentration.

The calculation of $k^h{}_M$ and K_S from Eqn. (3) requires a knowledge of the values of c.m.c. and $k^h{}_W$ under the present experimental conditions. The value of $k^h{}_W$ ($= 24.6 \times 10^{-4}$ s^{-1}) was obtained by carrying out the kinetic run under similar experimental conditions at $[C_{16}E_{20}]_T = 0$. The value of c.m.c. was obtained by an iterative technique which involved the calculation of $k^h{}_M$, K_S and Σd_i^2 (where $d_i = k_{obsi} - k_{calcdi}$, with k_{obsi} and k_{calcdi} representing the respective observed and calculated values of rate constants at the ith $[C_{16}E_{20}]_T$ and the best c.m.c. (~0) value was that at which the Σd_i^2 value was a minimum. It is worth noting that an increase in c.m.c from 0.0 to 4.0×10^{-4} M increased Σd_i^2 from 15.64×10^{-9} to 16.82×10^{-9}, $k^h{}_M$ from $(-2.0 \pm 2.0) \times 10^{-4}$ to $(-1.7 \pm 2.0) \times 10^{-4}$ s^{-1} and K_S from 6.3 ± 0.8 to 6.5 ± 0.8 M^{-1}. It is therefore clear that an increase in c.m.c. from 0.0 to 4.0×10^{-4} mol dm^{-3} did not change Σd_i^2, $k^h{}_M$ and K_S significantly and hence an appreciable error in c.m.c. (~0) is not a setback for data analysis. The reported values of c.m.c. for $C_{12}E_{12}$ and $C_{16}E_{12}$ are 1.4×10^{-4} and 2.3×10^{-6} M, respectively, obtained in the absence of any ionic or non-ionic solute.[10] The calculated value of $k^h{}_M$ $(-2.0 \pm 2.0) \times 10^{-4}$ s^{-1} is negative (which is physically/chemically meaningless and not different from zero) and is associated with an extremely high standard deviation. Hence the $k^h{}_M$ value is statistically unreliable, which could be due to the fact that $k^h{}_M K_S [D_n] \ll k^h{}_W$ under the experimental conditions imposed. This inequality ($k^h{}_M K_S [D_n] \ll k^h{}_W$) reduced Eqn. (3) to

$$k^h{}_W / k_{obs} = (1 - \text{c.m.c.}K_S) + K_S[C_{16}E_{20}]_T \tag{4}$$

The least-squares calculated value of K_S and $(1 - \text{c.m.c.}K_S)$ are 7.5 ± 0.2 M^{-1} and 0.99 ± 0.02, respectively. The fitting of observed data to Eqn. (4) is evident from the standard deviations associated with the calculated parameters, K_S and $(1 - \text{c.m.c.}K_S)$, and from the calculated values of $k^h{}_W/k_{obs}$ (Table 1). It may be noted that the value of K_S is only 16% larger than that (6.3 M^{-1}) calculated from Eqn. (3) with c.m.c. = 0. Thus, a change in c.m.c. from 0 to 1.33×10^{-3} M [obtained from the calculated values of $(1 - \text{c.m.c.}K_S)$ of 0.99 and K_S of 7.5 M^{-1}] did not change the K_S value significantly. The fraction of micellar-bound PTH is 0.6 at 0.18 M $C_{16}E_{20}$ with $K_S = 7.5$ M^{-1} and $k^h{}_M = 0$. It is worth mentioning that the non-linear least-squares technique used in the calculation of $k^h{}_M$ and K_S from Eqn. (3) is a simulation process where it is 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 technique gives an exact solution of Eqn. (4) and hence there are no possible compensatory errors in the calculated values of K_S and $(1 - \text{c.m.c.}K_S)$.

The insignificant rate of hydrolysis of PTH in the micellar pseudophase compared with that in the aqueous pseudophase may be attributed to (i) the extremely low concentration of hydroxide ions in the vicinity of micellized PTH molecules, (ii) different average locations of HO^- and SH molecules in the micellar pseudophase and (iii) the micellar medium polarity effect. Similarly, the rate of non-ionic micellar-mediated hydrolysis of securinine was negligible compared with its rate of hydrolysis in the aqueous pseudophase.[11] The $C_{16}E_{20}$ micellar binding constant (K_S) for SH is expected to be much larger than that for S^- because of the much higher hydrophilicity of S^- compared with that of SH and in view of the reported values of $C_{12}E_{23}$ micellar binding constants of non-ionized and ionized peracids.[12] The low value of K_S (7.5 M^{-1}) indicates that $[SH]_T \approx 0$ under the experimental conditions imposed.

Table 2. Values of k_{obs}, E_{app} and A_∞ calculated from Eqn. (1) for alkaline hydrolysis of PTH at different $[C_{12}E_{23}]_T$[a]

$[C_{12}E_{23}]_T$ (M)	10^3k_{obs} (s^{-1})	E_{app} (M^{-1} cm^{-1})	A_∞
0.0	2.4		
0.00005	2.05 ± 0.08[b]	2240 ± 31[b]	−0.004 ± 0.005[b]
0.0005	2.04 ± 0.08	2245 ± 33	−0.005 ± 0.006
0.005	1.97 ± 0.08	2215 ± 34	0.001 ± 0.006
0.01	2.00 ± 0.08	2270 ± 33	0.010 ± 0.006
0.02	1.90 ± 0.06	2204 ± 27	0.021 ± 0.005
0.03	1.96 ± 0.04	2166 ± 19	0.034 ± 0.003
0.04	2.09 ± 0.05	2102 ± 17	0.082 ± 0.003
0.04	1.65 ± 0.06	2198 ± 28	0.030 ± 0.006
0.05	0.801 ± 0.013	1646 ± 10	0.155 ± 0.002
0.05	0.815 ± 0.010	1633 ± 8	0.158 ± 0.002
0.06	—[c]		
0.08	—[d]		

[a] Conditions: $[\text{phthalimide}]_0 = 2 \times 10^{-4}$ M, [NaOH] = 0.02 M, 35 °C, $\lambda = 300$ nm and aqueous reaction mixture for each kinetic run contained 2% (v/v) CH_3CN.
[b] Error limits are standard deviations.
[c] The rate of hydrolysis became too slow to determine k_{obs} with acceptable precision. The absorbance value remained at 0.492 for nearly 40 min.
[d] The rate of hydrolysis became too slow to determine k_{obs} with acceptable precision. The absorbance value remained at 0.504 for nearly 40 min.

Effects of $[C_{12}E_{23}]_T$ on k_{obs} for hydrolysis of PTH at 0.02 M NaOH and 35 °C

A few kinetic runs were carried out to determine the effects of $[C_{12}E_{23}]_T$ [where $C_{12}E_{23}$ represents $C_{12}H_{25}(OCH_2CH_2)_{23}OH$] on the rate of hydrolysis of PTH within the $[C_{12}E_{23}]_T$ range 5×10^{-5}–0.05 M. The calculated values of k_{obs}, E_{app} and A_∞ are summarized in Table 2. The values of k_{obs} in Table 2 show a sharp decrease with increase in $[C_{12}E_{23}]_T$ from 0.0 to 5×10^{-5} M and then level off until $[C_{12}E_{23}]_T$ reaches 0.04 M. Similar observations have been reported in the reaction of HO^- with *p*-nitrophenyl diphenylphosphate (pNPDPP) in the presence of non-ionic surfactants, $C_{12}E_{23}$ and $C_{12}E_{10}$.[13] The value of k_{obs} at 0.05 M $C_{12}E_{23}$ shows a further sharp decrease whereas at ≥0.06 M $C_{12}E_{23}$ the k_{obs} values became almost zero because under such experimental conditions the Abs values remained unchanged within a reaction period of many hours. The values of E_{app} (= 1630 M^{-1} cm^{-1}) and A_∞ (= 0.16) at 0.05 M $C_{12}E_{23}$ indicate that nearly 30% of PTH molecules are irreversibly trapped in the micellar region where $[HO^-_M] \approx 0$. These observations merely show that the concentration of hydroxide ions in the vicinity of micellized PTH molecules or ions begins to decrease at ~0.05 M $C_{12}E_{23}$ and becomes almost zero at ⩾0.06 M $C_{12}E_{23}$. Although the suggestion that at >0.06 M $C_{12}E_{23}$ all PTH molecules are irreversibly trapped by micelles in the micellar regions where $[HO^-_M] \approx 0$ is an unusual proposal in terms of our existing knowledge of micellar structure and its behavior towards solubilizates, no other explanation(s) can be extended at the moment. Curiously, such observations were not detected with $C_{16}E_{20}$ and we do not know the exact reason(s) for such unusual behavior of $C_{12}E_{23}$ micelles.

Although the values of k_{obs}, summarized in Table 2, do not appear to fit to PM model, the values of k_{obs}, obtained within the $[C_{12}E_{23}]_T$ range 5×10^{-5}–0.04 M, were treated with Eqn. (4) with $10^4k^h_W = 24$ s^{-1} and the least-squares calculated values of $(1 - \text{c.m.c.}K_s)$ and K_s

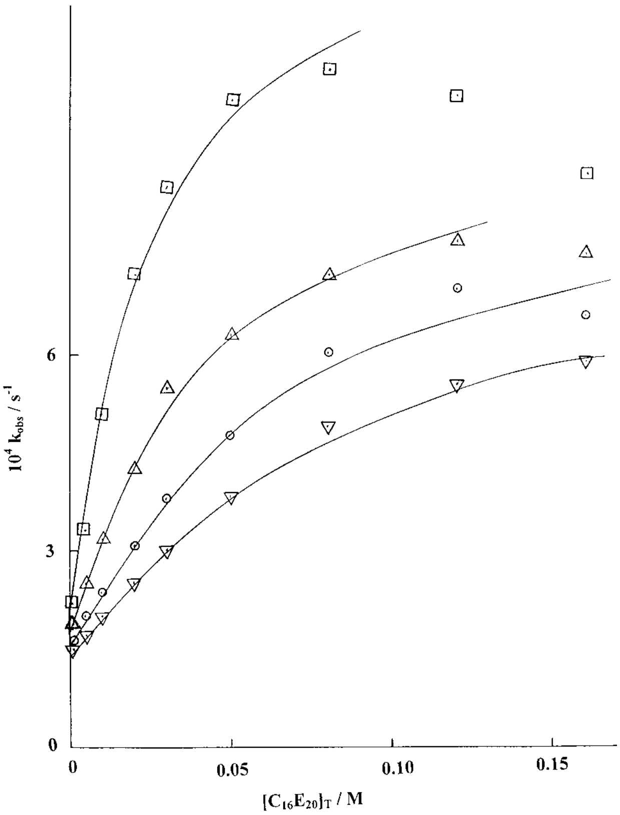


Figure 1. Plots showing the dependence of k_{obs} on $[C_{16}E_{20}]_T$ at 0.006 (□), 0.010 (△), 0.015 (○) and 0.020 M CTABr (▽) in mixed aqueous solvent containing 2% (v/v) CH_3CN, 0.02 M NaOH and 2×10^{-4} M phthalimide. The solid lines are drawn through the least-squares calculated points using Eqn. (6) as described in the text

are 1.16 ± 0.03 and $5.3 \pm 1.6\ \text{M}^{-1}$, respectively. This value of K_S is not very different from that ($7.5\ \text{M}^{-1}$) with $C_{16}E_{20}$ micelles.

It may be noted that the initial absorbance (A_0) increased from 0.444 to 0.504 with increase in $[C_{12}E_{23}]_T$ from 0.005 to 0.08 M and from 0.421 to 0.580 with a similar increase in $[C_{16}E_{20}]_T$. These observations show that the microturbidity is unexpectedly larger with $C_{16}E_{20}$ than that with $C_{12}E_{23}$ micelles under similar experimental conditions.

Effects of $[C_{16}E_{20}]_T$ on k_{obs} for hydrolysis of PTH in the presence of a constant $[CTABr]_T$ at 0.02 M NaOH and 35 °C

A series of kinetic runs were carried out within the $[C_{16}E_{20}]_T$ range 0.001–0.160 M at 0.006 M CTABr. Similarly, observations were made at 0.010, 0.015 and 0.020 M CTABr in the same $[C_{16}E_{20}]_T$ range (0.001–0.160 M). The results are shown as plots of k_{obs} versus $[C_{16}E_{20}]_T$ in Fig. 1. The values of E_{app} were independent of $[C_{16}E_{20}]_T$ and the mean values of E_{app} at 0.006, 0.010, 0.015 and 0.020 M CTABr are 1880 ± 70, 1850 ± 60, 1820 ± 40 and $1820 \pm 50\ \text{M}^{-1}\ \text{cm}^{-1}$, respectively. The values of A_∞ showed a non-linear increase from 0.01 to 0.34 with increase in $[C_{16}E_{20}]_T$ from 0.001 to 0.160 M at a constant $[CTABr]_T$. Similar results were obtained in the absence of CTABr under similar experimental conditions (Table 1). However, the values of A_∞ were essentially independent of $[CTABr]_T$ at a constant $[C_{16}E_{20}]_T$. This shows that the increase in microturbidity caused by the increasing concentration of $C_{16}E_{20}$ is insensitive to the presence of $[CTABr]_T$ within the range 0.006–0.020 M.

Each plot in Fig. 1 shows a continuous decrease in gradient with increase in $[C_{16}E_{20}]_T$ and the gradient becomes almost zero at very high values of $[C_{16}E_{20}]_T$. However, the addition of non-ionic surfactants ($C_{10}E_4$ and $C_{12}PO = C_{12}H_{25}PMe_2O$) to aqueous CTABr inhibited the micellar-mediated reaction of Br^- with methyl naphthalene-2-sulfonate (MeONs),[2] and such inhibitions were attributed to both the increase in the volume of the mixed micellar pseudophase and the decrease in the fractional micellar coverage, β. The increase in k_{obs} with increase in $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ may be explained as described below.

It is known that the voluminous head-group mantle of $C_{12}E_{23}$ and presumably $C_{16}E_{20}$ micelles is associated with a considerable amount of water.[14] The non-ionic micellar affinity of HO^- and Br^- must be much lower than that of S^- (ionized phthalimide) because of the much larger hydrophobicity and lower negative charge density of S^- compared with those of HO^- and Br^-. The CTABr and $C_{16}E_{20}$ micellar binding constants of S^- are 3000 (Ref. 5) and $7\ \text{M}^{-1}$, respectively. The strong cationic micellar binding affinity of S^- is purely electrostatic in nature. The pseudo-first-order rate constant (k^h_W) for the hydrolysis of PTH is $24 \times 10^{-4}\ \text{s}^{-1}$ at 0.02 M NaOH[6] and this value is 11–16-fold larger than k_{obs} at 0.006–0.020 M CTABr in the absence of non-ionic micelles. The increase in $[C_{16}E_{20}]_T$ increases the volume and hence $[H_2O]$ at the cationic micellar surface in mixed cationic–non ionic micelles. Such an increase in the water concentration and hence relative permittivity at the cationic micellar surface decreases the micellar affinity of counterions such as Br^-, HO^- and S^- owing to the decrease in the effectiveness of energetically favorable electrostatic interactions between the cationic head-group and counterions. However, such relative permittivity and dilution effects of addition of $C_{16}E_{20}$ to CTABr micelles make the most hydrophilic ion, HO^-, move first from the cationic micellar surface of the less hydrated region to the relatively more hydrated mixed micellar region including the aqueous pseudophase. Such an effect is expected to decrease k_{obs} compared with the value at $[C_{16}E_{20}]_T = 0$ only if the value of k^h_M is significant and the values of k^h_W and k^h_M are dependent on $[HO^-_W]$. However, the values of k^h_M and k^h_W turned out to be insignificant and independent of $[HO^-]$, respectively, under such conditions.[6] Once the decreasing effects of $[C_{16}E_{20}]_T$ on $[HO^-_M]$ and $[Br^-_M]$ have leveled off then a further increase in $[C_{16}E_{20}]_T$ causes S^- ions to move from the cationic surface of the less hydrated region to the relatively more hydrated mixed micellar region, i.e. poly(oxyethylene) mantle. Since the values of k_{obs} increase with increase in relative permittivity of the reaction medium, the increase in k_{obs} with increase in $[C_{16}E_{20}]_T$ is due to transfer of S^- ions from the less hydrated cationic surface to the more hydrated poly(oxyethylene) mantle region of the mixed micelles.

The occurrence of ion exchange between two different counterions on the ionic micellar surface has been unequivocally ascertained.[15] Although there are a few theoretical models to explain the occurrence of ion exchange, none of them seems to be perfect, at least at quantitative level.[16] The effects of inorganic and organic salts (MX) on the CTABr micellar binding constants (K_S) of ionized phenyl salicylate[17] and phthalimide[6] were found to follow the empirical equation

$$K_S = K_S{}^0/(1 + K_{X/S}[MX]) \qquad (5)$$

where $K_{X/S}$ is an empirical parameter (or constant) whose magnitude is a measure of the ability of X^- to expel another counterion, S^-, from cationic micellar pseudophase to the aqueous pseudophase. Although the decrease in the counterion affinity (which is proportional to β or K_S) of the CTABr micellar surface due to an increase in the concentration of non-ionic surfactants (such as $C_{10}E_4$, $C_{16}E_{20}$ and $C_{12}E_{23}$) is not due to the occurrence of direct ion exchange, the essence of the effect of the concentrations of non-ionic surfactants on β, i.e. the concentration of counterions (such as $[Br^-_M]$), is similar to that of the

Table 3. Values of k and K calculated from Eqn. (6) for alkaline hydrolysis of PTH at different $[CTABr]_T$[a]

Surfactant	$[CTABr]_T$ (M)	$10^4 k_0$ (s^{-1})	$10^4 k$ (s^{-1})	K (M^{-1})	$K_{X/S}$[b] (M^{-1})	$[NIS]_T$[c] (M)	$10^4 k_{obs}$[d] (s^{-1})
$C_{16}E_{20}$	0.006	2.01 ± 0.02[e]	13.6 ± 0.9[e]	38.6 ± 7.0[e]	730	0.08	15.4
	0.010	1.74 ± 0.03	9.97 ± 0.37	24.4 ± 2.60	760	0.12	12.9
	0.015	1.55 ± 0.02	9.80 ± 0.86	12.9 ± 2.9	590	0.12	12.9
	0.020	1.40 ± 0.04	9.19 ± 0.50	9.1 ± 1.1	560		
$C_{12}E_{23}$	0.006	2.01 ± 0.02	20.9 ± 1.7	31.0 ± 4.6		0.03	20.9
	0.010	1.74 ± 0.03	13.7 ± 2.2	23.5 ± 7.0		0.04	18.9
	0.015	1.55 ± 0.02	9.72 ± 1.08	27.3 ± 5.6			
	0.020	1.40 ± 0.04	6.96 ± 2.46	41 ± 32			

[a] Conditions: $[phthalimide]_0 = 2 \times 10^{-4}$ M, [NaOH] = 0.02 M, 35 °C, $\lambda = 300$ nm and aqueous reaction mixture for each kinetic run contained 2% (v/v) CH_3CN.

[b] $K_{X/S} = K(1 + K_S{}^0[CTABr]_T)$, where $K_S{}^0 = 3000\ M^{-1}$.

[c] Minimum optimum concentrations of non-ionic surfactants ($C_{16}E_{20}$ and $C_{12}E_{23}$) at which the maxima appeared in the plots of k_{obs} versus $[NIS]_T$ at different $[CTABr]_T$.

[d] The values of k_{obs} obtained under similar experimental conditions with $[CTABr]_T = 0$ (Tables 1 and 2).

[e] Error limits are standard deviations.

effect of the concentration of X^- ions on $[Br^-{}_M]$, i.e. X^-–Br^- ion exchange. Hence, if it is assumed that the decrease in the CTABr micellar affinity of S^- (i.e. K_S) due to the increase in $[C_{16}E_{20}]_T$ follows Eqn. (5), then Eqns (3) and (5) (with replacement MX by $C_{12}E_{20}$) can lead to

$$k_{obs} = \frac{k_0 + kK[C_{16}E_{20}]_T}{1 + K[C_{16}E_{20}]_T} \tag{6}$$

where $k_0 = (k^h{}_w + k^h{}_M K_S{}^0\ [D_n])/(1 + K_S{}^0\ [D_n])$, $K = K_{X/S}/(1 + K_S{}^0\ [D_n])$ with the empirical definition of $K_{X/S}$ modified to one which states that the magnitude of $K_{X/S}$ is a measure of the ability of $C_{16}E_{20}$ to decrease the cationic micellar affinity of S^- in mixed cationic–non-ionic micelles and $k = k^h{}_W$.

It is apparent from Eqn. (6) that the plot of k_{obs} versus $[C_{16}E_{20}]_T$ should be non-linear at a constant $[CTABr]_T$ provided that $K[C_{16}E_{20}]_T$ is not negligible compared to with unity within the $[C_{16}E_{20}]_T$ range applied in the present study. The observed data, shown graphically in Fig. 1, seem to fit this prediction. The unknown parameters, k and K, were calculated from Eqn. (6) using the non-linear least-squares technique considering k_0 as a known parameter. The values of k_0 at 0.006, 0.010, 0.015 and 0.020 M CTABr were determined by carrying out the kinetic runs under similar experimental conditions with $[C_{16}E_{20}]_T = 0$. The calculated values of k and K at different $[CTABr]_T$ are summarized in Table 3. The fitting of the observed data to Eqn. (6) appears to be satisfactory, as is evident from the standard deviations associated with the calculated parameters (Table 3) and from the plots in Fig. 1 where solid lines are drawn through the calculated data points.

Equation (6) predicts that k_{obs} should be independent of $[C_{16}E_{20}]_T$ at its optimum value where $1 \ll K[C_{16}E_{20}]_T$ and $k_0 \ll kK[C_{16}E_{20}]_T$. However, the plots in Fig. 1 show a decrease in k_{obs} with increase in $[C_{16}E_{20}]_T$ at ~0.08, ~0.12 and ~0.12 M $C_{16}E_{20}$ in the presence of 0.006, 0.010 and 0.015 M CTABr, respectively. These results show that the maxima in the plots of k_{obs} versus $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ occur at a $[C_{16}E_{20}]_T/[CTABr]_T$ ratio of ~9–12. In the presence of a constant $[CTABr]_T$, the optimum concentration of $C_{16}E_{20}$ is the minimum value of $[C_{16}E_{20}]_T$ at which the increasing effect of $[C_{16}E_{20}]_T$ on k_{obs} (compared with k_{obs} in pure CTABr

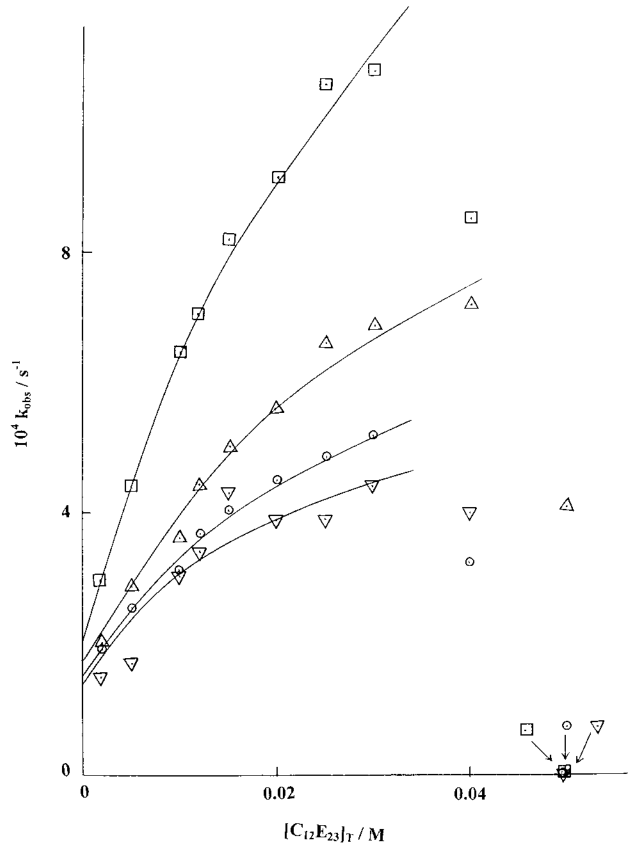


Figure 2. Plots showing the dependence of k_{obs} on $[C_{12}E_{23}]_T$ at 0.006 (□), 0.010 (△), 0.015 (○) and 0.020 M CTABr (▽) in mixed aqueous solvent containing 2% (v/v) CH_3CN, 0.02 M NaOH and 2×10^{-4} M phthalimide. The solid lines are drawn through the least-squares calculated points using Eqn. (6) as described in the text

micelles) is leveled off. A further increase in $[C_{16}E_{20}]_T$ from its optimum value causes a decrease in k_{obs} because the increase in $[C_{16}E_{20}]_T$ decreases k_{obs} compared with k_{obs} in the absence of any micelles, i.e. at $[CTABr]_T = [C_{16}E_{20}]_T = 0$ (Table 1).

The value of k should be equal to $k^h{}_W$ only when the optimum concentration of $C_{16}E_{20}$ makes $[PTH_M] = 0$. However, this can never happen in the present mixed micellar system because of the significant $C_{16}E_{20}$ micellar affinity of phthalimide at 0.02 M NaOH, as is evident from the observed data given in Table 1. The calculated values of k at different $[CTABr]_T$ are not very different from k_{obs} obtained at the corresponding optimum value of $[C_{16}E_{20}]_T$ with $[CTABr]_T = 0$ (Table 3). This shows that the mixed $C_{16}E_{20}$–CTABr micellar system behaves kinetically like pure $C_{16}E_{20}$ micelles above the minimum optimum concentration of $C_{16}E_{20}$ and the validity of Eqn. (6) exists only at or below the minimum optimum concentration of non-ionic surfactant.

The relationship $K = K_{X/S}/(1 + K_S{}^0[D_n])$ indicates that $K \approx K_{X/S}/(1 + K_S{}^0[CTABr]_T)$ because $[D_n] \approx [CTABr]_T$ at $[CTABr]_T \geq 0.006$ mol dm^{-3} as c.m.c. = 2×10^{-4} M under the present experimental conditions.[6] Hence it is apparent that $K(1 + K_S{}^0[CTABr]_T)$ (= $K_{X/S}$) should be constant in view of the empirical definition of $K_{X/S}$. Such calculated values of $K_{X/S}$ at different $[CTABr]_T$, as summarized in Table 3, are considered to be constant within the domain of the complex structural features of the mixed micellar system with a varying $[C_{16}E_{20}]_T/[CTABr]_T$ ratio and the empirical nature of Eqn. (5).

Effects of $[C_{12}E_{23}]_T$ on k_{obs} for hydrolysis of PTH in the presence of a constant $[CTABr]_T$ at 0.02 M NaOH and 35 °C

Several kinetic runs were carried out within the $[C_{12}E_{23}]_T$ range 0.002–0.040 M at 0.006 M CTABr. Similar kinetic runs were carried out at 0.010, 0.015 and 0.020 M CTABr. These observed data (k_{obs} versus $[C_{12}E_{23}]_T$) are shown graphically in Fig. 2. There appears to be a smooth monotonic increase in k_{obs} with increase in $[C_{12}E_{23}]_T$ from 0.002 to ~0.030 M and then the k_{obs} values drop sharply to almost zero at ⩾0.05 M $C_{12}E_{23}$ in the presence of 0.006–0.020 M CTABr (Fig. 2). Similar observations were obtained in the absence of CTABr (Table 2). This unusual effect of $[C_{12}E_{23}]_T$ on k_{obs} is similar to that obtained in the study on the effects of $[C_{12}E_{23}]_T$ on the pK_a of phenyl salicylate in the absence and presence of CTABr micelles.[3]

The initial absorbance (A_0) increased from ~0.37 to ~0.51 with increase in $[C_{12}E_{23}]_T$ from 0.002 to 0.05 M and these values of A_0 remained independent of $[CTABr]_T$ within the range 0.006–0.02 M. As noted earlier, similar observations were obtained in the absence of CTABr. These results show that the microturbidity produced due to the increase in $[C_{12}E_{23}]_T$ is independent of $[CTABr]_T$ within the range 0.006–0.02 M.

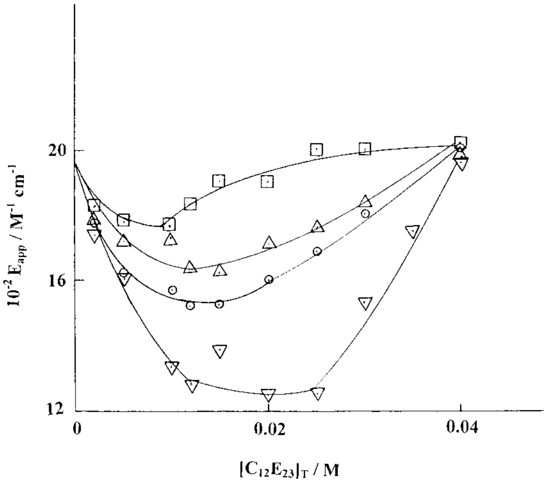


Figure 3. Effects of $[C_{12}E_{23}]_T$ on apparent molar absorptivity of the reaction mixture, E_{app}, at 0.006 (□), 0.010 (△), 0.015 (○) and 0.020 M CTABr (▽) in mixed aqueous solvent containing 2% (v/v) CH_3CN, 0.02 M NaOH and 2×10^{-4} M phthalimide

The values of E_{app} turned out to be independent of both $[C_{16}E_{20}]_T$ and $[CTABr]_T$, as mentioned earlier. However, the values of E_{app} show minima in the plots of E_{app} versus $[C_{12}E_{23}]_T$ at different $[CTABr]_T$ (Fig. 3). The magnitude of the minimum in the plot of E_{app} versus $[C_{12}E_{23}]_T$ decreases with decrease in $[CTABr]_T$ and becomes almost non-existent at 0.006 M CTABr (Fig. 3). It was mentioned in the Experimental section that $E_{app} = E_{PTH} - E_P \approx E_{PTH}$ because $E_{PTH} \gg E_P$ [molar absorptivity of the products(s) phthalamic acid and phthalic acid ~40 M^{-1} cm^{-1} (Ref. 5)]. The plots in Fig. 3 indicate that E_P is no longer negligible compared with E_{PTH}, especially at $[CTABr]_T \geq 0.01$ M and $[C_{12}E_{23}]_T \geq 0.01$ and ≤ 0.03 M.

A few representative plots of Abs. (observed absorbance) versus reaction time are shown in Fig. 4. These plots show a rapid monotonic decrease in Abs. in the initial phase of the reaction followed by a slow monotonic increase with reaction time in the latter phase of the reaction at 300 nm. The visibility of the minima in these plots decreases with decrease in $[C_{12}E_{23}]_T$ at 0.01 M CTABr and there is no minimum in the plot at 0.005 M $C_{12}E_{23}$ (Fig. 4). The minima in the plots in Fig. 4 demonstrate the formation of a stable intermediate product which absorbs significantly at 300 nm. The most probable stable intermediate is phthalic anhydride (PAn) because $E_{PAn} = 1600$ M^{-1} cm^{-1} and $E_{PTA} \approx E_P \approx 40$ M^{-1} cm^{-1}, where PTA and PA represent phthalamic acid and phthalic acid, respectively.[5]

It has been unequivocally ascertained that the aqueous cleavage of phthalamic acid, *N*-substituted phthalamic acids and related amides at pH ≤3 involves the formation of a stable intermediate cyclic anhydride.[6,18–23] Thus, at

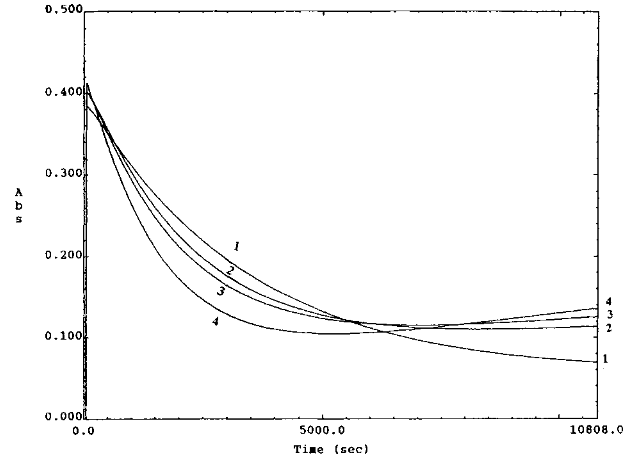


Figure 4. Plots of absorbance (Abs) (of reaction mixture) versus reaction time for hydrolysis of phthalimide at 0.005 (1), 0.012 (2), 0.015 (3) and 0.025 M $C_{12}E_{23}$ (4) in mixed aqueous solvent containing 2% (v/v) CH_3CN, 0.02 M NaOH, 0.01 M CTABr and 2×10^{-4} M phthalimide

pH ≤ 3, the aqueous cleavage of phthalimide (PTH) follows an irreversible consecutive reaction path:

$$\begin{tikzcd}\mathrm{PTH} \arrow[r, "k_1"] & \mathrm{PTA} \arrow[r, "k_2"] \arrow[rr, bend right, "k_2^1"'] & \mathrm{PAn} \arrow[r, "k_3"] & \mathrm{PA}\end{tikzcd} \quad (7)$$

The reported values of k_2 at 48 °C are 20×10^{-4} and 1×10^{-4} s^{-1} at pH 1.5 and 5.0, respectively.[5] The value of k_2 must be much smaller than 1×10^{-5} s^{-1} at 0.02 M NaOH and 35 °C because the reported value of k_2 is 2×10^{-5} s^{-1} at 0.02 M NaOH and 100 °C for *o*-methoxybenzamide.[24] The values of k_2 and k_3 (when PTA = *N*,*N*-dimethylphthalamic acid) changed from 3.2×10^{-4} to 6.4×10^{-4} s^{-1} and from 1.19×10^{-2} to 4.5×10^{-5} s^{-1}, respectively, with increasing CH_3CN content from 2 to 80% (v/v) in mixed aqueous solvents containing 0.005 M HCl at 25 °C.[23a,25] These results show that the presence of PAn in the hydrolysis of PTA can be easily detected spectrophotometrically by using water–aprotic organic solvents containing high contents of organic co-solvent.

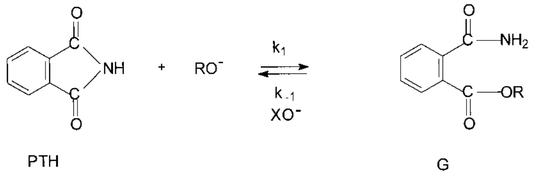
The studies on the effects of $[C_{12}E_{23}]_T$ on the pK_a of phenyl salicylate[3] and on k_{obs} for the hydrolysis of PTH, as described earlier, reveal that the concentration of hydroxide ions in the neighborhood of $C_{12}E_{23}$ micellized PTH molecules is extremely low and it becomes so low at 0.02 M NaOH and at ≥ 0.05 M $C_{12}E_{23}$ that the rate constants, k_{obs}, become almost zero under such conditions (Table 2 and Fig. 2). The anionic form of the product phthalamic acid is expected to have some binding affinity with cationic CTABr micelles. However, an increase in $[C_{12}E_{23}]_T$ at constant $[CTABr]_T$ increases the depletion of hydroxide ions in the vicinity of micellized phthalamic acid and consequently it increases the fraction of non-ionized phthalamic acid in the mixed micellar pseudophase. Extensive and detailed studies on the intramolecular carboxylic acid-catalyzed hydrolysis of phthalamic acid and related compounds reveal that the aqueous cleavage phthalamic acid at pH <7 involves non-ionized phthalamic acid as the reactant while ionized phthalamic acid remains non-reactive.[5,19–21]

An increase in $[C_{12}E_{23}]_T$ at a constant $[CTABr]_T$ increases the fraction of non-ionized phthalamic acid due to depletion of hydroxide ions (i.e. increase in $[H^+]$) in the mixed micellar pseudophase. Such an effect of $[C_{12}E_{23}]_T$ on the pH of the micellar environment of micellized phthalamic acid is bound to decrease its water content compared with that in the aqueous pseudophase. In view of the reported values of k_2 and k_3 [Eqn. (7)] at pH ≥ 1.5 and at different contents of organic co-solvent in mixed aqueous solvent for phthalamic acid[5] and PAn,[25] the respective values of k_2 and k_3 should increase and decrease sharply with increase in $[C_{12}E_{23}]_T$ at a constant $[CTABr]_T$ provided that the pH drops to ~2 and $[H_2O]$ drops to ~10 M under such conditions. The respective absence and presence of a minimum in the plots of Abs. versus reaction time at 0.005 and 0.025 M $C_{12}E_{23}$ (Fig. 4) are the consequence of the effects of $[C_{12}E_{23}]_T$ on the pH of the micellar environment of micellized PTA molecules. It is obvious that at 0.005 M $C_{12}E_{23}$, the pH of the micellar reaction environment remained considerably high and hence the conversion of PTA to PAn in the k_2 step was completely stopped [Eqn. (7)]. However, at 0.025 M $C_{12}E_{23}$, the pH of the micellar reaction environment dropped to a level where there was significant amount of non-ionized PTA which caused the kinetically detectable occurrence of the conversion of PTA to PAn [Eqn. (7)]. It is unlikely that the absence of a minimum in the plot of Abs. versus reaction time at 0.005 M $C_{12}E_{23}$ is due to the presence of the inequality $k_3 \gg k_2$ [Eqn. (7)] because 2×10^{-4} M phenyl salicylate (PSH) remained fully ionized under such conditions[3] and the pK_a of PSH is larger than that of PTA by more than 6 pK units.

The decrease in E_{app} with increase in $[C_{12}E_{23}]_T$ in the initial phase of the plots in Fig. 3 is due to the significance of the formation of PAn in the k_2 step [Eqn. (7)] which absorbs significantly at 300 nm. The respective rate constants k_2 and k_3 are expected to increase slightly and decrease sharply with decrease in $[H_2O]$ in mixed aqueous–acetonitrile solvents.[23a,25] An increase in $[C_{12}E_{23}]_T$ decreases $[H_2O]$ and $[HO^-]$ in the micellar region of micellized PTH and PTA molecules, which in turn increases the fraction of non-ionized micellized PTH and PTA. The increase in the fraction of non-ionized SAH_M (i.e. micellized non-ionized PTA) would slightly increase the rate of formation of PAn_M while decreasing sharply the rate of disappearance of PAn_M. The decrease in E_{app} with increase in $[CTABr]_T$ at a constant $[C_{12}E_{23}]_T$ (Fig. 3) is merely due to the increase in the total concentration of micellized PTH ($[PTH_M]_T = [SH_M] + [S^-_M]$, where SH and S^- represent non-ionized and ionized PTH, respectively) and PTA ($[PTA_M]_T$

$= [SAH_M] + [SA^-{}_M]$, where SAH and SA^- represent non-ionized and ionized PTA, respectively). The increase in E_{app} with increase in $[C_{12}E_{23}]_T$ after the attainment of minima in the plots in Fig. 3 is due merely to the medium effect on E_{PAn} (molar absorptivity of phthalic anhydride, PAn, in Eqn. (7)]. The values of E_{PAn} decreased from 690 to 170 M^{-1} cm^{-1} with increase in the acetonitrile content from 2 to 80% (v/v) in a mixed aqueous solvent at 310 nm.[25] Hence these results show indirectly the depletion of water molecules from the micellar environment of micellized PTA.

The hydroxyl groups of $C_{12}E_{10}$ [$=C_{12}H_{25}(OCH_2CH_2)_{10}OH$] and $C_{12}E_{23}$ have been shown to react with 2,4-dinitrochlorobenzene to form a nucleophilic product ether in the presence of 0.15 M KOD and 0.1 M non-ionic surfactant C_mE_n where the rate of ether product formation was much faster in $C_{12}E_{10}$ micelles than in $C_{12}E_{23}$ micelles.[13] However, such an ether product formation was not observed with *p*-nitrophenyl diphenylphosphate under similar experimental conditions.[13] Hence it seems possible that the presence of 0.01–0.03 M NaOH in $C_{12}E_{23}$ or $C_{16}E_{20}$ micellar solution might cause ionization of hydroxyl groups of these non-ionic surfactants, which might act as a nucleophile in its reaction with PTH. Although the apparent concentration of ionized $C_{12}E_{23}$ or $C_{16}E_{20}$ surfactant should be extremely low in the presence of 0.01–0.03 M NaOH and <0.2 M $C_{12}E_{23}$ or $C_{16}E_{20}$, because the effective or local concentrations of these anionic groups at the micellar surface may be considerably high and methoxide ion reacts nearly 60-fold faster than hydroxide ion with carbonyl carbon of esters,[26] the probable reaction between the ionized hydroxyl group of $C_{12}E_{23}$ or $C_{16}E_{20}$ surfactant and PTH may be as shown in Scheme 1. However, it has been shown elsewhere[27] that $k_{-1}/k_1 > 10^3$ for the reaction of methoxide ion with PTH owing to occurrence of an intramolecular nucleophilic addition–elimination mechanism in the k_{-1} step.[28] Hence it is apparent that even if the reaction in Scheme 1 is kinetically significant, the amount of AE would be negligible compared with that of PTH during the aqueous cleavage of PTH. It should also be noted that the molar absorptivity of AE (E_{AE}) should be similar to that of PTA ($E_{PTA} \approx 40$ M^{-1} cm^{-1}).



$XO^- = HO^-$ and RO^-

$R = C_{12}H_{25}(OCH_2CH_2)_{23}$— or $C_{16}H_{33}(OCH_2CH_2)_{20}$—

G = PTA if R = H

= AE if R = R

Scheme 1

Although the data are not sufficient to carry out a detailed kinetic analysis of the formation of PAn [Eqn. (7)], we attempted to fit the observed data for plot 4 in Fig. 4 (as shown in Table 4, where there is a maximum change in absorbance in the final phase of the reaction) to Eqn. (8), which is derived from the reaction scheme in Eqn. (7) with the conceivable conditions that $k_2 \gg k_3$ and k'_2:[23,29]

$$\mathrm{Abs} = E_{PTH}[X]_0 \exp(-k_1 t)$$

$$+ E_{PAn}[X]_0 \left\{ 1 + \frac{1}{k_1 - k_2} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \right\}$$

$$+ A_\infty \tag{8}$$

and $E_{PTA} \ll E_{PTH}$ and E_{PAn} at 300 nm.[5] The non-linear least-squares fit of the observed data (Table 4) to Eqn. (8) was carried out by considering k_1, k_2 and A_∞ as unknown parameters at the given values of E_{PTH} and E_{PAn}. The calculated values of least-squares Σd_i^2 (where $d_i = \mathrm{Abs}_i - \mathrm{Abs}_{calcd\,i}$) indicate that the best fit is at $E_{PTH} = 1950$ M^{-1} cm^{-1} and $E_{PAn} = 850$ M^{-1} cm^{-1}. However, a change in E_{PAn} from 850 to 600 M^{-1} cm^{-1} only slightly affected the percentage residual errors [$RE = 100(\mathrm{Abs}_i - \mathrm{Abs}_{calcd\,i})/\mathrm{Abs}_i$], as is evident from Table 4.

The calculated value of k_1 (5.84×10^{-4} s^{-1}) is similar to that (5.51×10^{-4} s^{-1}) calculated from Eqn. (1) (with $k_{obs} = k_1$) considering the Abs values within the reaction time range 98–2100 s (Table 4). The value of k_2 (8.7×10^{-5} s^{-1}) is nearly half of the corresponding value (20×10^{-5} s^{-1}) obtained in the absence of micelles at 0.024 M HCl and 70% (v/v) CH_3CN in mixed aqueous solvent.[23b] Although the calculated value of E_{PAn} is not so certain, an approximate value of $E_{PAn} = 750$ M^{-1} cm^{-1} is nearly half of that (1600 M^{-1} cm^{-1}) obtained at 300 nm in pure aqueous solvent.[5] The value of E_{PAn} at 310 nm reduced by nearly half with increase in the CH_3CN content from 2 to 70% (v/v) at 0.027 M HCl.[23c] Thus, the best fit values of k_2 (8.7×10^{-5} s^{-1}) and E_{PAn} ($\sim$750 M^{-1} cm^{-1}) show that the formation of PAn from PTA occurs in the mixed micellar environment of acidic pH and a low water concentration compared with that in the aqueous pseudophase.

The rates of hydrolysis of PTH strictly followed a first-order rate law for reaction periods of ~3–7 half-lives even for those kinetic runs (carried out at $[C_{12}E_{23}]_T > 0.005$ M and $[CTABr]_T > 0.01$ M) where the detectable formation of PAn was evident from the calculated values of E_{app}. However, the values of k_{obs} [$= k_1$ in Eqn. (7)] for these kinetic runs may be slightly augmented by the occurrence of the k_2 step [Eqn. (7)] in the latter phase of the reactions.

The pseudo-first-order rate constants (k_{obs}) for the hydrolysis of PTH, obtained at different values of

Table 4. Observed absorbance (Abs) versus reaction time (*t*) for alkaline hydrolysis of PTH at 300 nm[a]

Time (s)	Abs	$\mathrm{Abs_{calcd}}$[b]	RE[c]	$\mathrm{Abs_{calcd}}$[d]	RE[c]	$\mathrm{Abs_{calcd}}$[e]	RE[c]
98	0.406	0.408	−1	0.412	−1	0.410	−1
294	0.372	0.371	0	0.371	0	0.371	0
476	0.341	0.339	0	0.338	1	0.338	1
672	0.310	0.309	0	0.307	1	0.307	1
882	0.280	0.280	0	0.277	1	0.278	1
1106	0.252	0.253	0	0.250	1	0.251	1
1386	0.221	0.228	−1	0.221	0	0.222	0
1708	0.193	0.194	0	0.194	0	0.195	−1
2100	0.166	0.165	1	0.169	−1	0.167	−1
2800	0.135			0.138	−2	0.137	−2
5306	0.105			0.108	−2	0.105	0
8400	0.119			0.119	0	0.119	0
10808	0.136			0.131	4	0.135	1
$10^4\ k_{\mathrm{obs}}\ (\mathrm{s^{-1}}) = 5.51 \pm 0.25$[f]							
$E_{\mathrm{app}}\ (\mathrm{M^{-1}\ cm^{-1}}) = 1923 \pm 45$							
$A_\infty = 0.044 \pm 0.010$							
$10^4\ k_1\ (\mathrm{s^{-1}}) = 5.98 \pm 0.14$[f]		5.93 ± 0.13[f]		5.88 ± 0.11[f]	5.84 ± 0.10[f]	6.16 ± 0.17[f]	
$10^5\ k_2\ (\mathrm{s^{-1}}) = 14.4 \pm 1.2$		12.8 ± 0.9		10.4 ± 0.6	8.70 ± 0.40	11.4 ± 1.0	
$A_\infty = 0.044 \pm 0.03$		0.043 ± 0.003		0.042 ± 0.002	0.042 ± 0.002	0.054 ± 0.003	
$10^5 \Sigma d_i^2 = 11.837$		9.639		7.187	6.063	13.480	
$E_{\mathrm{PTH}}\ (\mathrm{M^{-1}\ cm^{-1}}) = 1950$		1950		1950	1950	1900	
$E_{\mathrm{PAn}}\ (\mathrm{M^{-1}\ cm^{-1}}) = 600$		650		750	850	600	

[a] Conditions: $[\text{phthalimide}]_0 = 2 \times 10^{-4}$ M, [NaOH] = 0.02 M, 35 °C and aqueous reaction mixture for each kinetic run contained 2% (v/v) $\mathrm{CH_3CN}$.

[b] Calculated from Eqn. (1) with $10^4\ k_{\mathrm{obs}} = 5.51\ \mathrm{s^{-1}}$, $E_{\mathrm{app}} = 1923\ \mathrm{M^{-1}\ cm^{-1}}$ and $A_\infty = 0.044$.

[c] RE = 100 $(\mathrm{Abs}_i - \mathrm{Abs}_{\mathrm{calcd}i})/\mathrm{Abs}_i$.

[d] Calculated from Eqn. (8) with $10^4\ k_1 = 5.98\ \mathrm{s^{-1}}$, $10^5\ k_2 = 14.4\ \mathrm{s^{-1}}$, $A_\infty = 0.044$, $E_{\mathrm{PTH}} = 1950\ \mathrm{M^{-1}\ cm^{-1}}$ and $E_{\mathrm{PAn}} = 600\ \mathrm{M^{-1}\ cm^{-1}}$.

[e] Calculated from Eqn. (8) with $10^4\ k_1 = 5.84\ \mathrm{s^{-1}}$, $10^5\ k_2 = 8.70\ \mathrm{s^{-1}}$, $A_\infty = 0.042$, $E_{\mathrm{PTH}} = 1950\ \mathrm{M^{-1}\ cm^{-1}}$ and $E_{\mathrm{PAn}} = 850\ \mathrm{M^{-1}\ cm^{-1}}$.

[f] Error limits are standard deviations.

$[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ and at a constant value of $[\mathrm{CTABr}]_\mathrm{T}$, appeared to fit Eqn. (6) (with $\mathrm{C_{16}E_{20}}$ replaced by $\mathrm{C_{12}E_{23}}$), as is evident from the plots in Fig. 2 where solid lines are drawn through the calculated data points. The non-linear least-squares calculated values of the unknown parameters *k* and *K* at different $[\mathrm{CTABr}]_\mathrm{T}$ are summarized in Table 3. The calculated values of *k* and *K* at $[\mathrm{CTABr}]_\mathrm{T} \geq 0.015$ M may not be reliable because of the uncertainties associated with k_{obs} values, obtained at $[\mathrm{C_{12}E_{23}}]_\mathrm{T} \geq 0.01$ and ≤ 0.03 M $\mathrm{C_{12}E_{23}}$ at a constant $[\mathrm{CTABr}]_\mathrm{T}$, possibly owing to a significant incursion of the k_2 step [Eqn. (7)] under such conditions, as pointed out earlier. Another possible source for the unreliability of the calculated values of *k* and *K*, especially at $[\mathrm{CTABr}]_\mathrm{T} \geq 0.01$ M, is the lack of the sufficient data points in the region of the k_{obs}–$[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ profiles where rate constants k_{obs} are almost independent of $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$. It is not possible to obtain k_{obs} at $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ where the k_{obs} values are almost independent of $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ because under such conditions k_{obs} become almost zero owing to the unusual effect of $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ on pH.

The values of *k* and *K* are relatively more reliable at 0.006 M CTABr and it is interesting to note that the value of *k* ($20.9 \times 10^{-4}\ \mathrm{s^{-1}}$) is similar to k_{obs} ($19.6 \times 10^{-4}\ \mathrm{s^{-1}}$) at $[\mathrm{C_{12}E_{23}}]_\mathrm{T} = 0.03$ M and $[\mathrm{CTABr}]_\mathrm{T} = 0$. This shows that the mixed $\mathrm{C_{12}E_{23}}$–CTABr micellar system behaves kinetically like pure $\mathrm{C_{12}E_{23}}$ micelles at the minimum optimum concentration of $\mathrm{C_{12}E_{23}}$, a feature similar to the mixed $\mathrm{C_{16}E_{20}}$–CTABr micellar system. The value of *K* ($31.0\ \mathrm{M^{-1}}$) is also not significantly different from that ($38.6\ \mathrm{M^{-1}}$) for $\mathrm{C_{16}E_{20}}$ under similar experimental conditions (Table 3).

CONCLUSION

It appears that the observed data for the rate of alkaline hydrolysis of PTH in the presence of $\mathrm{C_{16}E_{20}}$ micelles follow the pseudophase micellar (PM) model but similar data in the presence of $\mathrm{C_{12}E_{23}}$ do not strictly follow the PM model. The most unusual observation is the depletion of hydroxide ions and water molecules from the $\mathrm{C_{12}E_{23}}$ micellar environment of micellized PTH molecules and consequently irreversible trapping of PTH and its hydrolysis product PTA by micelles at higher concentrations of $\mathrm{C_{12}E_{23}}$. The presence of CTABr (0.006–0.020 M) has little or no influence on the unusual effect of $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ on the pH of the micellar environment of micellized solubilizates. Such characteristic behavior of non-ionic micelles in the absence and presence of CTABr surfactant has not been observed with $\mathrm{C_{16}E_{20}}$ micelles. The explanation for such unusual behavior of $\mathrm{C_{12}E_{23}}$ micelles may perhaps be found in a study on the structural details of such micelles under various conditions.

Acknowledgement

The authors thank the National Scientific Research Development Council of Malaysia under the IRPA program for financial support (Grant No. 09-02-03-0785).

REFERENCES

1. Rubingh DN, Bauer M. *ACS Symp. Ser.* 1992; **501**: 210–233.
2. Blasko A, Bunton CA, Toledo EA, Holland PM, Nome F. *J. Chem. Soc., Perkin Trans. 2* 1995; 2367–2373, and references cited therein.
3. Khan MN, Arifin Z, Yusoff MR, Ismail E. *J. Colloid Interface Sci.* 1999; **220**: 474–476.
4. Khan MN. *J. Chem. Soc., Perkin Trans. 2* 1990; 435–444.
5. Blackburn RAM, Capon B, McRitchie AC. *Bioorg. Chem.* 1977; **6**: 71–78.
6. Khan MN, Arifin Z. *J. Chem. Soc., Perkin Trans. 2* 2000; 2503–2510.
7. Khan MN. *Int. J. Chem. Kinet.* 1987; **19**: 143–153; Khan MN. *J. Pharm. Biomed. Anal.* 1989; **7**: 685–691.
8. Khan MN. *Int. J. Chem. Kinet.* 1991; **23**: 567–579.
9. (a) Menger FM, Portnoy CA. *J. Am. Chem. Soc.* 1967; **89**: 4698–4703; (b) Bunton CA. *Catal. Rev. Sci. Eng.* 1979; **20**: 1–56.
10. Huibers PDT, Lobanov VS, Katritzky AR, Shah DO, Karelson M. *Langmuir* 1996; **12**: 1462–1470.
11. Lajis NH, Khan MN. *J. Phys. Org. Chem.* 1998; **11**: 209–215.
12. Davies DM, Gillitt ND, Paradis PM. *J. Chem. Soc., Perkin Trans. 2* 1996; 659–666.
13. Bunton CA, Foroudian HJ, Gillitt ND, Whiddon CR. *Can. J. Chem.* 1998; **76**: 946–954.
14. (a) Phillies GDJ, Stott J, Ren SZ. *J. Phys. Chem.* 1993; **97**: 11563–11568; (b) Streletzky K, Phillies GDJ. *Langmuir* 1995; **11**: 42–47.
15. (a) Magid LJ, Han Z, Warr GG, Cassidy MA, Butler PD, Hamilton WA. *J. Phys. Chem. B* 1997; **101**: 7919–7927; (b) Bachofer SJ, Simonis U. *Langmuir* 1996; **12**: 1744–1754; (c) Cuccovia IM, da Silva IN, Chaimovich H. *Langmuir* 1997; **13**: 647–652; (d) Cuccovia IM, Agostinho-Neto A, Wendel CMA, Chaimovich H, Romsted LS. *Langmuir* 1997; **13**: 5032–5035; (e) Menger FM, Williams DY, Underwood AL, Anacker EW. *J. Colloid Interface Sci.* 1982; **90**: 546–548; (f) Gamboa C, Sepulveda L, Soto R. *J. Phys. Chem.* 1981; **85**: 1429–1434.
16. Bunton CA. In *Surfactants in Solution*, vol. 11, Mittal KL, Shah DO (eds). Plenum Press: New York, 1991; 17–40.
17. (a) Khan MN. *J. Org. Chem.* 1997; **62**: 3190–3193; (b) Khan MN, Arifin Z, Ismail E, Ali SFM. *J. Org. Chem.* 2000; **65**: 1331–1334; (c) Khan MN, Arifin Z, Ismail E, Ali SFM. *Colloids Surf. A* 2000; **161**: 381–389; (d) Khan MN, Yusoff MR. *J. Phys. Org. Chem.* 2001; **14**: 74–80.
18. (a) Bender ML. *J. Am. Chem. Soc.* 1957; **79**: 1258–1259; (b) Bender ML, Chow-L, Chloupek F. *J. Am. Chem. Soc.* 1958; **80**: 5380–5284.
19. (a) Kirby AJ, McDonald RS, Smith CR. *J. Chem. Soc., Perkin Trans. 2* 1974; 1495–1504; (b) Aldersley MF, Kirby AJ, Lancaster PW, McDonald RS, Smith CR. *J. Chem. Soc., Perkin Trans. 2* 1974; 1487–1495.
20. Hawkins MD. *J. Chem. Soc., Perkin Trans. 2* 1976; 642–647.
21. Kluger R, Lam C-H. *J. Am. Chem. Soc.* 1975; **97**: 5536–5540; 1978; **100**: 2191–2197.
22. Menger FM, Ladika M. *J. Am. Chem. Soc.* 1988; **110**: 6794–6796.
23. (a) Khan MN. *Indian J. Chem.* 1993; **32A**: 387–394; (b) Khan MN. *J. Org. Chem.* 1996; **61**: 8063–8068; (c) Khan MN. *J. Phys. Org. Chem.*, 1998; **11**: 216–222.
24. Bunton CA, Nayak B, O'Connor C. *J. Org. Chem.* 1968; **33**: 572–575.
25. Khan MN. *Indian J. Chem.* 1993; **32A**: 395–401.
26. (a) Hupe DJ, Jencks WP. *J. Am. Chem. Soc.* 1977; **99**: 451–464; (b) Khan MN, Gleen PC, Arifin Z. *Indian J. Chem.* 1996; **35A**: 758–765.
27. Khan MN. *Int. J. Chem. Kinet.* 2001; **33**: 29–40.
28. Shafer JA, Morawetz H. *J. Org. Chem.* 1963; **28**: 1899–1901.
29. Al-Lohedan H, Bunton CA, Mhala MM. *J. Am. Chem. Soc.* 1982; **104**: 6654–6660.