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# Effects of non-ionic and mixed non-ionic–cationic micelles on the rate of aqueous cleavages of phenyl benzoate and phenyl salicylate in alkaline medium

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ABSTRACT: Pseudo-first-order rate constants ($k_{\mathrm{obs}}$) for the hydrolysis of phenyl salicylate (PSH) and phenyl benzoate (PB) in the alkaline medium 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. These results show a characteristic difference between the effects of $[C_{16}E_{20}]_T$ and previously published effects of $[C_{12}E_{23}]_T$ (total concentration of Brij 35) on the rates of aqueous cleavage of PSH and PB at $[C_nE_m]_T$/[NaOH] $\geq \sim 3$. The values of $k_{\mathrm{obs}}$, obtained at different $[C_{16}E_{20}]_T$ in the presence of a constant amount of CTABr, follow the empirical relationship $k_{\mathrm{obs}} = (k_0 + \theta K[C_{16}E_{20}]_T)/(1 + K[C_{16}E_{20}]_T)$, where $\theta$ and $K$ are empirical parameters. The values of $\theta$ are not affected whereas the values of $K$ decrease with increase in $[\mathrm{CTABr}]_T$ in a mixed $C_{16}E_{20}$–CTABr micellar system. The values of $\theta$ at different $[\mathrm{CTABr}]_T$ show that $\theta > k_0$ for hydrolysis of PSH and $\theta < k_0$ for hydrolysis of PB in the presence of 0.01 M NaOH. The effects of $[\mathrm{CTABr}]_T$ on $K$ and $\theta$ are explained in terms of the pseudophase model of micelles coupled with the empirical relationship $K_S = K_S0/(1 + K_{C16E20/S}[C_{16}E_{20}]_T)$. Copyright © 2004 John Wiley & Sons, Ltd.

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

## INTRODUCTION

The study of the effects of pure micelles, formed from cationic, anionic and non-ionic surfactants, on reaction rates has been the subject of great interest for the last 4–5 decades. Most of the kinetic data obtained in these studies have been explained in terms of one of the various proposed micellar models [such as enzyme kinetic type,[1] pseudophase (PP),[2] pseudo-phase ion-exchange (PIE),[3] mass-action,[4] Coulombic[5] and multiple micellar pseudophase (MMPP),[6] micellar kinetic models]. All these micellar models appear to be very approximate and some of them have apparent weaknesses.[5a,7] One of the main reasons for the lack of a perfect micellar model to use in quantitative analysis of kinetic data on micellar-mediated reactions is the incomplete understanding of the fine details of micellar structure.[8] Structural aspects of mixed micelles have been studied theoretically in the last few years,[9] but the fine details of the structure of a mixed micellar system are far less clear than those of a pure micellar system. Kinetic studies on the effects of mixed micelles on reaction rates have been started only recently.[10] Most of the kinetic data on mixed micellar-mediated reactions have been attempted to explain in terms of micellar models used for the pure micellar system.[11] However, it is almost certain that the structural characteristics of mixed micelles, formed from two different surfactants S1 and S2, change from S1 micelle-type to S2 micelle-type as the X values increase from very low to very high where X = [S2]/[S1].[12]

Davies and Foggo[13] explained the observed data on the effects of mixed anionic–non-ionic micelles on the rate of reaction of *m*-chloroperbenzoic acid and iodide in terms of the MMPP model of the micelles. The effects of mixed cationic–non-ionic micelles on the rate of $S_N2$ reactions of $Br^-$ with fully bound sulfonate ester have been explained in terms of the PP micellar model coupled with a factor *R* defined as mole fraction of cationic surfactant.[14] This empirical approach appears to be incapable of explaining the observed data on the effects of mixed $C_{12}E_{23}$–CTABr [where CTABr = cetyltrimethylammonium bromide and $C_{12}E_{23} = C_{12}H_{25}$-$(OCH_2CH_2)_{23}OH$] micelles on aqueous cleavages of phenyl benzoate, phenyl salicylate,[15] 4-nitrophthalimide[16] and phthalimide[17] in alkaline medium.

We have previously reported the effects of pure $C_{12}E_{23}$ and mixed $C_{12}E_{23}$–CTABr micelles on the rates of

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alkaline hydrolysis of $PS^-$ and PB. However, the kinetic data could not be fully explained by any existing kinetic model, because the rate of reaction dropped to almost zero in a narrow range of $[C_{12}E_{23}]_T$. This behaviour of $C_{12}E_{23}$ we called as unusual behaviour of $C_{12}E_{23}$ micelles, and it restricted the attainment of a sufficiently high range of $[C_{12}E_{23}]_T$. However, we could explain the kinetic data obtained in the limited concentration range of pure $C_{12}E_{23}$ micelles in terms of the PP model of micelles. However, the kinetic data obtained in mixed $C_{12}E_{23}$–CTABr micelles did not appear to fit to PP model and, consequently, the observed results were explained only qualitatively.

We proposed the empirical equation $K_S = K_S^0/(1 + K_{X/S}[MX])$ in 1997[22] to explain the effects of inert inorganic salts on rates of methanolysis of $PS^-$. Since then, this empirical equation has been under test through rate studies of micellar-mediated reactions carried out under a variety of reaction conditions. In 2001,[16] this empirical equation was used in a modified form, Eqn (1), coupled with the PP model of micelles to explain the effects of mixed $C_{12}E_{23}$–CTABr micelles on the rates of alkaline hydrolysis of 4-nitrophthalimide.

$$K_S = K_S^0/(1 + K_{C_nE_m/S}[C_nE_m]) \tag{1}$$

where $K_S$ and $K_S^0$ are CTABr micellar binding constants of organic substrate (S) in the presence and absence of $C_nE_m$, respectively, and $K_{C_nE_m/S}$ is an empirical constant whose magnitude is a measure of the ability of the $C_nE_m$ surfactant to change the micellar affinity of S from pure cationic micelle to very close to pure $C_nE_m$ micelle (i.e. to change $K_S$ from $K_S^{\mathrm{CTABr}} \equiv K_S^0$ to $K_S^{C_nE_m}$, where $K_S^{\mathrm{CTABr}}$ and $K_S^{C_nE_m}$ are the CTABr and $C_nE_m$ micellar binding constants of S, respectively).Thus, the value of $K_{C_nE_m/S}$ is expected to depend on the nature of CTABr, $C_nE_m$ and S.

Recently, we studied the effects of pure $C_{12}E_{23}$, $C_{16}E_{20}$ and mixed $C_{12}E_{23}$–CTABr and $C_{16}E_{20}$–CTABr micelles on the rates of alkaline hydrolysis of phthalimide ($PT^-$).[17] The observed unusual behaviour of pure $C_{12}E_{23}$ and mixed $C_{12}E_{23}$–CTABr micelles beyond a certain $[C_{12}E_{23}]/[NaOH]$ ratio prompted us to include another non-ionic $C_{16}E_{20}$ surfactant and to compare the behaviour of both $C_{12}E_{23}$ and $C_{16}E_{20}$ micelles. Unlike $C_{12}E_{23}$ micelles, $C_{16}E_{20}$ micelles showed no unusual behaviour even up to 0.18 M $C_{16}E_{20}$ at 0.02 M NaOH, which is much higher than 0.015 M $C_{12}E_{23}$ at 0.02 M NaOH, where a sudden change in the micellar effect on reaction rate occurred. The effects of $[C_{16}E_{20}]_T$ on $k_{obs}$ followed the PP model of micelles within the $[C_{16}E_{20}]_T$ range 0.0–0.18 M. The effects of mixed $C_{16}E_{20}$–CTABr micelles on $k_{obs}$ were explained in terms of Eqn (1) coupled with the PP model of micelles. However, again, the observed data on the effects of $C_{12}E_{23}$ and mixed $C_{12}E_{23}$–CTABr micelles could not be explained in terms of PP model and Eqn (1) coupled with the PP model of micelles within a wide concentration range of micelles at 0.02 M NaOH.

It is well known that micellar structure, behaviour and characteristics are sensitive to the structural features and nature of additives. Although both phthalimide and phenyl salicylate exist in the anionic form at > 0.005 M NaOH, the hydrophobic and structural difference caused $PS^-$ and $PT^-$ to have very different CTABr and $C_{16}E_{20}$ micellar binding constants. Kinetic observations also showed a deeper micellar penetration of $PS^-$ than $PT^-$. It is logical that the generality of the empirical Eqn (1) and the conceivable chemical meaning of empirical constant, $K_{\mathrm{C}n\mathrm{E}_m}/\mathrm{S}$ or $K_{X/S}$, should be studied under variety of reaction conditions. This is the driving force that led us to carry out the present study and the observed results and their probable explanation(s) are described here.

## EXPERIMENTAL

### Materials

Reagent-grade chemicals such as phenyl salicylate (PSH), phenyl benzoate (PB), cetyltrimethylammonium bromide (CTABr) 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 and Aldrich and were of the highest commercially available purity. All other chemicals used were also of reagent grade. Stock solutions (0.01 M) of PSH and PB were prepared in acetonitrile.

### Kinetic measurements

The rate of hydrolysis of PSH, in an alkaline medium, was studied by monitoring the disappearance of reactant (PSH) spectrophotometrically at 350 nm. The rate of alkaline hydrolysis of PB was studied spectrophotometrically by monitoring the appearance of product (phenolate ion) at 290 nm. The details of the kinetic procedure have been described elsewhere.[18] All the kinetic runs were carried out under pseudo-first-order kinetic conditions. Pseudo-first-order rate constants ($k_{obs}$) were calculated from either Eqn (2) (if disappearance of reactant was monitored periodically) or Eqn (3) (if appearance of product was monitored periodically):

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

$$A_{obs} = E_{app}[X]_0[1 - \exp(-k_{obs}t)] + A_0 \tag{3}$$

by the use of the non-linear least-squares technique considering $E_{app}$ (apparent molar absorptivity of the reaction mixture) and $A_\infty$ (the absorbance at reaction time $t = \infty$) or $A_0$ (the absorbance at reaction time $t = 0$) also as unknown parameters. In Eqns (2) and (3), $A_{obs}$ is the absorbance value at any time *t* and $[X]_0$ is the initial concentration of PSH or PB. The reactions were carried out for up to 3–8 half-lives and the absorbance data ($A_{obs}$ versus *t*) fitted well Eqn (2) or (3).

## RESULTS AND DISCUSSION

### Effects of $[C_{16}E_{20}]_T$ on $k_{obs}$ for hydrolysis of $PS^-$ at 35 °C

A few kinetic runs were carried out within the total $C_{16}E_{20}$ [$= C_{16}H_{33}(OCH_2CH_2)_{20}OH$] concentration ($[C_{16}E_{20}]_T$) range $2 \times 10^{-4}$–0.18 M at 0.05 M NaOH and 35 °C in mixed aqueous solvent containing 2% (v/v) $CH_3CN$ and $2 \times 10^{-4}$ M phenyl salicylate. Similar observations were also obtained at 0.01 M NaOH. The calculated parameters, $k_{obs}$ and $A_\infty$, at both 0.01 and 0.05 M NaOH are shown graphically in Figs 1 and 2, respectively. Non-ionized (PSH) and ionized ($PS^-$) phenyl salicylate showed non-detectable and strong absorption, respectively, at 350 nm.[18] The hydrolysis products, phenol, salicylic acid, phenolate and salicylate ions, have essentially no absorption at 350 nm.[18] Hence, $E_{app}$ and $A_\infty$ must be equal to nearly $E_{PS^-}$ (molar absorptivity of $PS^-$) and zero, respectively, at different $[C_{16}E_{20}]_T$. However, the values of $A_\infty$ seem to be ~0 only at < 0.01 M $C_{16}E_{20}$ and the $A_\infty$ values show a modest but definite increase with increase in $[C_{16}E_{20}]_T$ at ≥ 0.01 M $C_{16}E_{20}$ followed by constancy of $A_\infty$ within the $[C_{16}E_{20}]_T$ range 0.06–0.18 M at both 0.01 and 0.05 M NaOH (Fig. 2). The values of $E_{app}$ remained essentially constant within the $[C_{16}E_{20}]_T$ range $2 \times 10^{-4}$–0.18 M, which revealed an increase in the initial absorbance ($A_0 = A_{obs}$ at reaction time $t = 0$) values with increase in $[C_{16}E_{20}]_T$ at ≥ 0.01 M $C_{16}E_{20}$ because $A_0 = E_{app}[X]_0 + A_\infty$. Such an increase in $A_0$ at high values of $[C_{16}E_{20}]_T$ may be attributed to the development of micro-turbidity under such conditions.[17] This micro-turbidity appeared to be independent of wavelength, as is evident from the results observed on hydrolysis of phthalimide[17] and phenyl benzoate, as described later.

The values of $E_{app}$ were found to be independent of $[C_{16}E_{20}]_T$ within the range $2 \times 10^{-4} - 0.18$ M at 0.01 M NaOH. However, the value of $E_{app}$ became almost zero at 0.03 M $C_{12}E_{23}$ and 0.01 M NaOH.[15] These observations show the characteristic behaviour of $C_{12}E_{23}$ [$C_{12}E_{23} = C_{12}H_{25}(OCH_2CH_2)_{23}OH$], which is different from that of $C_{16}E_{20}$.

The values of $k_{obs}$ (Fig. 1) show a monotonic decrease with increase in $[C_{16}E_{20}]_T$, which could be explained quantitatively in terms of the PP model of micelles.[1,2] It can easily be shown that the observed rate law and the rate law derived based on the reaction mechanism in terms of the PP model of micelles can lead to the equation

$$k_{obs} = \frac{k_W^h + k_M^h K_S\,[D_n]}{1 + K_S\,[D_n]} \tag{4}$$

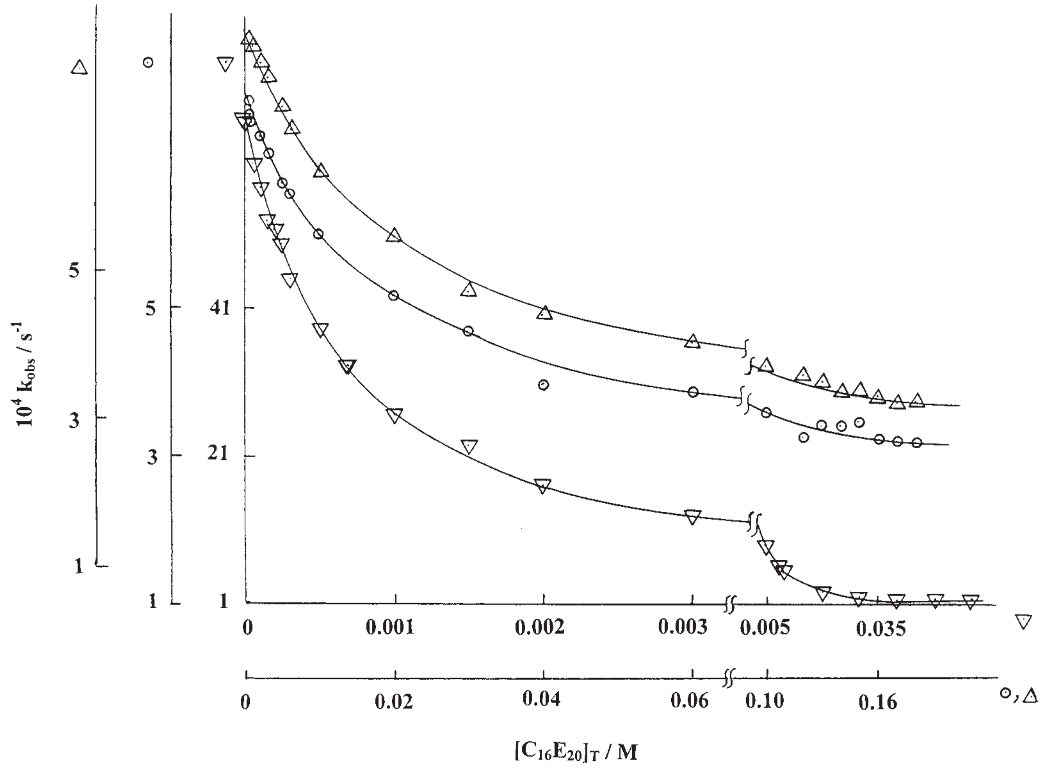

**Figure 1.** Plots of $k_{obs}$ versus $[C_{16}E_{20}]_T$ for hydrolysis of $PS^-$ at 0.01 M NaOH (○) and 0.05 M NaOH (△) and for hydrolysis of PB at 0.01 M NaOH (▽). Solid lines are drawn through the calculated data points as described in the text

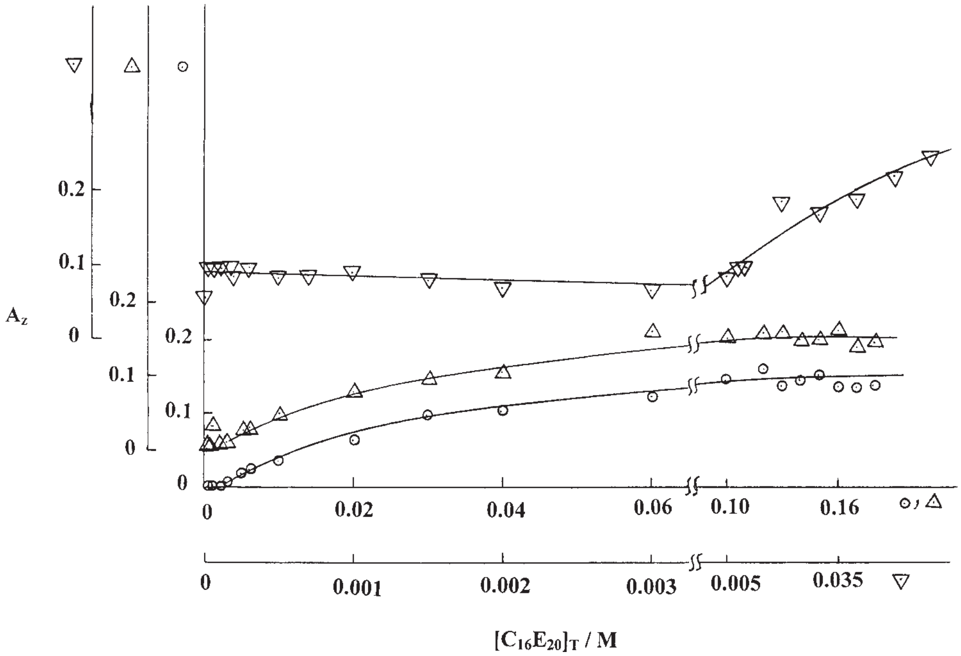

**Figure 2.** Plots of $A_z$ versus $[C_{16}E_{20}]_T$ where $A_z = A_\infty$ for hydrolysis of $PS^-$ at 0.01 M NaOH (○) and 0.05 M NaOH (△) and $A_z = A_0$ for hydrolysis of PB at 0.01 M NaOH (▽)

where the subscripts W and M represent aqueous pseudophase and micellar pseudophase, respectively, $k_W^h$ and $k_M^h$ are pseudo-first-order rate constants for the hydrolysis of $PS^-$ in the aqueous pseudophase and micellar pseudophase respective, $K_S$ is the apparent $C_{16}E_{20}$ micellar binding constant of $PS^-$ and $[D_n] = [C_{16}E_{20}]_T -$ c.m.c., c.m.c. being the critical micelle concentration. The value of c.m.c. was determined by an iterative technique.[19] The values of c.m.c. at 0.01 and 0.05 M NaOH turned out to be ~0 and $1 \times 10^{-4}$ M, respectively. The change in [NaOH] from 0.01 to 0.05 M is not expected to increase the c.m.c. The main reason for such unexpected values of c.m.c is the extremely low sensitivity of $k_{obs}$ to the c.m.c. value. For example, a change in c.m.c. from 0 to $1.0 \times 10^{-4}$ M changed $k_M^h$, $K_S$ and $\Sigma d_i^2$ (where $d_i = k_{obs\,i} - k_{cld\,i}$, with $k_{obs\,i}$ and $k_{cld\,i}$ being the observed and calculated values, respectivly of rate constants at the $i$th $[C_{16}E_{20}]_T$) by 0.4, 1.6 and 2–10%, respectively. Such an insignificant change in the kinetic parameters shows that an appreciable error in c.m.c. (~0) is not a setback for data analysis. The reported values of c.m.c. for $C_{12}E_{12}$, $C_{16}E_{12}$, $C_{12}E_{10}$ and $C_{12}E_{23}$ are $140 \times 10^{-6}$ and $2 \times 10^{-6}$, $100 \times 10^{-6}$ and $60 \times 10^{-6}$ M, respectively, obtained in the absence of any ionic or non-ionic solute.[20] The least-squares calculated respective values of $k_M^h$ and $K_S$ are $(2.79 \pm 0.06) \times 10^{-4}\,s^{-1}$ and $62.6 \pm 3.4\,M^{-1}$ with $10^4\ k_W^h = 7.90\,s^{-1}$ and c.m.c. = 0 M at 0.01 M NaOH and $(2.72 \pm 0.04) \times 10^{-4}\,s^{-1}$ and $52.7 \pm 1.9\,M^{-1}$ with $10^4\ k_W^h = 8.25\,s^{-1}$ and c.m.c. = 0 M at 0.05 M NaOH.

In view of the observed results described previously,[15,21,22] the cleavage of phenyl salicylate, under the present experimental conditions, involves $PS^-$ and $H_2O$ as reactants. The values of $k_{obs}$ remained unchanged with increase in $[C_{12}E_{23}]_T$ from 0.0 to 0.01 M at 0.01 M NaOH and from 0.0 to 0.03 M at 0.03 M NaOH.[15] However, the values of $k_{obs}$ revealed a monotonic decrease with increase in $[C_{16}E_{20}]_T$ from 0.0 to 0.18 M at both 0.01 and 0.05 M NaOH (Fig. 1). The values of $k_{obs}$ decreased by nearly 25 and 43% with respective increases in $[C_{16}E_{20}]_T$ from 0.0 to 0.01 M at 0.01 M NaOH and from 0.0 to 0.03 M at 0.05 M NaOH. The value of $k_{obs}$ dropped to ~0 and the concentration of $PS^-$ became zero at reaction time $t = 0$ at 0.03 M $C_{12}E_{23}$ and 0.01 M NaOH. However, such an abrupt drop in $k_{obs}$ was not found even up to $[C_{16}E_{20}]_T = 0.18$ M and the concentration of PSH remained zero until $[C_{16}E_{20}]_T = 0.18$ M at both 0.01 and 0.05 M NaOH (Fig. 1). Hence the present results show a very different behaviour of $C_{16}E_{20}$ micelles from that of $C_{12}E_{23}$ micelles[15], which may be considered unusual. The abrupt drop in $k_{obs}$ at a certain ratio of $[C_{12}E_{23}]_T$/[NaOH] has been attributed to the sudden drop in hydroxide ion concentration in the vicinity of micellized $PS^-$ ions.[15] The real mechanism by which $C_{12}E_{23}$ micelles cause the expulsion of hydroxide ions from the neighbourhood of micellized $PS^-$ ions or cause the irreversible entrapment of phenyl salicylate molecules in the micellar environment of nearly zero hydroxide ion concentration at a certain value of $[C_{12}E_{23}]_T$/NaOH ($\geq 2$) is unknown, at least to these authors. However, the effects of $[C_{16}E_{20}]_T$ on $k_{obs}$ are not unusual.

The value of $k_M^h$ ($= 2.7 \times 10^{-4}\,s^{-1}$) is nearly three times smaller than that of $k_W^h$ ($= 8.1 \times 10^{-4}\,s^{-1}$). Hence the nearly threefold lower rate of hydrolysis of $PS^-$ in the micellar pseudophase than in the aqueous pseudophase shows that $PS_M^-$ ions remained in the micellar environment of considerably low water concentration compared with $[H_2O_W]$.

## Effects of $[C_{16}E_{20}]_T$ on $k_{obs}$ for hydrolysis of PB at 0.01 M NaOH and 35 °C

The effects of $[C_{16}E_{20}]_T$ on the rate of alkaline hydrolysis of phenyl benzoate (PB) [a molecule which is similar to phenyl salicylate (PSH), except that the PSH molecule contains an *o*-OH group in its benzoyl moiety] were studied by carrying out a series of kinetic runs at different $[C_{16}E_{20}]_T$ ranging from $2 \times 10^{-5}$ to 0.06 M in a mixed aqueous solvent containing 2% (v/v) $CH_3CN$. The kinetic parameters, $k_{obs}$ and $A_0$, calculated from Eqn (3) at different $[C_{16}E_{20}]_T$ are shown graphically in Figs 1 and 2, respectively. The increase in $[C_{16}E_{20}]_T$ from 0.0 to 0.06 M caused essentially no change in $E_{app}$ and a monotonic decrease in $k_{obs}$. The values of $A_0$ remain unchanged with increase in $[C_{16}E_{20}]_T$ from 0 to 0.01 M and a modest increase in $A_0$ is evident at $[C_{16}E_{20}]_T > 0.01$ M (Fig. 2). A similar increase in $A_0$ can be seen from the calculated values of $A_0$ $(= E_{app}\ [X]_0 + A_\infty)$ for $PS^-$ obtained at 350 nm (Fig. 2). These results are attributed to the presence of micro-turbidity.

The increase in $[C_{16}E_{20}]_T$ from $2 \times 10^{-5}$ to 0.06 M at 0.01 M NaOH did not affect the values of $E_{app}$. However, the values of $E_{app}$ remained independent of $[C_{12}E_{23}]_T$ only within the range 0–0.003 M and dropped from 2400 to ~250 $M^{-1}\,cm^{-1}$ with increase in $[C_{12}E_{23}]_T$ from 0.003 to 0.020 M at 0.01 M NaOH.[15]

The rate of alkaline hydrolysis of PB has been shown to involve PB and $HO^-$ as reactants.[23] Thus, under the present experimental conditions, $k_{obs} = k_{OH}[HO^-]$. The values of $k_{obs}$ at different $[C_{16}E_{20}]_T$ were found to fit reasonably well to the equation

$$k_{obs} = \frac{k_{OH,W}[HO^-]_T + k_M^{mr} K_{OH} K_S [HO^-]_T [D_n]}{1 + K_S[D_n]} \qquad (5)$$

which is derived based on the reaction mechanism described in terms of the PP model of micelles, where $1 \gg K_{OH}\ [D_n]$ and the rate of reaction ($v_M$) in the micellar pseudophase is defined as $v_M = k_M^{mr}\ m_{OH}\ [PB_M]$ with $m_{OH} = [HO_M^-]/[D_n]$, $[HO^-]_T$ is the total concentration of hydroxide ion, $k_{OH,W}$ is the second-order rate constant for the reaction between $HO_W^-$ and $PB_W$ and $K_{OH}$ is the micellar binding constant of $HO^-$.

The values of $k_M^{mr}\ K_{OH}[HO^-]_T$ and $K_S$ were calculated from Eqn (5) considering $k_{OH,W}[HO^-]_T$ and c.m.c. as known parameters. The value of $k_{OH,W}[HO^-]_T$ was obtained experimentally by carrying out kinetic run at $[C_{16}E_{20}]_T = 0$ and the value of c.m.c. was determined by an iterative technique.[19] The best c.m.c. value turned out to be nearly zero, which is similar to that obtained for $C_{16}E_{20}$ micellar-mediated hydrolysis of $PS^-$. However, a change in c.m.c. from 0 to $6 \times 10^{-6}$ M changed the respective values of $k_M^{mr}\ K_{OH}[HO^-]_T$ and $K_S$ from $(9.3 \pm 3.5) \times 10^{-5}\,s^{-1}$ and $1538 \pm 38\,M^{-1}$ to $(10.4 \pm 4.0) \times 10^{-5}\,s^{-1}$ and $1575 \pm 43\,M^{-1}$. In view of the reported c.m.c. values of $C_{12}E_{10}$ $(100 \times 10^{-6}\,M)$,[20] $C_{12}E_{23}$ $(60 \times 10^{-6}\,M)$,[20] $C_{12}E_{12}$ $(140 \times 10^{-6}\,M)$,[20] and $C_{16}E_{12}$ $(2 \times 10^{-6}\,M)$,[20] the c.m.c. value of $C_{16}E_{20}$ should probably be $< 2 \times 10^{-6}$ M.

Although it appeared that the values of $k_{obs}$ obtained in the presence of $C_{12}E_{23}$ micelles obeyed the PP model of micelles only within the $[C_{12}E_{23}]_T$ range where $[C_{12}E_{23}]_T/[NaOH] > 1.5$–2.0, the least-squares-calculated value of $K_S$ $(= 1 \times 10^3\,M^{-1})$[15] may be compared with $K_S$ $(= 1.5 \times 10^3\,M^{-1})$ obtained in the present study. However, the value of $k_M^{mr}\ K_{OH}[HO^-]_T$ for the $C_{12}E_{23}$ micellar-mediated alkaline hydrolysis of PB was not different from zero at a similar value of $[HO^-]_T$[15] whereas, although the value of $k_M^{mr}\ K_{OH}[HO^-]_T$ $[= (9.3 \pm 3.5) \times 10^{-5}\,s^{-1}]$ for $C_{16}E_{20}$ is associated with a considerably large standard deviation, it is not definitely zero. The rate of reaction of $PB_M$ with $HO_M^-$ seems to be much lower than that of $PB_W$ with $HO_W^-$, which may be attributed to both the medium effect and different average locations of $HO^-$ and PB in the micellar pseudophase.[24] The value of $K_S$ for S = PB is nearly 25–30 times larger than that for $S = PS^-$ which is conceivable because the $C_{12}E_{23}$ micellar binding constants of pernonanoic acid, pernonanoate ion, 3-chloroperbenzoic acid and 3-chlorperbenzoate ion are 1010, 282, 172 and ~0 $M^{-1}$, respectively.[6]

It may be of interest that an increase in $[C_{16}E_{20}]_T$ and $[C_{12}E_{23}]_T$[15] from 0 to 0.01 M decreased $k_{obs}$ from $66.3 \times 10^{-4}$ to $5.42 \times 10^{-4}\,s^{-1}$ (Fig. 1) and from $69.7 \times 10^{-4}$ to $7.42 \times 10^{-4}\,s^{-1}$, respectively. However, the value of $k_{obs}$ became almost zero at 0.02 M $C_{12}E_{23}$ and 0.01 M NaOH[15] whereas the value of $k_{obs}$ did not become zero even at 0.06 M $C_{16}E_{20}$ and 0.01 M NaOH (Fig. 1). A similar unexpected behaviour of $C_{12}E_{23}$ was observed in the pH-independent hydrolysis of $PS^-$.[15]

## Effects of $[C_{16}E_{20}]_T$ on $k_{obs}$ for hydrolysis of $PS^-$ in the presence of a constant $[CTABr]_T$ at 0.01 M NaOH and 35 °C

A series of kinetic runs were carried out within the $[C_{16}E_{20}]_T$ range 0–0.12 M at 0.006 M CTABr. Similar observations were obtained at 0.01 and 0.02 M CTABr. The values of $E_{app}$ were independent of $[C_{16}E_{20}]_T$ (range 0–0.12 M) and $[CTABr]_T$ (range 0.006–0.020 M). However, the value of $E_{app}$ dropped to almost zero at $[C_{12}E_{23}]_T > 0.015$ M and $[CTABr]_T$ in the range 0.01–0.03 M in the presence of 0.01 M NaOH.[15] The values of $A_\infty$ were not affected by the presence of CTABr within the concentration range 0.006–0.02 M. The value of $k_{obs}$ shows an almost monotonic increase with increase in $[C_{16}E_{20}]_T$ at constant $[CTABr]_T$ and [NaOH] (Table 1). However, the rate of hydrolysis of $PS^-$ at 0.01 M NaOH, >0.015 M $C_{12}E_{23}$ and within the $[CTABr]_T$ range 0.01–0.03 M became too slow to monitor easily. Mixed micelles behave as if pure CTABr micelles at $[CTABr]_T/[C_{16}E_{20}]_T \geq$ ~10 at both 0.01 and 0.02 M CTABr because under such conditions the $k_{obs}$ values remain independent of $[C_{16}E_{20}]_T$ (Table 1).

**Table 1.** Values of $k_{obs}$ and $K$ for hydrolysis of PS$^-$ at different $[C_{16}E_{20}]_T$ in the presence of a constant value of $[CTABr]_T$[a]

| | $[CTABr]_T$ (M) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.006 | | | 0.010 | | | 0.020 | | |
| $[C_{16}E_{20}]_T$ (M) | $10^4k_{obs}$ ($s^{-1}$) | $10^4k_{cld}$[b] ($s^{-1}$) | $K$ ($M^{-1}$) | $10^4k_{obs}$ ($s^{-1}$) | $10^4k_{cld}$[c] ($s^{-1}$) | $K$ ($M^{-1}$) | $10^4k_{obs}$ ($s^{-1}$) | $10^4k_{cld}$[d] ($s^{-1}$) | $K$ ($M^{-1}$) |
| 0.0 | $1.34 \pm 0.01$[e] | | | $1.28 \pm 0.012$[e] | | | | | |
| 0.0002 | | | | $1.30 \pm 0.01$ | 1.29 | 15[f] | $1.23 \pm 0.01$[e] | 1.22 | 15[f] |
| 0.0005 | | | | $1.34 \pm 0.01$ | 1.31 | 19[f] | $1.26 \pm 0.01$ | 1.23 | 16[f] |
| 0.0010 | | | | $1.32 \pm 0.00$ | 1.34 | 6.5[f] | $1.13 \pm 0.02$ | 1.24 | −13[f] |
| 0.0050 | $1.76 \pm 0.03$ | 1.67 | 17 | $1.61 \pm 0.01$ | 1.54 | 13 | $1.27 \pm 0.02$ | 1.37 | 2.2[f] |
| 0.0100 | $2.02 \pm 0.03$ | 1.88 | 17 | $1.67 \pm 0.02$ | 1.71 | 9.0 | $1.42 \pm 0.02$ | 1.48 | 4.6 |
| 0.0200 | $2.01 \pm 0.02$ | 2.17 | 11 | $1.94 \pm 0.02$ | 1.92 | 10 | $1.68 \pm 0.02$ | 1.63 | 6.8 |
| 0.0240 | $2.15 \pm 0.03$ | 2.24 | 12 | | | | | | |
| 0.0260 | $2.14 \pm 0.02$ | 2.27 | 12 | | | | | | |
| 0.0280 | $2.37 \pm 0.02$ | 2.30 | 16 | | | | | | |
| 0.0300 | $2.40 \pm 0.02$ | 2.35 | 16 | $2.06 \pm 0.03$ | 2.06 | 10 | $1.78 \pm 0.03$ | 1.74 | 6.6 |
| 0.0400 | $2.55 \pm 0.03$ | 2.46 | 17 | $2.09 \pm 0.04$ | 2.13 | 9 | $1.85 \pm 0.03$ | 1.81 | 6.6 |
| 0.0500 | | | | $2.18 \pm 0.04$ | 2.19 | 10 | $1.91 \pm 0.04$ | 1.87 | 6.5 |
| 0.0600 | $2.65 \pm 0.04$ | 2.60 | 18 | $2.25 \pm 0.04$ | 2.23 | 10 | $1.83 \pm 0.03$ | 1.91 | 5.1 |
| 0.1000 | $2.81 \pm 0.04$ | 2.80 | 19 | $2.41 \pm 0.05$ | 2.40 | 10 | $2.06 \pm 0.04$ | 2.10 | 5.6 |
| 0.1200 | $2.88 \pm 0.05$ | 2.87 | 26 | | | | $2.10 \pm 0.05$ | 2.07 | 6.4 |
| Average | $16 \pm 4$[e] | | | $10 \pm 1$ | | | $6.0 \pm 0.8$ | | |

[a] Conditions: $[\text{phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, [NaOH] = 0.01 M, 35 °C, $\lambda = 350$ nm, aqueous reaction mixture for each kinetic run contained 2% (v/v) $CH_3CN$ and the values of $K$ were calculated from Eqn (6) with $F = 1$ and $k_{obs}^{C_{16}E_{20}}$ $(= k_{obs})$ values shown in Fig. 1.

[b] Calculated from Eqn (6) with $10^4k_0 = 1.34\ s^{-1}$, $k_{obs}^{C_{16}E_{20}}$ $(= k_{obs})$ values shown in Fig. 1, $F = 1.23$ and $K = 10\ M^{-1}$.

[c] Calculated from Eqn (6) with $10^4k_0 = 1.28\ s^{-1}$, $k_{obs}^{C_{16}E_{20}}$ $(= k_{obs})$ values shown in Fig. 1, $F = 0.98$ and $K = 10\ M^{-1}$.

[d] Calculated from Eqn (6) with $10^4k_0 = 1.21\ s^{-1}$, $k_{obs}^{C_{16}E_{20}}$ $(= k_{obs})$ values shown in Fig. 1, $F = 1.01$ and $K = 5.9\ M^{-1}$.

[e] Error limits are standard deviations.

[f] These values were not included in the calculation of the average value of $K$.

The value of the CTABr micellar binding constant of PS$^-$ is ~7000 $M^{-1}$ and the pseudo-first-order rate constant for hydrolysis of PS$^-$ is nearly eight times larger in the aqueous pseudophase than that in pure CTABr micellar pseudophase;[25] probable causes of such an inhibitory effect have been discussed in detail elsewhere.[21] This shows that PS$^-$ ions are almost fully micellized at $[CTABr]_T \geq 0.006$ M in the absence of any additive. The increase in $k_{obs}$ with increase in $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ is therefore attributed to the transfer of PS$^-$ ions from the less to the more hydrated mixed micellar environment. A limited number of studies on the effects of mixed cationic–non-ionic micelles on the rates of reactions showed that an increase in non-ionic surfactant concentration at a constant cationic surfactant concentration increased both the volume of mixed micelles and the degree of micellar ionization ($\alpha$).[11,14] Voluminous polyoxyethylene headgroups of $C_nE_m$ micelles are known to be extensively hydrated.[26] The increase in $\alpha$ values due to the increase in $[C_nE_m]_T$ at a constant $[CTABr]_T$ is most likely due to a decrease in the electrostatic affinity of counterions for the cationic headgroups because of the apparent increase in both $[H_2O]$ and size of the cationic headgroups. It is apparent that an increase in $[C_nE_m]_T$ at a constant [cationic surfactant]$_T$ is bound to decrease the cationic micellar affinity of both counterions and non-ionic solubilizates. It should be noted that the cationic headgroups of CTABr micelles surfactant are buried deep inside the voluminous headgroup mantle of $C_{16}E_{20}$.[27] It has been reported that polar solubilizates reside in the headgroup mantle rather than in the hydrophobic core of $C_{12}E_{23}$.[28]

The kinetic data on the effects of mixed micelles on reaction rates show that the characteristic features of mixed micellar system (S1–S2 with S1 and S2 representing two different surfactants) change gradually from very close to pure S1 micelle type to very close to pure S2 micelle type as the X values increase from very low to very high, where X = [S2]/[S1]. Hence it is obvious that the increase in $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ will change CTABr micellar binding constant of PS$^-$ from $K_S{}^{CTA}$ $(= K_S0)$ to very close to $K_S{}^{C16E20}$ (pure $C_{16}E_{20}$ micellar binding constant of PS$^-$). Based on related studies,[16,17] such an effect of $[C_{16}E_{20}]$ on $K_S^{CTA}$ is expected to follow Eqn (1) with $C_nE_m$ replaced by $C_{16}E_{20}$.

Recently, the effects of $[C_{12}E_{23}]_T$ and $[C_{16}E_{20}]_T$ on the CTABr micellar binding constants, $K_S$, of anionic 4-nitrophthalimide[16] and phthalimide[17] have been explained in terms of the pseudophase model of micelles coupled with an empirical relationship shown by Eqn (1). The pseudophase model of micelles i.e. Eqns (4) and (1), with replacement of $C_nE_m$ by $C_{16}E_{20}$, and with $k_W^h = k_{obs}$

at $[\mathrm{CTABr}]_\mathrm{T} = [\mathrm{C_{16}E_{20}}]_\mathrm{T} = 0$ and $k_\mathrm{W}^\mathrm{h} = k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}}$ at $[\mathrm{CTABr}]_\mathrm{T} = 0$ but $[\mathrm{C_{16}E_{20}}]_\mathrm{T} \neq 0$, can lead to the equation

$$k_\mathrm{obs} = \frac{k_0 + F\,k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}} K[\mathrm{C_{16}E_{20}}]_\mathrm{T}}{1 + K[\mathrm{C_{16}E_{20}}]_\mathrm{T}} \tag{6}$$

where

$$k_0 = \frac{k_\mathrm{W}^\mathrm{h} + k_\mathrm{M}^\mathrm{h} K_\mathrm{S}^0\,[\mathrm{D}_n]}{1 + k_\mathrm{S}^0[\mathrm{D}_n]} \tag{7}$$

$$K = K_{\mathrm{C_{16}E_{20}/S}}/(1 + K_\mathrm{S}^0\,[\mathrm{D}_n]) \tag{8}$$

and $F = \theta / k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}}$ with $F$ representing the fraction of pure CTABr micellized $\mathrm{PS^-}$ transferred to pure $\mathrm{C_{16}E_{20}}$ micelles by the limiting concentration of $\mathrm{C_{16}E_{20}}$ (the limiting concentration of $\mathrm{C_{16}E_{20}}$ is the optimum value of $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ at which $k_\mathrm{obs}$ values become independent of $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$). Hence, conceptually, the value of $F$ should be $\leq 1.0$. It may be noted that a slightly different form of Eqn (6) was used in the previous work.[16,17]

The values of the unknown parameters $F$ and $K$ were calculated from Eqn (6) by the use of the non-linear least-squares technique. The values of $k_0$ and $k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}}$ were obtained experimentally by carrying out experiments under similar experimental conditions with $[\mathrm{C_{16}E_{20}}]_\mathrm{T} = 0$, $[\mathrm{CTABr}]_\mathrm{T} \neq 0$ and $[\mathrm{C_{16}E_{20}}]_\mathrm{T} \neq 0$, $[\mathrm{CTABr}]_\mathrm{T} = 0$. The least-squares calculated values of $F$ and $K$ are summarized in Table 2. The fitting of observed data to Eqn (6) appears to be satisfactory, as is evident from the values of the calculated rate constants ($k_\mathrm{cld}$) summarized in Table 1. The larger value of $F$ (= 1.23 at 0.006 M CTABr) compared with its expected maximum value of 1.0 is considered to be fortuitous and therefore $K$ values were also calculated from the equation

$$K = \frac{k_\mathrm{obs} - k_0}{(k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}} - k_\mathrm{obs})[\mathrm{C_{16}E_{20}}]_\mathrm{T}} \tag{9}$$

which is the rearranged form of Eqn (6) with $F = 1$. These calculated values of $K$ are shown in Table 1. It should be noted that the calculation of $K$ from Eqn (9) with $F = 1$ has the disadvantage that the calculated values of $K$ may not be reliable at both very low and very high values of $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ because, under such conditions, $k_\mathrm{obs} \to k_0$ and $k_\mathrm{obs} \to k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}}$, respectively, and consequently ($k_\mathrm{obs}$–$\mathrm{k}_0$) $\to 0$ and $(k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}} - k_\mathrm{obs})^{-1} \to \infty$. These mathematical limits show that under such conditions, the values of ($k_\mathrm{obs}$–$\mathrm{k}_0$) and $(k_\mathrm{obs}^{\mathrm{C_{16}E_{20}}} - k_\mathrm{obs})^{-1}$ should be very sensitive to errors.

The values of $k_\mathrm{obs}$ in Fig. 1 and Table 1 reveal that an increase in $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ decreases $k_\mathrm{obs}$ compared with $k_\mathrm{W}^\mathrm{h}$ and increases $k_\mathrm{obs}$ compared with $k_\mathrm{obs}$ at $[\mathrm{CTABr}]_\mathrm{T} \geq 0.006$ M and $[\mathrm{C_{16}E_{20}}]_\mathrm{T} = 0$. It is evident from Eqn (6) that the maximum value of $k_\mathrm{obs}$ should be $\sim\leq k_\mathrm{M}^\mathrm{h}$ (i.e. first-order rate constant for the hydrolysis of $\mathrm{PS^-}$ in pure $\mathrm{C_{16}E_{20}}$ micelles).

**Table 2.** Values of $F$ and $K$, calculated from Eqn (6), for hydrolyses of $\mathrm{PS^-}$ and PB at different values of $[\mathrm{CTABr}]_\mathrm{T}$

| Ester (S) | $[\mathrm{CTABr}]_\mathrm{T}$ (M) | $F$ | $K$ ($\mathrm{M^{-1}}$) | $K_\mathrm{X/S}$[a] ($\mathrm{M^{-1}}$) |
|---|---|---|---|---|
| $\mathrm{PS^-}$ | 0.006 | 1.23 ± 0.10[b] | 10 ± 2[b] | |
| | | 1.0 | (16 ± 4)[c] | 688 |
| | 0.010 | 0.98 ± 0.04 | 10 ± 1 | |
| | | 1.0 | (10 ± 1) | 710 |
| | 0.020 | 1.01 ± 0.12 | 5.9 ± 1.4 | |
| | | 1.0 | (6.0 ± 0.8) | 848 |
| PB | 0.006 | 1.73 ± 0.48 | 651 ± 126 | |
| | | 1.0 | (505 ± 84) | 2020 |
| | 0.010 | 3.35 ± 0.32 | 495 ± 74 | |
| | | 1.0 | (269 ± 55) | 1614 |
| | 0.020 | 0.70 ± 0.53 | 121 ± 13 | |
| | | 1.0 | (142 ± 25) | 1562 |
| $\mathrm{PT^-}$[d] | 0.006 | 1.08 ± 0.04 | 16 ± 1 | |
| | | 1.0 | 19 ± 3 | 390 |
| | 0.010 | 1.26 ± 0.05 | 5.7 ± 0.3 | |
| | | 1.0 | 8.0 ± 0.9 | 268 |
| | 0.015 | 2.44 ± 0.79 | 1.7 ± 0.7 | |
| | | 1.0 | 5.2 ± 1.5 | 259 |
| | 0.020 | 6.50 ± 4.10 | 0.4 ± 0.3 | |
| | | 1.0 | 3.6 ± 1.0 | 238 |

[a] $K_\mathrm{X/S} = K(1 + K_\mathrm{S}^0\ [\mathrm{CTABr}]_\mathrm{T})$ with $\mathrm{X} = \mathrm{C_{16}E_{20}}$, $K_\mathrm{S}{}^0 = 7000\ \mathrm{M^{-1}}$ for $\mathrm{S} = \mathrm{PS^-}$, $K_\mathrm{S}^0 = 500\ \mathrm{M^{-1}}$ for S = PB and $K_\mathrm{S}^0 = 3250\ \mathrm{M^{-1}}$ for $\mathrm{S} = \mathrm{PT^-}$.
[b] Error limits are standard deviations.
[c] Values in parentheses were obtained from Tables 1 and 3.
[d] The values of $K$ were calculated from Eqn (6) by the use of data obtained from Ref. 17.

### Effects of $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ on $k_\mathrm{obs}$ for hydrolysis of PB in the presence of a constant $[\mathrm{CTABr}]_\mathrm{T}$ at 0.01 M NaOH and 35 °C

Several kinetic runs were carried out with $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ in the range 0.0–0.06 M at 0.006 M CTABr. Similar observations were obtained at 0.01 and 0.02 M CTABr. These results, as $k_\mathrm{obs}$ versus $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$, are shown in Table 3. The values of $E_\mathrm{app}$ were independent of $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ (range 0–0.06 M) and $[\mathrm{CTABr}]_\mathrm{T}$ (range 0.006–0.020 M). However, the values of $E_\mathrm{app}$ remained almost unchanged within the $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ range 0–0.015 M and dropped from ~2100 to 300–500 $\mathrm{M^{-1}\,cm^{-1}}$ with increase in $[\mathrm{C_{12}E_{23}}]_\mathrm{T}$ from 0.015 to 0.025 M at 0.01 M NaOH and $[\mathrm{CTABr}]_\mathrm{T}$ in the range 0.006–0.030 M.[15] It is evident from these results that mixed micelles behave as pure CTABr micelles at $[\mathrm{CTABr}]_\mathrm{T}/[\mathrm{C_{16}E_{20}}]_\mathrm{T} \geq \sim$10–20. The values of both $E_\mathrm{app}$ and $A_0$ were not affected by the presence of 0.006–0.020 M CTABr. The values of $k_\mathrm{obs}$ decrease with increase in $[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ at $[\mathrm{CTABr}]_\mathrm{T}/[\mathrm{C_{16}E_{20}}]_\mathrm{T}$ of $< \sim$10–20. However, the value of $k_\mathrm{obs}$ even at 0.06 M $\mathrm{C_{16}E_{20}}$ with $[\mathrm{CTABr}]_\mathrm{T}/[\mathrm{C_{16}E_{20}}]_\mathrm{T} = 0.1$ is about double the value obtained at 0.06 M $\mathrm{C_{16}E_{20}}$ with $[\mathrm{CTABr}]_\mathrm{T} = 0$. Similar observations were obtained in the alkaline hydrolysis of PB in the presence of mixed CTABr–$C_{12}E_{23}$ micelles.[15]

The value of $k_{obs}(=k_W^h)$ for hydrolysis of PB is $6.77 \times 10^{-3}\,s^{-1}$ at 35 °C, 0.01 M NaOH and $[CTABr]_T = [C_{16}E_{20}]_T = 0$.[23] The values of $k_{obs}$ at different $[CTABr]_T$ with $[C_{16}E_{20}]_T = 0$ are significantly higher than $k_W^h$ (Table 3), which is due to $HO^-$–$Br^-$ ion exchange at the cationic micellar surface.[23] The increase in $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ is expected to alter gradually the characteristic features of the mixed micellar system from cationic micelle type to non-ionic micelle type and consequently it should change the micellar affinity of the reactants, $HO^-$ and PB, from cationic to non-ionic micelles. Such a change in $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ is expected to change the CTABr micellar binding constants of both reactants, $HO^-$ and PB. If we assume that the changes in $K_S$ and $K_{OH}$ due to increase in $[C_{16}E_{20}]_T$ at a constant $[CTABr]_T$ follow empirical equations similar to Eqn (1), then

$$K_S = K_S^0/(1 + K_{X/S}[C_{16}E_{20}]_T) \tag{10}$$

and

$$K_{OH} = K_{OH}^0/(1 + K_{X/HO}[C_{16}E_{20}]_T) \tag{11}$$

where the subscript X represents $C_{16}E_{20}$ and $K_{X/S}$ and $K_{X/HO}$ are empirical constants. Equation (5) with the condition that 1 is not negligible compared with $K_{OH}[D_n]$, and Eqns (10) and (11) can lead to

$$k_{obs} = \frac{k_0' + (\theta K^{PB} + \mu K^{HO})[C_{16}E_{20}]_T + \theta\mu K^{PB}K^{HO}[C_{16}E_{20}]_T^2}{(1 + K^{PB}[C_{16}E_{20}]_T)(1 + K^{HO}[C_{16}E_{20}]_T)} \tag{12}$$

**Table 3.** Values of $k_{obs}$ and $K$ for hydrolysis of PB at different $[C_{16}E_{20}]_T$ in the presence of a constant value of $[CTABr]_T$[a]

| | $[CTABr]_T$ (M) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.006 | | | 0.010 | | | 0.020 | | |
| $[C_{16}E_{20}]_T$ (M) | $10^3k_{obs}$ ($s^{-1}$) | $10^3k_{cld}$[b] ($s^{-1}$) | $K$ ($M^{-1}$) | $10^3k_{obs}$ ($s^{-1}$) | $10^3k_{cld}$[c] ($s^{-1}$) | $K$ ($M^{-1}$) | $10^3k_{obs}$ ($s^{-1}$) | $10^3k_{cld}$[d] ($s^{-1}$) | $K$ ($M^{-1}$) |
| 0.0 | 13.5 ± 0.1[e] | | | 10.7 ± 0.02[e] | | | 7.81 ± 0.11[e] | | |
| 0.02 | 13.7 ± 0.1 | | | | | | | | |
| 0.00005 | 13.6 ± 0.2 | | | 10.8 ± 0.5 | | | 7.44 ± 0.18 | | |
| 0.00010 | | | | 11.3 ± 0.1 | | | 7.67 ± 0.08 | | |
| 0.00015 | 13.6 ± 0.1 | | | | | | | | |
| 0.00020 | 12.8 ± 0.2 | | | 11.1 ± 0.3 | | | 7.43 ± 0.10 | | |
| 0.00025 | 13.0 ± 0.1 | | | | | | | | |
| 0.0003 | 12.8 ± 0.1 | | | 11.7 ± 0.5 | | | 7.25 ± 0.09 | | |
| 0.0005 | 11.5 ± 0.2 | 11.6 | 468 | 11.3 ± 0.2 | | | 7.20 ± 0.07 | | |
| 0.0007 | 10.9 ± 0.1 | 10.9 | 452 | | | | | | |
| 0.0010 | 10.1 ± 0.1 | 9.86 | 430 | | | | | | |
| 0.0012 | 9.66 ± 0.13 | 9.28 | 417 | 10.2 ± 0.4 | | | 6.83 ± 0.09 | 6.88 | 152 |
| 0.0014 | 9.34 ± 0.07 | 8.74 | 394 | 9.78 ± 0.30 | 9.46 | 114[f] | | | |
| 0.0015 | 7.88 ± 0.12 | 8.50 | 639 | | | | | | |
| 0.0016 | | | | 8.81 ± 0.12 | 9.07 | 200 | 6.52 ± 0.07 | 6.62 | 154 |
| 0.002 | 6.60 ± 0.12 | 7.42 | 681 | 8.14 ± 0.09 | 8.33 | 221 | 6.26 ± 0.13 | 6.37 | 151 |
| 0.003 | 6.07 ± 0.09 | 5.98 | 504 | 6.99 ± 0.07 | 7.01 | 234 | 5.94 ± 0.09 | 5.84 | 122 |
| 0.004 | 5.35 ± 0.09 | 4.95 | 457 | 6.20 ± 0.10 | 5.94 | 231 | 5.52 ± 0.07 | 5.37 | 118 |
| 0.005 | 4.61 ± 0.05 | 4.30 | 467 | 5.15 ± 017 | 5.29 | 274 | 5.10 ± 0.09 | 4.99 | 121 |
| 0.006 | 3.94 ± 0.02 | 3.72 | 486 | 4.84 ± 0.10 | 4.61 | 250 | 4.59 ± 0.09 | 4.63 | 132 |
| 0.007 | 3.35 ± 0.05 | 3.31 | 526 | 4.42 ± 0.05 | 4.15 | 249 | 4.35 ± 0.08 | 4.34 | 127 |
| 0.008 | 2.89 ± 0.05 | 2.98 | 563 | 3.80 ± 0.09 | 3.77 | 280 | 4.20 ± 0.09 | 4.07 | 119 |
| 0.010 | 2.41 ± 0.05 | 2.58 | 583 | 3.22 ± 0.04 | 3.36 | 290 | 3.64 ± 0.08 | 3.66 | 129 |
| 0.020 | 1.05 ± 0.01 | 1.36 | 770[f] | 1.58 ± 0.01 | 1.79 | 362 | 2.64 ± 0.04 | 2.35 | 105 |
| 0.030 | 0.638 ± 0.009 | 0.949 | 928[f] | 1.07 ± 0.01 | 1.27 | 373 | 1.51 ± 0.01 | 1.74 | 154 |
| 0.040 | 0.422 ± 0.005 | 0.734 | 1162[f] | 0.707 ± 0.005 | 0.992 | 458[f] | 1.09 ± 0.01 | 1.39 | 173 |
| 0.050 | 0.342 ± 0.006 | 0.658 | 1393[f] | 0.534 ± 0.004 | 0.930 | 554[f] | 0.851 ± 0.006 | 1.17 | 195 |
| 0.060 | 0.284 ± 0.008 | 0.585 | 1619[f] | | | | | | |
| Average | | | 505 ± 84[e] | | | 269 ± 55[e] | | | 142 ± 25[e] |

[a] Conditions: [phenyl benzoate]$_0 = 2 \times 10^{-4}$ M, [NaOH] = 0.01 M, 35 °C, $\lambda = 290$ nm, aqueous reaction mixture for each kinetic run contained 2% (v/v) $CH_3CN$ and the values of $K$ were calculated from Eqn (6) with $F = 1$ and $k_{obs}^{C_{16}E_{20}}$ ($= k_{obs}$) values shown in Fig. 1.

[b] Calculated from Eqn (6) with $10^3k_0 = 13.3\,s^{-1}$, $k_{obs}^{C_{16}E_{20}}$ ($= k_{obs}$) values shown in Fig. 1, $F = 1.73$ and $K = 651\,M^{-1}$.

[c] Calculated from Eqn (6) with $10^3k_0 = 11.0\,s^{-1}$, $k_{obs}^{C_{16}E_{20}}$ ($= k_{obs}$) values shown in Fig. 1, $F = 3.35$ and $K = 495\,M^{-1}$.

[d] Calculated from Eqn (6) with $10^3k_0 = 7.64\,s^{-1}$, $k_{obs}^{C_{16}E_{20}}$ ($= k_{obs}$) values shown in Fig. 1, $F = 0.70$ and $K = 121\,M^{-1}$.

[e] Error limits are standard deviations.

[f] These values were not included in the calculation of the average value of $K$.

where

$$k'_0 = \frac{(k_{\mathrm{OH,W}} + k_{\mathrm{M}}^{\mathrm{mr}} K_{\mathrm{OH}}^0 K_{\mathrm{S}}^0 [\mathrm{D}_n])[\mathrm{HO}^-]_{\mathrm{T}}}{(1 + K_{\mathrm{S}}^0[\mathrm{D}_n])(1 + K_{\mathrm{OH}}^0[\mathrm{D}_n])} \quad (13)$$

$$\theta = k_{\mathrm{OH,W}}^{\mathrm{X}}[\mathrm{HO}^-]_{\mathrm{T}}/(1 + K_{\mathrm{OH}}^0\,[\mathrm{D}_n]) \quad (14)$$

$$\mu = k_{\mathrm{OH,W}}^{\mathrm{X}}[\mathrm{HO}^-]_{\mathrm{T}}/(1 + K_{\mathrm{S}}^0\,[\mathrm{D}_n]) \quad (15)$$

$$K^{\mathrm{PB}} = K_{\mathrm{X/S}}/(1 + K_{\mathrm{S}}^0\,[\mathrm{D}_n]) \quad (16)$$

and

$$K^{\mathrm{HO}} = K_{\mathrm{X/HO}}/(1 + K_{\mathrm{OH}}^0\,[\mathrm{D}_n]) \quad (17)$$

In Eqns (14) and (15), $k_{\mathrm{OH,W}}^{\mathrm{X}} = k_{\mathrm{OH,W}}$ at [X] $(=[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}) = 0$.

It is evident from the empirical definition of $K_{\mathrm{X/S}}$ or $K_{\mathrm{X/HO}}$ that the magnitude of say $K_{\mathrm{X/S}}$ should be directly and inversely proportional to $K_{\mathrm{S}}^{\mathrm{X}}$ and $K_{\mathrm{S}}^{\mathrm{CTA}}$ ($\equiv K_{\mathrm{S}}^0$), respectively, where $K_{\mathrm{S}}^{\mathrm{X}}$ and $K_{\mathrm{S}}^{\mathrm{CTA}}$ are the respective pure $\mathrm{C}_{16}\mathrm{E}_{20}$ and CTABr micellar binding constants of S (= PB). The values of kinetically determined CTABr micellar binding constants of anionic acetyl salicylic and 4-acetoxybenzoic acids are in the range ~200–300 $\mathrm{M}^{-1}$.[29] The values of the ion-exchange constants, $K_{\mathrm{Bz}}^{\mathrm{Br}}$ ($= K_{\mathrm{Bz}}^0/K_{\mathrm{Br}}^0$, where Bz represents benzoate ion) and $K_{\mathrm{Br}}{}^{\mathrm{OH}}$ ($= K_{\mathrm{Br}}^0/K_{\mathrm{OH}}^0$), for the respective ion-exchange processes $\mathrm{Bz}^-$–$\mathrm{Br}^-$ and $\mathrm{Br}^-$–$\mathrm{HO}^-$ at the CTABr micellar surface are ~6[22,30] and 2–20,[3,29,31] respectively. These results show that $K_{\mathrm{Br}}^0 \approx 33$–$50\ \mathrm{M}^{-1}$ and $K_{\mathrm{OH}}^0 \approx 2$–$25\ \mathrm{M}^{-1}$. The value of $K_{\mathrm{OH}}^{\mathrm{X}}$(i.e. the $\mathrm{C}_{16}\mathrm{E}_{20}$ micellar binding constant of $\mathrm{HO}^-$) should be much smaller than $K_{\mathrm{OH}}^0$ ($= K_{\mathrm{OH}}^{\mathrm{CTA}}$). The values of $K_{\mathrm{S}}^{\mathrm{X}}$ and $K_{\mathrm{S}}^{\mathrm{CTA}}$ ($= K_{\mathrm{S}}^0$) are ~1550 (Table 2) and 300–700 $\mathrm{M}^{-1}$,[23] respectively. In view of the empirical definition of $K_{\mathrm{X/S}}$ and $K_{\mathrm{X/HO}}$ and the estimated values of $K_{\mathrm{S}}^{\mathrm{X}}$, $K_{\mathrm{S}}^0$, $K_{\mathrm{OH}}^{\mathrm{X}}$ and $K_{\mathrm{OH}}^0$, it seems that the value of $K_{\mathrm{X/S}}$ should be much higher than that of $K_{\mathrm{X/HO}}$ and consequently $\mu K^{\mathrm{HO}}$ may be neglected compared with $\theta K^{\mathrm{PB}}$ in Eqn (12). It can also be shown that $1 \gg \mu K^{\mathrm{HO}}\ [\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}$ under the experimental conditions of the present study. These inequalities reduced Eqn (12) to Eqn (6) provided $1 \gg K^{\mathrm{HO}}[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}$ with $K^{\mathrm{PB}} = K$ and $k_{\mathrm{W}}^{\mathrm{h}} = k_{\mathrm{OH,W}}\ [\mathrm{HO}^-]_{\mathrm{T}} = k_{\mathrm{obs}}$ at $[\mathrm{CTABr}]_{\mathrm{T}} = [\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}} = 0$ and $k_{\mathrm{W}}^{\mathrm{h}} = k_{\mathrm{obs}}^{\mathrm{C16E20}}$ at $[\mathrm{CTABr}]_{\mathrm{T}} = 0$ but $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}} \neq 0$.

The unknown parameters $F$ and $K$ ($= K^{\mathrm{PB}}$) were calculated from Eqn (6) by the use of the non-linear least-squares technique considering $k_0{}'$ and $k_{\mathrm{obs}}{}^{\mathrm{C16E20}}$ as known parameters. Although the residual errors ($= k_{\mathrm{obs}\,i} - k_{\mathrm{cld}\,i}$) appear to be reasonably low at $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}} < \sim 1.5$ (Table 3), the calculated values of $F$ are unreliable. This is not an unusual problem encountered in solving an equation similar to Eqn (6) by the use of the non-linear least-squares technique. This is a mathematical paradox which requires careful attention in such data analysis. The likely possibility that the low residual errors and fortuitous values of $F$ were due to compensatory effects of the errors in $F$ and $K$ because of the term $FK$ in the numerator of Eqn (6) may be ruled out for the reason that exactly the same values of $F$, $K$ and residual errors were obtained from Eqn (18), which is a rearranged form of Eqn (6):

$$k_{\mathrm{obs}} = \frac{k'_0\,K' + FK_{\mathrm{obs}}^{\mathrm{C_{16}E_{20}}}[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}}{K' + [\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}} \quad (18)$$

where $K' = 1/K$. Perhaps the more reliable values of $K$ were obtained from Eqn (6) with $F = 1$. These calculated values of $K$ are shown in Table 3. The values of $K$ seem to be constant within the $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}}$ range ~0.1–1.5 (Table 3). However, the $K$ values increase with increase in $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}}$ beyond a value of ~1.5 (Table 3).

The larger values of $K$ than expected at $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}} > \sim 1.5$ may be due to the following reasons: (i) an unexpected faster decrease in $k_{\mathrm{obs}}$ with increase in $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}}$ beyond ~1.5; (ii) the value of $F$ is no longer 1 at $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}} > \sim 1.5$ and drops sharply with increase in $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}}$ beyond ~1.5; (iii) the value of the empirical constant $K_{\mathrm{X/S}}$ does not remain constant at $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}} > \sim 1.5$; (iv) the inequality $1 \gg K^{\mathrm{HO}}[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}$ is probably no longer true at $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}/[\mathrm{CTABr}]_{\mathrm{T}} > \sim 1.5$. All these possibilities may be the consequence of the fact that the nature and characteristics of the mixed micellar environment of a mixed micellar-mediated reaction cannot be expected to remain the same within the entire range of $[\mathrm{C}_{16}\mathrm{E}_{20}]_{\mathrm{T}}$ at a constant $[\mathrm{CTABr}]_{\mathrm{T}}$. Sommer *et al.*[32] recently reported the formation of giant worm-like nonionic micelles in the presence of small amounts of ionic surfactants. However, such a probable characteristic mixed micellar structural change due to changes in the mole fraction of mixed micellar components at a specific value appeared to be kinetically insensitive to the rate of non-catalysed hydrolysis of $\mathrm{PS}^-$, which involves $\mathrm{PS}^-$ and $\mathrm{H_2O}$ as the reactants, and sensitive to the rate of hydroxide ion-catalysed hydrolysis of PB, which involves PB and $\mathrm{HO}^-$ as the reactants.

Equation (8) or (16) predicts that the value of $K$ should decrease with increase in $[\mathrm{CTABr}]_{\mathrm{T}}$ provided that $K_{\mathrm{S}}[\mathrm{D}_n]$ is not negligible compared with 1 within the $[\mathrm{CTABr}]_{\mathrm{T}}$ range considered in this study. The values of $K$ for $\mathrm{S} = \mathrm{PS}^-$, PB and $\mathrm{PT}^{-17}$ ($\mathrm{PT}^-$ represents ionized phthalimide) decrease with increase in $[\mathrm{CTABr}]_{\mathrm{T}}$ within the range 0.006–0.020 M (Table 2). The CTABr micellar binding constants ($K_{\mathrm{S}}^0$) for $\mathrm{S} = \mathrm{PS}^-$, $\mathrm{PT}^-$ and PB are 7000,[25] 3250[24e] and 500 $\mathrm{M}^{-1}$,[23] respectively. The values of the c.m.c. of CTABr vary in the range $1 \times 10^{-4}$–$3 \times 10^{-4}$ M in the presence of $2 \times 10^{-4}$ M S and therefore $[\mathrm{D}_n] = [\mathrm{CTABr}]_{\mathrm{T}} - \mathrm{c.m.c.} \approx [\mathrm{CTABr}]_{\mathrm{T}}$ at $[\mathrm{CTABr}]_{\mathrm{T}} \geq 0.006$ M. The known values of $K_{\mathrm{S}}{}^0$ were used to calculate $K_{\mathrm{X/S}}$ from Eqn (8) or (16) with $[\mathrm{D}_n] = [\mathrm{CTABr}]_{\mathrm{T}}$ and the results obtained are shown in Table 2.

The values of $K_{X/S}$ are almost independent of $[CTABr]_T$ within the range 0.006–0.020 M. The average values of $K_{X/S}$ for $S = PS^-$ ($K_{X/S} = 750 \pm 90\,M^{-1}$), $S = PB$ ($K_{X/S} = 1730 \pm 250\,M^{-1}$) and $S = PT^-$ ($K_{X/S} = 290 \pm 70\,M^{-1}$)[17] are conceivable in view of the empirical definition of $K_{X/S}$, which suggests that the magnitude of $K_{X/S}$ should be proportional to the magnitude of $K_S{}^X$ (X, $C_{16}E_{20}$, micellar binding constant of S) and inversely proportional to the magnitude $K_S^{CTA}$ (CTA, CTABr, micellar binding constant of S). Thus, $K_{X/S} = \delta_S\ K_S^X/K_S^{CTA}$, where $\delta_S$ is a proportionality constant with dimensions $M^{-1}$. The value of $\delta_S$ depends only on the nature and micellar affinity of S. The value of $K_{X/S}$ for $S = PS^-$ ($K_{X/S} = 750\,M^{-1}$) is nearly three times larger than $K_{X/S}$ ($= 290\,M^{-1}$) for $S = PT^-$ because $K_S^X$ ($= 62\,M^{-1}$) for $S = PS^-$ is about 10 times larger than $K_{X/S}$ ($= 6\,M^{-1}$)[17] for $S = PT^-$, whereas $K_S^{CTA}$ ($= 7000\,M^{-1}$) for $S = PS^-$ is slightly more than double $K_S^{CTA}$ ($= 3250\,M^{-1}$) for $S = PT^-$. The many-fold larger value of $K_{X/S}$ ($= 1730\,M^{-1}$) for $S = PB$ than for $S = PS^-$ and $PT^-$ is due to (i) $K_S^X$ ($= 1550\,M^{-1}$) for $S = PB$ is ~25 and 250 times larger than those for $S = PS^-$ and $PT^-$, respectively, and (ii) $K_S^{CTA}$ ($= 500\,M^{-1}$) for $S = PB$ is ~14 and 6.5 times smaller than the corresponding values of $K_S^{CTA}$ for $S = PS^-$ and $PT^-$. The values of $\delta_S$ (proportionality constant) for $S = PS^-$, $PT^-$ and PB are $8.47 \times 10^4$, $15.7 \times 10^4$ and $5.60 \times 10^2\,M^{-1}$, respectively.

## CONCLUSIONS

The effect $[C_{16}E_{20}]_T$ on $k_{obs}$ for the hydrolysis of $PS^-$ reveals a nearly three times lower reactivity in the $C_{16}E_{20}$ micellar pseudophase compared with that in the aqueous pseudophase. This shows the presence of $PS^-{}_M$ ions in the micellar region of considerably low $[H_2O_M]$. An increase in $[C_{16}E_{20}]_T$ from 0 to 0.06 M decreased $k_{obs}$ for alkaline hydrolysis of PB from $66.3 \times 10^{-4}$ to $1.5 \times 10^{-4}\,s^{-1}$ at 0.01 M NaOH and 35 °C. Although the rate of alkaline hydrolysis of PB in the $C_{16}E_{20}$ micellar pseudophase turned out to be extremely low, it is definitely not zero. This shows the presence of $PB_M$ molecules in the micellar region where $[HO^-{}_M]$ is kinetically insignificant. The observed data for the effects of $[C_{16}E_{20}]_T$ on the rate of hydrolysis of both $PS^-$ and PB follow the pseudophase model of micelles reasonably well.

The effects of mixed micelles, $C_{16}E_{20}$–CTABr, on the rate of alkaline hydrolysis of both $PS^-$ and PB have been explained in terms of the pseudophase model of micelles coupled with the empirical equation $K_S = K_S^0/(1 + K_{C_{16}E_{20}/S}[C_{16}E_{20}]_T)$, where $K_S$ and $K_S^0$ are the CTABr micellar binding constants of S ($= PS^-$ and PB) in the presence and absence of $C_{16}E_{20}$, respectively, and $K_{C_{16}E_{20}/S}$ is an empirical constant whose magnitude is the measure of the ability of $C_{16}E_{20}$ surfactant to change the micellar affinity of S from pure cationic micelles to very close to pure $C_{16}E_{20}$ micelles. The calculated values of $K_{C_{16}E_{20}/S}$ for $S = PS^-$, PB and $PT^-$ (anionic phthalimide) at different $[CTABr]_T$ ranging from 0.006 to $0.020\,M^{-1}$ are conceivable in view of the empirical definition of $K_{C_{16}E_{20}/S}$.

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## REFERENCES

1. Menger FM, Portnoy CA. *J. Am. Chem. Soc.* 1967; **89**: 4698–4703.
2. Bunton CA. *Catal. Rev. Sci. Eng.* 1979; **20**: 1–56.
3. Romsted LS. In *Surfactants in Solution*, vol. 2, Mittal KL, Lindman B (eds). Plenum Press: New York, 1984; 1015–1068.
4. (a) Bunton CA, Savelli G. *Adv. Phys. Org. Chem.* 1986; **22**: 213–309; (b) Bertoncini CRA, Neves MdeFS, Nome F, Bunton CA. *Langmuir*, 1993; **9**: 1274–1279; (c) Cuenca A. *Int. J. Chem. Kinet.* 1998; **30**: 777–783.
5. (a) Bunton CA. In *Surfactants in Solution*, vol. 11, Mittal KL, Shah DO (eds). Plenum Press: New York, 1991; 17–40; (b) Bunton CA, Moffatt JR. *Langmuir* 1992; **8**: 2130–2134.
6. Davies DM, Gillitt ND, Paradis PM. *J. Chem. Soc., Perkin Trans. 2* 1996; 659–666.
7. (a) Germani RR, Savelli G, Romeo T, Spreti N, Cerichelli G, Bunton CA. *Langmuir* 1993; **9**: 55–60; (b) Lajis NH, Khan MN. *J. Phys. Org. Chem.* 1998; **11**: 209–215; (c) Khan MN, Ismail E. *J. Chem. Soc., Perkin Trans. 2* 2001; 1346–1350; (d) Bunton CA. In *Encyclopedia of Surface and Colloid Science*, Hubbard A (ed.). Marcel Dekker: New York, 2002; 980–994; (e) Khan MN. In *Encyclopedia of Surface and Colloid Science*, Hubbard A (ed.). Marcel Dekker: New York, 2002; 3178–3191.
8. Menger FM. *Acc. Chem. Res.* 1979; **12**: 111–117, and references cited therein.
9. (a) Herrington KL, Kaler EW, Miller DD, Zasadzinski JA, Chiruvolu S. *J. Phys. Chem.* 1993; **97**: 13792–13802; (b) Maques E, Khan A, Miguel MdeG, Lindman B. *J. Phys. Chem.* 1993; **97**: 4729–4736; (c) Kondo Y, Uchiyama H, Yoshino N, Nishiyama K, Abe M. *Langmuir* 1995; **11**: 2380–2384.
10. Rubingh DN, Bauer M. *ACS Symp. Ser.* 1992; **501**: 210–233.
11. Blasko A, Bunton CA, Toledo EA, Holland PM, Nome F. *J. Chem. Soc., Perkin Trans. 2* 1995; 2367–2373, and references cited therein.
12. Khan MN. *J. Colloid Interface Sci.* 1996; **182**: 602–605.
13. Davies DM, Foggo SJ. *J. Chem. Soc., Perkin Trans. 2* 1998; 247–251.
14. (a) Bunton CA, Wright S, Holland PM, Nome F. *Langmuir* 1993; **9**: 117–120; (b) Foroudian HJ, Bunton CA, Holland PM, Nome F. *J. Chem. Soc., Perkin Trans. 2* 1996; 557–561; (c) Froechner SJ, Nome F, Zanette D, Bunton CA. *J. Chem. Soc., Perkin Trans. 2* 1996; 673–676; (d) Freire L, Iglesias E, Bravo C, Leis JR, Pena ME. *J. Chem. Soc., Perkin Trans. 2* 1994; 1887–1894; (e) Calvaruso G, Cavasino FP, Sbriziolo C, Liveri MLT. *J. Chem. Soc., Faraday Trans.* 1995; **91**: 1075–1079.
15. Khan MN, Ismail E, Yusoff MR. *J. Phys. Org. Chem.* 2001; **14**: 669–676.
16. Khan MN, Ismail E. *J. Colloid Interface Sci.* 2001; **240**: 636–639.
17. Khan MN, Ismail E. *J. Phys. Org. Chem.* 2002; **15**: 374–384.
18. Khan MN. *J. Chem. Soc., Perkin Trans. 2* 1990; 445–457.
19. Khan MN. *Langmuir* 1996; **12**: 261–269.
20. Huibers PDT, Lobanov VS, Katritzky AR, Shah DO, Karelson M. *Langmuir* 1996; **12**: 1462–1470.
21. Khan MN, Arifin Z. *J. Colloid Interface Sci.* 1996; **180**: 9–14.
22. Khan MN. *J. Org. Chem.* 1997; **62**: 3190–3193.
23. Khan MN. *Colloids Surf. A* 1998; **139**: 63–74.

24. (a) Bunton CA, Foroudian HJ, Gillitt ND, Whiddon CR. *Can. J. Chem.* 1998; **76**: 946–954; (b) Bravo C, Garcia-Rio L, Leis JR, Pena ME, Iglesias E. *J. Colloid Interface Sci.* 1994; **166**: 316–320, and references cited therein; (c) Fernandez A, Iglesias E, Garcia-Rio L, Leis JR. *Langmuir* 1995; **11**: 1917–1924; (d) Khan MN, Arifin Z, Lasedik AMN, Hanifiah MAM, Alex G. *Langmuir* 1997; **13**: 3959–3964; (e) Khan MN, Arifin Z. *J. Chem. Soc., Perkin Trans. 2* 2000; 2503–2510.
25. Khan MN, Arifin Z, Wahab IA, Ali SFM, Ismail E. *Colloids Surf. A* 2000; **163**: 271–281.
26. (a) Phillies GDJ, Yambert JE. *Langmuir* 1996; **12**: 3431–3436; (b) Romsted LS, Yao J. *Langmuir* 1996; **12**: 2425–2432.
27. Gao H-C, Zhao S, Mao S-Z, Yuan H-Z, Yu J-Y, Shen L-F, Du Y-R. *J. Colloid Interface Sci.* 2002; **249**: 200–208.
28. Mukerjee P. In *Solution Chemistry of Surfactants*, vol. 1, Mittal KL (ed.). Plenum Press: New York, 1979; 153–174.
29. Vera S, Rodenas E. *Tetrahedron* 1986; **42**: 143–149.
30. (a) Khan MN, Ahmad FB. *React. Kinet. Catal. Lett.* 2001; **72**: 321–329; (b) Khan MN, Yusoff MR. *J. Phys. Org. Chem.* 2001; **14**: 74–80; (c) Khan MN, Ismail E. *J. Chem. Res. (S)* 2001; 143–145.
31. Bravo C, Herves P, Leis JR, Pena ME. *J. Colloid Interface Sci.* 1992; **153**: 529–536.
32. Sommer C, Pedersen JS, Egelhaaf SU, Cannavacciuolo L, Kohlbrecher J, Schurtenberger P. *Langmuir* 2002; **18**: 2495–2505.