Effects of inorganic ions on rate of alkaline hydrolysis of phthalimide in the presence of cationic micelles

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Pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of phthalimide (PTH) show a monotonic decrease with the increase in the total concentration of cetyltrimethylammonium bromide ($[CTABr]_T$) † at a constant [NaOH] and [NaBr]. The pseudophase micellar (PM) model and the pseudophase ion-exchange (PIE) model reveal that the rate of alkaline hydrolysis of PTH is insignificant in the micellar pseudophase compared to that in the aqueous pseudophase under different reaction conditions. The CTABr micellar binding constants (K_S) of ionized phthalimide (S^-) follow an empirical relationship: $K_S = K_S^0/(1 + \Psi[MX])$ where MX represents NaOH or NaBr. The value of the empirical parameter Ψ for HO^- is nearly 30-fold smaller than that for Br^-. The decrease in K_S with the increase in $[HO^-]$ or $[Br^-]$ is attributed to the expulsion of S^- ions from the micellar pseudophase to the aqueous pseudophase by HO^- or Br^-. Pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of PTH in the presence of CTABr micelles vary with [MX] (MX = NaBr, KCl and Na_2CO_3) according to the empirical relationship: $k_{obs} = (k_{obs}^0 + \theta K[MX])/(1 + K[MX])$ where θ and K are empirical parameters. Based upon the values of θ, it is concluded that the respective anions Br^-, Cl^- and CO_3^{2-} can expel nearly 100, 60 and 15% of the total amount of micellized S^- from the micellar pseudophase to the aqueous pseudophase under the limiting conditions where $1 \ll K[MX]$.

Introduction

The first kinetic model known as the pseudophase micellar (PM) model of Menger and Portnoy[1] was developed to explain the effects of micelles on rates of reactions where a monotonic decrease or increase in pseudo-first-order rate constants (k_{obs}) with the increase in the concentration of micelles ($[D_n]$) was observed. In the presence of ionic micelles, many bimolecular reactions involving a neutral and an ionic reactant with the ionic reactant carrying charge similar to that of counterions of the ionic micelles exhibited maxima in the plots of k_{obs} *versus* $[D_n]$. These results cannot be explained in terms of the original PM model and hence in order to explain these results, Romsted[2] proposed an addition of ion-exchange to the original PM model. The modified model of Romsted known as the pseudophase ion-exchange (PIE) model involves more assumptions than the original PM model and yet some serious weaknesses of the PIE model have recently been realized.[3]

The effects of cationic micelles on the rate of a bimolecular reaction involving anionic reactants could not easily be explained in terms of the PIE model[2] because this model originally considered only one ion-exchange process. The kinetic data on the effects of [KBr] on the rate of hydroxide ion-catalyzed hydrolysis of a few anionic esters[4] and anionic *N*-hydroxyphthalimide[5] were explained in terms of the PIE model considering the usual Br^-–HO^- ion-exchange process coupled with an empirical equation [eqn. (1)] where the magnitude of empirical parameter L gives a measure of the ability of an inert anion (Br^-) to expel an anionic organic solute from the micellar pseudophase to the aqueous pseudophase. It should be noted that the effects of $[HO^-]$ upon K_S were ignored in these studies which is conceivable for the reasons that (i) very low values of $[HO^-]$ were maintained in these studies and (ii) the hydrophilicity of HO^- is much larger than that of Br^-. In eqn. (1), K_S represents the cationic micellar binding constant of

$$K_S = K_S^0 - L[KBr] \qquad (1)$$

the anionic organic solute and $K_S = K_S^0$ at [KBr] = 0. The effects of cationic micelles on benzimidazole deprotonation equilibria, in the absence and presence of added inert salt (with the anion carrying charge similar to that of counterions), were explained by the PIE model considering two ion-exchange processes (HO^-–X^- and S^-–X^- where S^- is ionized benzimidazole) with more restrictive conditions and assumptions compared to one involving only one ion-exchange process.[6] Oliveira *et al.* have claimed a successful fit of observed data on a cetyltrimethylammonium bromide (CTABr) micellar-mediated bimolecular reaction involving two anionic reactants (S^- and HO^-) in terms of the PIE model considering only two ion-exchange processes, S^-–Br^- and HO^-–Br^-, and ignoring other possible ion-exchange S^-–HO^- as well as ion-exchange processes involving anionic buffer components used in the study.[7]

The observed data on the effects of [KBr] on the rate of methanolysis of ionized phenyl salicylate did not obey eqn. (1).[8] In the continuation of our investigation of the effects of inert inorganic and organic salts on rates of hydrolysis, alkanolysis and aminolysis of esters and imides in the presence of micelles, we studied the effects of some inorganic salts on the rate of alkaline hydrolysis of phthalimide in the presence of CTABr micelles. The observed results and plausible explanations of them are described.

Experimental

Materials

All the reagents used were supplied by Fluka or Aldrich and were of the highest commercially available purity. Stock solutions (0.01 mol dm^{-3}) of phthalimide were prepared in acetonitrile.

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† The IUPAC name for cetyl is hexadecyl.

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Kinetic measurements

Nonionized (SH) and ionized (S^-) phthalimide showed significant absorption while phthalamic acid (hydrolysis product of SH and S^-) did not show detectable absorption at 300 nm. Thus, the rate of hydrolysis of phthalimide (PTH), in an alkaline medium, was studied by monitoring the disappearance of PTH spectrophotometrically at 300 nm using a Shimadzu model UV 2101/3101PC UV–VIS–NIR scanning spectrophotometer. The reactions were carried out for up to 2–6 halflives and the observed data fitted well to an equation derived from the first-order rate law. Details of the experimental procedure are the same as described elsewhere.[9]

Product analysis

The expected immediate product of the cleavage of PTH, in the presence of sodium hydroxide and cetyltrimethylammonium bromide (CTABr),† is ionized phthalamic acid. The molar absorptivities of ionized and nonionized phthalamic acid and phthalic acid at 300 nm are nearly zero. Therefore, the apparent molar absorptivity of the reaction mixture, $E_{app} \approx E_{PTH}$ at 300 nm because $E_{app} = E_{PTH} - E_P$ where E_{PTH} and E_P represent the molar absorptivity of PTH and products, respectively. The calculated values of E_{app} turned out to be almost independent of the total concentration of CTABr and NaOH in the presence of inert inorganic ions. These results show that the products of the reaction do not absorb to a detectable level at 300 nm and the products are most likely ionized phthalamic acid and phthalic acid. Although the rate of alkaline hydrolysis of phthalamic acid is more than 10^6-fold slower than that of PTH,[10,11] the formation of a small amount of phthalic acid from phthalamic acid within the reaction periods attained in the kinetic runs cannot be completely ruled out. However, the rate of formation of phthalic acid would not affect the rate of disappearance of PTH (monitored in the present study).

Results and discussion

Effects of $[CTABr]_T$ on k_{obs} for hydrolysis of PTH at a constant [NaOH]

The cleavage of PTH was studied within the total concentration of cetyltrimethylammonium bromide ($[CTABr]_T$) range 0–0.01 mol dm^{-3} at 0.005 mol dm^{-3} NaOH. Pseudo-first-order rate constants (k_{obs}) showed a nonlinear monotonic decrease with the increase in $[CTABr]_T$. Similar observations were obtained at 0.02, 0.05, 0.1, 0.3, 0.5 and 0.8 mol dm^{-3} NaOH. These observed data are shown graphically in Fig. 1.

The rate constants, k_{obs} ($=k_W$), obtained within the $[HO^-]_T$ range 0.005 to 0.8 mol dm^{-3} in the absence of CTABr micelles, were found to fit eqn. (2), where k_0 and k_{OH} represent

$$k_W = k_0 + k_{OH}[HO^-] \qquad (2)$$

uncatalyzed and hydroxide ion-catalyzed first- and second-order rate constants, respectively, for hydrolysis of PTH. The least-squares calculated values of k_0 and k_{OH} are $(21.9 \pm 1.1) \times 10^{-4}$ s^{-1} and $(38.4 \pm 2.9) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, respectively. The calculated values of k_0 and k_{OH} are comparable with the corresponding values obtained in the earlier studies.[12]

It is easily shown that the rate $= k_0$[PTH] (where [PTH] = [SH] + $[S^-]$ with SH and S^- representing nonionized and ionized PTH) corresponds to either rate $= k_{H_2O}[S^-][H_2O]$ or rate $= k'_{OH}[HO^-][SH]$ in the $[HO^-]$ range ~0.0025–0.10 mol dm^{-3} [12] where the rate of hydrolysis is $[HO^-]$-independent and in such a $[HO^-]$ range, $[H^+] \ll K_a$ (with K_a representing the ionization constant of PTH). The value of K_a is 3.05×10^{-10} dm^3 mol^{-1} at 30 °C.[13] But, it has been concluded elsewhere[14] that $[HO^-]$-independent hydrolysis of PTH involved the rate law: rate $= k'_{OH}[HO^-][SH]$. The mechanistic details for the rate terms $k'_{OH}[HO^-][SH]$ and $k_{OH}[HO^-][S^-]$ may be expected to be similar to the corresponding rate terms discussed for alkaline hydrolysis of maleimide.[15]

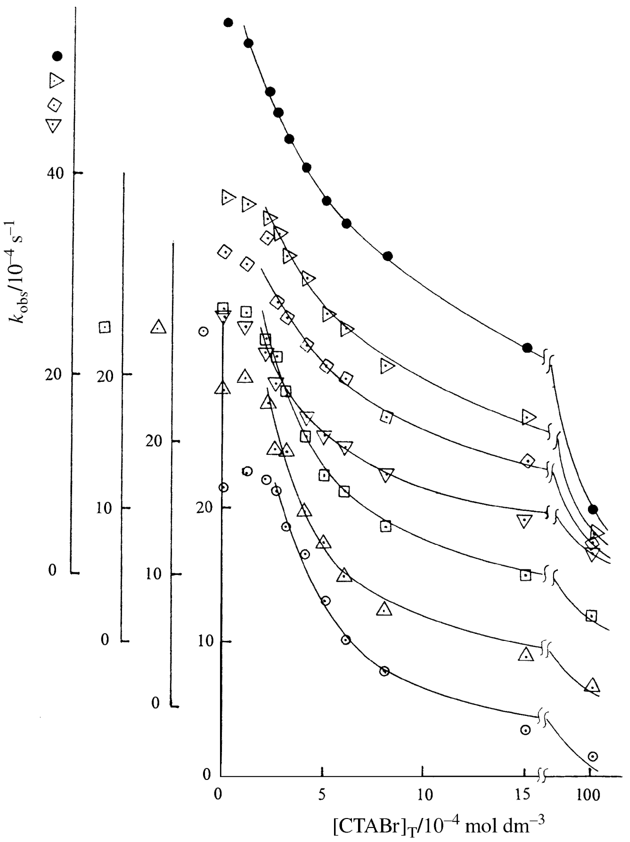

Fig. 1 Effects of $[CTABr]_T$ on pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of PTH at 35 °C and [NaOH] = 0.005 (○), 0.02 (△), 0.05 (□), 0.1 (▽), 0.3 (◇), 0.5 (▷) and 0.8 mol dm^{-3} (●). The solid lines are drawn through the calculated data points using eqn. (3) and unknown parameters, k_M and K_S, listed in Table 1.

The increase in $[CTABr]_T$ decreased k_{obs} for the hydrolysis of PTH at a constant [NaOH] (Fig. 1). These observations may be explained using the pseudophase micellar (PM) model[1] which consists of several assumptions.[2,16] The reaction scheme for the hydrolysis of PTH, in the presence of CTABr micelles (D_n), is shown in Scheme 1, where subscripts W and M represent

$$PTH_W + D_n \xrightleftharpoons{K_S} PTH_M$$
$$HO^-_W + D_n \xrightleftharpoons{K_{OH}} HO^-_M$$
$$PTH_W \xrightarrow{k'_{0,W}} \text{Product(s)}$$
$$PTH_W + HO^-_W \xrightarrow{k'_{OH,W}} \text{Product(s)}$$
$$PTH_M \xrightarrow{k'_{0,M}} \text{Product(s)}$$
$$PTH_M + HO^-_M \xrightarrow{k'_{OH,M}} \text{Product(s)}$$

Scheme 1

aqueous pseudophase and micellar pseudophase, respectively. The observed rate law (rate $= k_{obs}$[PTH], where [PTH] = $[PTH_W] + [PTH_M]$) and Scheme 1 can lead to eqn. (3) where

$$k_{obs} = \frac{k_W + k_M K_S[D_n]}{1 + K_S[D_n]} \qquad (3)$$

$k_W = k'_{0,W} + k'_{OH,W}[HO^-_W]$, $k_M = k'_{0,M} + k''_{OH,M} m_{OH}$ with $m_{OH} = [HO^-_M]/[D_n]$ and $k''_{OH,M} = k'_{OH,M}/V_M$ (where V_M is the molar volume of CTABr micelles).

An attempt to fit the observed data to eqn. (3) requires knowledge of the c.m.c. values under the present experimental

Table 1 Values of k_M and K_s calculated from eqns. (3) and (5) for alkaline hydrolysis of PTH at different [NaOH][a]

[NaOH]/ M_1[f]	10^4 c.m.c./ M_1[f]	$10^4 k_w$/ s^{-1}	$10^4 k_M/s^{-1}$	K_s/ $dm^3\ mol^{-1}$	$10^9 \Sigma\ d_i^2$[b]	Q[c] (%)	$10^4 k'_{0,M}$[d]/ s^{-1}	$10^4 k''_{OH,M}$[d]/ s^{-1}	K_s[d]/ $dm^3\ mol^{-1}$	$10^9 \Sigma\ d_i^2$[e]
0.005	2.4	22.1	−0.2 ± 1.0[g]	2900 ± 377[g]	55.96	−ve	3.80 ± 1.87[g]	−70 ± 36[g]	1128 ± 383[g]	20.72
	(2.2)[h]						−0.1 ± 1.0	0	2898 ± 377	56.01
			0	(3203 ± 715)[i]						
0.020	2.0	23.8	0.61 ± 0.62	3439 ± 326	52.58	46	4.53 ± 1.16	−26 ± 12	1525 ± 366	24.01
	(1.8)						0.5 ± 0.7	0	3018 ± 325	62.42
0.050	1.8	24.9	0.81 ± 0.54	3111 ± 210	22.99	50	4.75 ± 1.80	−15 ± 6	1842 ± 296	15.81
	(1.7)						0.6 ± 0.7	0	2713 ± 237	36.04
0.100	1.3	25.8	1.12 ± 0.50	2615 ± 150	18.77	53	2.55 ± 2.04	−4 ± 5	2356 ± 324	17.12
	(1.1)						1.10 ± 0.5	0	2594 ± 148	18.65
0.300	1.2	32.3	1.34 ± 0.28	1541 ± 43	8.21	39	−3.2 ± 3.0	8.8 ± 5.4	1944 ± 170	7.19
	(1.2)						0	2.94 ± 0.76	1795 ± 78	8.81
0.500	1.5	37.6	1.87 ± 0.63	1248 ± 55	19.38	38	−26 ± 8	48 ± 13	3038 ± 524	55.90
	(1.5)						0	6.28 ± 2.28	1982 ± 237	123.5
0.800	0.6	55.2	2.32 ± 0.39	1109 ± 19	8.23	32	43 ± 39	−66 ± 61	697 ± 157	75.75
	(0.5)						1.1 ± 1.4	0	900 ± 57	93.64

[a] $[PTH]_0 = 2 \times 10^{-4}$ mol dm^{-3}, 35 °C, $\lambda = 300$ nm, aqueous reaction mixture for each kinetic run contained 2% v/v CH_3CN. [b] $\Sigma\ d_i^2 = \Sigma\ (k_{obs\ i} - k_{calcd\ i})^2$ where $k_{calcd\ i}$ represents calculated value of rate constant using eqn. (3) at the *i*th $[CTABr]_T$. [c] $Q = 100(k_M K_S[D_n])/(k_W + k_M K_S[D_n])$ at $[D_n] \approx [CTABr]_T = 0.01$ mol dm^{-3}. [d] Calculated from eqn. (5) with $K_{Br}^{OH} = 20$ and $\beta = 0.8$. [e] $\Sigma\ d_i^2 = \Sigma\ (k_{obs\ i} - k_{calcd\ i})^2$ where $k_{calcd\ i}$ represents the calculated value of the rate constant using eqn. (5) at the *i*th $[CTABr]_T$. [f] M_1 = mol dm^{-3}. [g] Error limits are standard deviations. [h] Parenthesized values were obtained from a graphical technique as described in the text. [i] Calculated from the relationship $(k_W/k_{obs}) - 1 = K_S[D_n]$.

conditions. The values of c.m.c. were determined by the iterative[17] and graphical[18] techniques and both techniques gave nearly the same c.m.c. values (Table 1). The values of k_M and K_S were calculated from eqn. (3) using the nonlinear least-squares technique. The calculated values of k_M and K_S as well as least-squares ($\Sigma\ d_i^2$ where $d_i = k_{obs\,i} - k_{calcd\,i}$ at the *i*th $[CTABr]_T$) at different [NaOH] are summarized in Table 1. The values of k_W at different [NaOH] (Table 1) were obtained by carrying out kinetic runs at $[CTABr]_T = 0$ as well as at $[CTABr]_T <$ c.m.c. (Table 1). The fitting of the observed data (k_{obs} *versus* $[D_n]$) to eqn. (3) appears to be satisfactory as is evident from the plots of Fig. 1 where solid lines are drawn through the calculated data points and from the standard deviations associated with the calculated values of K_S (Table 1).

The calculated values of k_M, especially at low values of [NaOH], are associated with high standard deviations (Table 1). The negative or positive values of k_M with very high standard deviations merely indicate the statistical unreliability of k_M values and insignificance of the $k_M K_S[D_n]$ term compared with k_W in eqn. (3). The maximum contributions of $k_M K_S[D_n]$ [obtained at the maximum concentration of CTABr (=0.01 mol dm^{-3}) attained in the study] compared with k_W in eqn. (3) are within the range 32–53% at different [NaOH] (Table 1). But the contributions of $k_M K_S[D_n]$ compared with k_W in eqn. (3) are ≤13% at 0.0015 mol dm^{-3} CTABr. The negative value of k_M with a standard deviation of nearly 500% at 0.005 mol dm^{-3} NaOH shows that statistically it is not different from zero. Thus, a relatively more reliable value of K_S at 0.005 mol dm^{-3} NaOH was obtained from the relationship $(k_W/k_{obs}) - 1 = K_S[D_n]$ which is derived from eqn. (3) with $k_M = 0$ and such a calculated value of K_S is also shown in Table 1.

The occurrence of ion-exchange has been unequivocally ascertained in several ionic micellar mediated bimolecular reactions with one or both reactants carrying charge similar to the charge of counterion of the micelle. The possible ion-exchange processes in the present reacting system are HO^-–Br^-, HO^-–S^- and Br^-–S^-. The ion-exchange HO^-–S^- is expected to be the least effective among these three ion-exchange processes because the hydrophilicity of these ions varies in the order $HO^- > Br^- > S^-$. The ion-exchange Br^-–S^- may be also ignored under the present experimental conditions for the reason that the total concentration of bromide ions attained is not sufficiently high ($[Br^-]_T \le 0.01$ mol dm^{-3}) to make this ion-exchange relatively effective. Such an ion-exchange was not kinetically detected in the alkaline hydrolysis of several anionic esters,[19] carried out under essentially similar experimental conditions including concentration range of cationic micelles, where some of the anionic ester molecules were equally or even less hydrophobic than anionic phthalimide. Furthermore, as discussed in the Appendix, the value of K_S will remain unchanged with the change in $[D_n]$ at a constant [PTH] and [NaOH] even if ion-exchange HO^-–S^- is kinetically effective. Thus, the ion-exchange HO^-–Br^- is considered in the present reaction conditions.

In addition to the assumptions made in the pseudophase micellar model,[16] the PIE model assumes that the anionic nucleophile (HO^-) and inert counterion (Br^-) of the CTABr micelle compete for the micellar surface according to an ion-exchange equilibrium described by eqn. (4) where $K_{Br}^{OH} = K_{Br}/K_{OH}$ with $K_{Br} = [Br_M^-]/[Br^-_W][D_n]$. The observed rate law (rate = k_{obs}[PTH]), Scheme 1 and eqn. (4) can lead to eqn. (5) where

$$HO_M^- + Br_W^- \xrightleftharpoons{K_{Br}^{OH}} HO_W^- + Br_M^- \qquad (4)$$

$$k_{obs} = \frac{k'_{0,W} + k'_{OH,W}[HO_W^-] + (k'_{0,M} + k''_{OH,M} m_{OH}) K_S[D_n]}{1 + K_S[D_n]} \qquad (5)$$

$[HO^-]_T = [HO_W^-] + [HO_M^-]$, $m_{OH} = [HO_M^-]/[D_n]$ and $k''_{OH,M} = k'_{OH,M}/V_M$ (where V_M is the molar volume of CTABr micelles). The values of m_{OH} at different $[D_n]$ and at a constant $[HO^-]_T$ (≈[NaOH]) were calculated from eqn. (6) at a given value of

$$m_{OH}{}^2 + m_{OH} \left\{ \frac{[HO^-]_T + [Br^-]_T K_{Br}^{OH}}{(K_{Br}^{OH} - 1)[D_n]} - \beta \right\} - \frac{\beta [HO^-]_T}{(K_{Br}^{OH} - 1)[D_n]} = 0 \qquad (6)$$

K_{Br}^{OH} with known values of $[HO^-]_T$, $[Br^-]_T$ and β (=0.8) where $[Br^-]_T = [Br_W^-] + [Br_M^-]$ (=$[D_n]$ + c.m.c.), $\beta = m_{OH} + m_{Br}$ and $m_{Br} = [Br_M^-]/[D_n]$. These calculated values of m_{OH} were subsequently used in eqn. (5) to calculate $k'_{0,M}$, $k''_{OH,M}$, K_S and least-squares ($\Sigma\ d_i^2$) values using the nonlinear least-squares technique with $k'_{0,W}$ (=0.00219 s^{-1}) and $k'_{OH,W}$ (=0.00384 dm^3 mol^{-1} s^{-1}) obtained from the kinetic runs carried out at different [NaOH] in the absence of CTABr micelles. Such calculations were carried out at different arbitrarily assigned values of K_{Br}^{OH}. But the values of $\Sigma\ d_i^2$ differ only slightly with the increase in the value of K_{Br}^{OH} from 5 to 500 at $\beta = 0.8$.

For example, the respective calculated values of $\Sigma\ d_i^2$ at $K_{Br}^{OH} = 5$, 20 and 500 are 24.70×10^{-9}, 24.01×10^{-9} and

23.75×10^{-9} at 10^4 c.m.c. = 2.0 mol dm^{-3} and 0.02 mol dm^{-3} NaOH and 76.09×10^{-9}, 75.75×10^{-9} and 77.48×10^{-9} at 10^4 c.m.c. = 0.6 mol dm^{-3} and 0.8 mol dm^{-3} NaOH. The calculated values of rate constants, k_{calcd}, within the K_{Br}^{OH} range of 5–500 at $\beta = 0.8$ remained almost unchanged. In view of these values of $\Sigma\, d_i^2$ and k_{calcd}, it is not easy to ascertain which value of K_{Br}^{OH} is the most appropriate. This is a general weakness of the PIE model.[3] It is interesting to note that a change in K_{Br}^{OH} from 5 to 500 changes (i) $k'_{0,M}$ from $(5.90 \pm 2.17) \times 10^{-4}$ to $(2.85 \pm 1.16) \times 10^{-4}$ s^{-1} at 0.02 mol dm^{-3} NaOH and from $(140 \pm 129) \times 10^{-4}$ to $(14.1 \pm 18.3) \times 10^{-4}$ s^{-1} at 0.8 mol dm^{-3} NaOH, (ii) $k''_{OH,M}$ from $(-17 \pm 7) \times 10^{-4}$ to $(-225 \pm 177) \times 10^{-4}$ s^{-1} at 0.02 mol dm^{-3} NaOH and from $(-185 \pm 173) \times 10^{-4}$ to $(-84 \pm 120) \times 10^{-4}$ s^{-1} at 0.8 mol dm^{-3} NaOH, and (iii) K_S from 1854 ± 336 to 1099 ± 390 dm^3 mol^{-1} at 0.02 mol dm^{-3} NaOH and from 711 ± 150 to 426 ± 329 dm^3 mol^{-1} at 0.8 mol dm^{-3} NaOH. Similar results were obtained at other concentrations of NaOH.

There is evidence that β decreases with the increase in the concentration of cationic surfactants with highly hydrophilic anions such as HO$^-$ and F$^-$.[20] Although Bunton[3c] has pointed out that the addition of a weakly-bound dilute anion, *e.g.*, HO$^-$, to CTABr probably does not markedly reduce β, the presence of a high concentration of HO$^-$ might decrease β. In order to check the effect of varying β values on the quality of data fitting to eqn. (5), the observed data (k_{obs} *versus* [D$_n$]) at 0.02 and 0.80 mol dm^{-3} NaOH (the lowest and the highest [NaOH] attained in the present study) were used to calculate $k'_{0,M}$, $k''_{OH,M}$ and K_S from eqn. (5) at $K_{Br}^{OH} = 20$ and $\beta = 0.05$, 0.50 and 0.95. It is surprising to note that the values of $\Sigma\, d_i^2$ differ only slightly (from 22.61×10^{-9} to 24.12×10^{-9} at 10^4 c.m.c. = 2.0 mol dm^{-3} and 0.02 mol dm^{-3} NaOH and from 75.69×10^{-9} to 75.71×10^{-9} at 10^4 c.m.c. = 0.6 mol dm^{-3} and 0.80 mol dm^{-3} NaOH) with the increase in β from 0.05 to 0.95 at $K_{Br}^{OH} = 20$. Thus, it is apparent that the quality of data fitting to eqn. (5) remains almost independent of the β value within its range 0.05–0.95 at constant K_{Br}^{OH} (=20). It may also be noted that similar calculational analysis was observed in a reaction system involving only one possible ion exchange (HO$^-$–Br$^-$).[3d] It may be noted that, at $K_{Br}^{OH} = 20$, the change in β from 0.05 to 0.95 changes (i) $k'_{0,M}$ from $(2.42 \pm 0.89) \times 10^{-4}$ to $(5.64 \pm 2.21) \times 10^{-4}$ s^{-1} at 0.02 mol dm^{-3} NaOH and from $(36.1 \pm 32.4) \times 10^{-4}$ to $(44.7 \pm 40.6) \times 10^{-4}$ s^{-1} at 0.8 mol dm^{-3} NaOH, (ii) $k''_{OH,M}$ from $(-492 \pm 226) \times 10^{-4}$ to $(-23.7 \pm 10.5) \times 10^{-4}$ s^{-1} at 0.02 mol dm^{-3} NaOH and from $(-899 \pm 835) \times 10^{-4}$ to $(-57 \pm 53) \times 10^{-4}$ s^{-1} at 0.8 mol dm^{-3} NaOH, and (iii) K_S from 1307 ± 369 to 1526 ± 367 dm^3 mol^{-1} at 0.02 mol dm^{-3} NaOH and from 703 ± 153 to 696 ± 158 dm^3 mol^{-1} at 0.8 mol dm^{-3} NaOH.

The calculated values of $k'_{0,M}$ and $k''_{OH,M}$ at different K_{Br}^{OH} with a constant β (=0.8) and at different β with a constant K_{Br}^{OH} (=20) are statistically unreliable because they are either negative or positive associated with very large standard deviations. A mild change in K_S values with change in K_{Br}^{OH} from 5 to 500 at $\beta = 0.8$ and in β from 0.05 to 0.95 at $K_{Br}^{OH} = 20$ is due to an insignificant contribution of $(k'_{0,M} + k''_{OH,M} m_{OH}) K_S [D_n]$ compared with $k'_{0,W} + k'_{OH,W}[HO_W^-]$ in eqn. (5).

Since most of the reported values of K_{Br}^{OH} lie between 2 to 31,[3b,4,19,21] an arbitrary value of $K_{Br}^{OH} = 20$ was chosen in the calculation of $k'_{0,M}$, $k''_{OH,M}$ and K_S from eqn. (5). The calculated values of $k'_{0,M}$, $k''_{OH,M}$, K_S and $\Sigma\, d_i^2$ at different [NaOH] are summarized in Table 1. The calculated values of $k'_{0,M}$, and $k''_{OH,M}$ are either negative or positive and are associated with very high standard deviations and hence, as discussed earlier, these values of $k'_{0,M}$ and $k''_{OH,M}$ are statistically unreliable. The values of $\Sigma\, d_i^2$ and the standard deviations associated with K_S values at all concentrations of NaOH are higher with the use of eqn. (5) than with the use of eqn. (3) (Table 1). This shows that the data fitting is better with the pseudophase micellar (PM) model than with the PIE model.

The values of K_S (associated with reasonably good standard deviations), obtained from eqn. (3), decreased from 3439 to 1109 dm^3 mol^{-1} with the increase in [NaOH] from 0.02 to 0.80 mol dm^{-3} (Table 1). These results show that hydroxide ions expel phthalimide anions (S$^-$) from the micellar pseudophase to the aqueous pseudophase. The values of K_S were found to fit the empirical equation [eqn. (7)] where K_S^0 and Ψ are empirical

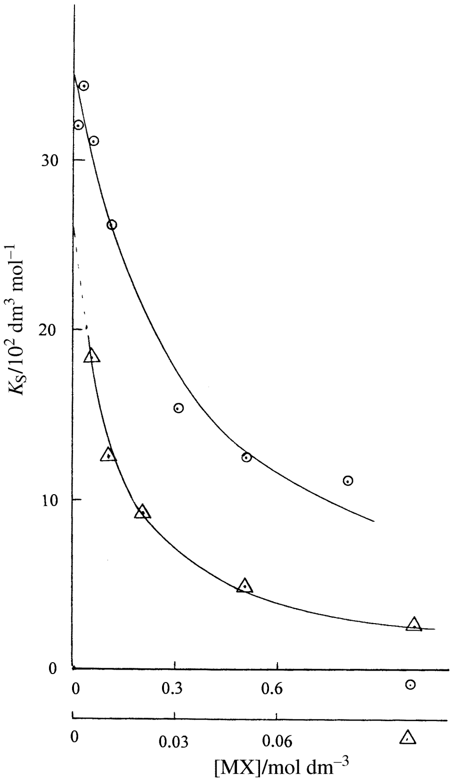

Fig. 2 Plots showing the dependence of CTABr micellar binding constants (K_S) of ionized PTH upon [MX] where MX = NaOH (○) and NaBr (△). The solid lines are drawn through the calculated data points using eqn. (7) and unknown parameters, K_S^0 and Ψ, mentioned in the text.

$$K_S = \frac{K_S^0}{1 + \Psi[\text{NaOH}]} \qquad (7)$$

parameters. The magnitude of Ψ is the measure of the ability of an ion (such as HO$^-$) to expel another ion of similar charge (such as S$^-$ with cationic micellar binding constant K_S^0 at [NaOH] where $1 \gg \Psi$ [NaOH]) from the micellar pseudophase to the aqueous pseudophase. A similar empirical equation was found to fit the observed data (K_S *versus* [inert salt]) on the effects of [KBr] on methanolysis of ionized phenyl salicylate (PS$^-$)[8] and on the effects of [C$_6$H$_5$COONa][22a] and [NaBr][22b] on aminolysis of PS$^-$ in the presence of CTABr micelles. The apparent relationship between eqn. (7) and ion-exchange between $^-$OH and S$^-$ at the CTABr micellar surface may be realized from the text described in the Appendix. The magnitude of Ψ represents the ability of $^-$OH to expel S$^-$ from the micellar pseudophase to the aqueous pseudophase. The nonlinear least-squares calculated values of K_S^0 and Ψ are 3482 ± 129 and 3.4 ± 0.5 dm^3 mol^{-1}, respectively. The fitting of K_S values to eqn. (7) is evident from the standard deviations associated with the values of K_S^0 and Ψ and from the plot of Fig. 2 where the solid line is drawn through the calculated data points.

Effects of [CTABr]$_T$ on k_{obs} for the hydrolysis of PTH at constant [NaBr] in the presence of 0.1 mol dm^{-3} NaOH

The kinetic runs carried out to study the effects of [CTABr]$_T$ on k_{obs} for the hydrolysis of PTH in the presence of a constant concentration of NaOH revealed a nonlinear decrease in K_S

Table 2 Values of k_M and K_S calculated from eqns. (3) and (5) for alkaline hydrolysis of PTH at different [NaBr][a]

[NaBr]/M$_1^f$	10^4 c.m.c./M$_1^f$	10^4k_W/s^{-1}	10^4k_M/s^{-1}	K_S/dm^3 mol^{-1}	$10^9\Sigma\, d_i^{2b}$	Q^c (%)	$10^4k'_{0,M}{}^d$/s^{-1}	$10^4k''_{OH,M}{}^d$/s^{-1}	$K_S{}^d$/dm^3 mol^{-1}	$10^9\Sigma\, d_i^{2e}$
0.005	1.6	26.7	1.24 ± 0.24^g	1836 ± 45^g	3.40	46	6.35 ± 4.03^g	−20 ± 1.5^g	1365 ± 167^g	9.51
	(1.2)^h						0.9 ± 0.5	0	1600 ± 80	13.01
0.010	1.1	26.3	0.65 ± 0.44	1246 ± 53	9.92	23	19.5 ± 6.7	−95 ± 34	837 ± 86	4.57
	(1.0)						0.4 ± 0.5	0	1143 ± 58	13.22
0.020	1.3	26.2	0.60 ± 0.82	924 ± 72	28.40	17	87.8 ± 48.6	−643 ± 359	457 ± 126	14.25
	(1.3)						0.4 ± 0.9	0	853 ± 72	31.44
0.050	0.8	25.3	1.06 ± 0.62	490 ± 29	8.46	17	−68 ± 53	1027 ± 781	736 ± 195	8.05
	(0.9)						0	21.7 ± 9.4	549 ± 35	9.81
0.100	0.9	25.5	−0.76 ± 1.05	236 ± 21	11.05	−ve	^{j}	^{j}	^{j}	
	1.1^i		0	(261 ± 2)^i			0	−1.9 ± 27.7	262 ± 24	12.59

[a] $[PTH]_0 = 2 \times 10^{-4}$ mol dm^{-3}, [NaOH] = 0.1 mol dm^{-3}, 35 °C, $\lambda = 300$ nm, aqueous reaction mixture for each kinetic run contained 2% v/v CH_3CN. Footnotes *b*, *c*, *d*, *e*, *f*, *g* and *h* are the same as described in Table 1. [i] Calculated from the relationship: $k_W/k_{obs} = \Phi + K_S[CTABr]_T$ where $\Phi = 1 - \text{c.m.c.}\ K_S$ and the calculated values of $\Phi = 0.97 \pm 0.006$ and $K_S = 261 \pm 2$ dm^3 mol^{-1}. [j] The observed data did not fit eqn. (5) with $k'_{0,M}$, $k''_{OH,M}$ and K_S as unknown parameters.

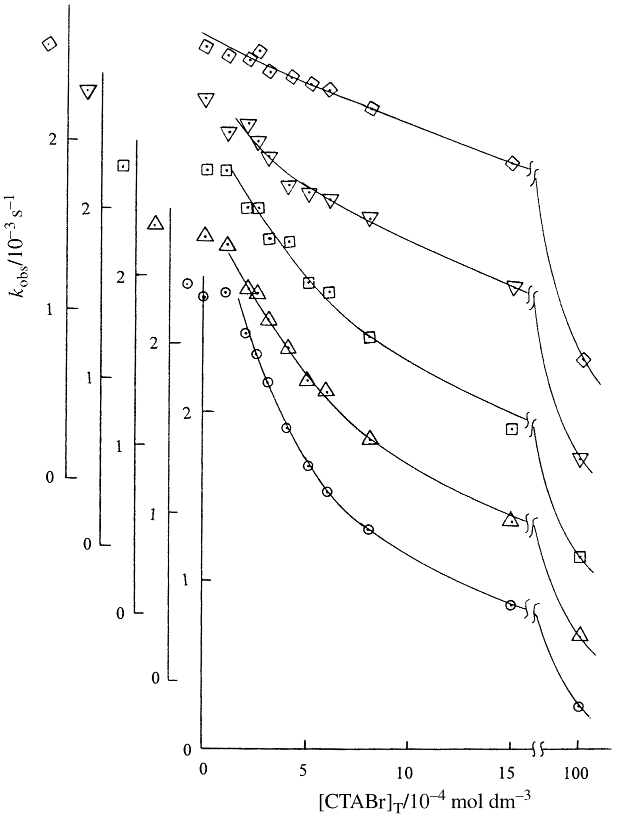

Fig. 3 Effects of $[CTABr]_T$ on pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of PTH at 35 °C, 0.1 mol dm^{-3} NaOH and [NaBr] = 0.005 (○), 0.01 (△), 0.02 (□), 0.05 (▽), 0.1 mol dm^{-3} (◇). The solid lines are drawn through the calculated data points using eqn. (3) and unknown parameters, k_M and K_S, listed in Table 2.

with the increase in [NaOH] and this was attributed to the occurrence of ion-exchange $^-OH–S^-$. Relatively more effective ion-exchange $Br^-–S^-$ was ignored because of the very low total concentration of Br^- attained in these kinetic runs (maximum $[Br^-]_T = 0.01$ mol dm^{-3}). In order to discover the effect of [NaBr] on the CTABr micellar binding constant (K_S) of S^-, a series of kinetic runs were carried out within the $[CTABr]_T$ range 0–0.01 mol dm^{-3} at 0.005 mol dm^{-3} NaBr and 0.1 mol dm^{-3} NaOH. The increase in $[CTABr]_T$ caused a nonlinear decrease in pseudo-first-order rate constants (k_{obs}). Similar observations were obtained at 0.01, 0.02, 0.05 and 0.10 mol dm^{-3} NaBr. These observed data are shown graphically in Fig. 3.

The observed data (k_{obs} *versus* $[CTABr]_T$) revealed a reasonably good fit to eqn. (3). The procedure to obtain the values of c.m.c. and k_W was the same as described earlier in the text. The nonlinear least-squares technique was used to calculate k_M and K_S from eqn. (3). The calculated values of k_M, K_S and $\Sigma\, d_i^2$ (where $d_i = k_{obs\ i} - k_{calcd\ i}$) at different [NaBr] are summarized in Table 2. The fitting of observed data to eqn. (3) is evident from the plots of Fig. 3 where the solid lines are drawn through the calculated data points.

The values of K_S are associated with low standard deviations while most of the k_M values are associated with very high standard deviations (Table 2). The maximum contributions of the $k_MK_S[D_n]$ term (obtained at 0.01 mol dm^{-3} CTABr) compared with k_W are ≤46% (Table 2). Thus, the calculated values of k_M are unreliable. The negative value of k_M at 0.1 mol dm^{-3} NaBr is chemically meaningless and hence a more reliable value of K_S (=261 ± 2 dm^3 mol^{-1}) was obtained from the relationship $(k_W/k_{obs}) = \Phi + K_S[CTABr]_T$ where $\Phi = 1 - \text{c.m.c.}\ K_S$.

The observed data were also treated with the PIE model. The nonlinear least-squares technique was used to calculate $k'_{0,M}$, $k''_{OH,M}$ and K_S from eqn. (5) and these calculated values of $k'_{0,M}$, $k''_{OH,M}$ and K_S as well as least-squares ($\Sigma\, d_i^2$) values at different [NaBr] are shown in Table 2. The values of $k'_{0,M}$ and $k''_{OH,M}$ are either negative or positive associated with very high standard deviations while the values of K_S are associated with relatively low standard deviations. The high standard deviations associated with $k'_{0,M}$ and $k''_{OH,M}$ values and with some of their negative values make these values unreliable. It may be noted that the values of K_S calculated from eqns. (3) and (5) at a particular [NaBr] are not very different from each other (Table 2). This is the consequence of the insignificant contribution of $k_MK_S[D_n]$ and $(k'_{0,M}, + k''_{OH,M}m_{OH})K_S[D_n]$ compared with k_W in eqn. (3) and with $k'_{0,W}, + k'_{OH,W}[HO^-_W]$ in eqn. (5), respectively.

The increase in [NaBr] from 0.005 to 0.100 mol dm^{-3} decreased K_S from 1836 to 261 dm^3 mol^{-1}. These values of K_S fit well to eqn. (7) with [NaOH] replaced by [NaBr]. The nonlinear least-squares calculated values of K_S^0 and Ψ are 2699 ± 248 dm^3 mol^{-1} and 101 ± 20 dm^3 mol^{-1}, respectively. The value of K_S^0 (=2699 dm^3 mol^{-1}) is comparable with K_S (=2615 dm^3 mol^{-1}) calculated from eqn. (3) using observed data (k_{obs} *versus* $[CTABr]_T$) obtained at 0.1 mol dm^{-3} NaOH in the absence of added NaBr. The value of Ψ (=101 dm^3 mol^{-1}) for Br^- is nearly 30-fold larger than Ψ (=3.4 dm^3 mol^{-1}) for HO^- which is conceivable for the reason that the hydrophobicity of the bromide ion is much larger than that of the hydroxide ion. The empirical definition of Ψ_{X-S} [=Ψ in eqn. (7)] where the magnitude of Ψ_{X-S} is the measure of the ability of X^- to expel S^- from the cationic micellar pseudophase to the aqueous pseudophase, shows that Ψ_{X-S} should be proportional to K_X^S (ion-exchange constant in PIE formalism). Thus, the ratio Ψ_{Br-S}/Ψ_{OH-S} (=Ψ_{Br-OH}) should be equal to K_{Br}^{OH}. The calculated value of Ψ_{Br-OH} (=101/3.4 = 30) may be compared with the reported values of K_{Br}^{OH} (=7–31).[3b,4,19,21]

Probable source of inhibitory effect of CTABr micelles on rate of alkaline hydrolysis of PTH

Although most of the calculated values of k_M are not statistically different from zero because of the very high standard deviations associated with them (Tables 1 and 2), relatively more reliable values of k_M, obtained at ≥0.3 mol dm^{-3} NaOH (Table 1) and at 0.005 mol dm^{-3} NaBr, 0.1 mol dm^{-3} NaOH (Table 2), are more than 20-fold smaller than the corresponding values of k_W. Thus, these results show that CTABr micelles strongly inhibit the rate of alkaline hydrolysis of PTH.

The micellar inhibition of the rate of alkaline hydrolysis of PTH cannot be attributed to the ionic strength effect. The ionic strength of the surface of the micelle is believed to be nearly 3.5 mol dm^{-3}.[23] The increase in [Na_2CO_3] and [KCl] from 0.1 to 2.5 mol dm^{-3} decreased the pseudo-first-order rate constants (k_{obs}) for hydrolysis of PTH at 0.01 mol dm^{-3} NaOH by only 30 and 20%. Similarly, k_{obs} decreased by nearly 65% with the increase in [$(CH_3)_4NCl$] from 0.1 to 2.3 mol dm^{-3} at 0.01 mol dm^{-3} NaOH in aqueous solvents containing 1% v/v CH_3CN.[24]

The polarity of the micellar surface is reported to be significantly lower than the polarity of the aqueous pseudophase.[25] The relative permittivity of the micellar surface is 36–46.[26] The rate constants, k_{obs}, for the hydrolysis of PTH at 0.01 mol dm^{-3} KOH or NaOH decreased by nearly 20-fold with an increase in the content of organic co-solvent CH_3CN from 1 to 65% v/v in mixed aqueous solvents. Similarly, k_{obs} decreased by nearly 12-fold with an increase in the content of CH_3OH from 1 to 70% v/v in mixed aqueous solvents. In view of the very high sensitivity of k_{obs} to the polarity of the reaction medium, it may not be unreasonable to propose that the micellar-mediated hydrolysis of PTH takes place in a micellar environment of considerably low polarity. However, the polarity effect may not be the only source of micellar inhibition of alkaline hydrolysis of PTH.

The micelles are dynamic molecular aggregates and as such the micellar pseudophase may not be expected to be similar to the aqueous pseudophase in terms of medium properties. Experimental observations indirectly show that the micellar pseudophase is nonhomogeneous in terms of polarity, concentration of water and the distribution of different types of micellized molecules. It is certain that the hydrophilicity of HO^- is much larger than that of SH (nonionized PTH). Hence, it is conceivable to propose that the different average locations of HO^- and SH molecules in the micellar pseudophase are partly responsible for the lower values of k_M compared with k_W. A similar proposal has been put forward in a few related studies.[27,28]

Probable reason(s) why the PIE model did not give better data fitting than the pseudophase micellar (PM) model

The occurrence of ion-exchange in micellar-mediated bimolecular reactions can be kinetically detected only if (i) the rate of uncatalyzed reaction of a substrate (Sub) is much slower than the rate of co-ion-catalyzed reaction of the same substrate (co-ion represents ionic reactant or catalyst carrying charge similar to the charge of the counterion of the micelle) because under such conditions, the rate of uncatalyzed reaction cannot mask any change in the reaction rate caused by co-ion-catalyzed reaction due to ion-exchange between co-ion and counterion, and (ii) the value of the second-order rate constant for co-ion-catalyzed reaction of Sub is large enough to show any reaction rate change caused by the change in the concentration of reactive co-ion due to ion-exchange. Pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of ionized *N*-hydroxyphthalimide (NHP^-)[5] and phenyl benzoate (PB)[29] were explained by the use of the PIE model. The values of $k_{OH,W}/k_{0,W}$ for alkaline hydrolysis of S^-, NHP^- and PB are 2, 5×10^5 and 3×10^7 dm^3 mol^{-1}, respectively. The values of $k_{OH,W}$ for alkaline hydrolysis of S^-, NHP^-, and PB are 3.8×10^{-3}, 1.3 (30 °C),[14] and 0.68 dm^3 mol^{-1} s^{-1} (35 °C),[29] respectively. The effectiveness of ion-exchange HO^-–Br^- could not be kinetically detected in the present reacting system because the values of $k_{OH,W}/k_{0,W}$ (=2 dm^3 mol^{-1}) and $k_{OH,W}$ (=38×10^{-3} dm^3 mol^{-1} s^{-1}) are not sufficiently large to detect kinetically the occurrence of ion-exchange HO^-–Br^-. Similarly, the effectiveness of ion-exchange HO^-–Br^- could not be detected in the alkaline hydrolysis of securinine where the values of $k_{OH,W}/k_{0,W}$ and $k_{OH,W}$ are $>2 \times 10^6$ dm^3 mol^{-1} and 36×10^{-3} dm^3 mol^{-1} s^{-1} (35 °C),[3d] respectively.

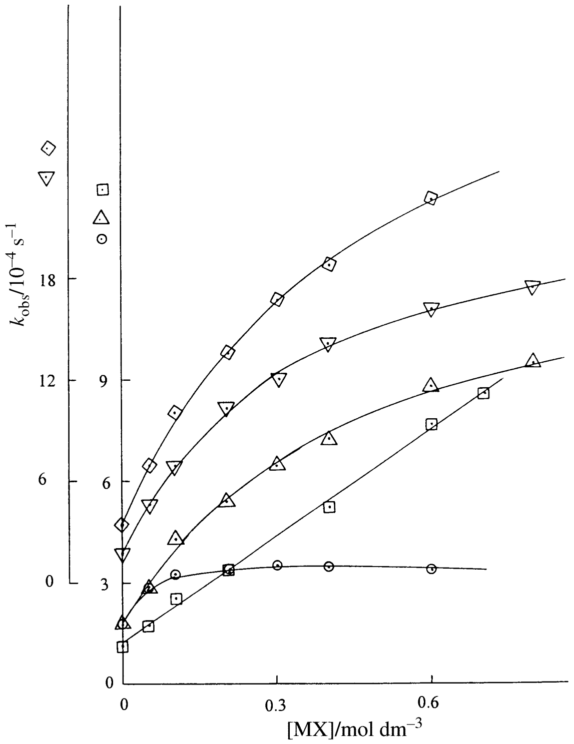

Fig. 4 Effects of [MX] (where MX = NaBr, KCl and Na_2CO_3) on pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of PTH at 35 °C and for MX = NaBr, 0.01 mol dm^{-3} CTABr, 0.02 mol dm^{-3} NaOH (▽), 0.01 mol dm^{-3} CTABr, 0.3 mol dm^{-3} NaOH (◇) and 0.04 mol dm^{-3} CTABr, 0.02 mol dm^{-3} NaOH (□); for MX = KCl, 0.01 mol dm^{-3} CTABr and 0.02 mol dm^{-3} NaOH (△) and MX = Na_2CO_3, 0.01 mol dm^{-3} CTABr and 0.02 mol dm^{-3} NaOH (○). The solid lines for (▽), (◇), (△) and (○) were drawn through the calculated data points using eqn. (8) and unknown parameters, *θ* and *K*, listed in Table 3. The solid line for (□) was drawn from the linear equation: $k_{obs} = k^0_{obs} + \theta K[\mathrm{NaBr}]$ with $10^4 k^0_{obs} = 1.28 \pm 0.12$ s^{-1} and $10^3\theta K = 1.04 \pm 0.03$ dm^3 mol^{-1} s^{-1}.

Effects of [NaBr], [KCl] and [Na_2CO_3] on k_{obs} for alkaline hydrolysis of PTH at constant [NaOH] and [CTABr]$_T$

The studies on the effects of [CTABr]$_T$ on k_{obs} at constant concentrations of NaOH and NaBr revealed that the increase in [NaOH] and [NaBr] decreased K_S (CTABr micellar binding constant of S^-). In order to find out the effects of a few inorganic salts (MX) on k_{obs}, kinetic runs were carried out at different concentrations of MX in the presence of a constant amount of NaOH and CTABr. The observed data are shown graphically as the plot of k_{obs} against [MX] in Fig. 4. Pseudo-first-order rate constants (k_{obs}) were found to fit eqn. (8) where *θ*

$$k_{obs} = \frac{k^0_{obs} + \theta K[\mathrm{MX}]}{1 + K[\mathrm{MX}]} \qquad (8)$$

and *K* were considered as unknown empirical parameters. The values of k^0_{obs} at different [NaOH] and [CTABr]$_T$ were obtained experimentally by carrying out the kinetic runs at [MX] = 0. The nonlinear least-squares technique was used to calculate *θ* and *K* from eqn. (8) and these results are summarized in

Table 3 Values of empirical parameters, θ and K calculated from eqn. (8)[a]

MX	[NaOH]/M_1[g]	$[C]_T$[b]/M_1[g]	$10^4k^0_{obs}$[c]/s^{-1}	10^4k_W[d]/s^{-1}	$10^4\theta/s^{-1}$	K/M_1[h]	B[e]/s	W[e]/M_1[i]	Ψ[f]/M_1[h]
NaBr	0.02	0.01	1.74 ± 0.03[j]	23.8	24.0 ± 0.6[j]	3.01 ± 0.18[j]			101[k]
					(24.5)[l]	(2.89)[l]	439 ± 14[j]	152 ± 2[j]	
	0.30	0.01	3.42 ± 0.02	32.3	35.4 ± 1.8	2.39 ± 0.25			65[m]
					(34.9)	(2.50)	318 ± 31	127 ± 3	
	0.02	0.04	1.06 ± 0.01	23.8	(28.1)	(0.512)	371 ± 294	725 ± 31	67[k]
KCl	[n]	0.01	1.74 ± 0.03	23.8	13.8 ± 0.7	2.24 ± 0.28			75[k]
					(14.3)	(1.93)	739 ± 186	383 ± 21	
Na_2CO_3	0.02	0.01	1.74 ± 0.03	23.8	3.55 ± 0.09	37.4 ± 12.6			1035[k]
					(3.59)	(30.8)	5393 ± 291	175 ± 31	

[a] $[PTH]_0 = 2 \times 10^{-4}$ mol dm^{-3}, 35 °C, $\lambda = 300$ nm, aqueous reaction mixture for each kinetic run contained 2% v/v CH_3CN. [b] $[C]_T = [CTABr]_T$. [c] Pseudo-first-order rate constant for the hydrolysis of PTH obtained under the experimental conditions of the kinetic runs for the study of the effects of [MX] on k_{obs} with [MX] = 0. [d] Pseudo-first-order rate constant for the hydrolysis of PTH obtained under the experimental conditions of the kinetic runs for the study of the effects of [MX] on k_{obs} with $[MX] = [CTABr]_T = 0$. [e] Calculated from eqn. (9) where $B = 1/(k_W - k^0_{obs})$ and $W = B/K$. [f] The value of Ψ was calculated from the relationship: $\Psi = K(1 + K^0_S[D_n])$ with $[D_n] \approx [CTABr]_T$. [g] M_1 = mol dm^{-3}. [h] M_1 = dm^3 mol^{-1}. [i] M_1 = mol dm^{-3} s. [j] Error limits are standard deviations. [k] $K^0_S = 3262$ dm^3 mol^{-1}. [l] Parenthesized values were obtained from the relationships: $\theta = k^0_{obs} + 1/B$ and $K = B/W$. [m] $K^0_S = 2603$ dm^3 mol^{-1}. [n] [KOH] = 0.02 mol dm^{-3}.

Table 3. The fitting of the observed data to eqn. (8) is evident from the plots of Fig. 4 where solid lines are drawn through the calculated points.

Pseudo-first-order rate constants (k_{obs}) obtained within [NaBr] range 0.0–0.70 mol dm^{-3} at 0.04 mol dm^{-3} CTABr did not fit well to eqn. (8) presumably because of the lack of curvature in the plot of k_{obs} *versus* [NaBr] (Fig. 4). The plot of k_{obs} *versus* [NaBr] turned out to be linear which is due to the inequality $1 \gg K[MX]$ under such conditions. The least-squares calculated values of intercept (k^0_{obs}) and slope (θK) are $(1.28 \pm 0.12) \times 10^{-4}$ s^{-1} and $(1.04 \pm 0.03) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}, respectively. The value of the intercept ($=1.28 \times 10^{-4}$ s^{-1}) is slightly larger than the experimentally determined value of k^0_{obs} ($=1.06 \times 10^{-4}$ s^{-1}, Table 3). The value of the slope (θK) became $(1.19 \pm 0.17) \times 10^{-3}$ dm^3 mol^{-1} s^{-1} by setting the intercept equal to 1.06×10^{-4} s^{-1}. The expected value of θ is 2.4×10^{-3} s^{-1} because $k_W = 2.38 \times 10^{-3}$ s^{-1} at 0.02 mol dm^{-3} NaOH with $[CTABr]_T = 0$ and $\theta = 2.4 \times 10^{-3}$ s^{-1} at 0.01 mol dm^{-3} CTABr (Table 3). Thus the value of K is 0.44 or 0.50 dm^3 mol^{-1}.

An attempt was also made to fit the observed data at 0.04 mol dm^{-3} CTABr to eqn. (9) which is the rearranged form of eqn. (8). The linear least-squares calculated values of $1/(\theta - k^0_{obs})$ and $1/K(\theta - k^0_{obs})$ are summarized in Table 3. The observed data (k_{obs} *versus* [MX]) for MX = KBr, KCl and Na_2CO_3 were also treated with eqn. (9) and the calculated values of $1/(\theta - k^0_{obs})$ and $1/K(\theta - k^0_{obs})$ are shown in Table 3. The values of $1/(\theta - k^0_{obs})$ and $1/K(\theta - k^0_{obs})$ were used to calculate θ and K. The values of θ and K obtained from eqn. (9) are

$$(k_{obs} - k^0_{obs})^{-1} = (\theta - k^0_{obs})^{-1} + \{K(\theta - k^0_{obs})[NaBr]\}^{-1} \quad (9)$$

comparable with the corresponding values derived from eqn. (8) (Table 3). Although the value of the intercept, $1/(\theta - k^0_{obs})$ ($=371 \pm 294$ s) for NaBr at 0.04 mol dm^{-3} CTABr is associated with high standard deviation, it gives θ as 2.80×10^{-3} s^{-1} which is not significantly different from θ ($=2.40 \times 10^{-3}$ s^{-1}) obtained at 0.01 mol dm^{-3} CTABr.

It may be noted that the reaction mixture containing 2×10^{-4} mol dm^{-3} PTH, 0.02 mol dm^{-3} NaOH, 0.04 mol dm^{-3} CTABr and 0.4 mol dm^{-3} NaBr became very viscous at ambient temperature (~27 °C). The increase in [NaBr] beyond 0.4 mol dm^{-3} (*i.e.* at 0.6 and 0.7 mol dm^{-3} NaBr) caused precipitation into the reaction mixtures at ambient temperature. But the precipitate disappeared and the reaction mixtures became clear solutions at 35 °C. Such observations were not obtained at 0.01 mol dm^{-3} CTABr. These observations demonstrate that the addition of NaBr to CTABr micellar solution changes the structure of the micelle. However, such a micellar structural change appeared to be kinetically insensitive.

Eqn. (8) can be derived from eqns. (3) and (7) with [NaOH] replaced by [MX] in eqn. (7). Thus, in terms of eqns. (3), (7) and (8), $k^0_{obs} = (k_W + k_M K^0_S[D_n])/(1 + K^0_S[D_n])$, $\theta = k_W$ and $K = \Psi/(1 + K^0_S[D_n])$. The values of K were used to calculate Ψ from the relationship $K = \Psi/(1 + K^0_S[D_n])$ assuming $[D_n] \approx [CTABr]_T$ at $\geqslant 0.01$ mol dm^{-3} CTABr. These calculated values of Ψ are shown in Table 3. The value of Ψ ($=101$ dm^3 mol^{-1}) for Br$^-$, obtained at 0.02 mol dm^{-3} NaOH and 0.01 mol dm^{-3} CTABr, is similar to Ψ ($=101$ dm^3 mol^{-1}) obtained from K_S values using eqn. (7) as described earlier in the text. But the value of Ψ ($=65$ dm^3 mol^{-1}) for Br$^-$ at 0.3 mol dm^{-3} NaOH is lower than Ψ at 0.02 mol dm^{-3} NaOH in the presence of 0.01 mol dm^{-3} CTABr. Similarly, the value of Ψ at 0.01 mol dm^{-3} CTABr is larger than Ψ at 0.04 mol dm^{-3} CTABr in the presence of 0.02 mol dm^{-3} NaOH (Table 3). It is likely that the Ψ value may be micellar structure-dependent and it is well known that the structure of an ionic micelle changes from spherical to rod- to disk-shaped with the increase in the concentration of micelle forming surfactant in the absence and presence of inorganic and organic salts.[30] However, a definite explanation for the decrease in Ψ with the increase in $[CTABr]_T$ or [NaOH] probably requires more observations on the related system.

The value of θ/k_W (where k_W represents the pseudo-first-order rate constant for hydrolysis of PTH under the experimental conditions of the determination of θ values with $[MX] = [CTABr]_T = 0$) is the measure of the extent of the expulsion of S$^-$ ions from the cationic micellar pseudophase to the aqueous pseudophase by X$^-$ ions provided S$^-$ ions are fully micellized in the absence of X$^-$. The values of θ/k_W are nearly 1.0 for the Br$^-$ ion under different concentrations of NaOH and CTABr (Table 3). This shows that Br$^-$ ions, under the experimental conditions imposed, can transfer completely (nearly 100%) S$^-$ ions from the micellar pseudophase to the the aqueous pseudophase if the limiting concentration of Br$^-$ ions, where $1 \ll K$[NaBr] in eqn. (8), is achieved.

The value of θ/k_W for the Cl$^-$ ion is 0.6 which shows that Cl$^-$ ions are capable of transferring only 60% of the total micellized S$^-$ ions under the limiting conditions where $1 \ll K$[KCl] in eqn. (8). Similarly, the value of θ/k_W of 0.15 for CO_3^{2-} ion indicates that the CO_3^{2-} ions can expel only 15% of the total number of micellized S$^-$ ions under the limiting conditions where $1 \ll K[Na_2CO_3]$ in eqn. (8). The respective values of θ/k_W for Br$^-$, Cl$^-$ and CO_3^{2-} as 1.0, 0.60 and 0.15 are conceivable in terms of the relative hydrophilicity of these anions which varies in the order Br$^-$ < Cl$^-$ < CO_3^{2-}.

Conclusions

Pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of phthalimide appeared to obey the pseudophase micellar

(PM) model satisfactorily. The pseudophase ion-exchange (PIE) model did not improve the quality of the fitting of observed data compared to the PM model. The residual errors ($=k_{\mathrm{obs}\,i} - k_{\mathrm{calcd}\,i}$ where $k_{\mathrm{calcd}\,i}$ is the calculated first-order rate constant using the PIE model at the *i*th concentration of CTABr) which measure the quality of data fitting remained almost unchanged with the change in $K_{\mathrm{Br}}^{\mathrm{OH}}$ from 5 to 500 at a constant β and in β from 0.05 to 0.95 at a constant $K_{\mathrm{Br}}^{\mathrm{OH}}$. This apparent weakness of the PIE model cannot be attributed to the use of K_S (binding constant) rather than K_S^{Br} (ion-exchange constant) in the data treatment using the PIE model because similar results were obtained in a reaction system involving only one possible ion-exchange (HO^-/Br^-).[3d] It has been shown qualitatively that K_S should remain independent of $[\mathrm{CTABr}]_T$ at a constant concentration of added salt (MX). The values of K_S at different [MX] (MX = NaOH and NaBr) obeyed an empirical equation $K_S = K_S^0/(1 + \Psi\,[\mathrm{MX}])$ where Ψ is the measure of the ability of an ion (X^-) to expel another ion of similar charge (S^- with cationic micellar binding constant K_S^0 at [MX] where $1 \gg \Psi[\mathrm{MX}]$) from the micellar pseudophase to the aqueous pseudophase.

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Appendix

For the ion-exchange system given in eqn. (10) where C^- represents the counterion of cationic micelle D_n, the ion-exchange constant K_X^C may be expressed by eqns. (11)–(13).

$$X_W^- + C_M^- \overset{K_X^C}{\rightleftharpoons} X_M^- + C_W^- \qquad (10)$$

$$K_X^C = K_X/K_C = ([X_M^-][C_W^-])/([X_W^-][C_M^-]) \qquad (11)$$

$$K_X = [X_M^-]/([X_W^-][D_n]) \qquad (12)$$

$$K_C = [C_M^-]/([C_W^-][D_n]) \qquad (13)$$

It may be noted that in the presence of a constant concentration of salt, MX, ($[\mathrm{MX}]_T$), an increase in $[D_n]$ will decrease $[X_W^-]$ and increase $[X_M^-]$ due to ion-exchange or in terms of eqn. (12). Under such conditions, K_X and K_C may remain constant in view of eqns. (12) and (13).

A similar situation may develop with the ion-exchange system given in eqn. (14).

$$Y_W^- + C_M^- \overset{K_Y^C}{\rightleftharpoons} Y_M^- + C_W^- \qquad (14)$$

Thus, it appears that at constant values of $[\mathrm{MX}]_T$ and $[\mathrm{MY}]_T$ (total concentration of salt MY), the increase in $[D_n]$ should not change K_X or K_Y. But for the ion-exchange system shown by eqn. (15), if the total concentrations of cationic surfactants ($[\mathrm{Surf}]_T$) *i.e.* $[D_n]$ (provided c.m.c. $\ll [\mathrm{Surf}]_T$) and Y^- ($[Y]_T$) are kept constant then the increase in $[X_W^-]$, due to increase in $[X]_T$ (where $[X]_T = [X_W^-] + [X_M^-]$), should increase $[X_M^-]$ (in view of eqn. (12) where $[D_n]$ is constant) and decrease $[Y_M^-]$ due to ion-exchange [eqn. (15)] at constant $[D_n]$. The decrease in $[Y_M^-]$ must increase $[Y_W^-]$ because $[Y]_T$ $(=[Y_W^-] + [Y_M^-])$ is constant under the experimental conditions imposed. Thus, the increase in $[X]_T$ increases $[Y_W^-]$ and decreases $[Y_M^-]$ at constant $[D_n]$ and $[Y]_T$ and consequently it decreases K_Y $\{= [Y_M^-]/([Y_W^-][D_n])\}$. This shows that K_X^Y is no longer constant if $[X]_T$ increases at constant $[Y]_T$ and $[D_n]$ or $[Y]_T$ increases at constant $[X]_T$ and $[D_n]$. Similarly, it can be shown that K_X^C or K_Y^C cannot remain constant if the total concentration of the inert salt MC, $[\mathrm{MC}]_T$, (where MC represents an inert salt whose anion is also the counterion of cationic micelle) is increased at constant $[\mathrm{Surf}]_T$ and $[X]_T$ or $[Y]_T$. Eqn. (15) shows that the change in $[D_n]$ should not affect K_X^Y at constant values of $[X]_T$ and $[Y]_T$.

$$X_W^- + Y_W^- \overset{K_X{}^Y}{\rightleftharpoons} X_M^- + Y_W^- \qquad (15)$$

References

1 F. M. Menger and C. A. Portnoy, *J. Am. Chem. Soc.*, 1967, **89**, 4698.

2 L. S. Romsted, in *Surfactants in Solution*, eds. K. L. Mittal and B. Lindman, Plenum Press, New York, 1984, vol. 2, p. 1015.

3 (*a*) C. A. Bunton, F. Nome, F. Quina and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357; (*b*) R. Germani, G. Savelli, T. Romeo, N. Spreti, G. Cerichelli and C. A. Bunton, *Langmuir*, 1993, **9**, 55; (*c*) C. A. Bunton, in *Surfactants in Solution*, eds. K. L. Mittal and D. O. Shah, Plenum Press, New York, 1991, vol. 11, p. 17; (*d*) N. H. Lajis and M. N. Khan, *J. Phys. Org. Chem.*, 1998, **11**, 209.

4 S. Vera and E. Rodenas, *J. Phys. Chem.*, 1986, **90**, 3414.

5 M. N. Khan, *Colloids Surf. A*, 1997, **127**, 211.

6 L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5107; L. S. Romsted, *J. Phys. Chem.*, 1985, **89**, 5113.

7 A. G. Oliveira, I. M. Cuccovia and H. Chaimovich, *J. Pharm. Sci.*, 1990, **79**, 37.

8 M. N. Khan, *J. Org. Chem.*, 1997, **62**, 3190.

9 M. N. Khan, *J. Chem. Soc., Perkin Trans. 2*, 1989, 199.

10 B. Zerner and M. L. Bender, *J. Am. Chem. Soc.*, 1961, **83**, 2267.

11 C. A. Bunton, B. Nayak and C. O'Connor, *J. Org. Chem.*, 1968, **33**, 572.

12 M. N. Khan, *Int. J. Chem. Kinet.*, 1987, **19**, 143; M. N. Khan, *J. Pharm. Biomed. Anal.*, 1989, **7**, 685.

13 M. N. Khan, *J. Chem. Soc., Perkin Trans. 2*, 1990, 435.

14 M. N. Khan, *Int. J. Chem. Kinet.*, 1991, **23**, 567.

15 M. N. Khan, *J. Pharm. Sci.*, 1984, **73**, 1767.

16 C. A. Bunton, *Catal. Rev. Sci. Eng.*, 1979, **20**, 1.

17 M. N. Khan and Z. Arifin, *J. Colloid Interface Sci.*, 1996, **180**, 9.

18 T. J. Broxton and S. Wright, *J. Org. Chem.*, 1986, **51**, 2965.

19 (*a*) S. Vera and E. Rodenas, *Tetrahedron*, 1986, **42**, 143 and references cited therein; (*b*) M. J. Segovia, F. Martinez and J. M. Alvarez, *Colloids Surf. A*, 1996, **106**, 1.

20 M. de F. S. Neves, D. Zanette, F. Quina, M. T. Moretti and F. Nome, *J. Phys. Chem.*, 1989, **93**, 1502.

21 C. Bravo, P. Herves, J. R. Leis and M. E. Pena, *J. Colloid Interface Sci.*, 1992, **153**, 529.

22 (*a*) M. N. Khan, Z. Arifin, E. Ismail and S. F. M. Ali, *Colloids Surf. A*, 2000, **161**, 381; (*b*) M. N. Khan, Z. Arifin, E. Ismail and S. F. M. Ali, *J. Org. Chem.*, 2000, **65**, 1331.

23 E. H. Cordes, *Pure Appl. Chem.*, 1978, **50**, 617 and references cited therein.

24 M. N. Khan, M. B. U. Sumaila and A. M. Mohammad, *J. Chem. Res.* (*S*), 1991, 233; M. N. Khan, M. R. U. Sumaila and A. M. Mohammed, *J. Chem. Res.* (*M*), 1991, 2301.

25 (*a*) C. A. Bunton and G. Savelli, *Adv. Phys. Org. Chem.*, 1986, **22**, 213 and references cited therein; (*b*) K. A. Zachariasse, N. V. Phac and B. Kozankiewicz, *J. Phys. Chem.*, 1981, **85**, 2672; (*c*) C. Ramchandran, R. A. Pyter and P. Mukerjee, *J. Phys. Chem.*, 1982, **86**, 3198; (*d*) A. D. Angeli, A. Cipiciani, R. Germani, G. Savelli, G. Cerichelli and C. A. Bunton, *J. Colloid Interface Sci.*, 1988, **121**, 42.

26 P. Mukerjee, in *Solution Chemistry of Surfactants*, ed. K. L. Mittal, Plenum Press, New York, 1979, vol. 1, p. 153 and references cited therein.

27 C. Bravo, L. Garcia-Rio, J. R. Leis, M. E. Pena and E. Iglesias, *J. Colloid Interface Sci.*, 1994, **166**, 316 and references cited therein.

28 A. Fernandez, E. Iglesias, L. Garcia-Rio and J. R. Leis, *Langmuir*, 1995, **11**, 1917.

29 M. N. Khan, *Colloids Surf. A*, 1998, **139**, 63.

30 (*a*) A. Heindl, J. Strnad and H. H. Kohler, *J. Phys. Chem.*, 1993, **97**, 742; (*b*) U. Olsson, O. Soderman and P. Guering, *J. Phys. Chem.*, 1986, **90**, 5223; (*c*) T. M. Clausen, P. K. Vinson, J. R. Minter, H. T. Davis, Y. Talmon and W. G. Miller, *J. Phys. Chem.*, 1992, **96**, 476 and references cited therein; (*d*) P. M. Lindemuth and G. L. Bertrand, *J. Phys. Chem.*, 1993, **97**, 7769; (*e*) B. K. Mishra, S. D. Samant, P. Pradhan, S. B. Mishra and C. Manohar, *Langmuir*, 1993, **9**, 894; (*f*) R. K. Prud'homme and G. G. Warr, *Langmuir*, 1994, **10**, 3419; (*g*) K. Bijma, M. J. Blandamer and J. B. F. N. Engberts, *Langmuir*, 1998, **14**, 79.