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An apparent weakness of the pseudophase ion-exchange (PIE) model for micellar catalysis by cationic surfactants with nonreactive counterions †

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Pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of phenyl benzoate (PB) show maxima in k_{obs}–[D_n] profiles at constant [NaOH] in the presence of cetyltrimethylammonium chloride (CTACl) micelles (D_n). These observed data have been explained in terms of the pseudophase ion-exchange (PIE) model. But the quality of the data fit to the kinetic equation derived from the PIE model approach remains essentially unchanged with a large change in ion-exchange constant (K_{Cl}^{OH}) and in fractional micellar neutralization (β). The use of the PIE model for k_{obs}, obtained under varying concentrations of added NaCl salt at a constant [NaOH] and [CTACl]$_T$, gives a K_S value significantly different from the K_S value obtained from k_{obs}–[D_n]. These observed data (k_{obs}–[MX], where X = Cl and Br) were also treated in terms of the pseudophase micellar (PM) model coupled with an empirical relationship: $K_{OH} = K_{OH}{}^0/(1 + \Psi_{X\text{–}OH}[MX])$ where K_{OH} is the CTACl micellar binding constant of HO$^-$ in the presence of MX and $\Psi_{X\text{–}OH}$ is an empirical parameter. This data treatment, which does not require the constancy of K_X^{OH} and β as needed in the PIE model, gives data fitting as good as the PIE model. The values of $\Psi_{X\text{–}OH}$ for Cl$^-$ and Br$^-$ are explained with conceivable chemical reasoning.

Introduction

The pseudophase ion-exchange (PIE) model[1] was developed due to failure of the kinetic model of micellar-mediated reaction[2] to explain the k_{obs}–[D_n] profiles involving maxima obtained for ionic micellar-mediated bimolecular reactions where one of the reactants was ionic with charge similar to the charge of counterions of micelles (D_n). The success of the PIE model is generally emphasized within the domain of considerably lower residual errors between observed and calculated rate constants at varying concentrations of micelles. The increase in the number of assumptions decreases the diverse applicability of a model. There are a greater number of assumptions in the PIE model than in the kinetic model of micellar-mediated reaction,[2] and hence the applicability of the PIE model should be expected to be more limited than the kinetic model of micellar-mediated reaction.[2] The applicability of the PIE model has been subjected to experimental verification using various non-kinetic techniques.[3] Although the PIE model explained quantitatively or semi-quantitatively a large amount of kinetic data on bimolecular semi-ionic or ionic reactions in the presence of ionic micelles,[1b,4] vesicles,[5] reversed micelles[6] and microemulsions,[7] it failed to explain the rates of reactions of very hydrophilic ions such as HO$^-$ and F$^-$.[1b,8] These data have been explained in terms of the mass action (MA) model,[9] the Poisson–Boltzmann equation (PBE) in spherical symmetry[10] and allowing different β values (estimated conductimetrically) at different concentrations of CTAOH and CTAF (where CTA represents the cetyltrimethylammonium group ‡).[11] Poor agreement between values of selectivity coefficients for exchange of highly hydrophilic counterions determined by different methods is also attributed to the breakdown of the PIE model.[12]

Bunton,[13] in an excellent review, called this whole exercise a somewhat jaundiced view of quantitative models of micellar rate effects. Germani *et al.*[14] have pointed out, without giving the details of analytical data, that a major problem in using ion-exchange treatments is that rate data can be fitted by using a variety of values for parameters such as β, K_{Br}^{OH}, or K_X'. Recently, it has been reported that the quality of the fitting of observed data on alkaline hydrolysis of securinine in terms of the PIE model remained almost unchanged with the change in K_{Br}^{OH} from 5 to 10^4 at $\beta = 0.8$.[15] In this study,[15] the k_{obs}–[CTABr] profile revealed an insignificant maximum. Very strong maxima in k_{obs}–[CTABr] profiles were obtained in the alkaline hydrolysis of phenyl benzoate in the presence of CTABr micelles.[16] In order to test the apparent weakness of the PIE model described in ref. 15, we considered the present reacting system which is expected to show strong maxima in the k_{obs}–[CTACl] profiles. The observed rate data on alkaline hydrolysis of phenyl benzoate and insensitivity of the fitting of these rate data (k_{obs} *versus* [D_n] at a constant [HO$^-$]) in terms of the PIE model to a large change (i) in K_{Cl}^{OH} at a constant β and (ii) in β at a constant K_{Cl}^{OH}, are described in this manuscript.

Experimental

Materials

All the chemicals used were supplied by Fluka, Sigma or Aldrich and were of the highest commercially available purity. The stock solutions of phenyl benzoate (PB) were prepared in acetonitrile.

Kinetic measurements

The rate of hydrolysis of PB was studied spectrophotometrically by monitoring the appearance of the product, the

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† Electronic supplementary information (ESI) available: Tables I–IV listing k_{obs} at different [CTACl] and at 0.005, 0.010, 0.015 and 0.020 M NaOH; Tables V–VII listing k_{obs} at different [NaCl] and at 0.01 M NaOH and at 0.007 and 0.01 M CTACl; Table VIII listing k_{obs} at different [NaBr] and at 0.007 and 0.01 M CTACl in the presence of 0.01 M NaOH. See http://www.rsc.org/suppdata/p2/b1/b101840j/

‡ The IUPAC name for cetyl is hexadecanyl.

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phenolate ion, as a function of time at 290 nm and 35 °C. The details of the kinetic procedure, and data analysis are described elsewhere.[17]

Results and discussion

Several kinetic runs were carried out within the total cetyltrimethylammonium chloride concentration ($[\mathrm{CTACl}]_\mathrm{T}$) range of 0.0 to 0.1 mol dm^{-3} at 0.005 mol dm^{-3} NaOH at 35 °C in an aqueous solvent containing 2% v/v $\mathrm{CH_3CN}$. Similar observations were obtained at 0.01, 0.015 and 0.02 mol dm^{-3} NaOH. Pseudo-first-order rate constants (k_obs) for these runs are summarized in Tables I–IV in the electronic supplementary information (ESI). These results show the presence of maxima in the k_obs–$[\mathrm{CTACl}]_\mathrm{T}$ profiles at a constant [NaOH] within the range 0.005–0.020 mol dm^{-3}.

A few kinetic runs were also carried out within the [NaX] (where $\mathrm{X^-} = \mathrm{Cl^-}$ and $\mathrm{Br^-}$) range of 5×10^{-4} to ≤ 0.3 mol dm^{-3} at 0.007 mol dm^{-3} CTACl, 0.01 mol dm^{-3} NaOH, 35 °C and 2% v/v $\mathrm{CH_3CN}$ in aqueous solvent. Similar observations were carried out at 0.01 mol dm^{-3} CTACl. Pseudo-first-order rate constants (k_obs) for these runs are summarized in Tables V–VIII in the ESI. The increase in [NaX] from 0.0 to ≤ 0.3 mol dm^{-3} decreased k_obs monotonically by ~16- to 27-fold at 0.007 and 0.01 mol dm^{-3} CTACl.

Pseudo-first-order rate constants (k_obs), obtained at [CTACl] = 0, show a linear increase with the increase in [NaOH] from 0.005 to 0.020 mol dm^{-3} with the intercept essentially at zero and slope = 0.68 ± 0.02 dm^3 mol^{-1} s^{-1}. Similar observations have been reported previously.[18] The appearance of an intercept at zero was concluded to be due to the insignificance of $k_{\mathrm{H_2O}}[\mathrm{H_2O}][\mathrm{PB}]$ compared to $k_\mathrm{OH}[\mathrm{HO^-}][\mathrm{PB}]$ in the rate law for alkaline hydrolysis of PB.[18] Thus, under the present experimental conditions, the rate of hydrolysis of PB involves $\mathrm{HO^-}$ and PB as the reactants.

The maxima in the k_obs–$[\mathrm{CTACl}]_\mathrm{T}$ profiles (Tables I–IV in the ESI) are typical for ionic micellar-mediated bimolecular reactions involving neutral and ionic reactants with the charge on the ionic reactant similar to the charge of the counterion of the ionic micelle, D_n. Such observed rate data are generally explained in terms of the PIE model.[1] This model contains essentially all the assumptions involved in the kinetic model of micellar-mediated reaction[2] and some additional assumptions which are well documented in several excellent reviews.[1,4] In view of the PIE model, the concentrations of $\mathrm{HO^-}$ (ionic reactant) and $\mathrm{Cl^-}$ (micellar counterion) in the micellar pseudophase are governed by an ion-exchange equilibrium, eqn. (1)

$$K_\mathrm{Cl}^\mathrm{OH} = [\mathrm{HO^-}_\mathrm{W}][\mathrm{Cl^-}_\mathrm{M}]/([\mathrm{HO^-}_\mathrm{M}][\mathrm{Cl^-}_\mathrm{W}]) = [\mathrm{HO^-}_\mathrm{W}]m_\mathrm{Cl}/(m_\mathrm{OH}[\mathrm{Cl^-}_\mathrm{W}]) \qquad (1)$$

where subscripts W and M represent aqueous pseudophase and micellar pseudophase, respectively, $m_\mathrm{Cl} = [\mathrm{Cl^-}_\mathrm{M}]/[\mathrm{D}_n]$ and $m_\mathrm{OH} = [\mathrm{HO^-}_\mathrm{M}]/[\mathrm{D}_n]$. The fraction of counterions bound to the micelle, β, total concentrations of $\mathrm{Cl^-}$, $[\mathrm{Cl^-}]_\mathrm{T}$, and $\mathrm{HO^-}$, $[\mathrm{HO^-}]_\mathrm{T}$, may be given by eqns. (2)–(4).

$$m_\mathrm{Cl} + m_\mathrm{OH} = \beta \qquad (2)$$

$$[\mathrm{Cl^-}]_\mathrm{T} = [\mathrm{Cl^-}_\mathrm{W}] + m_\mathrm{Cl}[\mathrm{D}_n] \qquad (3)$$

$$[\mathrm{HO^-}]_\mathrm{T} = [\mathrm{HO^-}_\mathrm{W}] + m_\mathrm{OH}[\mathrm{D}_n] \qquad (4)$$

Eqns. (1)–(4) yield eqn. (5).

$$m_\mathrm{OH}{}^2 + m_\mathrm{OH}\left\{\frac{[\mathrm{HO^-}]_\mathrm{T} + K_\mathrm{Cl}^\mathrm{OH}[\mathrm{Cl^-}]_\mathrm{T}}{(K_\mathrm{Cl}^\mathrm{OH} - 1)[\mathrm{D}_n]} - \beta\right\} - \frac{\beta[\mathrm{HO^-}]_\mathrm{T}}{(K_\mathrm{Cl}^\mathrm{OH} - 1)[\mathrm{D}_n]} = 0 \qquad (5)$$

The reaction scheme, in terms of the PM model, can lead to eqn. (6) where $k_{2,\mathrm{W}}$ is the second-order rate constant for the

$$k_\mathrm{obs} = \frac{k_{2,\mathrm{W}}[\mathrm{HO^-}]_\mathrm{T} + (k'_{2,\mathrm{M}}K_\mathrm{S} - k_{2,\mathrm{W}})\, m_\mathrm{OH}[\mathrm{D}_n]}{1 + K_\mathrm{S}[\mathrm{D}_n]} \qquad (6)$$

reaction of $\mathrm{HO^-}$ with phenyl benzoate (PB) in the aqueous pseudophase, K_S is the CTACl micellar binding constant of PB and the rate of bimolecular reaction in the micellar pseudophase is defined as rate = $k'_{2,\mathrm{M}}\, m_\mathrm{OH}\, [\mathrm{PB_M}]$.

The unknown parameters, $k'_{2,\mathrm{M}}$ and K_S, as well as the least-squares (Σd_i^2, where $d_i = k_{\mathrm{obs}\ i} - k_{\mathrm{calcd}\ i}$) value were calculated from eqn. (6) using observed data, k_obs *versus* $[\mathrm{D}_n]$, and calculated values of m_OH. The values of m_OH at different $[\mathrm{D}_n]$ were calculated by solving quadratic eqn. (5) at constant given values of β and $K_\mathrm{Cl}^\mathrm{OH}$ with known values of $[\mathrm{HO^-}]_\mathrm{T}$, $[\mathrm{Cl^-}]_\mathrm{T}$, and critical micellization concentration (c.m.c). The values of c.m.c. at different [NaOH] were obtained by a graphical technique.[19] The calculated values of $k'_{2,\mathrm{M}}$, K_S and Σd_i^2 at different combinations of $K_\mathrm{Cl}^\mathrm{OH}$ and β and at different [NaOH] are summarized in Table 1. The quality of the fit of observed data to eqn. (6) in terms of the PIE model is evident from the calculated values of rate constants (k_calcd) and the least-squares values (Tables I–IV in the ESI and Table 1).

In order to find out the effects of a large variation in $K_\mathrm{Cl}^\mathrm{OH}$ values at a constant β and in β values at a constant $K_\mathrm{Cl}^\mathrm{OH}$ on the quality of the fit of the observed data to eqn. (6), the values of k_calcd at different $[\mathrm{D}_n]$ were obtained by the nonlinear least-squares calculated values of $k'_{2,\mathrm{M}}$ and K_S at constant values of $K_\mathrm{Cl}^\mathrm{OH}$ and β (Table 1). The values of $K_\mathrm{Cl}^\mathrm{OH}$ were arbitrarily varied from 2 to 500 at $\beta = 0.7$ (the reported value of β, not strictly obtained under the kinetic conditions of the present study, is 0.7[11]). Similarly, the values of β were varied from 0.1 to 0.9 at $K_\mathrm{Cl}^\mathrm{OH} = 5$ (the value of $K_\mathrm{Cl}^\mathrm{OH} = 5$ was considered for the reason that the experimentally determined values of $K_\mathrm{Br}^\mathrm{OH}$, $K_\mathrm{Cl}^\mathrm{OH}$ and $K_\mathrm{Br}^\mathrm{Cl}$ are 7–31,[1b] 3–11[1b] and 2.5,[3d] respectively). Among the various possible inferences that could be drawn from the values of $k'_{2,\mathrm{M}}$, K_S, Σd_i^2 (Table 1), percentage residual error (PRE) and k_calcd at different values of $K_\mathrm{Cl}^\mathrm{OH}$ and β (Tables I–IV in the ESI), the most obvious one may be described as follows.

Although the least-squares Σd_i^2 values show a change with the change in $K_\mathrm{Cl}^\mathrm{OH}$ from 2 to 500 at $\beta = 0.7$ and in β from 0.1 to 0.9 at $K_\mathrm{Cl}^\mathrm{OH} = 5$, the calculated values of rate constants (k_calcd) and residual error do not differ appreciably under such conditions (Tables I–IV in the ESI). The lowest values of Σd_i^2 for the observed data at 0.005, 0.01, 0.015 and 0.02 mol dm^{-3} NaOH are at $K_\mathrm{Cl}^\mathrm{OH} = 2$, $\beta = 0.7$; $K_\mathrm{Cl}^\mathrm{OH} = 5$, $\beta = 0.1$; $K_\mathrm{Cl}^\mathrm{OH} = 5$, $\beta = 0.1$ and $K_\mathrm{Cl}^\mathrm{OH} = 5$, $\beta = 0.9$, respectively (Table 1). The values of both $k'_{2,\mathrm{M}}$ and K_S vary by many-fold in an irregular order under such specific conditions (Table 1). Thus, the criterion of minimum value of Σd_i^2 for the best fit is meaningless in this case. Furthermore, at 0.01 mol dm^{-3} NaOH, the value of Σd_i^2 ($= 22.36 \times 10^{-6}$) at $K_\mathrm{Cl}^\mathrm{OH} = 2$, $\beta = 0.7$ is not appreciably different from Σd_i^2 ($= 21.63 \times 10^{-6}$) at $K_\mathrm{Cl}^\mathrm{OH} = 5$, $\beta = 0.1$. But the values of $k'_{2,\mathrm{M}}$ and K_S at $K_\mathrm{Cl}^\mathrm{OH} = 2$, $\beta = 0.7$ are very much different from the corresponding values at $K_\mathrm{Cl}^\mathrm{OH} = 5$, $\beta = 0.1$ (Table 1). It may also be noted that at any set of values of $K_\mathrm{Cl}^\mathrm{OH}$ and β, the values of K_S change by more that 50% with the change in [NaOH] from 0.005 to 0.02 mol dm^{-3} (Table 1) which cannot be explained easily. Thus, it is difficult to ascertain with confidence the exact values of $K_\mathrm{Cl}^\mathrm{OH}$ and β in terms of the PIE model. It is apparent that k_calcd values change only slightly with a large change in either $K_\mathrm{Cl}^\mathrm{OH}$ at constant β or β at constant $K_\mathrm{Cl}^\mathrm{OH}$ (Tables I–IV in the ESI). It is therefore necessary to determine the exact values of β and the ion-exchange constant (K_X^Y) under the typical experimental conditions of kinetic runs by using methods other than a kinetic one in order to get reliable values of the unknown parameters $k'_{2,\mathrm{M}}$ and K_S by using the PIE model. Alternatively,

Table 1 Values of kinetic parameters ($k'_{2,M}$ and K_S) and least-squares (Σd_i^2) at different [NaOH] (in the absence of added inert salt) calculated from eqn. (6)[a]

[NaOH]/mol dm^{-3}	10^4 c.m.c./mol dm^{-3}	K_{Cl}^{OH}	β	10^3 $k'_{2,M}$/s^{-1}	K_S/dm^3 mol^{-1}	10^6 Σd_i^2	10^4 [CTACl]$_T$ range/mol dm^{-3}
0.005	3.4	2	0.7	77.3 ± 3.6[b]	247 ± 24[b]	4.724	4–1000
		10	0.7	220 ± 15	150 ± 18	8.111	
		500	0.7	8910 ± 855	81 ± 12	11.15	
		5	0.1	1846 ± 144	96 ± 12	8.237	
		5	0.7	133 ± 8	186 ± 21	6.740	
		5	0.9	78.3 ± 4.6	259 ± 32	8.415	
0.010	2.6	2	0.7	88.8 ± 4.0	332 ± 38	22.36	3–1000
		10	0.7	237 ± 15	164 ± 20	30.84	
		500	0.7	9537 ± 1224	57 ± 10	62.51	
		5	0.1	1803 ± 107	116 ± 12	21.63	
		5	0.7	147 ± 8	221 ± 25	25.90	
		5	0.9	93.3 ± 5.4	291 ± 39	34.65	
0.015	3.2	2	0.7	96.7 ± 2.9	430 ± 39	20.58	4–1000
		10	0.7	243 ± 8	191 ± 14	18.36	
		500	0.7	8888 ± 661	61 ± 7	42.01	
		5	0.1	1749 ± 50	141 ± 8	10.77	
		5	0.7	155 ± 5	267 ± 20	18.14	
		5	0.9	102 ± 4	347 ± 37	33.79	
0.020	2.7	2	0.7	89.1 ± 2.1	568 ± 46	19.32	3–1000
		10	0.7	211 ± 7	219 ± 16	22.58	
		500	0.7	7481 ± 449	53 ± 5	35.06	
		5	0.1	1447 ± 66	172 ± 17	41.65	
		5	0.7	138 ± 4	324 ± 23	19.33	
		5	0.9	94.1 ± 2.2	412 ± 29	17.91	

[a] $[PB]_0 = 2 \times 10^{-4}$ mol dm^{-3}, $\lambda = 290$ nm, 35 °C and the aqueous reaction mixture in each kinetic run contains 2% v/v CH_3CN. [b] Error limits are standard deviations.

β and K_S or K_X^Y and K_S or β, K_X^Y and K_S should not be considered as disposable parameters in order to get reliable values of $k'_{2,M}$ and K_X^Y or $k'_{2,M}$ and β or $k'_{2,M}$. Although, in principle, all the parameters except $k'_{2,M}$ can be measured independently, practically it is not so simple to measure these parameters under typical reaction kinetic conditions. Furthermore, it has been shown that the value of the ion-exchange constant of an ion[20] and most likely the micellar binding constant of a molecule are technique-dependent.

If the ion-exchange constant K_{Cl}^{OH} is defined as $K_{Cl}^{OH} = K_{Cl}/K_{OH}$ where K_{Cl} and K_{OH} represent CTACl micellar binding or association constants for Cl^- and HO^-, respectively, then it may be shown that K_{Cl}^{OH} cannot remain constant for the kinetic runs carried out under varying concentrations of added inert salt (NaCl) at constant [NaOH] and [CTACl]$_T$. The mathematical complexity in the use of the PIE model would be increased compared to one exhibited by eqns. (1)–(6) if the added inert salt is NaBr or MX instead of NaCl in the presence of CTACl micelles.

The rate constants (k_{obs}), obtained at a constant [CTACl]$_T$, 0.01 mol dm^{-3} NaOH and under varying concentrations of NaCl, were treated in terms of the PIE model, *i.e.* through eqns. (1)–(6). The values of $k'_{2,M}$, K_S, Σd_i^2 and PRE, k_{calcd} at $\beta = 0.7$ and different values of K_{Cl}^{OH} are summarized in Table 2 and Tables V and VI in ESI, respectively. The value of the c.m.c. of CTACl micelles is 2.6×10^{-4} mol dm^{-3} at 0.01 mol dm^{-3} NaOH and [NaCl] = 0. The increase in [NaCl] is expected to decrease the c.m.c. Thus, the value of c.m.c. should be $<2.6 \times 10^{-4}$ mol dm^{-3} in the presence of NaCl. But the lowest value of [CTACl]$_T$ is 0.007 mol dm^{-3} which shows that $[D_n]$/c.m.c. ≈ 26 at [NaCl] = 0. It is therefore evident that $[D_n] \approx$ [CTACl]$_T$ at 0.007 mol dm^{-3} and 0.01 mol dm^{-3} CTACl. The calculated values of $k'_{2,M}$, K_S and Σd_i^2 at $K_{Cl}^{OH} = 2$, 3 and 5 do not show any appreciable change with the change in c.m.c. from 0 to 2×10^{-4} mol dm^{-3} (Table 2) which supports the assumption that $[D_n] \approx$ [CTACl]$_T$ under the experimental conditions imposed. It may be noted that the absolute values of residual errors increase appreciably with the increase or decrease in K_{Cl}^{OH} from its value at 3, especially at ≥ 0.01 mol dm^{-3} NaCl (Tables V and VI in the ESI). But such characteristic residual errors are not noticeable in the treatment of the observed data k_{obs}–$[D_n]$ shown in Tables I–IV in the ESI.

The minimum value of Σd_i^2 turned out to be at $K_{Cl}^{OH} = 3$ and $\beta = 0.7$ at 0.007 and 0.01 mol dm^{-3} CTACl for k_{obs} obtained at 0.01 mol dm^{-3} NaOH (Table 2). But the minimum value of Σd_i^2 was found to be at $K_{Cl}^{OH} \le 2$ and $\beta = 0.7$ for k_{obs} obtained at 0.01 mol dm^{-3} NaOH, [NaCl] = 0 and a different value of [CTACl]$_T$ (Table 1). It may be noted that statistical significance of the calculated value of K_S seems to be reliable and unreliable in the absence of NaCl (Table 1) and presence of NaCl (Table 2), respectively, at $K_{Cl}^{OH} \le 2$ and $\beta = 0.7$. The values of K_S, obtained at $K_{Cl}^{OH} = 3$ (*i.e.* the minimum values of Σd_i^2), are nearly 3-fold smaller in the absence than in the presence of NaCl at 0.01 mol dm^{-3} NaOH (Tables 1 and 2) which cannot be explained easily. The CTABr micellar binding constants (K_S) of neutral benzimidazole, obtained at different [NaCl], increased from 43 to 68 dm^3 mol^{-1} with the increase in [NaCl] from 0.0 to 1.0 mol dm^{-3} at 0.01 mol dm^{-3} CTACl and this salt effect on K_S was most probably attributable to the salting out effect.[21] But the increase in [NaBr] from 0.0 to 0.3 mol dm^{-3} did not reveal an appreciable effect on K_S for the sodium dodecyl sulfate micellar binding constant of PB.[18] Thus, it seems unlikely that <3-fold larger values of K_S in the presence (Table 2) than in the absence (Table 1) of varying concentrations of NaCl are due merely to the salt effect. It may be noted from the values of calculated parameters ($k'_{2,M}$ and K_S) in Table 2 that although the values of Σd_i^2 change, the values of $k'_{2,M}$ and K_S remain essentially unchanged with the change in [CTACl]$_T$ from 0.007 to 0.01 mol dm^{-3} at a constant K_{Cl}^{OH} (within the K_{Cl}^{OH} range 3–500).

As has been mentioned earlier in the text the use of the PIE model for the observed data listed in Tables V and VI in the ESI is rather suspect and for the observed data listed in Table VIII in the ESI, the use of the PIE model becomes even more difficult and complex because of the increased mathematical complexity in arriving at a practically workable kinetic equation. An alternative kinetic model to explain kinetic data similar to those listed in Tables V, VI and VIII in the ESI may be described as follows. The CTABr micellar binding constant (K_S) of ionized

Table 2 Values of kinetic parameters ($k'_{2,M}$ and K_S) and least-squares (Σd_i^2) at different $[CTACl]_T$ (in the presence of NaCl) calculated from eqn. (6)[a]

$[CTACl]_T$/mol dm^{-3}	10^4 c.m.c./mol dm^{-3}	K_{Cl}^{OH}	$10^3\ k'_{2,M}$/s^{-1}	K_S/dm^3 mol^{-1}	$10^7\ \Sigma d_i^2$	10^3 [NaCl] range/mol dm^{-3}
0.007	0.0	2	67.8 ± 1.7[b]	10366 ± 27218[b]	28.90	0–300
	2.0	2	67.3 ± 1.6	7446 ± 13165	26.43	
	0.0	3	89.1 ± 1.4	1142 ± 224	9.595	
	2.0	3	88.5 ± 1.4	1107 ± 210	9.902	
	0.0	5	129 ± 5	507 ± 119	46.02	
	2.0	5	128 ± 5	502 ± 121	50.50	
	0.0	7	168 ± 10	360 ± 104	102.7	
		10	225 ± 20	270 ± 92	185.2	
		20	411 ± 63	177 ± 76	384.6	
		100	1922 ± 560	101 ± 60	799.6	
		500	9589 ± 3467	83 ± 56	970.2	
0.010	0.0	2	66.2 ± 1.0	7278 ± 11480	9.608	0–300
	2.0	2	65.8 ± 0.9	5661 ± 6564	8.826	
	0.0	3	86.4 ± 1.1	944 ± 178	6.339	
	2.0	3	85.8 ± 1.1	919 ± 174	6.890	
	0.0	5	124 ± 4	438 ± 107	35.81	
	2.0	5	122 ± 4	434 ± 108	38.24	
	0.0	7	159 ± 8	320 ± 90	72.43	
		10	210 ± 14	248 ± 78	122.2	
		20	374 ± 38	173 ± 64	235.2	
		100	1648 ± 267	113 ± 52	447.7	
		500	7974 ± 1484	100 ± 49	526.6	

[a] $[PB]_0 = 2 \times 10^{-4}$ mol dm^{-3}, [NaOH] = 0.01 mol dm^{-3}, $\beta = 0.7$, $\lambda = 290$ nm, 35 °C and the aqueous reaction mixture in each kinetic run contains 2% v/v CH_3CN. [b] Error limits are standard deviations.

phenyl salicylate (PS^-), obtained at different [KBr] in methanolysis[22] and [NaBr] in aminolysis,[23] followed an empirical relationship [eqn. (7)] where MX = KBr or NaBr and Ψ_{Br-PS}

$$K_S = K_S^0/(1 + \Psi_{Br-PS}[MX]) \qquad (7)$$

is an empirical parameter whose magnitude is the measure of the ability of a counterion (such as Br^-) to expel another counterion (such as PS^-) from the micellar pseudophase to the aqueous pseudophase. The validity of eqn. (7) has been tested in a few more related studies.[24] If we assume that eqn. (7) is applicable for the expulsion of HO^- from the CTACl micellar pseudophase to the aqueous pseudophase by externally added NaCl or NaBr at a constant [NaOH] and $[CTACl]_T$, then the kinetic model of the micellar-mediated reaction[2] and eqn. (7) can lead to eqn. (8) where $k_0 = \{k_W + k_M K_{OH}{}^0 K_S\ [D_n]\}/\{(1 + K_S[D_n])(1 + K_{OH}{}^0[D_n])\}$, $k = k_W/(1 + K_S\ [D_n])$ and $K = \Psi_{X-OH}/(1 + K_{OH}{}^0[D_n])$ with k_W, k_M and $K_{OH}{}^0$ representing the pseudo-first-order rate constants for alkaline hydrolysis of PB in aqueous pseudophase and micellar pseudophase, and the CTACl micellar binding constant of HO^- at [MX] = 0, respectively.

$$k_{obs} = \frac{k_0 + kK[MX]}{1 + K[MX]} \qquad (8)$$

Eqn. (8) was applied to the rate constants (k_{obs}), obtained at constant $[CTACl]_T$, [NaOH] (= 0.01 mol dm^{-3}) and different concentrations of NaCl and NaBr. The nonlinear least-squares calculated values of k and K at 0.007 mol dm^{-3} and 0.01 mol dm^{-3} CTACl for NaCl and NaBr are shown in Table 3. The values of k_0 used in the calculation of k and K from eqn. (8) were obtained experimentally by carrying out kinetic runs at [MX] = 0. The quality of the fit of k_{obs} to eqn. (8) is evident from the standard deviations associated with the values of calculated parameters, k and K (Table 3), as well as from the values of calculated rate constants (k_{calcd}) as shown in Tables VII and VIII in the ESI. Incidentally, the values of Σd_i^2 (Table 3) for k_{obs} obtained at 0.007 and 0.01 mol dm^{-3} CTACl through eqn. (8) are almost similar to the corresponding minimum values of Σd_i^2 obtained through PIE treatment (Table 2). But, as concluded earlier, the criterion of minimum least-squares value for the best fit in the use of the PIE model seems to be meaningless. The reasonably good fit of observed data in Table VIII in the ESI to eqn. (8) indicates that the ion-exchange Br^- to Cl^- is insignificant compared with ion-exchange Br^- to HO^- which is conceivable for the reason that $K_{Br-OH} \gg K_{Br-Cl}$. The effect of ion-exchange from Cl^- to HO^- may be also ignored compared with Br^- to HO^- for the reasons that (i) $\psi_{Br-OH}/\psi_{Cl-OH} \approx 2$ and (ii) the value of $[Cl^-]_T$ is constant and rather low and its effect is a maximum at [NaBr] = 0.

The calculated values of k are associated with considerably high standard deviations and consequently these values of k are statistically unreliable. The values of k and K (Table 3) show that the contribution of the kK[MX] term compared with k_0 in eqn. (8) is <20% at [NaCl] ≤ 0.1 mol dm^{-3}. The low contribution of kK[MX] compared with k_0 in eqn. (8) is the cause of the unreliability in the values of k summarized in Table 3. The values of K were also calculated from eqn. (8) with $k = 0$. These K values (Table 3) are not very much different from the corresponding K values obtained with $k \neq 0$. This shows the negligible contribution of kK[MX] compared with k_0 in eqn. (8) under the present experimental conditions.

In view of the empirical definition of ψ_{X-Y} (= ψ_{Br-PS} in eqn. (7)) where the magnitude of ψ_{X-Y} is the measure of the ability of counterion X to expel another counterion Y from ionic micellar pseudophase to the aqueous pseudophase, the value of ψ_{X-Y} must be proportional to K_X^Y (ion-exchange constant in PIE formalism where $K_X^Y = K_X/K_Y$ with K_X and K_Y representing ionic micellar binding constants of counterions X and Y, respectively). Thus, ψ_{Cl-OH} and ψ_{Br-OH} must be proportional to K_{Cl}^{OH} and K_{Br}^{OH} respectively and consequently, $\psi_{Br-OH}/\psi_{Cl-OH}$ should be equal to K_{Br}^{Cl} (= K_{Br}^{OH}/K_{Cl}^{OH}). The average value of K_{Br-OH}/K_{Cl-OH} (= $\psi_{Br-OH}/\psi_{Cl-OH} \approx 2$) may be compared with the reported values of K_{Br}^{Cl} = 2–3.[1b,3d] Similar relationships between K_{X-S}/K_{Y-S} (= ψ_{X-S}/ψ_{Y-S}) and ion-exchange constant K_X^Y have been obtained for various ions X and Y with S = anionic phthalimide[16,24b] and anionic phenyl salicylate.[24a,c–e] These results strengthen the validity of eqn. (7).

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Table 3 Values of kinetic parameters (k and K) and least-squares (Σd_i^2) calculated from eqn. (8)[a]

Salt	$[\mathrm{CTACl}]_\mathrm{T}$/mol dm^{-3}	10^3 k/s^{-1}	K/dm^3 mol^{-1}	10^7 Σd_i^2	10^3 [salt] range/mol dm^{-3}
NaCl	0.007	0.51 ± 0.22[b]	104 ± 4[b]	12.86	0–300
		0	88 ± 17		
	0.010	0.38 ± 0.15	86 ± 3	5.263	
		0	79 ± 14		
NaBr	0.007	−0.01 ± 0.29	192 ± 11	23.43	0–200
		0	177 ± 33		
	0.010	−0.13 ± 0.21	167 ± 7	12.08	
		0	169 ± 21		

[a] $[\mathrm{PB}]_0 = 2 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{NaOH}] = 0.01$ mol dm^{-3}, $\lambda = 290$ nm, 35 °C and the aqueous reaction mixture in each kinetic run contains 2% v/v $\mathrm{CH_3CN}$. [b] Error limits are standard deviations.

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