Effects of organic salts on the rate of intramolecular general base-catalyzed piperidinolysis of ionized phenyl salicylate in the presence of cationic micelles

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Pseudo-first-order rate constants (k_{obs}), obtained for the cleavage of ionized phenyl salicylate (PS^-) at constant [NaOH], [MeCN], $[CTABr]_T$ (total concentration of cetyltrimethylammonium bromide), $[Pip]_T$ (total concentration of piperidine) and varying concentrations of sodium *o*-, *m*- and *p*-toluate ([MX]), follow the relationship: $k_{obs} = (k_0 + \theta K[MX])/(1 + K[MX])$, where θ and K are empirical parameters. The values of θ are almost independent of $[CTABr]_T$, while the K values decrease with increasing $[CTABr]_T$ within its range 0.005–0.020 mol dm^{-3}. The values of θ and K are explained in terms of a pseudophase model of the micelle coupled with an empirical relationship: $K_S = K_S^0/(1 + k_{X/S}[MX])$, where K_S is the CTABr micellar binding constant of PS^- in the presence of MX. The value of $K_{X/S}$, for the *o*-toluate ion is nearly 2.5-fold smaller than those for the *m*- and *p*-toluate ions. The values of $\theta/(k^n_w[Pip]_T)$ {where $k^n_w[Pip]_T = k_{obs}$ at $[CTABr]_T = [MX] = 0$} vary from nearly 0.5 to 0.6 within the $[CTABr]_T$ range 0.005–0.020 mol dm^{-3}.

Introduction

The ion exchange between HO^- and Br^- was first detected kinetically in the reactions of HO^- with neutral organic substrates in the presence of cationic surfactants such as cetyltrimethylammonium bromide (CTABr). A pseudophase ion-exchange (PIE) model,[1] which is the extension of the older pseudophase micellar (PM) model,[2] has been developed to explain quantitatively such ion exchange. However, some serious weaknesses in the PIE model have recently been realized.[3] The use of the PIE model in micellar-mediated reaction systems containing two or more ion-exchange processes is rare. To best of our knowledge, there are only a few reports where the PIE model has been used in reaction systems involving two ion-exchange processes with relatively more restrictive experimental conditions (because of the conceptual and mathematical complexity involved in formulating a practically workable kinetic equation for data analysis) compared to those involving only one ion-exchange process.[4] The effects of an inert inorganic salt (here, KBr) on the pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis of moderately hydrophobic anionic esters[5] and imides,[6] in the presence of cationic micelles, have been explained in terms of the PIE model coupled with an empirical equation [eqn. (1)], where K_S and K_S^0

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

represent the micellar binding constant of a moderately hydrophobic anionic organic substrate in the presence and absence of KBr, respectively, and L is an empirical parameter, the measure of the ability of an ion (such as Br^-) to expel another counterion (such as S^-) from a micellar pseudophase to the aqueous pseudophase.

The effects of [KBr] on the rate of methanolysis of ionized phenyl salicylate (PS^-) revealed the occurrence of eqn. (2),[7]

$$K_S = K_S^0/(1 + K_{X/S}[KBr]) \quad (2)$$

where $K_{X/S}$ is an empirical parameter, the measure of the ability of an ion, X^- (such as Br^-) to expel another counterion, S^- (such as PS^-) from a micellar pseudophase to the aqueous pseudophase. The results of the effects of $[C_6H_5COONa]$ on the rate of reactions of PS^- with piperidine and *n*-butylamine supported the validity of eqn. (2).[8] Spectrophotometric techniques have been also used to determine K_S (CTABr micellar binding constant of PS^-) at different [NaBr] and $[C_6H_5COONa]$ in the absence of any amine and these data also support the validity of eqn. (2).[9] In the continuation of our work on testing the validity of eqn. (2), the effects of a few organic salts on the rate of piperidinolysis of PS^- in the presence of cationic micelles have been studied. The observed results and their probable explanation(s) are described in this paper.

Experimental

Materials

Reagent grade chemicals such as phenyl salicylate, cetyltrimethylammonium bromide (CTABr), piperidine and toluic acids were supplied by Fluka, BDH or Aldrich and were of the highest commercially available purity. All other chemicals used were also of reagent grade. Stock solutions (0.01 mol dm^{-3}) of phenyl salicylate were prepared in acetonitrile. Stock solutions (1 mol dm^{-3}) of piperidine were freshly prepared in distilled water. Stock solutions (y mol dm^{-3}) of toluic acids were freshly prepared in (y + 0.05) mol dm^{-3} NaOH.

Kinetic measurements

The rate of piperidinolysis of ionized phenyl salicylate (PS^-) was studied by monitoring the disappearance of PS^- spectrophotometrically at 350 nm in the presence of CTABr micelles. Stock solutions (0.25 or 0.5 mol dm^{-3}) of NaOH were used to produce 0.02 mol dm^{-3} NaOH into the reaction mixture for each kinetic run. The concentrations of NaOH produced by the stock solutions of sodium toluates were in the range 0.001 to 0.050 mol dm^{-3} within the [sodium toluate] range 0.01 to 0.40 mol dm^{-3} or 0.60 mol dm^{-3}. Thus, the total concentrations of

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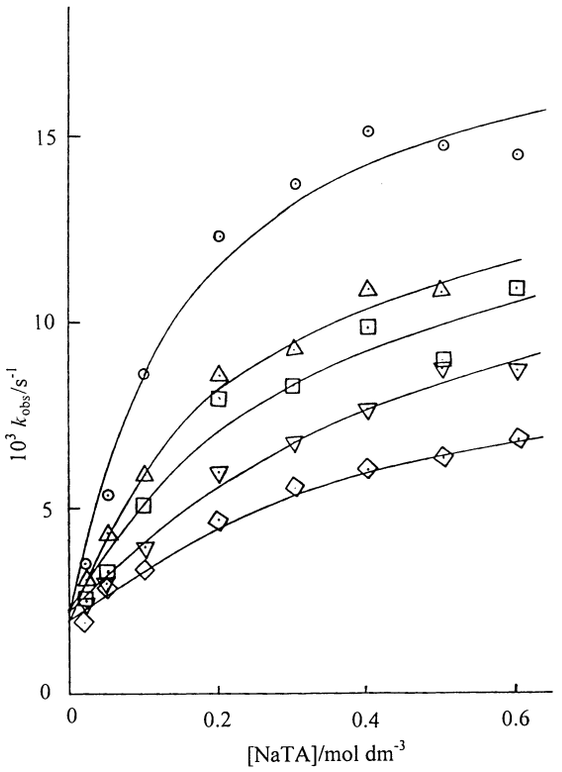


Fig. 1 Plots showing the dependence of k_{obs} upon [NaTA] where NaTA represents sodium *o*-toluate at 0.005 (○), 0.007 (△), 0.010 (□), 0.015 (▽) and 0.020 mol dm^{-3} (◇) CTABr. The solid lines are drawn through the least-squares calculated points.

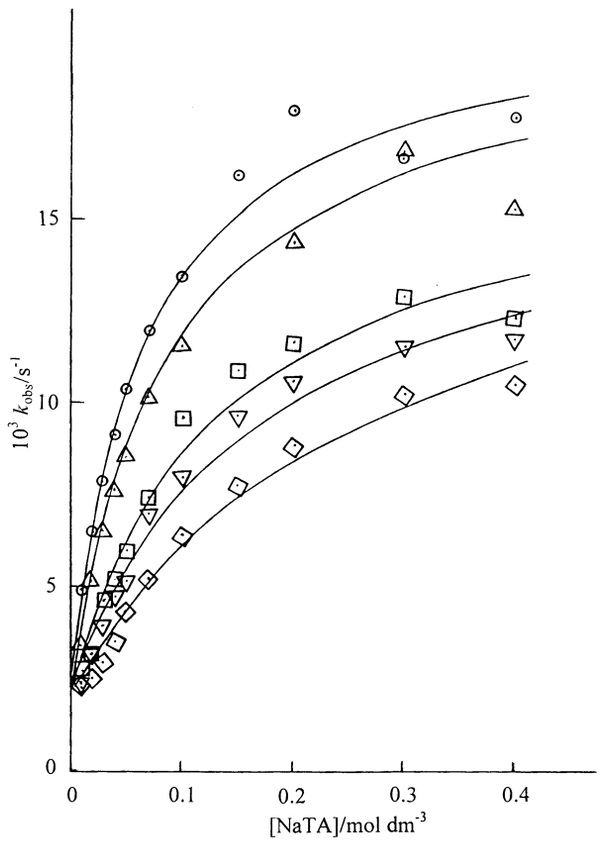


Fig. 2 Plots showing the dependence of k_{obs} upon [NaTA] where NaTA represents sodium *m*-toluate at 0.005 (○), 0.007 (△), 0.010 (□), 0.015 (▽) and 0.020 mol dm^{-3} (◇) CTABr. The solid lines are drawn through the least-squares calculated points.

added NaOH into the reaction mixtures were in the range 0.021 to 0.070 mol dm^{-3}. The final concentration of PS^- in each kinetic run was kept constant at 2×10^{-4} mol dm^{-3}. The details of the kinetic procedure, data analysis and product characterization have been described elsewhere.[10] The products of the reaction of piperidine with phenyl salicylate are *N*-piperidinylsalicylamide and phenol.

Results and discussion

A series of kinetic runs was carried out within a [*o*-$CH_3C_6H_4COONa$] range of 0.0–0.60 mol dm^{-3} at 0.1 mol dm^{-3} piperidine (Pip), ≥0.021 mol dm^{-3} NaOH, 0.005 mol dm^{-3} CTABr and 35 °C. The pseudo-first-order rate constants (k_{obs}) obtained under these conditions are shown in Fig. 1. Similar results were obtained at 0.007, 0.010, 0.015 and 0.020 mol dm^{-3} CTABr. These results are also shown as the plots of k_{obs} *versus* [*o*-$CH_3C_6H_4COONa$] in Fig. 1. The effects of [*m*-$CH_3C_6H_4COONa$] and [*p*-$CH_3C_6H_4COONa$] on k_{obs} were also studied at different $[CTABr]_T$ (= total concentration of CTABr) and these results are shown in Figs. 2 and 3, respectively.

The nonlinear increase in k_{obs} with increasing concentration of the sodium salt of toluic acid, [NaTA] (Figs. 1–3), cannot be attributed to the salt effect or to the probable nucleophilic reaction between PS^- and toluate ion because carboxylate groups are poorer nucleophiles than amines toward esters.[11] Furthermore, the increase in [sodium benzoate] from 0.0 to 0.8 mol dm^{-3} at ≥0.01 mol dm^{-3} NaOH and in the absence of micelles changed k_{obs} for the hydrolysis of PS^- from 7.59×10^{-4} to 6.40×10^{-4} s^{-1} at 35 °C. Pseudo-first-order rate constants (k_{obs}) for the reaction of piperidine with PS^- showed monotonic decrease with the increase in $[CTABr]_T$ from 0.0 to ≤0.004 mol dm^{-3} and almost leveled off at $[CTABr]_T > 0.004$ mol dm^{-3}.[12] The effects of [NaTA] on k_{obs} were studied under $[CTABr]_T$ (≥0.005 mol dm^{-3}) where the PS^- ions are fully micellar bound in the absence of NaTA. The value of k_{obs} is nearly 13-fold larger at $[CTABr]_T = 0$ than at $[CTABr]_T \geq 0.004$ mol dm^{-3} (see ref. 12 and Table 1). Thus, the most obvious cause for the increase in k_{obs} with the increase in [NaTA] at ≥0.005 mol dm^{-3} CTABr may be attributed to the transfer of micellized ionized

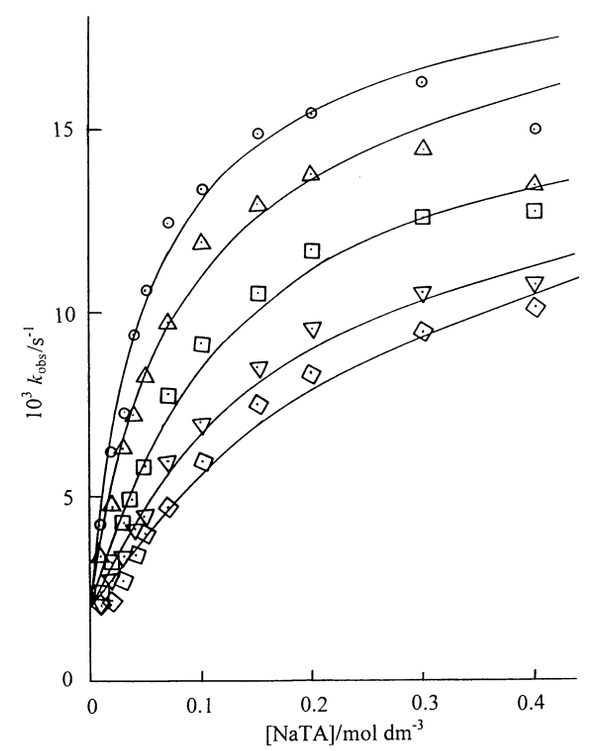


Fig. 3 Plots showing the dependence of k_{obs} upon [NaTA] where NaTA represents sodium *p*-toluate at 0.005 (○), 0.007 (△), 0.010 (□), 0.015 (▽) and 0.020 mol dm^{-3} (◇) CTABr. The solid lines are drawn through the least-squares calculated points.

Table 1 Values of the empirical parameters, θ and K, calculated from eqn. (3)[a]

$[CTABr]_T$/ mol dm^{-3}	$10^3 k_0$[b]/s^{-1}	$10^3 \theta$/s^{-1}	K/dm^3 mol^{-1}	$K_{X/S}$[c]/ dm^3 mol^{-1}	F[d]
o-Toluate					
0.005	2.42 ± 0.08[e]	19.1 ± 1.4[e]	6.00 ± 1.48[e]	216	0.59
0.007	1.95 ± 0.11	15.2 ± 0.9	4.48 ± 0.72	224	0.47
0.010	2.30 ± 0.07	15.2 ± 2.5	2.95 ± 1.22	209	0.47
0.015	2.21 ± 0.09	15.8 ± 2.3	1.67 ± 0.47	177	0.49
0.020	2.07 ± 0.07	11.3 ± 1.4	1.82 ± 0.49	257	0.35
m-Toluate					
0.005	2.62 ± 0.06	21.0 ± 0.9	14.6 ± 1.9	526	0.65
0.007	2.52 ± 0.04	20.5 ± 2.0	10.9 ± 3.1	545	0.63
0.010	2.11 ± 0.06	17.0 ± 1.3	7.80 ± 1.60	554	0.53
0.015	2.36 ± 0.05	16.6 ± 1.3	5.90 ± 1.20	625	0.51
0.020	2.12 ± 0.06	17.1 ± 1.9	3.60 ± 0.80	508	0.53
p-Toluate					
0.005	2.37 ± 0.07	19.4 ± 0.8	17.3 ± 2.2	623	0.60
0.007	2.26 ± 0.08	18.3 ± 0.9	11.5 ± 1.5	575	0.56
0.010	2.10 ± 0.09	17.4 ± 1.3	7.12 ± 1.31	506	0.54
0.015	2.00 ± 0.07	15.8 ± 1.3	5.30 ± 1.00	562	0.49
0.020	1.99 ± 0.07	16.8 ± 2.1	3.30 ± 0.80	465	0.52

[a] Conditions: $[\text{phenyl salicylate}]_0 = 2 \times 10^{-4}$ mol dm^{-3}; [NaOH] > 0.02 mol dm^{-3}; [Pip] = 0.1 mol dm^{-3}; 35 °C; λ = 350 nm; the aqueous solvent for each kinetic run contained 2% v/v MeCN. [b] $k_0 = k_{obs}$ at [MX] = 0. [c] $K_{X/S} = K(1 + K_S^0[CTABr]_T)$ where $K_S^0 = 7000$ dm^3 mol^{-1}. [d] $F = \theta/(k^n_W[Pip]_T)$ where $k^n_W = 0.324$ dm^3 mol^{-1} s^{-1} and $[Pip]_T = 0.1$ mol dm^{-3}. [e] Error limits are standard deviations.

phenyl salicylate (PS^-_M) to the aqueous pseudophase by the added toluate ions (TA^-) through the ion exchange TA^-_W/PS^-_M (subscripts W and M represent the aqueous pseudophase and micellar pseudophase, respectively). The concentrations of nonionic piperidine in aqueous and micellar pseudophases should not be affected by the occurrence of ion exchange within the domain of the assumptions of the pseudophase model of the micelle.[1–3]

The values of k_{obs} obtained at 0.1 mol dm^{-3} Pip, ≥0.021 mol dm^{-3} NaOH, a constant concentration of CTABr and different values of [NaTA] were found to fit to the empirical equation, eqn. (3), where $k_0' = k_{obs}$ at [NaTA] = 0, and θ and K are empirical parameters. Values of k_0 for different reaction conditions were obtained by carrying out experiments in the absence of NaTA. The values θ and K were calculated from eqn. (3) using

$$k_{obs} = \frac{k_0' + \theta K[\text{NaTA}]}{1 + K[\text{NaTA}]} \quad (3)$$

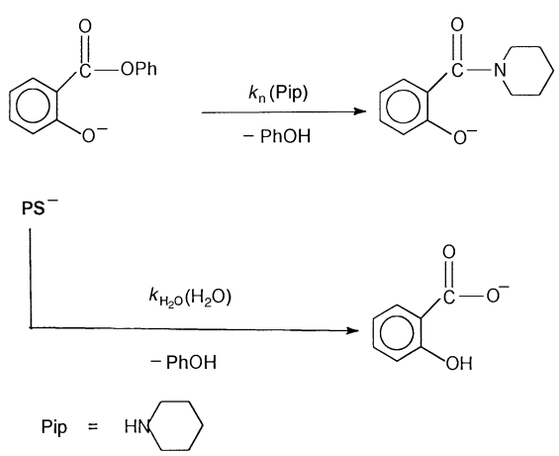
the nonlinear least-squares technique. These calculated values of θ and K at different $[CTABr]_T$ for *o*-, *m*- and *p*-$CH_3C_6H_4COONa$ are summarized in Table 1. The fitting of the observed data to eqn. (3) is evident from the plots of Figs. 1–3, where solid lines are drawn through the calculated data points.

The spectral evidence, as described elsewhere,[12] revealed the presence of 100% ionized form of phenyl salicylate (PS^-) under the experimental conditions of the entire kinetic runs of the present study. The rate constants k_{obs} for the cleavage of PS^- under the present experimental conditions have been found to follow eqn. (4),[12] where $[Pip] \approx [Pip]_T$ (= [Pip] + [$PipH^+$]), k_0 is

$$k_{obs} = k_0 + k_n[Pip] \quad (4)$$

the pseudo-first-order rate constant for the intramolecular general base (IGB)-catalyzed hydrolysis of PS^- and k_n is the second-order rate constant for the IGB-catalyzed nucleophilic reaction of Pip with PS^-. The source for IGB catalysis is the ionized *o*-OH group in PS^-, which acts as an intramolecular general base catalyst for the nucleophilic reactions of the nucleophiles (with a hydrogen atom attached to the nucleophilic atom such as H_2O, ROH, RNH_2 and R_2NH) with PS^-.[10,13,14] But the contribution of k_0 is negligible compared to that of $k_n[Pip]_T$ at 0.1 mol dm^{-3} Pip.[12] Thus, under the present experimental conditions, $k_{obs} \approx k_n[Pip]_T$.

The brief reaction scheme for the cleavage of PS^- may be shown in Scheme 1, where $k_{H_2O}(H_2O)$ [= k_0 in eqn. (4)] is negligible compared with k_n(Pip) under the present reaction conditions. The detailed reaction mechanisms for the k_n and k_0 steps in the absence of micelles have been described elsewhere.[13,14]

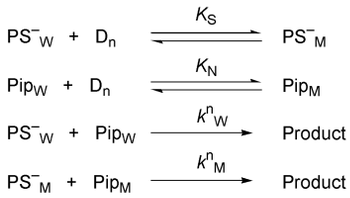


Scheme 1

The rate of reaction of Pip with PS^- in the presence of CTABr micelles may be explained quantitatively in terms of a pseudophase model (PM) of the micelle, *i.e.* Scheme 2.[2] The assumptions involved in this model and its usefulness, as well as weaknesses, are critically discussed by Bunton.[3c,15]

In Scheme 2, K_S and K_N are the CTABr micellar binding constants of PS^- and Pip, respectively, k^n_W and k^n_M represent the nucleophilic second-order rate constants for the reactions of Pip with PS^- in the aqueous and micellar pseudophases, respectively, and D_n stands for the CTABr micelle. Scheme 2 and the observed rate law (rate = $k_{obs}[PS^-]_T$) can lead to eqn. (5), where $k^{ns}_M = k^n_M/V_M$ (V_M is the micellar molar

$$k_{obs} = \frac{(k^n_W + k^{ns}_M K_N K_S[D_n])[Pip]_T}{(1 + K_S[D_n])(1 + K_N[D_n])} \quad (5)$$



Scheme 2

volume[15]) and $[D_n] = [CTABr]_T - cmc$ (cmc is the critical micelle concentration). The reported value of the cmc is $<1 \times 10^{-4}$ mol dm^{-3} in the presence of 2×10^{-4} mol dm^{-3} PS^- and the absence of any inert salt.[12,16] The presence of an inert salt is expected to decrease the cmc and, thus, under the present experimental conditions, the cmc value must be much lower than 1×10^{-4} mol dm^{-3}. Since the lowest value of $[CTABr]_T$ is 50×10^{-4} mol dm^{-3}, it is therefore apparent that $[D_n] \approx [CTABr]_T$.

The reported value of K_N for a tetradecyltrimethylammonium bromide (TTABr) micelle is 0.3 dm^3 mol^{-1}.[17,18] The value of K_N for a CTABr micelle should not be significantly different from the K_N for TTABr.[19] The value of K_N would not be expected to change appreciably in the presence of sodium toluate of varying concentrations because piperidine is a neutral and highly hydrophilic molecule. The value of the cetyltrimethylammonium chloride (CTACl) micellar binding constant of neutral benzimidazole, a relatively much more hydrophobic molecule than piperidine, increased from 43 to 68 dm^3 mol^{-1} with the increase in [NaCl] from 0.0 to 1.0 mol dm^{-1} at 0.01 mol dm^{-3} CTACl.[4b] Thus, it is apparent that $1 \gg K_N[D_n]$ at $[CTABr]_T \leq 0.02$ mol dm^{-3} and, under such conditions, eqn. (5) can be reduced to eqn. (6).

$$k_{obs} = \frac{(k^n_W + k^{ns}_M K_N K_S[D_n])[Pip]_T}{(1 + K_S[D_n])} \quad (6)$$

The occurrence of the ion-exchange phenomenon in ionic micellar-mediated bimolecular reactions involving both ionic, or one ionic and one neutral, reactants appears to be a ubiquitous feature of such reacting systems. The possible ion-exchange processes in the present reacting system are PS^-/TA^-, PS^-/Br^-, PS^-/HO^-, TA^-/Br^-, TA^-/HO^- and HO^-/Br^-. Here the ion-exchange processes TA^-/Br^-, TA^-/HO^- and HO^-/Br^- may be ignored, as the rate of the piperidinolysis of PS^- would remain unaffected by their occurrence. The rate constant for the reaction of Pip with PS^- is more than 95-fold larger in the aqueous pseudophase than in the micellar pseudophase.[12] The rate of hydrolysis of PS^- remained independent of $[HO^-]$ within its range 0.005–0.060 mol dm^{-3} at $[CTABr]_T = 0$[10,20] and 0.01–0.04 mol dm^{-3} at 0.0015 mol dm^{-3} CTABr.[16] The effectiveness of an ion-exchange process decreases as the difference in the hydrophilicity or hydrophobicity of the exchanging ions increases. The relative effectiveness of two or more ion-exchange processes is also determined by the relative concentrations of the exchanging ions. The hydrophobicity of HO^-, Br^-, TA^- and PS^- is expected to vary in the order $PS^- > TA^- > Br^- > HO^-$ and their maximum concentrations, attained in the present study, are ≤ 0.07, 0.02, ≤ 0.6 and 2×10^{-4} mol dm^{-3}, respectively. Thus, the ion-exchanges PS^-/Br^- and PS^-/HO^- may be ignored compared to PS^-/TA^- under the experimental conditions of the present study. The ion-exchange process which should most affect the rate of piperidinolysis of PS^- is PS^-/TA^-. The TA^- ions, being moderately hydrophobic and present in large amounts, can expel PS^- ions from the micellar pseudophase to the aqueous pseudophase, which, in turn, causes the increase in k_{obs} with the increase in $[TA^-]$. Such an effect of $[TA^-]$ on the distribution of PS^- between the aqueous and micellar pseudophases is represented by the empirical eqn. (2).

Eqns. (2) (with replacement of KBr by NaTA) and (6) lead to eqn. (3) with k_0', θ and K defined by eqns. (7)–(9).

$$k_0' = (k^n_W[Pip]_T + k^{ns}_M K_N K_S^0[D_n][Pip]_T)/(1 + K_S^0[D_n]) \quad (7)$$

$$\theta = k^n_W[Pip]_T \quad (8)$$

$$K = K_{X/S}/(1 + K_S^0[D_n]) \quad (9)$$

The reported value of k^n_W is 0.324 dm^3 mol^{-1} s^{-1} at 35 °C.[12] Thus, the maximum value of θ should be 0.0324 s^{-1} at 0.1 mol dm^{-3} Pip, which could be obtained only if the limiting concentration of TA^- can cause 100% transfer of micellized PS^- ions (PS^-_M) from the micellar pseudophase to the aqueous pseudophase, provided the PS^- ions are completely micellar bound in the absence of MX. The limiting concentration of a salt such as NaTA is defined as the concentration of the salt at which the rate of a reaction becomes independent of the salt concentration [*i.e.*, at the limiting concentration of NaTA, $K[NaTA] \gg 1$ and $\theta K[NaTA] \gg k_0'$ in eqn. (3)]. Thus, the ratio $F \{= \theta/(k^n_W[Pip]_T)\}$ may be considered to be the measure of the fraction of the fully micellized PS^- ions transferred from the micellar pseudophase to the aqueous pseudophase by the limiting concentration of an inert salt such as NaTA.

It is well known that the structure of a cationic micelle changes from spherical to disk to rod with increasing concentration of the micelle-forming surfactant.[21] This micellar structural transition is enhanced in the presence of inert inorganic or organic salts.[22,23] Such structural changes might affect $K_{X/S}$, and hence, the value of $K_{X/S}$ should not be expected to remain constant for a wide range of [NaTA] at constant $[CTABr]_T$. Such a salt effect on $K_{X/S}$ could also indirectly affect θ. It might also cause the observed data to deviate from fitting to eqn. (3). This could possibly be the reason for the negative deviations of the observed data points from the theoretical lines at very high values of [NaTA] and low values of $[CTABr]_T$ (Figs. 1–3).

Eqn. (8) shows that the value of θ ($= k^n_W[Pip]_T$) should be independent of $[CTABr]_T$. But the calculated values of θ indicate a slight decrease with the increase in $[CTABr]_T$ for all *o*-, *m*- and *p*-toluate ions (Table 1). This might be attributed to the micellar structural changes discussed above.

In view of eqn. (9), $K = K_{X/S}/(1 + K_S^0[D_n]) \approx K_{X/S}/(1 + K_S^0[CTABr]_T)$ under the experimental conditions imposed in the present study. The values of $K_{X/S}$, obtained at different $[CTABr]_T$ with $K_S^0 = 7000$ dm^3 mol^{-1},[24] are summarized in Table 1. They turn out to be almost independent of $[CTABr]_T$ within its range from 0.005 to 0.020 mol dm^{-3}. These results show that the $K_{X/S}$ values are insensitive to any micellar structural changes there might be. The value of $K_{X/S}$ for an anion such as toluate ion can be rationalized in terms of the hydrogen bonding, electrostatic, hydrophobic and steric (*i.e.*, packing constraints) interactions between the anion and the ionic micellar pseudophase. The hydrogen bonding and electrostatic interactions between the CTABr micellar pseudophase or surface and the *o*-, *m*- and *p*-toluate ions are expected to be the same, but the hydrophobic and possibly steric interactions are not. The hydrophobicity of *m*- and *p*-nitrobenzoate anions is nearly the same, while the *o*-nitrobenzoate ion is significantly less hydrophobic.[25] The relative values of hydrophobicity of the *o*-, *m*- and *p*-toluate ions are also similar to the corresponding values of hydrophobicity of *o*-, *m*- and *p*-nitrobenzoate ions.[26] Thus, the hydrophobicity argument may be used to explain (i) the lower (~2.5-fold) $K_{X/S}$ value for the *o*-toluate ion (217 ± 19 dm^3 mol^{-1}) compared to those for the *m*- (552 ± 45 dm^3 mol^{-1}) and *p*-toluate ions (546 ± 62 dm^3 mol^{-1}) and (ii) the almost similar $K_{X/S}$ values for the *m*- and *p*-toluate ions (Table 1). Similar hydrophobicity arguments have been used to explain the values of ion-exchange constants, obtained by ^{1}H NMR

Table 2 Values of the empirical constants, $K_{X/S}$ and $K_{Y/S}$, and ion-exchange constants, K_X^Y, obtained from empirical constants as well as from physical techniques[a]

X	Y	$K_{X/S}$/dm^3 mol^{-1}	$K_{Y/S}$/dm^3 mol^{-1}	K_X^Y[b]	K_X^Y[c]
$C_6H_5CO_2^-$	Br^-	(124)[d,e]	(25)[e,f]	(5)[g]	
o-$CH_3C_6H_4CO_2^-$	Br^-	217 (102)	(25)	9 (4)	
m-$CH_3C_6H_4CO_2^-$	Br^-	552 (315)	(25)	22 (13)	
p-$CH_3C_6H_4CO_2^-$	Br^-	546 (295)	(25)	22 (12)	
$C_6H_5SO_3^-$	Br^-				11[h]
p-$CH_3C_6H_4SO_3^-$	Br^-				19
o-$O^-C_6H_4CO_2^-$	Br^-				20[i]
o-$NO_2C_6H_4CO_2^-$	Br^-				3.8
m-$NO_2C_6H_4CO_2^-$	Br^-				11
p-$NO_2C_6H_4CO_2^-$	Br^-				3.3
2,6-$Cl_2C_6H_4CO_2^-$	Cl^-				13–22[j]
Br^-	Cl^-	(100)	75 (44)[k]	1.3 (2.3)	2.65,[l] 5[h]

[a] Unless otherwise noted, the surfactant used is cetyltrimethylammonium halide, S is ionized phenyl salicylate and the values of K_X^Y were determined by using physical techniques at a single concentration of the surfactant. [b] $K_X^Y = K_{X/S}/K_{Y/S}$. [c] The values of K_X^Y were obtained by using physical techniques. [d] Ref. 8. [e] Parenthesized values are normalized empirical constants, $K_{X/S}^n$, (= $F_X K_{X/S}$). [f] Ref. 34. [g] Parenthesized values are derived from normalized values of empirical constants, $K_{X/S}^n$. [h] Ref. 36. [i] Ref. 25. [j] Ref. 37, where K_X^Y values were determined within $[CTA^+]_T$ range 0.01–0.03 mol dm^{-3} by the use of ^{1}H NMR spectroscopic techniques. [k] Ref. 35, where S represents ionized phthalimide. [l] Ref. 38.

techniques, for the competition between Br^- and *o*-, *m*- and *p*-nitrobenzoate ions for a tetradecyltrimethylammonium bromide (TTABr) micellar surface, where the ion-exchange constant for *o*-nitrobenzoate was found to be 2.9-fold smaller than that for the *m*-nitrobenzoate ion.[25] Menger *et al.*[27] reported that the *m*-phthalate dianion binds more strongly to the decyltrimethylammonium micellar interface compared to the *o*-phthalate dianion.

As mentioned earlier, the magnitude of F {$= \theta/(k^n_W[Pip]_T)$} is a measure of the fraction of the fully micellized PS^- ions expelled from the micellar pseudophase to the aqueous pseudophase by the limiting concentration of sodium toluate. The value of F varies from 0.5 to 0.6 within the $[CTABr]_T$ range 0.005–0.020 mol dm^{-3} for all *o*-, *m*- and *p*-toluate ions, which indicates that the optimum concentrations of toluate ions can expel only nearly 50–60% of the total $[PS^-_M]$ (= $[PS^-]_T$) to the aqueous pseudophase. These observations show that *o*-, *m*- and *p*-toluate ions cannot penetrate the CTABr micellar pseudophase to the same extent as PS^-_M ions. The phenyl salicylate ion is apparently more hydrophobic than *o*-, *m*- and *p*-toluate ions and it is perhaps because of this that the depth of penetration into the micellar pseudophase is different for PS^- and toluate ions. The results described in this manuscript indirectly show that the micellar pseudophase is not strictly a two-state microenvironment (*i.e.*, Stern layer and core) in terms of polarity, water concentration and the distribution of ionic solubilizates of different hydrophibicity. This conclusion is also supported by other kinetic data, which indirectly show that the micellar surface is not uniform in terms of water concentration,[28–31] polarity,[10,22] ionic strength[22,32] and distribution of solubilizates of different hydrophobicity.[10,18] The fact that fluorescence spectroscopy shows that very hydrophilic anions, *e.g.* HO^- and F^-, are singularly ineffective in displacing Br^- from the micellar pseudophase to the aqueous pseudophase, while kinetic data are fitted with values of K_{Br}^{OH} {$= ([Br^-_M][HO^-_W])/([Br^-_W][HO^-_M])$} generally in the range of 12–30,[3c] indirectly shows the different degrees of penetration of Br^-, HO^- or F^- to the cationic micellar surface.† Recently Davies and co-workers[33] proposed a multiple micellar pseudophase (MMPP) model of micelles and this model leads to a kinetic equation similar to the one obtained from the PM model with modified definitions of the kinetic parameters. The rate constant for a micellar-mediated reaction and the micellar binding constants of the reactants are composite and phase-average parameters in view of the MMPP model.

The empirical definition of $K_{X/S}$ implies that the value of $K_{X/S}$ is proportional to the value of K_X (micellar binding constant of X) and inversely proportional to the value of K_S (micellar binding constant of S). Thus, $K_{X/S} = \delta_S K_X/K_S$, where δ_S is a proportionality constant with dimensions dm^3 mol^{-1}. The value of δ_S depends only upon the nature and micellar affinity of S (the ion *expelled* by another counterion from the micellar pseudophase to the aqueous pseudophase); it is independent of the nature and micellar affinity of X (the ion which *expels* another counterion S from the micellar pseudophase to the aqueous pseudophase). Similarly, for another ion Y, $K_{Y/S} = \delta_S K_Y/K_S$. It is thus apparent that the ratio $K_{X/S}/K_{Y/S}$ should be equal to the usual ion-exchange constant K_X^Y (where $K_X^Y = K_X/K_Y = \{[X^-_M][Y^-_W]\}/\{[X^-_W][Y^-_M]\}$). It should be noted that the relationship: $K_{X/S}/K_{Y/S} = K_X^Y$ is correct only if $K_{X/S}$ and $K_{Y/S}$ were obtained experimentally using eqn. (2). If the values of $K_{X/S}$ and $K_{Y/S}$ were obtained from eqn. (3), then these values should be normalized, *i.e.* $K_{X/S}^n = F_X K_{X/S}$ and $K_{Y/S}^n = F_Y K_{Y/S}$, where $F = \theta/(k^n_W[Pip]_T)$ and, under such conditions, $K_{X/S}^n/K_{Y/S}^n = K_X^Y$. The reported values of $K_{X/PS}$ (X = $C_6H_5CO_2^-$)[8] and $K_{Y/PS}$ (Y = Br^-)[34] as well as $K_{X/PT}$ and $K_{Y/PT}$ (where PT represents ionized phthalimide)[35] for various X and Y (Table 2) and listed values of $K_{X/PS}$ in Table 1 were used to calculate the usual ion-exchange constants, K_X^Y (= $K_{X/PS}/K_{Y/PS}$ or $K_{X/PT}/K_{Y/PT}$). These results are summarized in Table 2. The values of $K_{Br/PS}$ and $K_{Bz/PS}$ (Bz = $C_6H_5CO_2^-$) were obtained from the kinetic relationships, where the values of F (= $\theta/k^n_W[Pip]_T$) were inherently maintained as 1. But the values of $K_{X/PS}$ (Table 1) were obtained from the kinetic relationship where the F values are 0.47, 0.57 and 0.54 for X = *o*-, *m*- and *p*-toluate ions, respectively. The normalized values of the empirical constants, $K_{X/PS}^n$ (*i.e.*, $K_{X/PS}$ values at $F = 1$) would therefore be equal to $FK_{X/PS}$. These normalized values of $K_{X/PS}^n$ where X = *o*-, *m*- and *p*-toluate ions, respectively, are shown in parenthesis in Table 2. These values of $K_{X/PS}^n$ and $K_{Br/PS}^n$ (= 25 dm^3 mol^{-1}) were also used to calculate K_X^{Br}, the values for which are shown in Table 2. These values of K_X^{Br} for benzoate, *o*-, *m*- and *p*-toluate ions may be compared with K_X^Y obtained directly by the use of spectrophotometric,[36] ^{1}H NMR spectroscopic[25,37] and trapping of free counterions measurement[38] techniques. Magid and co-workers[37] have also concluded that the value of such an ion-exchange constant is technique-dependent.

† One of the referees has correctly pointed out that the $Br^-/HO^-/F^-$ competition is not governed by location but by the balance between Coulombic and non-Coulombic ion–micelle interactions. But, in a multisite or multistate micellar model, each site or state differs from others in terms of the balance between the Coulombic and non-Coulombic ion–micelle interaction energies, and a specific ion should reside in a specific site or state (in view of the energy barrier) in a multistate micellar model.

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