SHORT PAPER

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Spectrophotometric determination of cationic micellar binding constant of ionised phenyl salicylate in the presence of inert salts[†]

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A spectrophotometric technique has been used to determine the cetyltrimethylammonium bromide (CTABr) micellar binding constant (K_S) of ionised phenyl salicylate (PS^-) in the presence of a constant amount of inert salt (MX = NaBr or C_6H_5COONa). The values of K_S at different [MX] follow an empirical relationship: $K_S = K_S{}^0/(1 + K_{X/S}[MX])$ where the magnitude of the empirical parameter $K_{X/S}$ is the measure of the ability of X^- to expel S^- (= PS^-) from the CTABr micellar pseudophase to the aqueous pseudophase. The value of $K_{X/S}$ is nearly 13-fold larger for $C_6H_5COO^-$ than for Br^-.

Keywords: cationic micellar binding constant, ionised phenyl salicylate

The pseudophase ion-exchange (PIE) model was developed to explain the kinetic data for micellar-mediated reactions involving a single ion-exchange process.[1] The application of the PIE model has been extended to reactions involving two ion-exchange processes by imposing relatively more assumptions and restrictive conditions.[2] The effects of inert inorganic salts (MX) on pseudo-first-order rate constants for cationic micellar-mediated methanolysis,[3] *n*-butylaminolysis[4] and piperidinolysis[4] of ionised phenyl salicylate (PS^-) revealed that the values of K_S, at different concentrations of MX, obeyed the following empirical equation

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

where $K_{X/S}$ is an empirical parameter. The magnitude of $K_{X/S}$ is the measure of the ability of X^- to expel S^- from micellar pseudophase to the aqueous pseudophase. The validity of equation (1) has been supported by only kinetic data.[3–6] The present study was initiated with the aim of providing non-kinetic data, obtained by spectrophotometric measurements, in the support of equation (1). The observed data and their possible explanation(s) are described in this manuscript.

Experimental

Details of spectrophotometric measurements have been described elsewhere.[7,8]

Results and discussion

The initial absorbance values ($A^0{}_{obs}$) were measured at 360 and 370 nm (these are the wavelengths where maximum initial absorbance changes occurred due to increase in the total concentration of cetyltrimethylammonium bromide, $[CTABr]_T$, from 0 to 0.01 mol/dm^3) within the $[CTABr]_T$ range 2×10^{-5} to 2×10^{-2} mol/dm^3 at 35 °C. The CTABr micellar binding constant (K_S) of PS^- and $A^0{}_M$ (= $A^0{}_{obs}$ at $[D_n]$ where $A^0{}_W << A^0{}_M K_S[D_n]$ and $1 << K_S[D_n]$) were calculated from equation (2) by the nonlinear least-squares technique. The subscripts W and M represent aqueous

$$A^0{}_{obs} \;=\; \frac{A^0{}_W + A^0{}_M K_S[D_n]}{1 + K_S[D_n])} \qquad (2)$$

pseudophase and micellar pseudophase, respectively, and $[D_n]$ = [CTABr]T – cmc (where cmc is the critical micelle concentration). The values of $A^0{}_W$ (= $A^0{}_{obs}$ at $[D_n]$ = 0) were either the values of $A^0{}_{obs}$ at [CTABr]T = 2×10^{-5} mol/dm^3 (when cmc > 2×10^{-5} mol/dm^3) or the extrapolated values of $A^0{}_{obs}$ at [CTABr]T = 0 (when cmc < 2×10^{-5} mol/dm^3). The values of cmc of CTABr at a constant [MX] was determined as follows, The unknown parameters $A^0{}_M$ and K_S as well as the least-squares, $\Sigma\, d_i{}^2$ (where $d_i = A^0{}_{obs\ i} - A^0{}_{calcd\ i}$ with $A^0{}_{obs\ i}$ and $A^0{}_{calcd\ i}$ representing observed and calculated initial absorbance at ith total concentration of CTABr) values were calculated from equation (2) at a given value of cmc using the non-linear least-squares technique. This calculation was repeated for different given values of cmc and the best value of the cmc considered was the one for which the $\Sigma\, d_i{}^2$ value was minimum. Such calculated values of cmc, $A^0{}_M$ and K_S at different [NaBr] and [C_6H_5COONa] are summarised in Table 1. The quality of the fitting of observed data to equation (2) is evident from the standard deviations associated with the calculated parameters, $A^0{}_M$ and K_S, and from a few typical plots of Fig. 1 where solid lines are drawn through the calculated values of absorbance using equation (2) with parameters $A^0{}_M$ and K_S listed in Table 1. It may be noted that the calculated values of $A^0{}_M$ are essentially similar to the corresponding values of $A^0{}_{obs}$ at 0.02 mol/dm^3 CTABr (Table 1).

The increase in [MX] (MX = NaBr and C_6H_5COONa) caused a nonlinear decrease in K_S (Table 1). These data show a good fit to equation (1). The nonlinear least squares calculated respective values of $K_S{}^0$ and $K_{X/S}$ are 6495 ± 227 dm^3/mol and 11.4 ± 1.3 dm^3/mol for $X^- = Br^-$ and 6841 ± 432 dm^3/mol and 145 ± 24 dm^3/mol for $X^- = C_6H_5COO^-$. The values of $K_{S,\ calcd}$ (Table 1) and standard deviations associated with the calculated parameters, $K_S{}^0$ and $K_{X/S}$, reveal the quality of fit of KS – [MX] data to equation (1). The values of $K_S{}^0$ are comparable with K_S (= 6710 dm^3/mol obtained from kinetic data on hydrolysis of PS^- [9] and to K_S (= 6994 dm^3/mol) obtained spectrophotometrically8 in the absence of MX.

The value of $K_{X/S}$ (= 145 dm^3/mol) for $C_6H_5COO^-$ may be compared with the $K_{X/S}$ values for $C_6H_5COO^-$ (= 124 and 127 dm^3/mol) obtained from kinetic data on *n*-butylaminolysis and piperidinolysis of PS^- in aqueous solvent containing 2 % v/v CH_3CN.[5a] Similarly, the value of $K_{X/S}$ (= 11.4 dm^3/mol) for Br^- may be compared with $K_{X/S}$ (= 19–23 dm^3/mol obtained for KBr from kinetic data on methanolysis of PS^- in mixed aqueous solvent containing 2 % v/v CH_3CN and 10 % v/v CH_3OH[3] and with $K_{X/S}$ (= 25–50 dm^3/mol) obtained for NaBr

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Values of parameters, A^0_M and K_S, calculated from equation (2) by using A^0_{obs} values at 360 and 370 nm[a]

MX	[MX] mol/dm^3	A^0_W[b]	10^5 cmc mol/dm^3	A^0_M	A^0_M[c]	K_S dm^3/mol	$K_{S,calcd}$[d] dm^3/mol	No. of data points
NaBr	0.01	0.784 (0.360)	7.5 (7.5)	1.251 ± 0.008[e] (0.810 ± 0.008)	1.256 (0.811)	5398 ± 381[e] (6171 ± 478)	5829	14
	0.02	0.808 (0.378)	8.0 (8.0)	1.289 ± 0.012 (0.860 ± 0.012)	1.270 (0.850)	4945 ± 498 (5396 ± 563)	5286	14
	0.03	0.810 (0.378)	7.0 (7.0)	1.301 ± 0.009 (0.865 ± 0.009)	1.300 (0.850)	4986 ± 381 (5405 ± 432)	4837	14
	0.04	0.830 (0.384)	7.0 (6.5)	1.321 ± 0.010 (0.876 ± 0.010)	1.322 (0.877)	4087 ± 324 (4482 ± 368)	4457	14
	0.06	0.832 (0.396)	7.5 (7.0)	1.323 ± 0.012 (0.890 ± 0.012)	1.310 (0.878)	3510 ± 336 (3820 ± 354)	3853	14
	0.06	0.811 (0.377)	5.0 (5.0)	1.299 ± 0.004 (0.864 ± 0.005)	1.287 (0.850)	3889 ± 123 (4292 ± 175)	3853	14
	0.10	0.790 (0.357)	5.0 (5.0)	1.271 ± 0.006 (0.844 ± 0.006)	1.260 (0.828)	2738 ± 123 (3094 ± 139)	3031	14
	0.20	0.832 (0.396)	2.0 (2.5)	1.371 ± 0.016 (0.929 ± 0.016)	1.356 (0.912)	1951 ± 181 (2097 ± 205)	1977	17
	0.50	0.832 (0.396)	0.0 (0.0)	1.456 ± 0.019 (1.027 ± 0.019)	1.455 (1.027)	932 ± 81 (973 ± 86)	967	17
C_6H_5COONa	0.002	0.825 (0.385)	6.5 (6.5)	1.286 ± 0.013 (0.837 ± 0.014)	1.260 (0.817)	5015 ± 591 (5761 ± 781)	5305	15
	0.003	0.841 (0.387)	6.5 (6.5)	1.324 ± 0.011 (0.864 ± 0.011)	1.310 (0.848)	4683 ± 445 (5226 ± 517)	4769	15
	0.005	0.854 (0.401)	5.0 (4.5)	1.346 ± 0.012 (0.882 ± 0.013)	1.321 (0.850)	3446 ± 310 (3533 ± 355)	3964	15
	0.010	0.844 (0.386)	3.5 (3.5)	1.342 ± 0.008 (0.875 ± 0.008)	1.32 (0.858)	62732 ± 153 (2937 ± 169)	2794	15
	0.020	0.837 (0.393)	3.0 (3.0)	1.323 ± 0.011 (0.886 ± 0.011)	1.300 (0.864)	1922 ± 136 (1983 ± 144)	1756	15
	0.040	0.860 (0.405)	0.5 (1.0)	1.413 ± 0.011 (0.965 ± 0.009)	1.405 (0.946)	1044 ± 59 (1000 ± 45)	1007	15
	0.100	0.856 (0.402)	0.0 (0.0)	1.400 ± 0.018 (0.962 ± 0.016)	1.388 (0.946)	641 ± 57 (703 ± 57)	442	17

[a] [phenyl salicylate]0 = 2 x 10-4 mol/dm^3, [NaOH] = 0.01 mol/dm^3, 35 ˚C, reaction mixture for each measurement contains 2 % v/v CH_3CN and parenthesised values were obtained from A^0_{obs} values at 370 nm. [b] Observed values of A^0_{obs} at $[D_n] = 0$. [c] Observed values of A^0_{obs} at [CTABr]T = 0.02 mol/dm^3. [d] Calculated from equation (1) as described in the text. [e] Error limits are standard deviations.

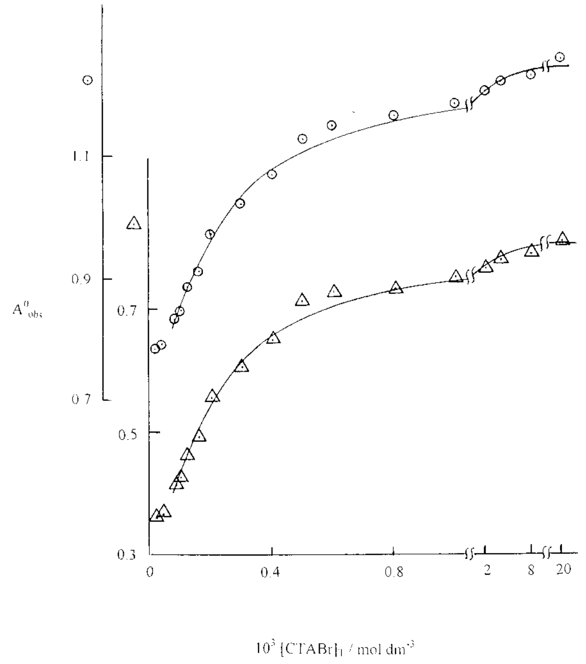

Fig. 1 Plots showing the dependence of initial absorbance (A^0_{obs}) upon the total concentration of cetyltrimethylammonium bromide ([CTABr]$_T$) for the micellar reaction mixtures containing 2 × 10^{-4} mol/dm phenyl salicylate, 0.01 mol/dm NaOH and 0.01 mol dm^{-3} NaBr at 360 nm (O) and 370 nm (Δ). Solid lines are drawn through the least squares calculated data points using equation (2) and parameters listed in Table 1.

from kinetic data on piperidinolysis and *n*-butylaminolysis of PS^- in aqueous solvent containing 2 % v/v CH_3CN.[4]

The empirical definition of $K_{X/S}$ shows that the magnitude of $K_{X/S}$ should be proportional to ion-exchange constant (K_X^S = $\{[X_M][S_W]/[X_W][S_M]\}$). The value of $K_{C6H5COO/Br}$ = $K_{C6H5COO/S}/K_{Br/S}$ (= 145/11.4 = 12.7) is not very different from ^{1}H NMR spectrometrically determined values of K_X^{Br} for X = salicylate monoanion (K_X^{Br} = 20), *o*-nitrobenzoate (K_X^{Br} = 3.8), *m*-nitrobenzoate (K_X^{Br} = 11) and *p*-nitrobenzoate (K_X^{Br} = 3.3) in the presence of tetradecyltrimethylammonium bromide micelles.[10] Similarly, the reported value of K_{26ClBz}^{Cl} (= 16.8)[11], where 26ClBz represents 2,6-dichlorobenzoate, is equivalent to K_{26ClBz}^{Br} = 5.6–8.4 (because K_{Br}^{Cl} = 2–3).[11] Thus, the value of K_{26ClBz}^{Br} (^{a} 7) may not be considered to be significantly different from $K_{C6H5COO/Br}$ (= 12.7) within the domain of the uncertainties in the values of K_{26ClBz}^{Br} [11] and $K_{C6H5COO/Br}$ caused by various factors.[11]

Normal ionic micellar affinity of an ion is largely governed by electrostatic and hydrophobic interactions as well as steric hindrance or packing constraints. The nearly 13-fold larger value of $K_{C6H5COO/S}$ than that of $K_{Br/S}$ is due to larger hydrophobicity of $C_6H_5COO^-$ compared to that of Br^-. It may be noted that probably both $K_{X/S}$ and K_S^0 may not be completely independent of the size and shape of the micelle. It is known that both in the presence and absence of a solubilisate, the increase in the concentration of micelle-forming ionic surfactants changes the size and shape of the micelle.[11,12] Thus, a strict variation of K_S with [MX] may not be expected to follow equation (1) in a wide range of [MX]. This statement is supported by a recent report[11] on effect of counterion competition on cationic micellar growth horizons where the selectivity coefficient *i.e.* ion-exchange constant for two counterions, 2,6-dichlorobenzoate and chloride ions, turned out to be 13 ± 3 and 22 ± 5 at 0.010 and 0.030 M CTA^+ micellar surface (CTA^+ = cetyltrimethylammonium ion), respectively. This study[11] also revealed the fact that the values of ion-exchange constants are technique-dependent. Magid and coworkers[11] have suggested that there is a continuum of adsorption sites, with a considerable distribution of aromatic counterions about an average depth of penetration. This supports the idea of multi-state model of micelle.[13]

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