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SPECTROPHOTOMETRIC DETERMINATION OF ANIONIC MICELLAR BINDING CONSTANTS OF IONIZED AND NON-IONIZED PHENYL AND METHYL SALICYLATES

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The ionized (S^-) and non-ionized (SH) phenyl (PSH) and methyl (MSH) salicylates exhibit strong and undetectable absorption at 350 nm, respectively. These molecular absorption properties were used to determine the binding constants of S^- and SH with the micelles of sodium dodecyl sulphate in terms of the pseudophase model of micelles. The binding constants (K_1) of S^- are $4{\cdot}0 \pm 2{\cdot}0$ dm^3 mol^{-1} for PSH and $5{\cdot}7 \pm 1{\cdot}2$ dm^3 mol^{-1} for MSH and those (K_2) of SH are 2350 ± 90 dm^3 mol^{-1} for PSH and 100 ± 10 dm^3 mol^{-1} for MSH at 30 °C.

INTRODUCTION

The binding of phenols and phenoxide ions to micelles of cetyltrimethylammonium bromide have been studied spectrophotometrically.[1] The observed data were treated in terms of the pseudo-phase model of micelles. The spectrophotometric technique has also been used in the study of the binding of polychlorophenols, in their anionic and neutral forms, with cationic micelles of cetyltrimethylammonium chloride or anionic micelles of sodium dodecyl sulphate (SDS).[2,3] The concentration of polychlorophenols in the micellar pseudo-phase was determined from the measurements of the absorbance change versus detergent concentration.[2] The luminescence quenching of tris (2,2′-bipyridine)ruthenium(II) dichloride has been used to measure the concentration of a few anionic polychlorophenols in the intermicellar aqueous pseudo-phase.[3] The results in these studies[2,3] were interpreted in terms of binding to a single class of independent binding sites.

The micellar binding constant of a solute may be determined by various methods, including spectrophotometric and kinetic methods. However. the use of these methods depends on the characteristic features of the solute. Ionized phenyl and methyl salicylates show strong absorption while non-ionized forms of these esters do not show detectable absorption at 350 nm. Such characteristic properties of these salicylate esters may be easily used to determine the SDS micellar binding constants of ionized and non-ionized phenyl and methyl salicylates. Recently, we have determined the SDS micellar binding constants of ionized and non-ionized phenyl salicylate using a kinetic method.[4] However, this method could not be used to determine the SDS micellar binding constants of ionized and non-ionized methyl salicylate. The present work was initiated with the aim of determining SDS micellar binding constants of ionized and non-ionized phenyl and methyl salicylates using the spectrophotometric method. The results obtained and their probable explanations are described in this paper.

EXPERIMENTAL

Materials. Reagent-grade sodium dodecyl sulphate (SDS) and phenyl salicylate (PSH) were obtained from Aldrich and BDH. Methyl salicylate (MSH) was prepared from salicylic acid and methanol using a standard procedure. All other chemicals were of reagent grade.

Initial absorbance measurements. In a typical measurement, an aqueous reaction mixture containing the desired amounts of SDS and NaOH with a total volume of $4{\cdot}95$ cm^3 was allowed to equilibrate at 30 °C for a few minutes. The reaction was then started by adding $0{\cdot}05$ cm^3 (using a 50 µl syringe) of either $0{\cdot}02$ mol dm^{-3} PSH or $0{\cdot}03$ mol dm^{-3} MSH solution

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prepared in acetonitrile to the temperature equilibrated reaction mixture (4·95 cm^3). The decrease in absorbance at 350 nm (A_{obs}^{350}) was recorded as a function of time for a period from 30 to ≤180 s. The initial absorbance (A_0^{350}), i.e. A_{obs}^{350} at reaction time $t = 0$, was obtained from the extrapolation of the plot of A_{obs}^{350} versus t.

The pH of the reaction mixture was recorded within 3–5 min after the addition of the desired amount of salicylate ester to the reaction mixture.

RESULTS

The values of A_0^{350} for PSH were obtained at a constant [NaOH]$_T$ (total concentration of NaOH) and within the [SDS]$_T$ (total concentration of SDS) range 0·0–0·4 mol dm^{-3}. Similarly, the values of A_0^{350} were also obtained within the [NaOH]$_T$ range 5×10^{-4}–7×10^{-2} mol dm^{-3} and at a constant [SDS]$_T$. Similar observations were made for MSH. The temperature and the initial concentrations of PSH and MSH were kept constant at 30 °C and 2×10^{-4} and 3×10^{-4} mol dm^{-3}, respectively. The observed values of A_0^{350} at different [SDS]$_T$ and [NaOH]$_T$ for PSH and MSH are summarized in Tables 1 and 2. The pH values of the aqueous reaction mixtures (containing 2×10^{-4} mol dm^{-3} PSH and 3×10^{-4} mol dm^{-3} MSH) at different [SDS]$_T$ and [NaOH]$_T$1 are given in Tables 3 and 4.

Table 1. Initial absorbance (A_0^{350}) values of PSH at different [SDS]$_T$ and [NaOH]$_T$^{a}

	[SDS]$_T$ (mol dm^{-3})								
[$^-$OH]$_T$ (mol dm^{-3})	0·0	0·02	0·04	0·07	0·10	0·14	0·20	0·30	0·40
5×10^{-4}	0·850	0·347	0·184	0·136	0·122	0·120	0·120	0·126	0·093
0·001	0·983	0·551	0·363	0·257	0·210	0·173	0·188	0·181	0·155
0·002	1·119	0·798	0·619	0·453	0·401	0·347	0·313	0·339	0·271
0·003	1·160	0·909	0·761	0·586	0·516	0·476	0·433	0·443	0·360
0·004	1·146	0·933	0·842	0·693	0·621	0·568	0·546	0·541	0·513
0·005	1·152	1·008	0·976	0·768	0·697	0·650	0·624	0·618	0·607
0·0075		1·051	1·022	0·884	0·827	0·778	0·762	0·761	0·780
0·010	1·162	1·118	1·087	0·949	0·919	0·867	0·875	0·861	0·940
0·020		1·119	1·148	1·064	1·061	1·020	1·061	1·035	1·109
0·030	1·163	1·146	1·179	1·117	1·102	1·080	1·113	1·110	1·173
0·040	1·190	1·149	1·239	1·132	1·138	1·116	1·176	1·157	1·241
0·050		1·150	1·241	1·158	1·166	1·110	1·211	1·158	1·266
0·060	1·187	1·171	1·251	1·173	1·188	1·148	1·256	1·218	1·313
0·070		1·233	1·267	1·186	1·213		1·246		

Table 2. Initial absorbance (A_0^{350}) values of MSH at different [SDS]$_T$ and [NaOH]$_T$^{a}

	[SDS]$_T$ (mol dm^{-3})							
[$^-$OH]$_T$ (mol dm^{-3})	0·0	0·02	0·04	0·07	0·10	0·14	0·20	0·40
5×10^{-4}	0·509	0·445	0·295	0·259	0·235	0·182	0·151	0·100
0·001	0·803	0·670	0·529	0·435	0·387	0·302	0·250	0·165
0·002	0·901	0·800	0·749	0·640	0·586	0·567	0·459	0·293
0·003	0·914	0·868	0·831	0·734	0·706	0·663	0·596	0·408
0·004	0·926	0·855	0·863	0·782	0·773	0·718	0·662	0·520
0·005	0·926	0·899	0·866	0·821	0·804	0·767	0·727	0·587
0·0075	0·948	0·913	0·902	0·865	0·833	0·827	0·806	0·704
0·010	0·939	0·927	0·921	0·886	0·877	0·858	0·844	0·778
0·020	0·936	0·932	0·939	0·904	0·920	0·894	0·902	0·866
0·030	0·943	0·938	0·947	0·901	0·929	0·919	0·934	0·918
0·040		0·941		0·911	0·934	0·915	0·930	0·927
0·050		0·930			0·945		0·960	
0·060		0·952			0·933		0·942	
0·070		0·941			0·938		0·963	

^{a}Conditions: [MSH]$_0 = 3 \times 10^{-4}$ mol dm^{-3}, 30 °C, $\lambda = 350$ nm, 1% (v/v) MeCN in the aqueous reaction mixture.

Table 3. pH values of reaction mixtures containing 2×10^{-4} mol dm^{-3} PSH at different $[\mathrm{SDS}]_T$ and $[\mathrm{NaOH}]_T$[a]

	$[\mathrm{SDS}]_T$ (mol dm^{-3})							
$[^{-}\mathrm{OH}]_T$ (mol dm^{-3})	0·0	0·02	0·04	0·07	0·10	0·14	0·20	0·300
5×10^{-4}	9·55	10·26	10·24	10·25	10·32	10·39	10·35	10·04
0·001	9·98	10·56	10·63	10·65	10·62	10·60	10·64	10·17
0·002	10·40	10·94	10·99	11·00	10·99	11·01	10·96	10·54
0·003	10·63	11·10	11·21	11·21	11·16	11·19	11·11	10·75
0·004	10·83	11·20	11·30	11·32	11·25	11·31	11·20	10·92
0·005	11·04	11·29	11·45	11·42	11·34	11·36	11·27	11·07
0·0075	11·41	11·46	11·58	11·60	11·52	11·50	11·41	11·26
0·010	11·38	11·55	11·70	11·68	11·60	11·64	11·52	11·41
0·020		11·85	12·02	11·96	11·87	11·89	11·79	11·73
0·030	11·91	12·02	12·12	12·11	12·04	12·06	11·96	11·89
0·040	12·06	12·15	12·23	12·22	12·22	12·19	12·08	12·03
0·050		12·26	12·35	12·33	12·25	12·27	12·19	12·10
0·060	12·31	12·35	12·42	12·37	12·30	12·32	12·29	12·21
0·070		12·40	12·49	12·45	12·36		12·37	

Table 4. pH values of reaction mixtures containing 3×10^{-4} mol dm^{-3} MSH at different $[\mathrm{SDS}]_T$ and $[\mathrm{NaOH}]_T$[a]

	$[\mathrm{SDS}]_T$[b] (mol dm^{-3})							
$[^{-}\mathrm{OH}]_T$ (mol dm^{-3})	0·0	0·02	0·04	0·07	0·10	0·14	0·20	0·40
5×10^{-4}	9·65	10·11	10·23	10·19	10·32	10·18	10·33	10·13
0·001	10·14	10·43	10·69	10·56	10·69	10·49	10·61	10·33
0·002	10·63	10·85	10·99	10·93	11·10	10·98	11·04	10·75
0·003	10·89	11·06	11·11	11·16	11·31	11·15	11·25	10·93
0·004	11·03	11·19	11·22	11·29	11·45	11·27	11·36	11·06
0·005	11·20	11·34	11·30	11·43	11·55	11·38	11·46	11·16
0·0075	11·39	11·51	11·53	11·61	11·70	11·54	11·60	11·34
0·010	11·54	11·64	11·67	11·72	11·81	11·70	11·70	11·51
0·020	11·85	11·92	11·97	11·99	12·08	11·95	11·97	11·79
0·030	12·10	12·13	12·14	12·15	12·24	12·12	12·14	11·98
0·040		12·27		12·20	12·36	12·23	12·26	12·11
0·050		12·39			12·45		12·36	
0·060		12·48			12·53		12·43	
0·070		12·58			12·59		12·48	

DISCUSSION

The values of A_0^{350} decrease with increase in $[\mathrm{SDS}]_T$ at low $[\mathrm{NaOH}]_T$ ($\leqslant 0{\cdot}02$ mol dm^{-3}). The extent of the decrease in A_0^{350} with increase in $[\mathrm{SDS}]_T$ from 0·0 to 0·4 mol dm^{-3} decreases with increase in $[\mathrm{NaOH}]_T$ and the A_0^{350} values became almost independent of $[\mathrm{SDS}]_T$ and at $[\mathrm{NaOH}]_T \geqslant 0{\cdot}03$ mol dm^{-3}. The pH values of the reaction mixtures appear to be independent of $[\mathrm{SDS}]_T$ at a constant $[\mathrm{NaOH}]_T$ (Tables 3 and 4). This shows that at a constant $[\mathrm{NaOH}]_T$ the decrease in $[^{-}\mathrm{OH}]$ in the intermicellar aqueous region (i.e. aqueous pseudophase) due to micellar incorporation of $^{-}$OH molecules is nearly counterbalanced by the increase in $[^{-}\mathrm{OH}]$ due to the decrease in the effective volume of the intermicellar aqueous region with increase in $[\mathrm{SDS}]_T$.

The observed data (A_0^{350} versus $[\mathrm{SDS}]_T$) at a constant $[\mathrm{NaOH}]_T$ may be explained in terms of the pseudophase model of micelles.[5] The SDS micellar binding of ionized (S^-) and non-ionized (SH) salicylate esters may be represented by Scheme 1:

$$\mathrm{S_W^-} + \mathrm{D_n} \overset{K_1}{\rightleftharpoons} \mathrm{S_M^-}$$

$$\mathrm{SH_W} + \mathrm{D_n} \overset{K_2}{\rightleftharpoons} \mathrm{SH_M}$$

Scheme 1

where D_n is the micellized SDS and the subscripts W and M represent the aqueous pseudo-phase and micellar pseudo-phase, respectively.

Since SH does not absorb whereas S^- absorbs strongly at 350 nm,

$$A_0^{350} = \varepsilon_{S^-}[S_W^-] + \varepsilon_{S^-}[S_M^-] \tag{1}$$

where ε_{S^-} represents the molar absorptivity coefficient of S^-. It is assumed that ε_{S^-} for S_W^- is equal to ε_{S^-} for S_M^-. This assumption is substantiated by the observation that the A_0^{350} values are almost the same in the absence and presence of 0·4 mol dm^{-3} SDS at ≥ 0·04 mol dm^{-3} NaOH (Tables 1 and 2).

The apparent SDS micellar binding constant of salicylate esters (K_S^{app}) may be defined as

$$K_S^{app} = \frac{[S_M^-] + [SH_M]}{([S_W^-] + [SH_W])[D_n]} \tag{2}$$

where $[D_n] = [SDS]_T - \text{cmc}$, with cmc representing the critical micellar concentration of SDS. Equations (1) and (2) easily lead to equation

$$\frac{A_0^{350}}{\varepsilon_{S^-}[X]_0} = \frac{f_W^{S^-} + f_M^{S^-}K_S^{app}[D_n]}{1 + K_S^{app}[S_n]} \tag{3}$$

where $[X]_0$ is the total initial concentration of salicylate ester (i.e. $[X_0] = [S_W^-] + [SH_W] + [S_M^-] + [SH_M]$), $f_W^{S^-} = K_{a,W}/(a_{H,W} + K_{a,W})$, $f_M^{S^-} = K_{a,M}/(a_{H,M} + K_{a,M})$, $K_{a,W} = [S_W^-]a_{H,W}/(SH_W]$, $K_{a,M}[S_M^-]a_{H,M}/[SH_M]$ and $a_{H,W}$ and $a_{H,M}$ represent the proton activity in the aqueous pseudo-phase and micellar pseudo-phase, respectively.

At a constant $[NaOH]_T$, the value of $f_W^{S^-}$ was obtained from observed value of A_0^{350} at $[SDS]^T = 0$. The values of $f_M^{S^-}$ and K_S^{app} will remain constant if the pH values remain independent of $[D_n]$ at a constant $[NaOH]_T$. It is evident from Tables 3 and 4 that the pH values remain essentially constant within the $[SDS]_T$ range 0·02–0·20 mol dm^{-3} at a constant $[NaOH]_T$. The values of $f_M^{S^-}$ and K_S^{app} were calculated from equation (3) using the non-linear least squares technique. These calculated values at different $[NaOH]_T$ are summarized in Table 5 for PSH and MSH. The observed data at 0·4 mol dm^{-3} SDS were not included in the calculation of $f_M^{S^-}$ and K_S^{app} from equation (3) because it is known that micelles undergo structural transformation from spherical to rod-shaped and then to liquid crystalline phase with increase in the concentration of micelle-forming surfactant.[6]

The reported value of the cmc[7] of 0·008 mol dm^{-3} was used in the calculation of $f_M^{S^-}$ and K_S^{app} using equation (3). The values of cmc at different $[NaOH]_T$ were also calculated using an iterative technique described elsewhere.[8] The calculated values of cmc turned out to be independent of $[NaOH]_T$ within the range 5×10^{-4}–0·01 mol dm^{-3}. The average calculated value of the cmc was found to be $(8{\cdot}5 \pm 3{\cdot}7) \times 10^{-3}$ mol dm^{-3}, which is not significantly different from the literature value of 8×10^{-3} mol dm^{-3}. The fitting of the observed data to equation (3) is evident from the plots in Figures 1 and 2, where solid

Table 5. Values of the parameters $f_M^{S^-}$ and K_S^{app} calculated from equation (3)

Compound	$[NaOH]_T$ (mol dm^{-3})	pH[a]	$f_W^{S^-}$	$f_M^{S^-}$	K_S^{app} (dm^3 mol^{-1})	$K_{S\ cal}^{app}$[b] (dm^3 mol^{-1})
PSH	5×10^{-4}	10·36 ± 0·06[c]	0·710	0·075 ± 0·009[c]	178 ± 21[c]	172
	0·001	10·62 ± 0·03	0·830	0·110 ± 0·010	87·3 ± 7·0	99·3
	0·002	10·98 ± 0·03	0·940	0·205 ± 0·017	47·1 ± 5·1	46·6
	0·003	11·16 ± 0·05	0·970	0·284 ± 0·020	34·3 ± 4·0	32·3
	0·004	11·26 ± 0·05	0·960	0·377 ± 0·023	29·9 ± 4·4	26·5
	0·005	11·36 ± 0·07	0·970	0·404 ± 0·051	18·8 ± 5·3	21·9
	0·0075	11·52 ± 0·09	0·980	0·553 ± 0·034	19·0 ± 4·8	16·4
	0·010	11·62 ± 0·07	0·980	0·639 ± 0·045	14·5 ± 5·3	13·9
MSH	5×10^{-4}	10·21 ± 0·12	0·540	0·080 ± 0·040	22·8 ± 6·2	24·8
	0·001	10·58 ± 0·11	0·850	0·117 ± 0·032	19·1 ± 2·2	14·9
	0·002	10·98 ± 0·09	0·950	0·303 ± 0·083	11·3 ± 3·2	9·6
	0·003	11·17 ± 0·09	0·960	0·352 ± 0·086	6·1 ± 1·5	8·2
	0·004	11·30 ± 0·10	0·980	0·478 ± 0·155	6·6 ± 3·6	7·6
	0·005	11·41 ± 0·09	0·980	0·591 ± 0·038	6·0 ± 1·0	7·1
	0·0075	11·58 ± 0·07	0·990	0·762 ± 0·035	8·5 ± 2·6	6·7
	0·010	11·71 ± 0·06	0·990	0·779 ± 0·052	4·8 ± 1·9	6·4

[a] Average pH value obtained within the $[SDS]_T$ range 0·02–0·20 mol dm^{-3}; the pH values at different $[NaOH]_T$ are considered to be a measure of hydronium ion activity in the aqueous pseudo-phase only.

[b] Calculated from equation (4).

[c] Error limits are standard deviations.

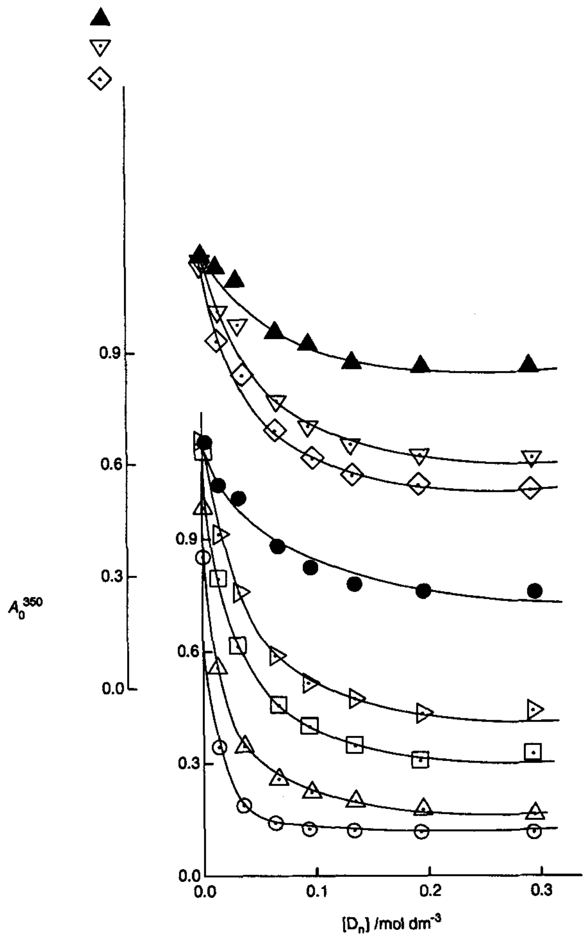

Figure 1. Effects of [D$_n$] on A_0^{350} for phenyl salicylate at (⊙) 5 × 10^{-4}, (△) 0·001, (⊡) 0·002, (▷) 0·003, (◇) 0·004, (▽) 0·005, (●) 0·0075 and (▲) 0·010 mol dm^{-3} NaOH. The solid lines are drawn through the least-squares calculated points

lines are drawn through the least-squares calculated points.

Equation (4) may be easily derived from Scheme 1 and equation (2):

$$K_S^{\text{app}} = \frac{K_1 K_{a,W} + K_2 a_{H,W}}{a_{H,W} + K_{a,W}} \tag{4}$$

The values of K_S^{app} at different pH (Table 5) were used to calculate K_1 and K_2 from equation (4) using the non-linear least-squares technique. The calculated respective values of K_1 and K_2 are 4·0 ± 2·9 and 2350 ± 90 dm^3 mol^{-1} for PSH and 5·7 ± 1·2 and 100 ± 10 dm^3 mol^{-1} for MSH. The values of K_1 (4·0 dm^3 mol^{-1}) and K_2 (2350 dm^3 mol^{-1}) at 30 °C may be compared with the corresponding values of K_1 (3·0 dm^3 mol^{-1} at 30 °C and 3·1 dm^3 mol^{-1} at 37 °C) and K_2 (1890 dm^3 mol^{-1} at 30 °C and 990 dm^3 mol^{-1} at 37 °C) obtained from kinetic data on the rate of hydrolysis of PSH.[4] Such a comparative study is not possible for methyl salicylate because the values of K_1 and K_2 for this ester could not be obtained from the kinetic data.[4]

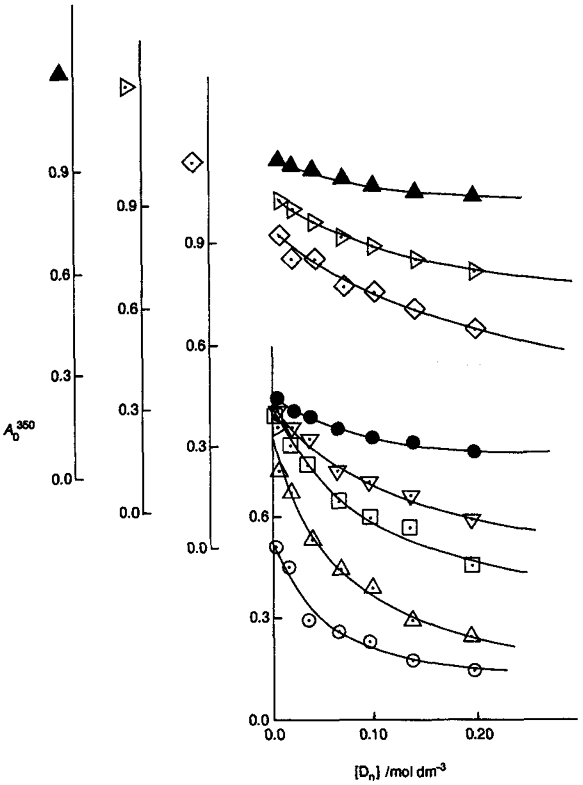

Figure 2. Effects of [D$_n$] on A_0^{350} for methyl salicylate at (⊙) 5 × 10^{-4}, (△) 0·001, (⊡) 0·002, (▽) 0·003, (◇) 0·004, (▷) 0·005, (●) 0·0075 and (▲) 0·010 mol dm^{-3} NaOH. The solid lines are drawn through the least squares calculated points

The value of K_1 for ionized PSH is not significantly different from that for ionized MSH whereas K_2 for non-ionized PSH is nearly 20 times larger than that for non-ionized MSH. The non-ionized PSH molecule is apparently more hydrophobic than the non-ionized MSH molecule. This characteristic difference in hydrphobicity may be partly or fully ascribed to the larger SDS micellar binding affinity towards non-ionized PSH compared with non-ionized MSH. The SDS micellar binding constant of phenyl benzoate (PB), which may be considered to be similar to non-ionized PSH in terms of hydrophobic behaviour, is 600 dm^3 mol^{-1} (obtained at 35 °C in an alkaline aqueous solvent containing 2% (v/v) MeCN).[9] The nearly 2–3 times larger value of K_2 for non-ionized PSH than that for PB is presumably due to significant hydrogen bonding between the anionic micellar head group and the phenolic hydrogen of non-ionized PSH. Such hydrogen bonding has been attributed to the larger anionic micellar binding affinity of amines.[10]

The values of K_1 for both ionized MSH and PSH are smaller by nearly 25 and 500 times, respectively. The extremely low SDS micellar binding affinity of ionized PSH and MSH may be attributed to the energetically unfavourable electrostatic effect. The very similar values of K_1 for both PSH and MSH indicate the unimportance of hydrophobicity towards SDS micellar incorporation of these anionic molecules.

It is interesting that the change in $[\mathrm{SDS}]_T$ from 0·0 to 0·4 $\mathrm{mol\,dm^{-3}}$ caused a nearly threefold decrease in pseudo-first-order rate constants (k_{obs}) for hydrolysis of ionized PSH at 0·04 $\mathrm{mol\,dm^{-3}}$ NaOH and 37 °C.[4] However, the k_{obs} for hydrolysis of ionized MSH decreased only 1·2-fold with increase in $[\mathrm{SDS}]_T$ from 0·0 to 0·4 $\mathrm{mol\,dm^{-3}}$ at 0·03 $\mathrm{mol\,dm^{-3}}$ NaOH and 37 °C.[4] Similarly, at 0·005 $\mathrm{mol\,dm^{-3}}$ NaOH and 35°C, the pseudo first-order rate constants (k_{obs}) decreased 2·3-fold for PSH whereas those for MSH remained unchanged with change in $[\mathrm{SDS}]_T$ from 0·0 to 0·2 $\mathrm{mol\,dm^{-3}}$.[11] These rate data on the hydrolysis of ionized MSH were ascribed to either of the following possibilities: (i) $K_1 \approx 0$ and (ii) $k_W^h \approx k_M^h$, where k_W^h and k_M^h represent pseudo-first-order rate constants for the hydrolysis of ionized MSH in the aqueous pseudo-phase and micellar pseudo-phase, respectively. The first possibility was ruled out and the second was preferred, although without any direct evidence for it.[4,11] The present data clearly demonstrate that the first possibility (i.e. $K_1 = 0$) is not correct.

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