JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 301-307 (1996)

EFFECTS OF Li^+ AND K^+ IONS ON THE RATE OF INTRAMOLECULAR GENERAL BASE-CATALYSED METHANOLYSIS OF IONIZED PHENYL SALICYLATE IN THE ABSENCE AND PRESENCE OF CATIONIC MICELLES IN MIXED H_2O-CH_3CN SOLVENTS

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Pseudo first-order rate constants (k_{obs1}) for methanolysis of ionized phenyl salicylate (PS^-) show a decrease of 3–5-fold with increase in CH_3CN content from 2 to 60 or 70% (v/v) in mixed aqueous solvents containing 0·01 mol dm^{-3} LiOH and a constant content of CH_3OH. At 0·01 mol dm^{-3} KOH, the rate constants, k_{obs1}, reveal a decrease of 15–20% and an increase of 70–130% with increase in the CH_3CN content from 2 to 30% (v/v) and from 30 to 60 or 70% (v/v) respectively. The values of $\Delta H‡$ and $\Delta S‡$ are not significantly affected by the presence of 2, 30 and 70% (v/v), CH_3CN in mixed aqueous solvents containing 10% (v/v) CH_3OH and 0.01 mol dm^{-3} KOH. The presence of 0.01 mol dm^{-3} LiOH causes the increases in $\Delta H‡$ and $\Delta S‡$ of 3·82 kcal mol^{-1} and 10·3 cal K^{-1} mol^{-1}, respectively, with increase in CH_3CN content from 2 to 60% (v/v) in mixed aqueous solvents containing 20% (v/v) CH_3OH. An increase in the total concentration of cetyltrimethylammonium bromide ($[CTABr]_T$) from 0·0 to 0·01 mol dm^{-3} decreases k_{obs1} by 3·6- and 4·0-fold in the presence of 0·01 mol dm^{-3} Li^+ and K^+ ion, respectively, in mixed aqueous solvents containing 2% (v/v) CH_3CN and 10% (v/v) CH_3OH.

1. INTRODUCTION

Studies on, e.g., solvent, temperature and specific cation effects on intermolecular and intramolecular general base catalysis have been of considerable interest because these catalyses are known to be involved in many enzymatic catalyses.[1] Micelles are believed to provide a microheterogeneous reaction medium which is similar to that for enzyme-catalysed reactions.[1b] We have studied the effects of salts,[2] solvent and temperature[3] on intramolecular general base (IGB)-catalysed hydrolysis of ionized phenyl and methyl salicylates. These studies were found to be useful in discussing the effects of micelles on these reactions.[4] It is known that the structures of the mixed aqueous- organic solvents are markedly influenced by the presence of different cations and anions.[5,6] The effect of micelles on the rate of a reaction may be described in terms of several factors, including polarity, non-uniformity in the concentration distribution of the reactants and specific solvent, cation and anion effects. Thus, studies aimed at discovering the effects of these factors on rate of a reaction in the absence of micelles are necessary to study the effects of micelles on the rate of such a reaction. Specific solvent and cation effects have been detected in the alkaline hydrolysis of ionized *N*-hydroxyphthalimide,[7] but such effects could not be detected in the alkaline hydrolysis of phthalimide.[8]

We started the present study with the aims of discovering (i) the effect of mixed H_2O-CH_3CN solvents in the presence of specific cations (K^+ and Li^+) and the absence of micelles and (ii) the effect of specific cations (K^+, and Li^+) in the presence of cationic micelles on the methanolysis of ionized phenyl salicylate (PS^-) at constant concentrations of the reactants, PS^- and CH_3OH.

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CCC 0894-3230/96/050301-07

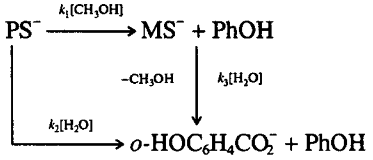
Received 29 March 1995
Revised 23 January 1996

EXPERIMENTAL

Materials. Reagent-grade chemicals (obtained from BDH, Aldrich and Fluka) were used throughout. Stock standard solutions of phenyl salicylate were frequently prepared in CH_3CN.

Kinetic measurements. The rate of methanolysis of PS^- in mixed H_2O-CH_3CN solvents containing a constant concentration of CH_3OH was studied spectrophotometrically by monitoring the appearance of product, phenolate ion, at 290 nm. A Shimadzu Model UV-2102/310/PC, UV-VIS-NIR scanning spectrophotometer equipped with a thermostated cell compartment was used. The details of the kinetic procedure have been described elsewhere.[9]

The complete reaction scheme for the methanolysis of PS^- using mixed H_2O-CH_3CN solvents is



(1)

where MS^- and PhOH represent ionized methyl salicylate and phenol, respectively. The ratio of the pseudo-first-order rate constants for pH-independent (i.e. [^-OH]

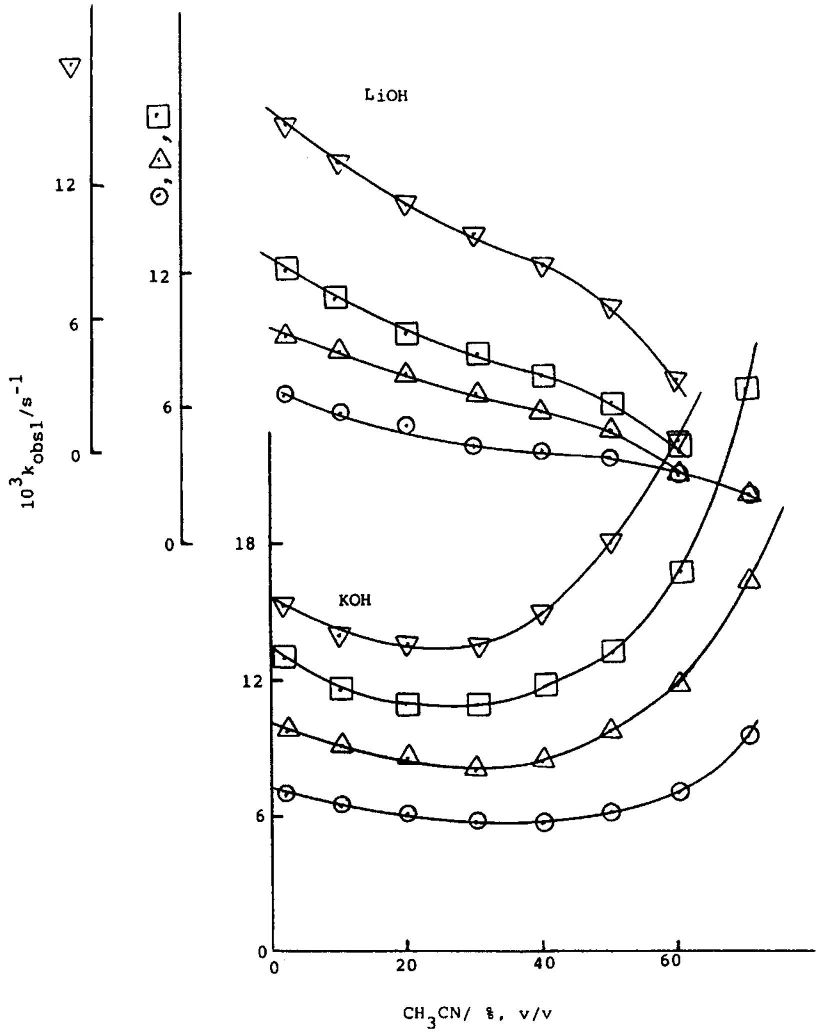


Figure 1. Plots showing the dependence of k_{obsl} on the concentration of CH_3CN at (○) 10, (△) 15, (□) 20 and (▽) 25% (v/v) CH_3OH in mixed CH_3CN-H_2O solvent

range ≈ 0·005–0·060 mol dm^{-3}) methanolysis and hydrolysis of phenyl salicylate, k_{obs1}/k_{obs2}, (where $k_{obs1} = k_1[CH_3OH]$ and $k_{obs2} = k_2[H_2O]$) is larger than 10 and, similarly, $k_{obs1}/k_{obs3} > 50$, where $k_{obs3} = k_3[H_2O]$.[10] Thus, under the experimental conditions of the present study, k_2 and k_3 may be neglected in comparison with k_1 in equation (1). The molar extinction coefficients (ε) of PhO^-, $o-{}^-OC_6H_4CO_2^-$, and MS^- and also as PS^- are 2350, 3250 and 700–900 dm^3 mol^{-1} cm^{-1}, respectively at 290 nm. The significantly larger value of ε for $o-{}^-OC_6H_4CO_2^-$ than for PhO^- and MS^- indicates the insignificance of k_3 compared with k_1 because the observed data (absorbance versus time) obeyed a first-order rate law. All the kinetic runs were carried out for periods of more than seven half-lives of the reactions. The details of the data analysis are described elsewhere.[11]

RESULTS

Effect of mixed H_2O–CH_3CN solvents on k_{obs1} at a constant concentration of CH_3OH

The rate of methanolysis of PS was studied under the conditions of 35 °C, 0·01 mol dm^{-3} KOH, 10% (v/v) CH_3OH and within the CH_3CN concentration range 2–70% (v/v) in mixed aqueous solvents. Similar rate studies were carried out at 15, 20 and 25% (v/v) CH_3OH. The results are shown as plots of k_{obs1} versus % (v/v) of CH_3CN in Figure 1. Similar observations were obtained in the presence of 0·01 mol dm^{-3} LiOH and the results are also shown in Figure 1.

At a constant content of CH_3OH and 0·01 mol dm^{-3} KOH, the rate constants, k_{obs1}, decreased by 15–20% with increase in the CH_3CN content from 2 to 30% (v/v). An increase in CH_3CN content from 30 or 40 to 60 or 70% (v/v) increased k_{obs1} by *ca* 70, 100, 130 and 70% at 10, 15, 20, and 25% (v/v) CH_3OH, respectively. The increase in the content of CH_3CN from 2 to 60 or 70% (v/v) in mixed aqueous solvents containing 0·01 mol dm^{-3} LiOH produced 3·1-, 4·5-, 3·0-, and 4·7-fold decreases in k_{obs1} at 10, 15, 20 and 25% (v/v) CH_3OH, respectively.

Effect of temperature on rate of methanolysis of PS^-

A series of kinetic runs were carried out within the temperature range 25–45 °C in mixed aqueous solvents containing 0·01 mol dm^{-3} KOH, 10% (v/v) CH_3OH and 2, 30 and 70% (v/v) CH_3CN. Similar kinetic runs were carried out in the presence of 0·01 mol dm^{-3} LiOH. The observed pseudo-first-order rate constants,

Table 1. Effect temperature on psuedo-first-order rate constants (k_{obs1}) for methanolysis of PS^- in the presence of K^+ and Li^+ ions[a]

		K^{+b}		Li^{+c}	
Temperature	$[CH_3CN]$	10^3k_{obs1} (s^{-1})	10^3k_{calc}[d] (s^{-1})	10^3k_{obs1} (s^{-1})	10^3k_{calc}[d] (s^{-1})
25	2	3·41 ± 0·03[e]	3·50	6·31 ± 0·03[e]	6·53
	30	2·72 ± 0·01	2·72	—	—
	60	—	—	1·85 ± 0·04	1·79
	70	4·59 ± 0·03	4·73	—	—
30	2	4·80 ± 0·03	4·91	8·49 ± 0·10	8·84
	30	3·81 ± 0·02	3·88	—	—
	60	—	—	2·52 ± 0·04	2·70
	70	6·34 ± 0·03	6·71	—	—
35	2	6·92 ± 0·03	6·80	12·2 ± 0·1	11·8
	30	5·62 ± 0·04	5·48	—	—
	60	—	—	4·01 ± 0·04	4·01
	70	9·46 ± 0·07	9·41	—	—
40	2	9·42 ± 0·08	9·34	16·2 ± 0·2	15·7
	30	7·58 ± 0·06	7·66	—	—
	60	—	—	6·08 ± 0·02	5·89
	70	13·8 ± 0·1	13·1	—	—
45	2	12·6 ± 0·2	12·7	20·4 ± 0·3	20·7
	30	10·6 ± 0·1	10·6	—	—
	60	—	—	8·46 ± 0·29	8·54
	70	17·6 ± 0·2	18·0	—	—

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ mol dm^{-3}, 290 nm and co-solvent H_2O.
[b] $[KOH] = 0·01$ mol dm^{-3} and $CH_3OH = 10\%$ (v/v).
[c] $[LiOH] = 0·01$ mol dm^{-3} and $CH_3OH = 20\%$ (v/v).
[d] Calculated from the Erying equator $k_{obs1} = (k_BT/h)\exp[-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT]$ with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as in Table 2.
[e] Error limits are standard deviations.

k_{obs1}, are summarized in Table 1. The activation parameters such as ΔH‡ and ΔS‡ were calculated from the Eyring equation using rate constants, k_{obs1}. These activation parameters are shown in Table 2.

Effect of CTABr micelles on rate of methanolysis of PS^- in the presence of K^+ and Li^+

Several kinetic runs were carried out within a range of total cetyltrimethylammonium bromide concentration, $[CTABr]_T$, of 0·0–0·01 mol dm^{-3} at 0·01 mol dm^{-3} KOH and 35 °C in mixed aqueous solvents containing 10% (v/v) CH_3OH and 2% (v/v) CH_3CN. Similar observations were also obtained in the presence of 0·01 mol dm^{-3} LiOH. The experimentally determined pseudo-first-order rate constants, k_{obs1} are shown in Table 3. An increase in $[CTABr]_T$ from 0·0 to 0·01 mol dm^{-3} decreased k_{obs1}, by *ca* 4·0- and 3·6-fold in the presence of

Table 2. Activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) for methanolysis of PS^- in the presence of K^+ and Li^+ ions[a]

	K^+		Li^+	
$[CH_3CN]$ (%, v/v)	$\Delta H^\ddagger$ (kcal mol^{-1})	$-\Delta S^\ddagger$ (cal K^{-1} mol^{-1})	$\Delta H^\ddagger$ (kcal mol^{-1})	$-\Delta S^\ddagger$ (cal K^{-1} mol^{-1})
2	11.52 ± 0.27[b]	31.1 ± 0.9[b]	10.26 ± 0.48[b]	34.1 ± 1.5[b]
30	12.17 ± 0.24	29.4 ± 0.8	—	—
60	—	—	14.08 ± 0.53	23.8 ± 1.7
70	11.96 ± 0.72	29.0 ± 2.3	—	—

[a] Conditions as in Table 1

[b] Error limits are standard deviations.

Table 3. Effect of $[CTABr]_T$ on pseudo-first-order rate constants (k_{obs1}) for methanolysis of PS^- in the presence of Li^+ and K^+ ions[a]

	Li^{+c}		K^{+d}	
$10^4[CTABr]_T$[b]	10^3k_{obs} (s^{-1})	10^3k_{calc}[e] (s^{-1})	10^3k_{obs} (s^{-1})	10^3k_{calc}[e] (s^{-1})
0·0	6·17 ± 0·06[f]	—	6·60 ± 0·08[f]	—
1·0	6·46 ± 0·05	—	6·74 ± 0·06	—
1·5	6·51 ± 0·06	—	6·65 ± 0·10	—
2·0	5·87 ± 0·14	6·17	6·14 ± 0·08	6·17
2·5	5·75 ± 0·08	5·35	5·36 ± 0·09	5·27
3·0	5·18 ± 0·12	4·77	4·90 ± 0·08	4·65
4·0	4·11 ± 0·07	4·00	3·86 ± 0·05	3·87
5·0	3·36 ± 0·04	3·51	3·35 ± 0·03	3·37
6·0	2·92 ± 0·03	3·17	2·92 ± 0·03	3·04
8·0	2·38 ± 0·02	2·73	2·44 ± 0·022	2·63
15·0	1·99 ± 0·02	2·09	1·96 ± 0·02	2·04
100·0	1·7 ± 0·02	1·44	1·65 ± 0·04	1·45
10^4cmc	1·9 mol dm^{-3} (2·0 mol dm^{-3})[g]		1·8 mol dm^{-3} (1·6 mol dm^{-3})[g]	
10^3k_M	1·32 ± 0·29 s^{-1} 1·34 ± 0·25 s^{-1}[h]		1·34 ± 0·13 s^{-1} 1·24 ± 0·21 s^{-1}[h]	
K_S	4200 ± 800 dm^3 mol^{-1} 4500 ± 800 dm^3 mol^{-1}[h]		5100 ± 400 dm^{3}mol^{-1} 4300 ± 500 dm^3 mol^{-1}[h]	

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ mol dm^{-3}, $[CH_3OH]$ = 10% (v/v), $[CH_3CN]$ = 2% (v/v), $[H_2O]$ = 88% (v/v), 35 °C and 290 nm.

[b] Total concentration of CTABr.

[c] [LiOH] = 0·01 mol dm^{-3}.

[d] [KOH] = 0·01 mol dm^{-3}.

[e] Calculated from equation (2) using cmc values obtained by iterative technique as described in the text.

[f] Error limits are standard deviations.

[g] Values in parentheses were obtained using Broxton *et al.*'s technique.[14g]

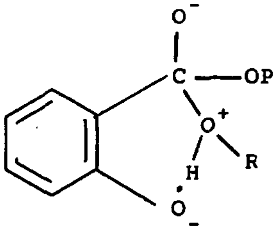
[h] Obtained from equation (2) using cmc values determined by Broxton *et al.*'s technique.[14g]

0·01 mol dm^3 KOH and LiOH, respectively.

DISCUSSION

The presence of the 100% ionized form (PS^-) of phenyl salicylate has been ascertained under the experimental conditions of the present study. The rate of methanolysis of PS^- has been shown to involve PS^- and CH_3OH as the reactants in the presence of 0·01 mol dm^{-3} HO^-.[3,12] Under such conditions, the rate of methanolysis is greatly enhanced owing to the occurrence of IGB catalysis.[10]

The suggested mechanism for methanolysis of PS^- involves an intramolecular intimate ion-pair (T).[10] This shows that the transition state is apparently more polar than the ground state. Thus, a decrease in the dielectric constant (i.e. the increase in the content of CH_3CN in mixed aqueous solvents) is expected to decrease the rate constants, k_{obs1}. One of the referees suggested that the desolvation of anions in the presence of a dipolar aprotic solvent (such as CH_3CN) results in a large catalytic effect on the rate of a reaction involving anionic reactant(s). Such an effect is expected to decrease k_{obs1} because the negative charge in the transition state is apparently more localized than in PS^- and **T**. The solvation energy of monomeric methanol (CH_3OH) in water solvent is presumably higher than in CH_3CN and therefore the increase in the content of CH_3CN should increase k_{obs1}. The decrease in k_{obs1} due to partial loss of the efficiency of IGB catalysis through ion-pair (IP) formation in mixed H_2O-CH_3CN solvents of decreasing dielectric constant cannot be completely ruled out. The observed effects of mixed H_2O-CH_3CN solvents on k_{obs1}, in the presence of K^+ and Li^+ ions (Figure 1), are a consequence of these four effects of the mixed H_2O-CH_3CN solvents. The characteristic difference in the effects of [K^+] and [Li^+] on k_{obs1} at CH_3CN contents of >40% (v/v) may be explained as follows. The monomeric methanol molecules and cations such as K^+ and Li^+ are solvated predominantly by water molecules in mixed aqueous–organic solvents containing low contents of organic co-solvent. However, as the content of the organic co-solvent, such as CH_3CN, is increased, its molecules also enter into the solvation shells of cations K^+ and Li^+, but because of the relatively high charge density of lithium ion, the solvation shell of Li^+ ion is much firmer than that of K^+ ion. This characteristic, in turn, makes Li^+ ion the methanol structure-forming agent while K^+ ion the methanol structure-breaking agent. Hence, the concentration of (CH_3OH) in mixed $CH_3OH-CH_3CN-H_2O$ solvents containing low contents of H_2O is expected to increase and decrease in the presence of K^+ and Li^+, respectively. This shows that the presence of K^+ ions should increase k_{obs1} whereas that of Li^+ ions should decrease k_{obs1} at low contents of H_2O in mixed $CHOH-CH_3CN-H_2O$ solvents.



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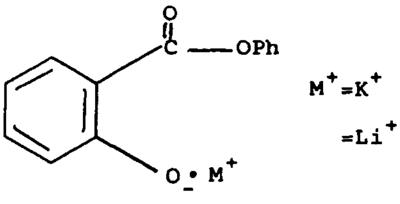

IP

The magnitudes of $\Delta H\ddagger$ and $\Delta S\ddagger$ are not significantly affected by the presence of 2, 30 and 70% (v/v) CH_3CN in mixed aqueous solvents containing 10% (v/v) CH_3OH and 0·01 mol dm^{-3} KOH. However, the values of $\Delta H\ddagger$ and $\Delta S\ddagger$ increased by *ca* 3·8 kcal mol^{-1} and 10·3 cal K^{-1} mol^{-1}, respectively, with increase in the content of CH_3CN from 2 to 60% (v/v) in mixed aqueous solvents containing 20% (v/v) CH_3OH and 0·01 mol dm^{-3} LiOH. These results may be attributed to (i) the relatively more stable IP formation in the presence of Li^+ compared with that of K^+, because the charge density of Li^+ is considerably larger than that of K^+, and (ii) Li^+ ions are methanol structure-forming agents whereas K^+ ions are methanol structure-breaking agents.[10] Hence the reactant state is more stabilized in the presence of Li^+ than of K^+ at 60% (v/v) CH_3CN in mixed aqueous solvents.

The rate of methanolysis of non-ionized phenyl salicylate (PSH) is $>10^3$-fold slower than that of PS.[12] The inhibitory effect of $[CTABr]_T$ on k_{obs1} may be ascribed to the possible increase in the concentration of PSH with increase in $[CTABr]_T$. This speculation is based on the fact that the micellized phenyl salicylate molecules exist in the micellar region where the polarity of the medium is considerably decreased compared with the polarity of the non-micellar region. The decrease in the polarity is expected to increase the pK_a of PSH. However, the observed absorbance values at time $t=0$ for all kinetic runs were found to be unchanged with change in $[CTABr]_T$ from 0·0 to 0·01 mol dm^{-3}. These observations rule out the possibility of the presence of PSH molecules in the reaction mixture under the experimental conditions imposed because the molar absorptivity of PSH is nearly double that of PS^- at 290 nm.

The rate of methanolysis of PS^- was found to be independent of [HO$^-$] within the range 0·01–0·15 mol dm^{-3} in mixed aqueous solvents containing 80% (v/v) CH_3OH and 0·8% (v/v) CH_3CN.[12] In view of these results, the rate of methanolysis of PS$^-$ involves PS$^-$ and CH_3OH as the reactants under the experimental conditions of present study.

The observed inhibitory effect of $[CTABr]_T$ on k_{obs1} (Table 3) may be explained in terms of the pseudo-phase model of micelles.[13] Equation (2) may be easily derived from the reaction scheme for methanolysis expressed in terms of pseudo-phase model of micelles:

$$k_{obs1} = \frac{k_{NM} + k_M K_S[Dn]}{1 + K_S[Dn]} \qquad (2)$$

where NM and M represent the non-micellar pseudo-phase and micellar pseudo-phase. respectively, $[Dn] = [CTABr]_T - cmc$ (where cmc is the critical micelle concentration) K_s is the binding constant for PS$^-$ with micelles and k_{NM} and k_M are pseudo-first-order rate constants for methanolysis of PS_{NM}^- and PS_M^-, respectively.

In order to calculate k_M and K_S from equation (2), the value of cmc must be known under the present kinetic conditions. A search of the literature revealed significant variations in the reported values of cmc $(8{\cdot}0 \times 10^{-5}–90{\cdot}0 \times 10^{-5}$ mol dm$^{-3})$[14] for CTABr, which may be attributed to the significant dependence of the cmc of CTABr on ionic strength, of the polarity medium and the nature of the substrate. The values of the cmc of CTABr under the present experimental conditions were obtained as follows. At a presumed value of cmc, the values of k_M, K_S and the least squares, Σd_i^2 (where $d_i = k_{obs1i} - k_{cldi}$, k_{obs1i} and k_{cldi} being the respective observed and calculated rate constant, respectively, at the *i*th concentration of CTABr), were calculated from equation (2) using the non-linear least-squares technique. The rate constants k_{NM} were obtained experimentally by carrying out kinetic runs in the absence of CTABr. The calculation of k_M and K_S was repeated at different presumed values of the cmc. The best value of the cmc was considered to be that for which Σd_i^2 was a minimum. Such values of cmc and the calculated values of k_M and K_S in the presence of 0·01 mol dm^{-3} KOH and LiOH are shown in Table 3. An alternative method advanced by Broxton *et al.*[14g] was also used to determine the values of cmc. These cmc values were also used to calculate k_M and K_S from equation (2) and the results obtained are summarized in Table 3. The cmc values obtained from these two alternative methods are not significantly different from each other. The least-squares value obtained with cmc $= 1{\cdot}6 \times 10^{-4}$ mol dm^{-3} was more than double that with cmc $= 1{\cdot}8 \times 10^{-4}$ mol dm^{-3} in the presence of K$^+$.

The polarity of the Stern layer (where almost all the micellar-mediated reactions are believed to occur) is considerably lower than that of aqueous pseudo-phase [the dielectric constant of the Stern layer is 36–49 (Ref. 15)]. The values of k_M and K_S (Table 3) appear to be unchanged with change from 0·01 mol dm^{-3} KOH to 0·01 mol dm^{-3} LiOH. This shows that neither K$^+$ nor Li$^+$ ions entered the microenvironment of low polarity where the micellar-mediated reactions occurred. This inference is based on the fact that the presence of 0·01 mol dm^{-3} K$^+$ caused an increase in k_{obs1} at 70% (v/v) CH_3CN compared to that at 2% (v/v), CH_3CN in mixed aqueous solvents (Figure 1). On the other hand, if we assume that both K$^+$ and Li$^+$ did enter the micellar region of low poarity where reaction occurred, then the value of k_M must have been much smaller in the presence of Li$^+$ than that of K$^+$, and this is contrast to the experimental observations (Table 3). These results show that the counterions for micellized HO$^-$ and perhaps PS$^-$ are micellar head-groups The rate constants k_{obs1} remained unchanged with change in $[Bu^n{}_4NI]$ from 0·0 to 0·09 mol dm^3 in mixed $CH_3CN–CH_3OH–H_2O$ (19·6 : 80·0 : 0·4, v/v) solvent.[12] Similarly, the plot of the rate constants k_{obs1} versus $[CH_3OH]_T$ turned out to be linear (with essentially a zero intercept) within the CH_3OH concentration range 15–97% (v/v) in mixed aqueous solvents containing 1% (v/v) CH_3CN and 0·07 mol dm^{-3} $Bu^n{}_4NBr$.[10] In view of these observations, the *ca* fourfold inhibitory effect of $[CTABr]_T$ on k_{obs1} cannot be attributed to the low polarity of the microenvironment where the micellar-mediated reactions occur.

The ionic strength of the Stern layer is significantly higher than that of the aqueous pseudo-phase.[16] The *ca* fourfold inhibitory effect of $[CTABr]_T$ on k_{obs1} is difficult to explain in terms of an ionic strength effect because the presence of 0·3 mol dm^{-3} Et_4NBr, 0·3 mol dm^{-3} $Pr^n{}_4NBr$ and 0·24 mol dm^{-3} $Bu_{n4}NBr$ decreased k_{NM} only by 26, 45 and 40%, respectively, in mixed $CH_3CN–CH_3OH–H_2O$ (1 : 15 : 84, v/v) solvents containing 0·01 mol dm^{-3} NaOH at 30 °C.[10]

The most plausible source of micellar inhibition of the methanolysis of PS$^-$ is the lower concentration of methanol in the micellar environment ($[CH_3OH_M]$) where PS_M^- molecules exist compared with $[CH_3OH_{NM}]$. An alternative source of micellar inhibition of methanolysis of PS$^-$ may be attributed to specific medium effects at the micellar surface where the PS_M^- molecule forms an ion-pair complex (similar to IP) with cationic head groups of the micelles. Although the present data are not sufficient to rule out this possibility completely, it appears to be the least conceivable possibility in view of the reported observations on the effects of $[Et_4NI]$ and $[Bu^n{}_4NI]$ on k_{obs1} in $H_2O–CH_3CN–CH_3OH$ (19·2 : 0·8 : 80·0, v/v) and $H_2O–CH_3CN–CH_3OH$ (0·4 : 19·6 : 80·0, v/v) solvents, respectively. With such solvent systems, the rate constants k_{obs1} remained unchanged with change in $[Et_4NI]$ from 0·0 to 0·15 mol dm^{-3} and in $[Bu^n{}_4NI]$ from 0·0 to 0·09 mol dm^{-3}, at 0·01 mol dm^{-3} NaOH.[12]

ACKNOWLEDGMENT

This work was supported by the Universiti Malaya Research Vote F161/94 granted to M.N.K.

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