# Effects of [NaOH] and [KBr] on Intramolecular General Base-Catalyzed Methanolysis of Ionized Phenyl Salicylate in the Presence of Cationic Micelles

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Pseudo-first-order rate constants obtained for methanolysis of ionized phenyl salicylate ($PS^-$) at constant [MeOH], [MeCN], [NaOH] or [KOH], and [KBr] and at 35 °C show a decrease with the increase in [CTABr] (where CTABr represents cetyltrimethylammonium bromide) from 0.0−0.01 M. These observed data obey a pseudophase model of the micelle. The micellar binding constants ($K_S$) of $PS^-$, pseudo-first-order rate constants ($k_M$) for methanolysis of $PS^-$ in the micellar pseudophase and cmc are almost unchanged with the change in [NaOH] from 0.005−0.050 M. The increase in [KBr] from 0.0 to 0.3 M at 0.01 M KOH decreases $K_S$ from 5140 to 653 $M^{-1}$ and cmc from $1.9 \times 10^{-4}$ to $0.2 \times 10^{-4}$ M. Pseudo-first-order rate constants, $k_M$, are almost independent of [KBr] at 0.01 M KOH.

## Introduction

Almost all kinetic data on the effects of micelles on rates of chemical reactions have been interpreted in terms of a pseudophase model of the micelle.[1] Among the various assumptions involved in this model,[2] perhaps, the most crucial one is that the binding constants of two or more than two chemical species with a micelle are independent of each other. This model also assumes that the presence of one chemical species does not affect the presence of other chemical species in the micellar pseudophase. This assumption, however, fails to explain the observed data on the effects of cationic micelles on rates of reactions between $^-OH$ (or any other anion) with neutral substrates.[3] In order to explain these observations, a pseudophase ion exchange (PIE) model has been proposed.[3,4] Although this model works well for many reactions,[5] its weaknesses have started appearing in the literature.[6] Probably, for the first time, Vera and Rodenas[7] have observed the expulsion of anionic esters (substrates) from cetyltrimethylammonium bromide (CTABr) micelles by the added bromide ions in the kinetic study on the effects of [KBr] on rates of reactions between $^-OH$ and anionic esters. In these reactions, the exchange of both the reactants (anionic ester and $^-OH$) by bromide ions has occurred. But the PIE model takes care of only the exchange between $^-OH$ and $Br^-$. Vera and Rodenas[7] explained their observations in terms of PIE model coupled with the assumption that the binding constants ($K_S$) of anionic esters with CTABr micelles varied with [KBr] according to the following empirical equation (eq 1) where $K_S{}^0$ and $L$ are adjustable empirical parameters.

$$K_S = K_S{}^0 - L[\mathrm{KBr}] \tag{1}$$

The present study aimed to test eq 1 kinetically by determining $K_S$ as a function of [KBr]. A solvolytic reaction (methanolysis of ionized phenyl salicylate in mixed $H_2O$−MeOH−MeCN solvents) was chosen to avoid the use of PIE model of micelles. The effects of CTABr micelles on pseudo-first-order rate constants for methanolysis of ionized phenyl salicylate have been determined at different [NaOH] and [KBr]. These results and their explanation(s) are described in this paper.

## Experimental Section

**Materials.** Phenyl salicylate and cetyltrimethylammonium bromide (CTABr) were commercial products of reagent grade from Fluka and Aldrich. All other chemicals used were also of reagent grade and were from Fluka, BDH, or Aldrich. The stock solutions of phenyl salicylate were prepared in acetonitrile.

**Kinetic Measurements.** In a typical kinetic run, the reaction mixture (4.9 mL) containing all reaction ingredients except phenyl salicylate was temperature equilibrated at 35 °C for about 10 min. The reaction was then initiated by adding 0.1 mL of 0.01 M phenyl salicylate (in MeCN) to the temperature-equilibrated reaction mixture (4.9 mL). Nearly 2.5 mL of the reaction mixture was quickly transferred to 3 mL quartz cuvette which was kept in the thermostated cell holder of the spectrophotometer. The progress of the reaction was monitored by recording the increase in absorbance ($A_{obs}$) as a function of time ($t$) at 290 nm using a double beam Shimadzu Model UV-2102/310/PC UV-VIS-NIR spectrophotometer equipped with thermostated cell holder. The constant temperature (35 °C) of the cell holder was maintained by using thermostated circulating water bath.

All the kinetic runs were carried out until 3−6 halflives. The observed data ($A_{obs}$ versus $t$) were found to fit well to eq 2.

$$A_{obs} = \delta_{app}[X_0][1 - \exp(-k_{obs}t)] + A_0 \tag{2}$$

The pseudo-first-order rate constant ($k_{obs}$), apparent molar extinction coefficient ($\delta_{app}$), and absorbance at $t = 0$ ($A_0$) were calculated from eq 2 using the nonlinear least squares technique. The standard deviations associated with $k_{obs}$, $\delta_{app}$, and $A_0$ were found to be <2% in all kinetic runs.

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**Table 1. Effects of $[CTABr]_T$ on Pseudo-First-Order Rate Constants ($k_{obs}$) for Methanolysis of $PS^-$ at Different [NaOH][a]**

| $10^4[CTABr]_T$,[b] M | [NaOH] = 0.005 M | | [NaOH] = 0.015 M | | [NaOH] = 0.030 M | | [NaOH] = 0.050 M | |
|---|---|---|---|---|---|---|---|---|
| | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ |
| 0.0 | 6.00 ± 0.05[d] | | 6.29 ± 0.04[d] | | 6.42 ± 0.04[d] | | 6.14 ± 0.05[d] | |
| 0.4 | | | | | 6.56 ± 0.06 | | | |
| 0.6 | 6.55 ± 0.05 | | 6.21 ± 0.05 | | | | 6.51 ± 0.03 | |
| 0.8 | | | | | 6.55 ± 0.07 | | | |
| 1.0 | 5.83 ± 0.06 | | 6.11 ± 0.07 | | 6.11 ± 0.06 | | 5.98 ± 0.05 | |
| 1.2 | 6.38 ± 0.08 | | 6.24 ± 0.06 | | | | 6.36 ± 0.09 | |
| 1.6 | | | | | | | 6.35 ± 0.09 | |
| 1.8 | 6.41 ± 0.08 | | 6.28 ± 0.10 | | | | | |
| 2.0 | 5.45 ± 0.16 | 5.76 | 5.60 ± 0.11 | 5.81 | 5.51 ± 0.17 | 5.70 | 5.21 ± 0.13 | 5.45 |
| 2.5 | 5.10 ± 0.15 | 4.86 | 5.19 ± 0.11 | 4.92 | 4.72 ± 0.11 | 4.87 | 4.79 ± 0.08 | 4.66 |
| 3.0 | 4.48 ± 0.14 | 4.26 | 4.64 ± 0.12 | 4.32 | 4.77 ± 0.08 | 4.30 | 4.31 ± 0.06 | 4.12 |
| 4.0 | 3.40 ± 0.10 | 3.51 | 3.55 ± 0.08 | 3.56 | 3.61 ± 0.05 | 3.58 | 3.51 ± 0.06 | 3.44 |
| 5.0 | 3.02 ± 0.05 | 3.05 | 3.01 ± 0.05 | 3.11 | 3.20 ± 0.04 | 3.14 | 3.00 ± 0.03 | 3.03 |
| 6.0 | | | 2.59 ± 0.05 | 2.80 | 2.75 ± 0.03 | 2.84 | 2.68 ± 0.03 | 2.76 |
| 8.0 | 2.17 ± 0.05 | 2.38 | 2.23 ± 0.04 | 2.41 | 2.18 ± 0.02 | 2.46 | 2.22 ± 0.03 | 2.41 |
| 15.0 | 1.73 ± 0.04 | 1.85 | 1.73 ± 0.03 | 1.86 | 1.77 ± 0.04 | 1.93 | 1.82 ± 0.03 | 1.92 |
| 100.0 | 1.55 ± 0.06 | 1.33 | 1.61 ± 0.04 | 1.32 | 1.66 ± 0.03 | 1.41 | 1.63 ± 0.02 | 1.44 |

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, 35 °C, $\lambda = 290$ nm, MeOH = 10% v/v, MeCN = 2% v/v, and $H_2O$ = 88% v/v. [b] Total concentration of CTABr. [c] Calculated from eq 4 using parameters $k_M$ and $K_S$ as listed in Table 4. [d] Error limits are standard deviations.

**Table 2. Effects of $[CTABr]_T$ on Pseudo-First-Order Rate Constants ($k_{obs}$) for Methanolysis of $PS^-$ at Different [KBr][a]**

| $10^4[CTABr]$,[b] M | [KBr] = 0.0 M | | [KBr] = 0.02 M | | [KBr] = 0.04 M | |
|---|---|---|---|---|---|---|
| | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ |
| 0.0 | 6.35 ± 0.05[d] | | 6.28 ± 0.05[d] | | 6.55 ± 0.06[d] | |
| 0.4 | 6.56 ± 0.04 | | 6.48 ± 0.05 | | 6.41 ± 0.05 | |
| 0.8 | 6.41 ± 0.08 | | 6.37 ± 0.06 | | 6.47 ± 0.07 | |
| 1.0 | 6.34 ± 0.05 | | 6.42 ± 0.13 | | 6.19 ± 0.05 | |
| 1.5 | | | | | 5.93 ± 0.06 | 6.13 |
| 1.6 | 6.31 ± 0.15 | | | | | |
| 2.0 | 5.94 ± 0.10 | 6.10 | 5.31 ± 0.07 | 5.45 | 5.71 ± 0.06 | 5.55 |
| 2.5 | 5.41 ± 0.14 | 5.14 | 5.02 ± 0.04 | 4.86 | 5.09 ± 0.05 | 5.11 |
| 3.0 | 4.70 ± 0.11 | 4.49 | 4.46 ± 0.06 | 4.42 | 4.83 ± 0.05 | 4.74 |
| 4.0 | 3.74 ± 0.07 | 3.68 | 3.89 ± 0.04 | 3.81 | 4.25 ± 0.04 | 4.20 |
| 5.0 | 3.17 ± 0.04 | 3.19 | 3.32 ± 0.03 | 3.41 | 3.85 ± 0.03 | 3.80 |
| 6.0 | 2.68 ± 0.05 | 2.87 | 3.03 ± 0.04 | 3.12 | 3.42 ± 0.06 | 3.50 |
| 8.0 | 2.26 ± 0.04 | 2.45 | 2.67 ± 0.03 | 2.74 | 2.98 ± 0.04 | 3.08 |
| 15.0 | 1.63 ± 0.03 | 1.88 | 2.26 ± 0.05 | 2.17 | 2.31 ± 0.03 | 2.38 |
| 100.0 | 1.66 ± 0.02 | 1.31 | 1.55 ± 0.04 | 1.55 | 1.63 ± 0.03 | 1.54 |

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, 35 °C, $\lambda = 290$ nm, [KOH] = 0.01 M, MeOH = 10% v/v, MeCN = 2% v/v, and $H_2O$ = 88%, v/v. [b-d] Notations have the same meanings as in Table 1.

The fact that the reaction rate being followed is predominantly the rate of methanolysis of ionized phenyl salicylate ($PS^-$) is described elsewhere.[8] The solvolytic cleavage of $PS^-$, in mixed MeOH−MeCN−$H_2O$ solvents, may be shown by the following reaction scheme (eq 3),

$$o\text{-}HOC_6H_4CO_2^- \xleftarrow[-\ \text{PhOH}]{k_2'H_2O} PS^- \xrightarrow[-\ \text{PhOH}]{k_1'\text{MeOH}} MS^- \xrightarrow[-\ \text{MeOH}]{k_3'H_2O} o\text{-}HOC_6H_4CO_2^- \quad (3)$$

where $MS^-$ and PhOH represent ionized methyl salicylate and phenol, respectively. In the mixed MeOH−MeCN−$H_2O$ (10:2:88) solvent containing 0.01 M NaOH, the values of $k_1/k_2 > 10$ [9] and $k_1/k_3 > 50$ [10] where $k_1 = k_1'[\text{MeOH}]$, $k_2 = k_2'[H_2O]$ and $k_3 = k_3'[H_2O]$. Thus, under the experimental conditions of this study, $k_2$ and $k_3$ may be neglected compared with $k_1$. In terms of eqs 2 and 3, pseudo-first-order rate constant $k_{obs} = k_1 + k_2$. But since $k_1/k_2 > 10$, therefore $k_{obs} \cong k_1$.

## Results

**Effect of CTABr Micelles on Rate of Methanolysis of $PS^-$ at Different [NaOH].** Several kinetic runs were carried out within $[CTABr]_T$ (total concentration of CTABr) range of 0.0−0.01 M at a constant [NaOH] and 35 °C in mixed aqueous solvents containing 10% v/v MeOH and 2% v/v MeCN. Pseudo-first-order rate constants ($k_{obs}$) decreased by nearly 4-fold with an increase in $[CTABr]_T$ from 0.0 to 0.01 M at 0.005 M NaOH. Similar results were obtained at 0.015, 0.030, and 0.050 M NaOH. These results are summarized in Table 1.

**Effect of CTABr Micelles on Rate of Methanolysis of $PS^-$ at Different [KBr].** A series of kinetic runs was carried out within $[CTABr]_T$ range of 0.0−0.01 M at 35 °C in mixed aqueous solvents containing 10% v/v MeOH, 2% v/v MeCN, 0.01 M KOH, and a constant [KBr]. Pseudo-first-order rate constants ($k_{obs}$), as shown in Tables 2 and 3, decreased nearly 3−4-fold with the increase in $[CTABr]_T$ from 0.0 to 0.01 M at diffrent [KBr].

## Discussion

The initial absorbance values (i.e. absorbance values at reaction time $t = 0$) of the reaction mixtures for entire kinetic runs were found to be unchanged with the change in $[CTABr]_T$ from 0.0 to 0.01 M and in $[^-OH]$ from 0.005 to 0.050 M. This shows the existence of phenyl salicylate in fully ionized form ($PS^-$) under the experimental conditions of the present study because the molar extinction coefficient of nonionized phenyl salicylate (PSH) is nearly 2-fold larger than that of $PS^-$ at 290 nm. The

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**Table 3. Effects of $[CTABr]_T$ on Pseudo-First-Order Rate Constants ($k_{obs}$) for Methanolysis of $PS^-$ at Different [KBr][a]**

| $[CTABr]_T$,[b] M | [KBr] = 0.1 M |  | [KBr] = 0.2 M |  | [KBr] = 0.3 M |  |
|---|---|---|---|---|---|---|
|  | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ | $10^3k_{obs}$, $s^{-1}$ | $10^3k_{cal}$,[c] $s^{-1}$ |
| 0.0 | 6.10 ± 0.05[d] |  | 5.91 ± 0.04[d] |  | 5.92 ± 0.04[d] |  |
| 0.1 |  |  |  |  | 5.87 ± 0.07 |  |
| 0.2 |  |  |  |  | 6.12 ± 0.06 |  |
| 0.4 | 6.35 ± 0.11 |  | 6.18 ± 0.04 |  |  |  |
| 0.8 | 6.27 ± 0.10 |  | 6.02 ± 0.07 |  |  |  |
| 1.0 | 5.96 ± 0.03 | 6.02 | 5.70 ± 0.04 | 5.73 | 5.72 ± 0.05 | 5.69 |
| 2.0 | 5.42 ± 0.13 | 5.39 | 5.33 ± 0.10 | 5.33 | 5.39 ± 0.11 | 5.44 |
| 2.5 | 5.12 ± 0.04 | 5.13 | 5.16 ± 0.06 | 5.15 | 5.30 ± 0.04 | 5.32 |
| 3.0 | 5.05 ± 0.05 | 4.90 | 4.98 ± 0.09 | 4.99 | 5.26 ± 0.03 | 5.21 |
| 4.0 | 4.57 ± 0.04 | 4.52 | 4.65 ± 0.06 | 4.71 | 4.92 ± 0.05 | 5.00 |
| 5.0 | 4.20 ± 0.04 | 4.21 | 4.50 ± 0.04 | 4.48 | 4.84 ± 0.03 | 4.82 |
| 6.0 | 3.90 ± 0.05 | 3.95 | 4.37 ± 0.05 | 4.27 | 4.69 ± 0.03 | 4.65 |
| 8.0 | 3.54 ± 0.03 | 3.55 | 3.95 ± 0.04 | 3.93 | 4.40 ± 0.04 | 4.36 |
| 15.0 | 2.65 ± 0.02 | 2.78 | 3.10 ± 0.03 | 3.19 | 3.63 ± 0.03 | 3.66 |
| 100.0 | 1.64 ± 0.02 | 1.57 | 1.82 ± 0.03 | 1.80 | 1.93 ± 0.03 | 1.93 |

[a–d] Notations have the same meanings as in Table 2.

**Table 4. Effects of [NaOH] and [KBr] on cmc, $K_S$, and $k_M$ for Methanolysis of $PS^-$ in the Presence of CTABr Micelles[a]**

| [NaOH], M | [KOH], M | [KBr], M | $10^4$cmc,[b] M | $10^3k_M$, $s^{-1}$ | $K_S$, $M^{-1}$ | $K_S$,calcd,[c] $M^{-1}$ | $10^3k_{NM}$,[d] $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.005 |  |  | 1.9 (1.9)[e] | 1.24 ± 0.19[f] | 5250 ± 753[f] |  | 6.00 ± 0.05 |
| 0.015 |  |  | 1.8 (1.9) | 1.22 ± 0.20 | 5300 ± 715 |  | 6.29 ± 0.04 |
| 0.030 |  |  | 1.7 (1.6) | 1.32 ± 0.21 | 5460 ± 778 |  | 6.42 ± 0.04 |
| 0.050 |  |  | 1.7 (1.6) | 1.36 ± 0.14 | 5630 ± 570 |  | 6.14 ± 0.05 |
|  | 0.01 | 0.0 | 1.9 (1.8) | 1.21 ± 0.20 | 5140 ± 690 |  | 6.35 ± 0.05 |
|  | 0.01 | 0.02 | 1.5 (1.4) | 1.43 ± 0.09 | 4150 ± 260 | 3860 | 6.28 ± 0.05 |
|  | 0.01 | 0.04 | 1.2 (1.2) | 1.37 ± 0.11 | 2980 ± 180 | 3060 | 6.55 ± 0.06 |
|  | 0.01 | 0.1 | 0.9 (0.8) | 1.28 ± 0.09 | 1580 ± 75 | 1810 | 6.10 ± 0.05 |
|  | 0.01 | 0.2 | 0.6 (0.7) | 1.41 ± 0.07 | 1060 ± 38 | 980 | 5.91 ± 0.04 |
|  | 0.01 | 0.3 | 0.2 (0.3) | 1.32 ± 0.07 | 653 ± 21 | 602 | 5.92 ± 0.04 |

[a] $[\text{Phenyl salicylate}]_0 = 2 \times 10^{-4}$ M, MeOH = 10% v/v, MeCN = 2% v/v, $H_2O$ = 88%, v/v, 35 °C, $\lambda = 290$ nm. [b] Calculated from iterative technique described elsewhere.[13] [c] Calculated from eq 5 with $L = 6087\ M^{-2}$ and $\Psi = 15\ M^{-1}$. [d] Obtained at $[CTABr]_T = 0.0$. [e] Calculated from the technique of Broxton et al.[14]. [f] Error limits are standard deviations.

rates of methanolysis and hydrolysis of PSH are more than $10^3$-fold slower than those of $PS^-$ in the absence of CTABr.[8b] Thus, the decrease in $k_{obs}$ with an increase in $[CTABr]_T$ cannot be attributed to the possible increase in [PSH] with the increase in $[CTABr]_T$.

The rate constants, $k_2$, (for hydrolysis of $PS^-$) were found to be independent of $[^-OH]$ within its range of 0.005−0.060 M[10] and 0.01−0.04 M[11] in the absence and presence of 0.0015 M CTABr, respectively. The rate constants, $k_1$, (for methanolysis of $PS^-$) were found to be independent of $[^-OH]$ within its range of 0.01−0.15 M in mixed aqueous solvents containing 80% v/v methanol and 0.8% v/v acetonitrile.[8b] The rate constants, $k_{obs}$ ($\cong k_1$), remained almost unchanged with the change in $[^-OH]$ from 0.005 to 0.050 M within the $[CTABr]_T$ range of 0.0−0.01 M. In view of these results, the rate of methanolysis of $PS^-$ may be considered to be pH-independent under the experimental conditions of this study.

The mechanism of pH-independent alkanolysis of phenyl salicylate involves intramolecular general base (IGB) catalysis where the ionized phenolic group of phenyl salicylate acts as an IGB catalyst. The possible occurrence of an alternative reaction mechanism involving intramolecular general acid (IGA) catalysis has been ruled out as discussed elsewhere.[12]

The inhibitory effect of CTABr micelles on the rate of methanolysis of $PS^-$ may be explained in terms of the pseudophase model of a micelle[1] as shown in Scheme 1.

## Scheme 1

$$PS^-_{NM} + D_n \underset{k_{NM}}{\overset{K_S}{\rightleftharpoons}} PS^-_M$$

$$PS^-_{NM} \xrightarrow[\text{MeOH}]{k_{NM}} MS^- + PhOH$$

$$PS^-_M \xrightarrow[\text{MeOH}]{k_M} MS^- + PhOH$$

In Scheme 1, $D_n$ represents micellized CTABr and subscripts NM and M represent nonmicellar pseudophase and micellar pseudophase, respectively. The observed rate law, rate = $k_{obs}[PS^-]_T$ (where $[PS^-]_T = [PS^-_{NM}] + [PS^-_M]$), and Scheme 1 yield eq 4 where $[D_n] = [CTABr]_T$ − cmc (critical micelle concentration).

$$k_{obs} = \frac{k_{NM} + k_M K_S[D_n]}{1 + K_S[D_n]} \tag{4}$$

The cmc of CTABr has been found to be highly sensitive to the reaction conditions such as nature of the substrate, salt, temperature, and solvent.[11] The cmc values under the present experimental conditions were determined by both an iterative technique and a graphical procedure as described elsewhere.[13,14] These results are summarized in Table 4. Pseudo-first-order rate constants, $k_M$, for methanolysis of $PS^-$ and binding constants, $K_S$, of $PS^-$ with CTABr micelles were calculated from eq 4 using the nonlinear least squares technique. These values at different [NaOH] and [KBr] are shown in Table 4. Pseudo-first-order rate constants, $k_{NM}$, for methanolysis of $PS^-$ were determined by carrying out experiments in the absence of CTABr. The fitting of the observed data to eq 4 is evident from the calculated

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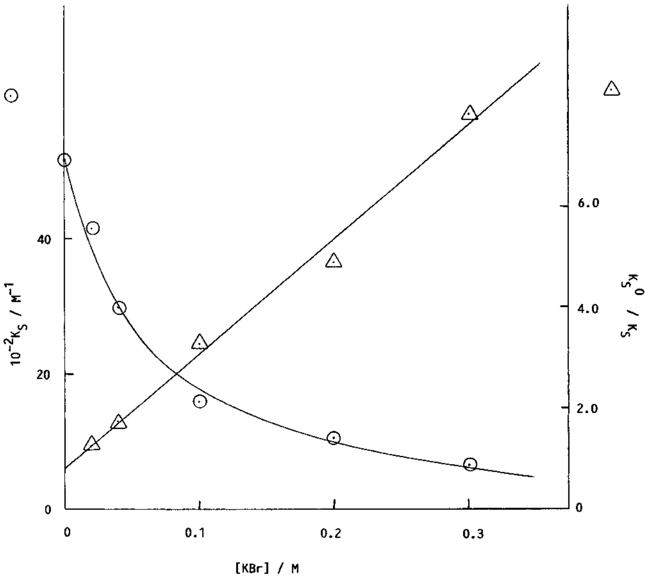

**Figure 1.** Plots showing the dependence of $K_S$ (⊙) and $K_S^0/K_S$ (△) upon [KBr] for methanolysis of $PS^-$. The solid lines are drawn through the calculated points using eq 5 with $L = 6087$ $M^{-2}$ and $\Psi = 15$ $M^{-1}$ for (⊙) and the equation $K_S^0/K_S = \Phi + \Psi[KBr]$ with $\Phi = 0.78$ and $\Psi = 22.8$ $M^{-1}$ for (△).

values of pseudo-first-order rate constants, $k_{cal}$, as summarized in Tables 1−3.

Both rate constants $k_{NM}$ and $k_M$ are almost independent of [NaOH] within its range of 0.005−0.050 M (Table 4). This shows that the mechanism for methanolysis of $PS^-$ remains essentially the same in both the nonmicellar pseudophase and the micellar pseudophase. Although the present data are not sufficient to differentiate between IGB and IGA catalytic mechanisms for methanolysis in the micellar pseudophase, the occurrence of the IGB mechanism is preferred because such a mechanism has been ascertained for methanolysis in the nonmicellar pseudophase.[12]

The change in [KBr] from 0.0 to 0.3 M did not bring any significant change in $k_M$ (Table 4). This is an expected result if the mechanism for methanolysis in micellar pseudophase is similar to that in nonmicellar pseudophase because rate constants, $k_{NM}$, are almost unchanged with the change in [KBr] from 0.0 to 0.3 M. Probable reasons for nearly 5-fold lower reactivity in the micellar pseudophase compared to that in the nonmicellar pseudophase (i.e. $k_{NM}/k_M \cong 5$) are discussed elsewhere.[13b]

The values of $K_S$ are almost independent of [NaOH] (Table 4). But the increase in [KBr] from 0.0 to 0.3 M decreased $K_S$ from 5140 to 653 $M^{-1}$. These observations show that both $PS^-$ and $Br^-$ ions compete for micellar incorporation. Such competitive micellar incorporation does not appear to occur between $PS^-$ and $^-OH$. However, the occurrence of competitive cationic micellar incorporation between $^-OH$ and $Br^-$ is well established.[2−5] Probably, Vera and Rodenas were the first to observe kinetically the expulsion of moderately hydrophobic anionic esters by bromide ions from cationic micelles.[7] These authors proposed that the variation of $K_S$ with [KBr] followed an empirical equation (eq 1). But these authors did not determine $K_S$ kinetically at different [KBr]. The values of $K_S$, as summarized in Table 4, did not follow eq 1.

The binding constants, $K_S$, obtained at different [KBr] were tried to fit to empirical eq 5

$$K_S = \frac{K_S{}^0 - L[\mathrm{KBr}]}{1 + \Psi[\mathrm{KBr}]} \tag{5}$$

where $L$ and $\Psi$ represent adjustable empirical parameters and $K_S^0 = K_S$ at [KBr] = 0.0 M. The nonlinear least squares calculated values of L and $\Psi$ are 6087 ± 4568 $M^{-2}$ and 15 ± 3 $M^{-1}$, respectively. Although the fitting of the observed data to eq 5 appears to be good (as evident from the plot of Figure 1 where a solid line is drawn through the calculated points), the value of $L$ is statistically unreliable because it is associated with a high standard deviation (≈75%). If one neglects $L$[KBr] compared with $K_S^0$, then eq 5 is reduced to eq 6.

$$K_S = \frac{K_S{}^0}{1 + \Psi[\mathrm{KBr}]} \tag{6}$$

The plot of $K_S^0/K_S$ versus [KBr] was found to be linear with intercept = 0.78 ± 0.24 and slope ($\Psi$) = 22.8 ± 1.4 $M^{-1}$ (Figure 1). However, the plot of $\{(K_S^0/K_S) - 1\}$ versus [KBr] yielded $\Psi = 18.9 \pm 4.4$ $M^{-1}$.

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