Kinetic Evidence for the Occurrence of Independent Ion-Exchange Processes in the Cationic Micellar-Mediated Reaction of Piperidine with Anionic Phenyl Salicylate

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A kinetic probe, which involves the determination of pseudo-first-order rate constants (k_{obs}) for the nucleophilic reaction of piperidine (Pip) with ionized phenyl salicylate (S^-) at constant $[Pip]_T$ (= 0.1 M), $[S^-]_T$ (= 2×10^{-4} M), $[CTABr]_T$, ≤ 0.10 M NaOH and varying concentration of MX (= $3\text{-}ClC_6H_4CO_2Na$ and $C_6H_5CH{=}CHCO_2Na$), gives the following information. The nonlinear plots of k_{obs} versus [MX] reveal indirectly the occurrence of more than one independent ion-exchange processes at the CTABr micellar surface. These observed data fit to a kinetic relationship derived from an empirical equation coupled with pseudophase micellar (PM) model. This relationship gives an empirical constant ($K_{X/S}$) that is used to determine the usual ion-exchange constant (K_X^Y). The values of K_X^{Br} (Y = Br) have been calculated for X = $3\text{-}ClC_6H_4CO_2^-$ and $C_6H_5CH{=}CHCO_2^-$. More than 12-fold larger value of K_X^{Br} for X = $3\text{-}ClC_6H_4CO_2^-$ than that for X = $2\text{-}ClC_6H_4CO_2^-$ is attributed to the presence and absence of viscoelasticity in the respective presence of $3\text{-}ClC_6H_4CO_2^-$ and $2\text{-}ClC_6H_4CO_2^-$.

Introduction

Although normal micelles are perhaps the most extensively studied nanoparticles/nanomaterials by the use of variety of physicochemical techniques, the dynamic structural features of these micelles at the molecular level are not completely understood.[1] The occurrence of ion-exchange (IE) between counterions at the ionic micellar surface appears to be a ubiquitous feature of such colloidal systems. Counterions in an ionic micelle play an important role in its stability[2] as well as in its physicochemical properties such as growth,[3] viscoelasticity,[4] and reaction rate of ionic or semi-ionic reactions.[5] However, the finely detailed mechanism(s) of the occurrence of IE at the ionic micellar surface have remained essentially a major problem in various areas of interest.[6]

Various physicochemical techniques have been used to study the effects of IE at the ionic micellar surface,[7] but the kinetic technique, being dynamic in nature, is expected to provide mechanistic aspects of the dynamic structural feature of micelles. Quantitative analysis of kinetic data on the ionic micellar mediated semi-ionic reactions involves largely the following two alternative, theoretical approaches for the distribution of the counterion-like reactants between aqueous and micellar pseudophases: (i) The most commonly used approach is the pseudophase ion-exchange (PIE) model[8] and (ii) a less commonly used model/approach (BPP) is to write micellar counterion binding in terms of ionic micellar surface electrical potential.[9] Both approaches are semiempirical and have limitations.[9] The apparent weaknesses of the PIE model and its various extensions have been realized recently.[10] Apart from the use of BPP,[9] PIE[8,11] and its various extensions,[12] a few empirical equations have been used to explain the effects of the occurrence of IE at the ionic micellar surface.[13,14]

Pseudophase micellar (PM) model, coupled with an empirical equation,[14] gives eq 1,[1,15]

$$k_{obs} = \frac{k_0 + \theta K^{X/S}[MX]}{1 + K^{X/S}[MX]} \qquad (1)$$

where k_{obs} represents the pseudo-first-order rate constant for the reaction of anionic reactant (ionized phenyl salicylate, S^-) with another nonionic reactant (piperidine, Pip) in the presence of a constant concentration of cationic micelles and different concentrations of inert salt MX. $k_0 = k_{obs}$ at [MX] = 0, θ and $K^{X/S}$ are empirical constants. It has been shown elsewhere[1] that the values of θ are related to the relative ionic micellar penetration of counterions (such as S^- and X^-), and the values of $K^{X/S}$ are related to the usual ion-exchange constant (K_X^S) for ion-exchange process X^-/S^-. In this manuscript, we present the indirect kinetic evidence for the occurrence of more than one independent ion-exchange process in the cationic micellar-mediated reaction of Pip with S^-.

Experimental Section

Materials. Reagent-grade cetyltrimethylammonium bromide (CTABr), phenyl salicylate (HS), piperidine, and 3-chlorobenzoic and cinnamic acids were commercial products of the highest available purity. All other chemicals were also reagent grade. Stock solutions (0.01 M) of HS and (1.0 M) of piperidine were freshly prepared in acetonitrile and distilled water, respectively.

Kinetic Measurements. The rate of nucleophilic reaction of piperidine with ionized phenyl salicylate was studied spectrophotometrically by monitoring the disappearance of the reactant S^- at 350 nm in the presence of cetyltrimethylammonium bromide micelles and the absence as well as the presence of inert salt MX (MX = sodium 3-chlorobenzoate and sodium cinnamate). The details of the kinetic procedure, data analysis, and the product characterization were the same as described elsewhere.[16−18]

Results and Discussion

A few kinetic runs were carried out at 0.1 M Pip, 2×10^{-4} M S^-, 0.01 M CTABr, 35 °C, [NaOH] range 0.030−0.065 M,

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TABLE 1: Pseudo-First-Order Rate Constants (k_{obs}) for the Reaction of Piperidine with Anionic Phenyl Salicylate (S^-) at 0.01 M CTABr and Different 3-$ClC_6H_4CO_2Na$ Concentrations[a]

[MX]/M	$10^3\ k_{obs}/s^{-1}$	$10^3\ k_{calcd1}{}^{b}\ /s^{-1}$	$10^3\ k_{calcd2}{}^{c}\ /s^{-1}$	$R1^d$	$R2^e$
0.0	2.67 ± 0.02[f]				
0.005[g]	2.56 ± 0.03				
0.010	3.12 ± 0.02	5.14	2.72	1.65	0.87
0.012	3.55 ± 0.02	5.58	3.69	1.57	1.04
0.015	4.77 ± 0.03	6.21	4.98	1.30	1.04
0.017	5.56 ± 0.02	6.61	5.76	1.19	1.04
0.020	6.97 ± 0.15	7.19	6.80	1.03	0.98
0.025	7.86 ± 0.04	8.09	8.29	1.03	1.05
0.030	10.1 ± 0.3	8.92	9.54	0.88	0.94
0.040	11.3 ± 0.1	10.4	11.5	0.92	1.02
0.050	13.0 ± 0.1	11.7	13.0	0.90	1.00
0.100	17.2 ± 0.1	16.2	17.0	0.94	0.99
0.200	19.6 ± 0.1	20.6	19.8	1.05	1.01
0.350[g]	18.9 ± 0.1				

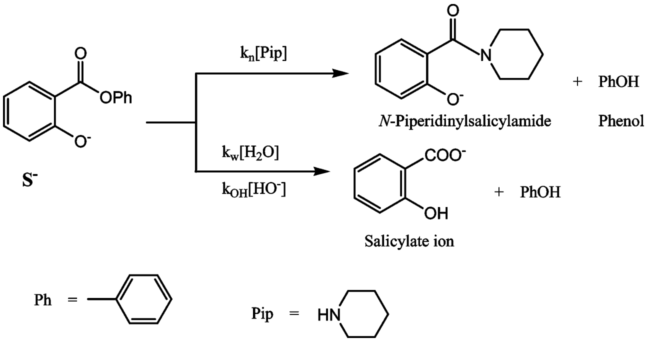
[a] [Phenyl salicylate]$_0$ 2×10^{-4} M, 35 °C, $\lambda = 350$ nm, [piperidine] = 0.1 M, and the aqueous reaction mixture for each kinetic run contained 2% v/v CH_3CN. The required amounts of 3-$ClC_6H_4CO_2Na$ ([MX]) were generated into the reaction mixture by using the stock solution (0.50 M) of 3-$ClC_6H_4CO_2H$ prepared in 0.55 M aqueous NaOH. The stock solution of NaOH was used to produce a fixed known concentration (0.03 M) of NaOH into the reaction mixture for each kinetic run, but the maximum concentration of added NaOH was 0.065 M. [b] Calculated from eq 1 with $[MX] = [MX] - [MX]_{op}^0$, where $[MX]_{op}^0 = 0$. [c] Calculated from eq 1 with $[MX] = [MX] - [MX]_{op}^0$, where $[MX]_{op}^0 = 9.9$ mM. [d] $R1 = k_{calcd1}/k_{obs}$. [e] $R2 = k_{calcd2}/k_{obs}$. [f] Error limits are standard deviations. [g] The k_{obs} at 0.005 and 0.350 M MX were not considered in the data treatment with eq 1.

TABLE 2: Pseudo-First-Order Rate Constants (k_{obs}) for the Reaction of Piperidine with Anionic Phenyl Salicylate (S^-) at 0.006 M CTABr and Different $C_6H_5CH{=}CH\ CO_2Na$ concentrations[a]

[MX]/M	$10^3\ k_{obs}/s^{-1}$	$10^3\ k_{calcd1}{}^{b}\ /s^{-1}$	$10^3\ k_{calcd2}{}^{c}\ /s^{-1}$	$R1^d$	$R2^e$
0.0	2.79 ± 0.01[f]				
0.005	3.27 ± 0.03	4.51	2.84	1.38	0.87
0.010	4.73 ± 0.03	6.01	4.97	1.27	1.05
0.020	7.75 ± 0.06	8.49	8.22	1.10	1.06
0.030	10.0 ± 0.1	10.5	10.6	1.05	1.02
0.040	12.2 ± 0.1	12.1	12.4	0.95	0.95
0.060	15.7 ± 0.1	14.5	14.9	0.92	0.98
0.080	17.0 ± 0.1	16.3	16.7	0.96	1.01
0.100	18.7 ± 0.3	17.7	17.9	0.95	0.96
0.150	19.3 ± 0.1	20.0	19.9	1.04	1.03
0.200	20.7 ± 0.2	21.4	21.1	1.03	1.02
0.300[g]	20.3 ± 0.1				
0.400[g]	18.7 ± 0.1				

[a] [Phenyl salicylate]$_0$ 2×10^{-4} M, 35 °C, $\lambda = 350$ nm, [piperidine] = 0.1 M, and the aqueous reaction mixture for each kinetic run contained 2% v/v CH_3CN. The required amounts of $C_6H_5CH{=}CHCO_2Na$ ([MX]) were generated into the reaction mixture by using the stock solution (0.50 M) of $C_6H_4CH{=}CHCO_2H$ prepared in 0.60 M aqueous NaOH. The stock solution of NaOH was used to produce a fixed known concentration (0.02 M) of NaOH into the reaction mixture for each kinetic run, but the maximum concentration of added NaOH was 0.100 M. [b] Calculated from eq 1 with $[MX] = [MX] - [MX]_{op}^0$, where $[MX]_{op}^0 = 0$. [c] Calculated from eq 1 with $[MX] = [MX] - [MX]_{op}^0$, where $[MX]_{op}^0 = 4.9$ mM. [d] $R1 = k_{calcd1}/k_{obs}$. [e] $R2 = k_{calcd2}/k_{obs}$. [f] Error limits are standard deviations. [g] The k_{obs} at 0.30 and 0.40 M MX were not considered in the data treatment with eq 1.

SCHEME 1



and [3-$ClC_6H_4CO_2Na$] range 0.0−0.35 M. Pseudo-first-order rate constants (k_{obs}) obtained under such conditions are summarized in Table 1. Similarly, a few kinetic runs were also carried out at 0.1 M Pip, 2×10^{-4} M S^-, 0.006 M CTABr, 35 °C, [NaOH] range 0.02−0.10 M, and [$C_6H_5CH{=}CHCO_2Na$] range 0.0−0.40 M, and the values of k_{obs} obtained for these kinetic runs are shown in Table 2. The values *of* k_{obs} show a mild decrease (<10%) with the increase in [sodium cinnamate] from 0.20 to 0.40 M (Table 2), which may be attributed to perhaps weak ionic strength or specific salt effect.

Spectrophotometric evidence[18] revealed the presence of nearly 100% of the ionized form (S^-) of phenyl salicylate under the experimental conditions of almost entire kinetic runs of this study. The rate of cleavage of S^- in the presence of Pip and CTABr micelles involves hydrolysis and piperidinolysis kinetic terms as represented by Scheme 1.[19]

The rate of hydrolysis of phenyl salicylate is independent of [HO^-] within its range ~0.005−0.060 M, and under such conditions, the rate of hydrolysis involves S^- and H_2O as the reactants.[20] The respective values of the pseudo-first-order rate constant, k'_w ($= k_w[H_2O]$), for pH-independent hydrolysis, and the second-order rate constant, k_{OH}, for the reaction of HO^- with S^- are 3.6×10^{-4} s^{-1} and 1.2×10^{-3} M^{-1} s^{-1} at 30 °C in the absence of CTABr micelles.[17] Thus, the value of k_0 ($= k'_w + k_{OH}[HO^-]$) at 35 °C are expected to vary from 5.9×10^{-4} to 7.3×10^{-4} s^{-1} within a [NaOH] range of 0.02−0.10 M. The value of k_0 decreased by more than 5-fold with the increase in the total concentration of CTABr ($[CTABr]_T$) from 0.0 to 0.002 M.[21] These results show that the lowest values of k_{obs} in Tables 1 and 2 (i.e. k_{obs} at [MX] = 0) are more than 20-fold larger than k_0 (i.e., k_{obs} at [Pip] = 0 and at $[CTABr]_T \geq 0.002$ M). Thus, the rate of hydrolysis is negligible compared to that of piperidinolysis of S^- under the present kinetic conditions (i.e., $k_n[Pip] \gg k_0$), and as a consequence, $k_{obs} = k_n[Pip]_T$ (where k_n represents nucleophilic second-order rate constant for the reaction of Pip with S^-) because the concentration of protonated piperidine ($PipH^+$) is nearly zero under the present kinetic conditions.

The values of k_{obs} (Tables 1 and 2) were treated with eq 1, and the nonlinear least-squares calculated values of θ and $K^{X/S}$ are shown in Table 3. The standard deviations associated with the values of θ and $K^{X/S}$ as well as the k_{calcd1} values in Tables 1 and 2 reveal the extent of reliable observed data fit to eq 1.

The nonlinear increase in k_{obs} with the increase in [MX] in the presence of a constant concentration of CTABr micelles cannot be explained in terms of the ionic strength or specific inert ion effect for the reasons described elsewhere.[22] The most obvious cause for such observations is the transfer of micellized ionized phenyl salicylate (S_M^-) to the aqueous phase through ion-exchange X^-/S^-. It is perhaps noteworthy that the value of k_n is >10-fold larger in the aqueous phase than in the micellar pseudophase.[23,24] The possible ion-exchange processes in the present reacting system are X^-/S^-, X^-/Br^-, X^-/HO^-, Br^-/HO^-,

TABLE 3: Values of Empirical Constants, θ and $K^{X/S}$, Calculated from eq 1(with $[MX] = [MX]_{ef}^{S}$) for Different MX's in the Pure CTABr Micelles

MX[a]	[NaOH]/M	$10^3\ k_0/s^{-1}$	$[MX]_{op}{}^0/M$	$10^3\ \theta/s^{-1}$	$K^{X/S}/M^{-1}$	$K_{X/S}\ /M^{-1}$	$F_{X/S}$	$K_{X/S}{}^{n}\ /M^{-1}$	$K_X{}^{Br}$
A	0.030−0.065	2.67[b]	0.0	29.4 ± 3.9[c]	10.2 ± 2.7[c]	724[d]	0.90[e]	652[f]	26[g]
A	0.030−0.065	2.67	9.9×10^{-3}	23.4 ± 0.5	24.6 ± 1.4	1747	0.72	1258	50
B	0.020−0.100	2.79	0.0	27.7 ± 1.9	14.8 ± 2.7	636	0.85	541	22
B	0.020−0.100	2.79	4.9×10^{-3}	25.6 ± 0.9	20.7 ± 2.2	890	0.78	694	28

[a] A: MX = $3\text{-ClC}_6H_4CO_2Na$ and $[CTABr]_T = 0.01$ M. B: MX = $C_6H_5CH{=}CHCO_2Na$ and $[CTABr]_T = 0.006$ M. [b] $k_0 = k_{obs}$ at $[MX] = 0$. [c] Error limits are standard deviations. [d] $K_{X/S} = K^{X/S}\ (1 + K_S{}^0[CTABr]_T)$, where $K_S{}^0 = 7 \times 10^3\ M^{-1}$. [e] $F_{X/S} = \theta/(k_W^n[Pip]_T)$, where $k_W^n = 0.327\ M^{-1}\ s^{-1}$ and $[Pip]_T = 0.1$ M. [f] $K_{X/S}^n = F_{X/S}K_{X/S}$. [g] $K_X^{Br} = K_{X/S}^n/K_{Br/S}^n$, where $K_{Br/S}^n = 25\ M^{-1}$.

Br^-/S^-, and HO^-/S^-, but in view of explanations described elsewhere,[22] the most effective ion exchange that could significantly affect k_{obs} is X^-/S^- under the experimental conditions of the present study. However, ion-exchange processes X^-/HO^- and X^-/Br^- may indirectly affect the ion exchange X^-/S^- by reducing the effective concentration of MX ($= [MX]_{ef}^S$) required for it. The addition of X^- to the reaction mixture containing NaOH and CTABr micelles causes the most hydrophilic ion, HO^-, to move first from the cationic micellar surface to the aqueous pseudophase once such decreasing effects of added [MX] on $[HO_M^-]$ and $[Br_M^-]$ are saturated (this means that the values of $[HO_M^-]$ and $[Br_M^-]$ become independent of [MX] beyond the respective $[MX] = [MX]_{op}^{OH}$ and $[MX] = [MX]_{op}^{Br}$). This statement is partially supported by the study on the effect of counterion competition on the micellar growth horizon[7] at the respective $[MX]_{op}^{OH}$ and $[MX]_{op}^{Br}$ (where $[MX]_{op}^{OH}$ and $[MX]_{op}^{Br}$ represent the optimum values of [MX] at which a further increase in [MX] has no effect on $[HO_M^-]$ and $[Br_M^-]$, respectively). A further increase in [MX] causes the expulsion of S^- ions from cationic micelles to the aqueous phase. Thus,

$$[MX]_{ef}^{S} = [MX] - [MX]_{op}^{OH} - [MX]_{op}^{Br} \tag{2}$$

and eq 2 predicts that $[MX]_{ef}^S \approx [MX]$ when $[MX] \gg [MX]_{op}^{OH} + [MX]_{op}^{Br}$.

The values of k_{calcd1} are significantly larger than the corresponding values of k_{obs} at lower values of [MX] (<~0.020 M for MX = $3\text{-ClC}_6H_4CO_2Na$ and ≤0.020 M for MX = $C_6H_5CH{=}CHCO_2Na$), and the ratio k_{calcd1}/k_{obs} (= R1) increases with the decrease in [MX] (Tables 1 and 2). These observations show that the magnitudes of ($[MX]_{op}^{OH} + [MX]_{op}^{Br}$) ($= [MX]_{op}^0$) are no longer negligible compared with [MX] at [MX] ≤ 0.020 M. This effect caused the significantly larger values of k_{calcd}/k_{obs} at [MX] ≤ 0.020 M. The values of $[MX]_{op}^0$ were estimated as follows: The nonlinear least-squares technique was used to calculate θ, $K^{X/S}$, and the least-squares, $\Sigma\, d_i^2$ (where $d_i = k_{obs\,i} - k_{calcd\,i}$, with $k_{obs\,i}$ and $k_{calcd\,i}$ representing experimentally determined and least-squares calculated first-order rate constants at the ith value of $[MX]_{ef}{}^S$, respectively), were calculated from eq 1 (with the replacement of [MX] with $[MX]_{ef}^S = [MX] - [MX]_{op}^0$) at a given (presumed) value of $[MX]_{op}^0$. The magnitudes of the least-squares, $\Sigma\, d_i^2$, were determined at different given (presumed) values of $[MX]_{op}^0$, and the specific $[MX]_{op}^0$ value at which the $\Sigma\, d_i^2$ value turned out to be nearly minimum was considered the best kinetic $[MX]_{op}^0$ value. Such kinetic $[MX]_{op}^0$ values as well as calculated values of θ and $K^{X/S}$ (at these $[MX]_{op}{}^0$ values) for different MX are shown in Table 3. It is evident from Tables 1 and 2 that the values of k_{calcd2} and k_{calcd2}/k_{obs} (= R2) are more reliable as compared to the corresponding values of k_{calcd1} and R1, especially at [MX] < 0.020 M. Thus, the calculated values of θ and $K^{X/S}$ were more reliable when the data treatment with eq 1 was carried out by considering $[MX] = [MX]_{ef}^S$ at $[MX]_{op}^0 \neq 0$.

The values of k_{obs} at [MX] = 0 (Tables 1 and 2) are more than 10-fold smaller than k_{obs} (= $31.0 \times 10^{-3}\ s^{-1}$,23 $34.4 \times 10^{-3}\ s^{-1}$ 24) for the reaction of Pip with S^- at 0.1 M Pip and $[CTABr]_T = 0$. Such CTABr micellar inhibitory effects have been explained in terms of a pseudophase micellar (PM) model which, coupled with the observed rate law (rate = $k_{obs}[S^-]_T$), leads to eq 3,[23,24]

$$k_{obs} = \frac{k_W + k_M^{nm}K_NK_S[Pip]_T[D_n]}{1 + K_S[D_n]} \tag{3}$$

where $k_W = k_W^n[Pip]_T$ (with k_W^n representing nucleophilic second-order rate constant for the reaction of Pip with S^- in water phase, $[Pip]_T = [Pip_W] + [Pip_M]$ and subscripts W and M represent water phase and micellar pseudophase, respectively), $k_M^{nm} = k_M^n/V_M$ (with V_M and k_M^n representing the micellar molar volume, in M^{-1}, of the micellar-mediated reaction and nucleophilic second-order rate constant for the reaction of Pip_M with $S^-{}_M$, respectively),[1] K_N and K_S are the respective micellar binding constants of Pip and S^-, D_n represents micelles and $1 \gg K_N[D_n]$ under the experimental conditions of the present study.[23,24]

The occurrence of ion-exchange X^-/S^- shows that at a constant $[D_n]$ and $[S^-]_T$, the increase in $[X^-]$ decreases K_S through the following empirical relationship,[1,14,15,22,25]

$$K_S = K_S^0/(1 + K_{X/S}[MX]) \tag{4}$$

where $K_{X/S}$ is an empirical constant whose magnitude is the measure of the ability of X^- to expel S^- from the cationic micellar pseudophase to the water phase, and $K_S^0 = K_S$ at [MX] = 0. Equations 3 and 4 can lead to eq 1 with

$$k_0 = \frac{k_W + k_M^{nm}K_NK_S^0[Pip]_T[D_n]}{1 + K_S^0[D_n]} \tag{5}$$

where $k_W = k_{obs}$ (= $k_W^n[Pip]_T$) at $[D_n] = [MX] = 0$, $1 \gg K_N[D_n]$,

$$\theta = F_{X/S}k_W^{MX} \tag{6}$$

where $k_W^{MX} = k_{obs}$ (= $k_W^n[Pip]_T$) at a typical value of [MX], and $[D_n] = 0$, $1 \gg K_N[D_n]$, and

$$K^{X/S} = K_{X/S}/(1 + K_S^0[D_n]) \tag{7}$$

In eq 6, $F_{X/S}$ represents the fraction of micellized S^- transferred to the water phase by the limiting concentration of X^- (the limiting concentration of X^- means the specific total concentration of MX at which the expulsion of S^- from the micellar pseudophase to the water phase due to ion-exchange X^-/S^- ceased almost completely, and hence, an increase in [MX] beyond its limiting value has no effect on such ion-exchange; thus, the value of $F_{X/S}$ must be within ≤1.0 to >0).

The satisfactory fit of observed data to eq 1 at ≤0.20 M MX reveals that θ is almost independent of [MX], and hence, $k_W = k_W^{MX}$ under such conditions. The values of $F_{X/S}$, calculated from eq 6 with $k_W^{MX} = k_W^n[\mathrm{Pip}]_T = 32.7 \times 10^{-3}\ \mathrm{s}^{-1}$ at $[\mathrm{Pip}]_T = 0.1$ M,[23,24] are summarized in Table 3. These $F_{X/S}$ values reveal almost similar CTABr micellar penetration of $3\text{-ClC}_6H_4CO_2^-$ and $C_6H_5CH{=}CHCO_2^-$ relative to that of S^- (= $2\text{-}^-OC_6H_4CO_2\text{-}C_6H_5$). The average value of $F_{X/S}$ of 0.75 (Table 3) shows that the limiting concentrations of $3\text{-ClC}_6H_4CO_2^-$ and $C_6H_5CH{=}CHCO_2^-$ could cause ~75% expulsion of S^- ions from the micellar pseudophase to the water phase.[1] The values of $F_{X/S}$ are significantly larger than $F_{X/S}$ (= 0.50−0.60) for X = $3\text{-CH}_3C_6H_4CO_2^-$, $4\text{-CH}_3C_6H_4CO_2^-$, and S = S^-.[1] Ions X^- are expected to expel almost completely ions S^- from the cationic micellar pseudophase to the water phase if $F_{X/S} \approx 1$, which could be possible only if ionic micellar penetration of ions X^- is the same as or deeper than that of ions S^-. Thus, the value of $F_{X/S}$ (= θ/k_W^{MX}) may be considered as the useful and important information about the relative ionic micellar locations of counterionic solubilizates, such as ions X and S.

The values of the critical micelle concentration (cmc) of CTABr must be $<1 \times 10^{-4}$ M in the presence of 2×10^{-4} M $S^-$and MX,[26] and hence, $[D_n] \approx [\mathrm{CTABr}]_T$ under the present experimental conditions. The values of $K_{X/S}$ were calculated from eq 7 with $K_S^0 = 7 \times 10^3\ \mathrm{M}^{-1}$.[1,16] These values of $K_{X/S}$ for $3\text{-ClC}_6H_4CO_2^-$ and $C_6H_5CH{=}CHCO_2^-$ are listed in Table 3.

It has been concluded elsewhere[1,22] that the normalized $K_{X/S}^n$ (= $F_{X/S}K_{X/S}$) and $K_{Y/S}^n$ (= $F_{Y/S}K_{Y/S}$) values (where the values of $K_{X/S}$ and $K_{Y/S}$ have been calculated from eq 7 using two different inert salts, MX and MY) are empirically related to the usual ion exchange constant, K_X^Y, through the relationship $K_X^Y = K_{X/S}^n/K_{Y/S}^n = ([X_M][Y_W])/([X_W][Y_M])$. The values of $K_{X/S}^n$ (Table 3) and the reported[1] value of 25 M^{-1} for $K_{Br/S}^n$ give the values of K_X^{Br} for X = $3\text{-ClC}_6H_4CO_2^-$ and $C_6H_5CH{=}CHCO_2^-$ that are shown in Table 3. The relatively more reliable value of K_X^{Br} (= 50)[1] for X = $3\text{-ClC}_6H_4CO_2^-$ is more than 12-fold larger than K_X^{Br} for X = $2\text{-ClC}_6H_4CO_2^-$ ($K_X^{Br} = 4.0$),[1] X = $C_6H_5CO_2^-$ ($K_X^{Br} = 5.0 - 6.0$),[1] X = $2\text{-CH}_3C_6H_4CO_2^-$ ($K_X^{Br} = 4.0$),[1] and X = $4\text{-CH}_3OC_6H_4CO_2^-$ ($K_X^{Br} = 5.2$).[1]

It is perhaps noteworthy that the structure of a cationic micelle changes from spherical to disk to cylindrical/rod with the increase in the concentration of the micelle-forming surfactant.[27] This structural transition is enhanced in the presence of inert inorganic or organic salts.[28−31] Such a micellar structural transition might affect the value of $K_{X/S}$, and hence, the $K_{X/S}$ value may not be expected to remain constant in a wide range of [MX] or [ionic surfactant]$_T$. However, such a micellar structural change appeared to be kinetically insensitive to the reaction rates and $K_{X/S}$.[15] This fact is also evident from the successful application of the PIE model to the kinetic data on bimolecular semi-ionic reactions in the presence of ionic micelles,[8,32] vesicles,[33] reversed micelles,[34] and microemulsions.[35]

Viscoelastic surfactant solutions have been of great interest because of their analogy to "living" polymers[36] and use as drag reducers in turbulent flow.[31] However, several aspects of the origin of viscoelasticity have remained unknown.[37] Aqueous solutions of cetyltrimethylammonium (CTA) with substituted benzoate (Bz) counterions, 3-[31] or 4-ClBz[31,38,39] or 3,4-diClBz[38] exhibit viscoelasticity. But the aqueous solutions of CTA with counterions 2-ClBz[31,38,39] or 2,6-diClBz[7,38] do not show detectable viscoelasticity. Viscoelastic behavior of surfactant solutions is generally determined by physical techniques that involve drag reduction, shear, and extensional rheometry and cryogenic transmission electron microscopy (cryo-TEM). A more than 12-fold larger value of K_X^{Br} for X = 3-ClBz than that for 2-ClBz may be attributed to the characteristic structural difference between the two counterions, which causes aqueous CTABr solutions to become viscoelastic and nonviscoelastic in the presence of 3-ClBz and 2-ClBz, respectively. Thus, the relative values of K_X^{Br} for 2-, 3-, and 4-XBz may predict the presence and absence of viscoelasticity in CTA solutions containing these substituted benzoate ions. The kinetic validity of eq 2 is attributed to the presence of more than one independent ion-exchange process in the present reaction conditions.

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