

Determination of an Ion Exchange Constant by the Use of a Kinetic Probe: A New Semiempirical Kinetic Approach Involving the Effects of 3-F- and 4-F-Substituted Benzoates on the Rate of Piperidinolysis of Anionic Phenyl Salicylate in Aqueous Cationic Micelles

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Pseudo-first-order rate constants (k_{obs}) for the nucleophilic substitution reaction of piperidine (Pip) with ionized phenyl salicylate (PS^-), obtained at a constant $[\text{Pip}]_{\text{T}} (= 0.1 \text{ M})$, $[\text{PS}^-]_{\text{T}} (= 2 \times 10^{-4} \text{ M})$, $[\text{CTABr}]_{\text{T}}$ (cetyltrimethylammonium bromide), $\leq 0.06 \text{ M}$ NaOH, and a varying concentration of MX ($= 3\text{-FC}_6\text{H}_4\text{CO}_2\text{Na}$, 3-FBzNa and 4- $\text{FC}_6\text{H}_4\text{CO}_2\text{Na}$, 4-FBzNa), follow the kinetic relationship $k_{\text{obs}} = (k_0 + \theta K^{\text{X/S}}[\text{MX}]) / (1 + K^{\text{X/S}}[\text{MX}])$ which is derived by the use of the pseudophase micellar (PM) model coupled with an empirical equation. The empirical equation explains the effects of $[\text{MX}]$ on CTABr micellar binding constant (K_{S}) of PS^- that occur through X^-/PS^- ion exchange. Empirical constants θ and $K^{\text{X/S}}$ give the parameters $F_{\text{X/S}}$ and $K_{\text{X/S}}$, respectively. The magnitude of $F_{\text{X/S}}$ gives the measure of the fraction of micellized PS^- transferred to the aqueous phase by the limiting concentration of X^- through X^-/PS^- ion exchange. The values of $F_{\text{X/S}}$ and $K_{\text{X/S}}$ have been used to determine the usual thermodynamic ion exchange constant (K_{X}^{Y}) for ion exchange process X^-/Y^- on the CTABr micellar surface. The values of K_{X}^{Br} (where $\text{Br} = \text{Y}$) have been calculated for $\text{X} = 3\text{-FBz}^-$ and 4-FBz^- . The mean values of K_{X}^{Br} are 12.8 ± 0.9 and 13.4 ± 0.6 for $\text{X}^- = 3\text{-FBz}^-$ and 4-FBz^- , respectively. Nearly 3-fold-larger values of K_{X}^{Br} for $\text{X} = 3\text{-FBz}^-$ and 4-FBz^- than those for $\text{X} = \text{Bz}^-$, 2- ClBz^- , 2- CH_3Bz^- , and the 2,6-dichlorobenzoate ion (2,6- Cl_2Bz^-) are attributed to the presence of wormlike micelles in the presence of $> 50 \text{ mM}$ 3-FBz $^-$ and 4-FBz $^-$ in the $[\text{CTABr}]_{\text{T}}$ range of 5–15 mM. Rheological properties such as shear thinning behavior of plots of shear viscosity versus the shear rate at a constant $[3\text{-FBz}^-]$ or $[4\text{-FBz}^-]$ as well as shear viscosity (at a constant shear rate) maxima as a function of the concentrations of 3-FBz $^-$ and 4-FBz $^-$ support the conclusion, derived from the values of K_{X}^{Br} , for the probable presence of wormlike/viscoelastic micellar solutions under the conditions of the present study.

I. Introduction

Quaternary ammonium surfactants with certain structurally typical counterions have been shown to form viscoelastic surfactant solutions¹ that have various potential commercial uses² including effective drag reducers in turbulent flow.³ Moderately hydrophobic organic anions binding to cationic micelles is believed to be important in stabilizing viscoelastic micellar structures.⁴ Similarly, a recent study concludes that rodlike micelle formation occurs because of an increase in headgroup-counterion association and dehydration on the micellar surface.⁵ These studies predict that (a) the cationic micellar binding constant (K_{X}) of viscoelastic counterion X should be larger than that (K_{Y}) of nonviscoelastic counterion Y with comparable molecular structural features and (b) the ion exchange constant for X, $K_{\text{X}}^{\text{Br}} (= K_{\text{X}}/K_{\text{Br}}$ where K_{Br} is the cationic micellar binding constant of counterion Br^-), should be larger than that for Y, $K_{\text{Y}}^{\text{Br}} (= K_{\text{Y}}/K_{\text{Br}})$. Practically, it is not easy to determine

accurately either K_{X} or K_{X}^{Br} because the magnitudes of K_{X} and K_{X}^{Br} are very technique-dependent.^{6,7} For instance, the reported values of K_{X}^{Cl} for $\text{X} = 2,6\text{-Cl}_2\text{Bz}^-$ on the CTACl micellar surface are 1.3 ± 0.1 , 16.2 ± 5.5 , and 16.8 ± 1.0 as determined by the use of respective ion-selective electrode measurements, ¹H NMR measurements, and a flotation technique.⁷ Similarly, the values of $K_{\text{Br}}^{\text{OH}}$, determined by the use of variety of physicochemical techniques, vary over the range of 3–34.⁸

A reliable correlation between the viscoelastic behavior of surfactant solutions and the values of K_{X}^{Br} for various counterions (X) is expected to be achieved if the values of K_{X}^{Br} have been determined by the use of the same technique. The values of K_{X}^{Br} have been determined for different X counterions by the use of a new technique⁹ involving an empirical kinetic approach that consists of the classical pseudophase micellar (PM) model coupled with an empirical equation (eq 1).^{8b,10}

$$K_{\text{S}} = \frac{K_{\text{S}}^{\circ}}{1 + K_{\text{X/S}}[\text{MX}]} \quad (1)$$

In eq 1, K_{S} and K_{S}° represent cationic micellar binding constants of reactive counterion S^- in the presence and absence of inert

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(1) (a) Ahmed, T.; Aramaki, K. *J. Colloid Interface Sci.* **2008**, *327*, 180–185. (b) Sharma, S. C.; Shrestha, R. G.; Shrestha, L. K.; Aramaki, K. *J. Phys. Chem. B* **2008**, *112*, 10520–10527.

(2) Attarzadeh, H. *J. Res. Med. Sci.* **2006**, *11*, 111–112.

(3) (a) Zakin, L.; Zhang, Y.; Ge, W. In *Giant Micelles: Properties and Applications*; Zana, R., Kaler, E. W., Eds.; Surfactant Science Series; CRC Press: Boca Raton, FL, 2007; Vol. 140, Chapter 16, pp 473–492. (b) White, A. *Nature* **1967**, *214*, 585–586.

(c) Roze, G. D.; Foster, K. L. *J. Non-Newtonian Fluid Mech.* **1989**, *31*, 59–85.

(d) Elson, T. P.; Garside, J. *J. Non-Newtonian Fluid Mech.* **1983**, *12*, 121–133.

(e) Ohlendorf, D.; Interthal, W.; Hoffmann, H. *Rheol. Acta* **1986**, *25*, 468–486.

(4) Rehage, H.; Hoffmann, H. *Rheol. Acta* **1982**, *21*, 561–563.

(5) Geng, Y.; Romsted, L. S.; Menger, F. *J. Am. Chem. Soc.* **2006**, *128*, 492–501.

(6) (a) Khan, M. N.; Naoliya, J.; Dahiru, M. *J. Chem. Res.* **1988**, 116–117. (S) Khan, M. N.; Naoliya, J.; Dahiru, M. *J. Chem. Res.* **1988**, 1168–1176. (M) (b) Khan, M. N. *J. Mol. Catal. A: Chem.* **1995**, *102*, 93–101. (c) Khan, M. N. *J. Phys. Org. Chem.* **1996**, *9*, 295–300.

(7) Magid, L. J.; Han, Z.; Warr, G. G.; Cassidy, M. A.; Butler, P. D.; Hamilton, W. A. *J. Phys. Chem. B* **1997**, *101*, 7919–7927.

(8) (a) Romsted, L. S. In *Surfactant in Solutions*; Mittal, K. L., Lindmann, B., Eds.; Plenum: New York, 1984; Vol. 2, pp 1015–1068. (b) Khan, M. N.; Ariffin, Z. *J. Chem. Soc., Perkin Trans 2* **2000**, 2503–2510.

(9) Khan, M. N. *Micellar Catalysis*; Surfactant Science Series; CRC/Taylor & Francis: Boca Raton, FL, 2007; Vol. 133, Chapter 3.

(10) (a) Khan, M. N. *J. Org. Chem.* **1997**, *62*, 3190–3193. (b) Khan, M. N.; Ariffin, Z.; Lasidek, M. N.; Hanifah, M. A. M.; Alex, G. *Langmuir* **1997**, *13*, 3959–3964. (c) Khan, M. N.; Ismail, E. *J. Mol. Liq.* **2003**, *107*, 277–287.

counterion X^- , respectively. The symbol $K_{X/S}$ represents an empirical constant whose magnitude is the measure of the ability of X^- to expel S^- from the cationic micellar pseudophase into the aqueous phase through the occurrence of ion exchange X^-/S^- on the cationic micellar surface. It has been concluded elsewhere^{8b,11} that the values of $K_{X/S}$ and $K_{Br/S}$ (for ion exchange Br^-/S^-) are related to the usual thermodynamic ion exchange constant, $K_X^{Br} (= K_X/K_{Br})$. The values of K_X^{Br} , obtained from this new approach/technique, for a few inorganic and organic anions (X) are listed elsewhere.^{8b,11} The value of K_X^{Br} with $MX = 3\text{-ClC}_6\text{H}_4\text{CO}_2\text{Na}$ (an inert salt with an anion acting as a viscoelastic counterion of a CTABr micelle¹²) was found to be more than 12-fold larger than that with $MX = 2\text{-ClC}_6\text{H}_4\text{CO}_2\text{Na}$ (an inert salt with an anion acting as a non-viscoelastic counterion of CTACl¹²).¹³ Thus, the values of K_X^{Br} for $X =$ viscoelastic as well as nonviscoelastic counterions would have predictive power for a counterion X to be either viscoelastic or nonviscoelastic. Furthermore, the kinetic approach of the present study is rather new and provides a quantitative interpretation of the effects of the inert salt concentration on the rate constants for cationic micellar-mediated organic reactions. The present study was aimed at using this new technique to determine the values of K_X^{Br} for $MX = 3\text{-FC}_6\text{H}_4\text{CO}_2\text{Na}$ (3-FBzNa) and $4\text{-FC}_6\text{H}_4\text{CO}_2\text{Na}$ (4-FBzNa) at different total concentrations of CTABr. The results and their probable explanation(s) are described in this article.

II. Experimental Section

Reagent-grade chemicals such as phenyl salicylate (PSL), cetyltrimethylammonium bromide (CTABr), piperidine (Pip), and 3-fluorobenzoic acid (3-FBzH) as well as 4-fluorobenzoic acid (4-FBzH) were commercial products of the highest available purity. However, these acids were recrystallized before use. Stock solutions (0.01 M) of PSL were prepared in acetonitrile.

Kinetic Measurements. The rate of the nucleophilic reaction of Pip with ionized phenyl salicylate (PS^-) was measured spectrophotometrically at 35 °C by monitoring the disappearance of reactant (PS^-) at 350 nm as a function of reaction time (t) in the presence of 2×10^{-4} M PS^- , 0.1 M Pip, and > 0.03 M NaOH and desired concentrations of CTABr and 3-FBzNa or 4-FBzNa. The details of the kinetic procedure and product characterization study were the same as described elsewhere.¹⁴

All of the kinetic runs were carried out under pseudo-first-order kinetic conditions ($[Pip]_T/[PS^-]_T = 500$ where $[]_T$ represents the total concentration). The observed kinetic data (A_{ob} vs t where A_{ob} represents the absorbance value at any reaction time t) were found to fit to eq 2 for a reaction period equivalent to ~ 6 to ~ 8 half-lives of the reaction.

$$A_{ob} = [R_0]\delta_{ap} \exp(-k_{obs}t) + A_{\infty} \quad (2)$$

In eq 2, $[R_0]$ is the initial concentration of PSL, δ_{ap} is the apparent molar absorptivity of the reaction mixture, k_{obs} is the pseudo-first-order rate constant, and $A_{\infty} = A_{ob}$ at $t = \infty$. The nonlinear least-squares technique was used to calculate k_{obs} , δ_{ap} , and A_{∞} from eq 2, and the observed data fit to eq 2 was found to be satisfactory in terms of the percent residual errors ($RE = 100 \times (A_{ob,i} - A_{cald,i})/A_{ob,i}$ where $A_{ob,i}$ and $A_{cald,i}$ represent observed and least-squares calculated values of absorbance at the i th reaction time (t_i)) as well as standard deviations associated with calculated parameters k_{obs} , δ_{ap} , and A_{∞} .

Rheological Measurements. Samples with total volume of 25 mL for each sample in the rheological measurements were prepared by mixing constant amounts of sodium hydroxide,

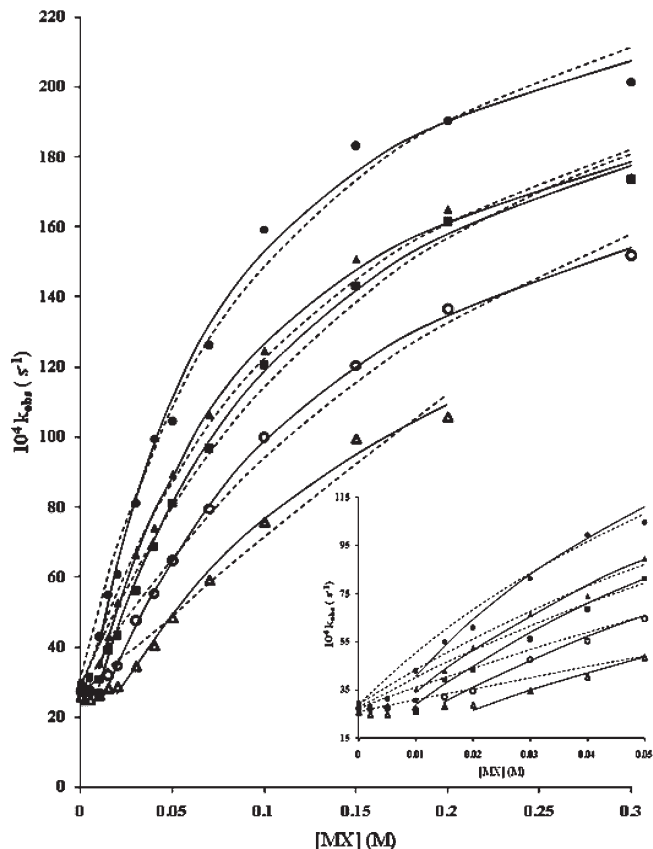


Figure 1. Plots showing the dependence of k_{obs} upon $[MX]$ ($MX = 3\text{-FBzNa}$) for the piperidinolysis of PS^- at 2.0×10^{-4} M PS^- , 0.1 M Pip, ≤ 0.06 to > 0.03 M NaOH, 35 °C, and $[CTABr]_T/mM = 5$ (●), 6 (▲), 7 (■), 10 (○), and 15 (△). The dashed lines are drawn through the calculated data points from eq 3 with kinetic parameters (k_0 , θ , and $K^{X/S}$) listed in Table 2 at $[MX]_0^{op} = 0.0$. The solid lines are drawn through the calculated data points from eq 3 with kinetic parameters (k_0 , θ , and $K^{X/S}$) listed in Table 2 at $[MX]_0^{op}/mM = 5.9$ (●), 7.3 (▲), 9.4 (■), 13.1 (○), and 18.8 (△).

piperidine, cetyltrimethylammonium bromide, phenyl salicylate, and $[MX]$ ($= 3\text{-FBzNa}$ or 4-FBzNa). The concentrations of 3-FBzNa and 4-FBzNa were varied within the range of 0.03–0.20 M. The sample solutions were left in a water bath at a constant temperature of 35 °C for at least 10 min. The rheological measurements were carried out using the Brookfield R/S+ rheometer, and the temperature was controlled by an external temperature controller. However, because of the air-conditioned room, the temperature varied slightly from 35 °C, which is expected to cause a negligible error. A coaxial double-gap cylinder (CC-DG) was used with the required volume of sample for every run as 16 mL. For every repeat measurement, a new sample was used. By fixing the shear rate ($\dot{\gamma}$) range at $1\text{--}15\text{ s}^{-1}$ in 2400 s and $1\text{--}100\text{ s}^{-1}$ in 800 s for all runs and $1\text{--}1000\text{ s}^{-1}$ in 8000 s for certain runs, the dependent shear stress (τ) and shear viscosity (η) detected by the machine were recorded after each 80 s.

III. Results

Effects of $[3\text{-FC}_6\text{H}_4\text{CO}_2\text{Na}]$ ($[3\text{-FBzNa}]$) and $[4\text{-FC}_6\text{H}_4\text{CO}_2\text{Na}]$ ($[4\text{-FBzNa}]$) on k_{obs} for the Reaction of Pip with PS^- at a Constant $[CTABr]_T$ and 35 °C. More than 10 kinetic runs were carried out within the $[MX]$ (where $MX = 3\text{-FBzNa}$ or 4-FBzNa) range of 0.0 to ≤ 0.30 M at constant values of $[CTABr]_T$, 0.1 M Pip, and 2×10^{-4} M PSL. The values of $[NaOH]$ were varied from 0.030 to 0.060 M. Similar observations were obtained at different $[CTABr]_T$ within the range of 0.005–0.015 M. The values of k_{obs} at different $[CTABr]_T$ are shown in Figures 1 and 2

(11) Khan, M. N.; Ismail, E. *J. Mol. Liq.* **2007**, *136*, 54–63.

(12) Lu., B.; Li, X.; Scriven, L. E.; Davis, H. T.; Talmon, Y.; Zakin, J. L. *Langmuir* **1998**, *14*, 8–16.

(13) Khan, M. N.; Ismail, E. *J. Phys. Chem. A* **2009**, *113*, 6484–6488 and references cited therein

(14) Khan, M. N. *J. Chem. Soc., Perkin Trans 2* **1989**, 199–208.

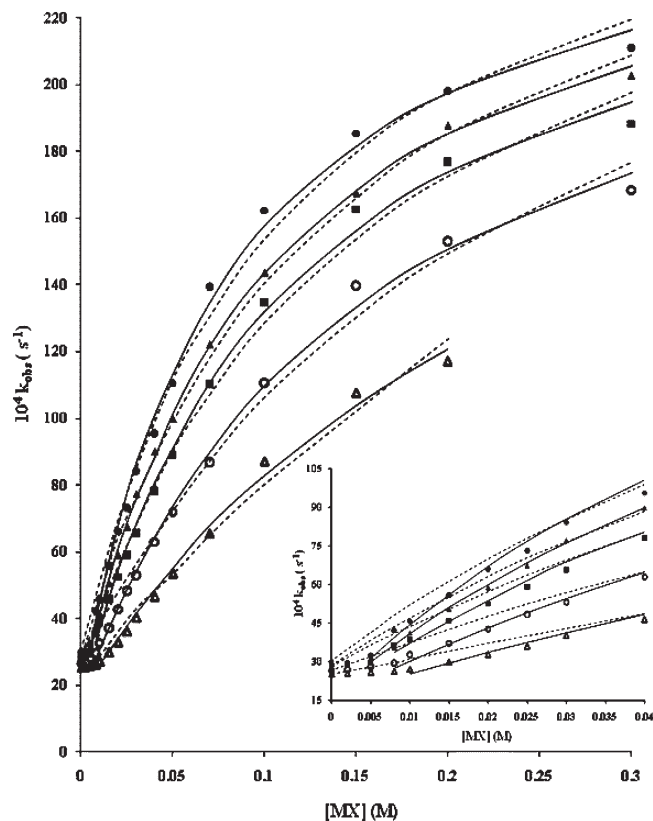


Figure 2. Plots showing the dependence of k_{obs} upon $[\text{MX}]$ ($\text{MX} = 4\text{-FBzNa}$) for the piperidinolysis of PS^- at 2.0×10^{-4} M PS^- , 0.1 M Pip, ≤ 0.06 to >0.03 M NaOH, 35°C , and $[\text{CTABr}]_{\text{T}}/\text{mM} = 5$ (●), 6 (▲), 7 (■), 10 (○), and 15 (△). The dashed lines are drawn through the calculated data points from eq 3 with kinetic parameters (k_0 , θ , and $K^{\text{X/S}}$) listed in Table 2 at $[\text{MX}]_0^{\text{op}} = 0.0$. The solid lines are drawn through the calculated data points from eq 3 with kinetic parameters (k_0 , θ , and $K^{\text{X/S}}$) listed in Table 2 at $[\text{MX}]_0^{\text{op}}/\text{mM} = 4.5$ (●), 4.7 (▲), 5.2 (■), 7.3 (○), and 9.8 (△).

as well as in Tables I–IV in the Supporting Information (SI). The values of δ_{ap} turned out to be almost independent of $[\text{MX}]$, and the mean values of δ_{ap} ($=\delta_{\text{ap}}^{\text{av}}$), at different $[\text{CTABr}]_{\text{T}}$, are shown in Tables I–IV (SI). The calculated values of A_∞ revealed a definite but mild absorption due to $3\text{-FC}_6\text{H}_4\text{CO}_2^-$ and $4\text{-FC}_6\text{H}_4\text{CO}_2^-$ at 350 nm ($\delta = \sim 10\text{--}14$ M $^{-1}$ cm $^{-1}$ with δ representing the molar absorptivity of $3\text{-FC}_6\text{H}_4\text{CO}_2^-$ or $4\text{-FC}_6\text{H}_4\text{CO}_2^-$). The values of δ remained unchanged within the $[\text{CTABr}]_{\text{T}}$ range of $0.005\text{--}0.015$ M.

Effects of [3-FBzNa] and [4-FBzNa] on k_{obs} for the Reaction of Pip with PS^- in the Absence of CTABr at 35°C . To determine the probable effect of inert salts 3-FBzNa and 4-FBzNa on k_{obs} in the absence of micelles, a few kinetic runs were carried out at 0.1 M Pip, 2×10^{-4} M PSL, and within the [3-FBzNa] or [4-FBzNa] range of 0.0 to ≤ 0.3 M. The concentration of NaOH was varied within the range of 0.030 to ≤ 0.060 M. The calculated values of kinetic parameters k_{obs} , δ_{ap} , and A_∞ at different [3-FBzNa] or [4-FBzNa] are summarized in Table 1.

Rheological Properties. The rheological behavior of CTABr/3-FBzNa and CTABr/4-FBzNa were examined at 34.3 ± 0.5 and $34.2 \pm 0.3^\circ\text{C}$ under steady shear. The micellar solutions contained constant concentrations of all of the additives (i.e., 2×10^{-4} M PS^- , 0.1 M Pip, 15 mM CTABr, constant $[\text{NaOH}]$ (≥ 0.03 to ≤ 0.05 M), and $[\text{MX}]$ (≥ 20 to 200 mM for $\text{MX} = 3\text{-FBzNa}$ as well as $\text{MX} = 4\text{-FBzNa}$). The log–log plots of shear viscosity (η) versus shear rate ($\dot{\gamma}$) at different values of $[\text{MX}]$ are shown in

Figures 3 and 4 for $\text{MX} = 3\text{-FBzNa}$ and 4-FBzNa , respectively. Figures 3 and 4 represent the shear thinning behavior that is a typical characteristic of wormlike micelles.^{15–19} The values of η at $\dot{\gamma} = 1.5$ s $^{-1}$ (i.e., $\eta_{1.5\dot{\gamma}}$) and constant $[\text{MX}]$ were obtained by the interpolation of the plots of η versus $\dot{\gamma}$ (Figures 3 and 4). The values of $\eta_{1.5\dot{\gamma}}$ were calculated from the empirical relationship $\eta = \eta_0 e^{-\alpha\dot{\gamma}}$ (where η_0 and α are considered to be empirical constants) by the use of observed data points (i.e., η vs $\dot{\gamma}$) at the lower $\dot{\gamma}$ values (< 10 s $^{-1}$). The calculated values of $\eta_{1.5\dot{\gamma}}$ at different $[\text{MX}]$ are shown graphically in Figure 5 for $\text{MX} = 3\text{-FBzNa}$ and $\text{MX} = 4\text{-FBzNa}$. Although the derivation of the value of η at a specific shear rate by the interpolation process using a small segment of the plot of η versus $\dot{\gamma}$ is considered to be reliable, the values of η at a shear rate of 100 s $^{-1}$ (i.e., $\eta_{100\dot{\gamma}}$) were directly obtained from the observed data of η versus $\dot{\gamma}$ at different $[\text{MX}]$. The values of $\eta_{100\dot{\gamma}}$ are shown graphically in Figure 6 for $\text{MX} = 3\text{-FBzNa}$ and $\text{MX} = 4\text{-FBzNa}$. Figures 5 and 6 reveal that the nature of the plots remained essentially unchanged with the change in the shear rate from 1.5 to 100 s $^{-1}$. Viscosity maxima as a function of salt and surfactant concentration are ubiquitous in the literature for wormlike micellar systems.^{16,19,20}

IV. Discussion

The details of the following observations have been described elsewhere.^{13,21} (a) The products of the reaction of Pip with PSL are *N*-piperidinylsalicylamide (P_1) and phenol (P_2). (b) The PSL exists in nearly 100% ionized form (PS^-) under the experimental conditions of entire kinetic runs of the present study (i.e., $[\text{PSL}]_{\text{T}} = [\text{PS}^-]_{\text{T}}$). (c) The rates of the uncatalyzed and hydroxide ion-catalyzed hydrolysis of PS^- are negligible compared with the rate of piperidinolysis of PS^- under the present experimental conditions. (d) The concentration of protonated piperidine ($[\text{PipH}^+]$) is negligible compared with $[\text{Pip}]$ in the presence of $0.03\text{--}0.060$ M NaOH and $0.0\text{--}0.015$ M CTABr, and thus $[\text{Pip}]_{\text{T}} \approx [\text{Pip}]$. This fact is also evident from the k_{obs} values listed in Table 1. (e) The values of k_{obs} at $[\text{MX}] = 0$ (Figures 1 and 2 as well as Tables I–IV, SI) are more than 10-fold smaller than k_{obs} for the reaction of Pip with PS^- at 0.1 M Pip and $[\text{CTABr}]_{\text{T}} = 0$ (Table 1).^{22,23} The mechanistic details of these observations have been described elsewhere.^{10b,22} In view of these observations, a brief reaction scheme for the cleavage of PS^- , under the present experimental conditions, may be represented by Scheme 1, where k_n represents the nucleophilic second-order rate constant for the reaction of Pip with PS^- at $[\text{Pip}] \approx [\text{Pip}]_{\text{T}}$ and consequently $k_{\text{obs}} = k_n[\text{Pip}]_{\text{T}}$.

A critical look at the observed data, represented by Figure 1 as well as Tables I and II, reveals that the values of k_{obs} are almost independent of [3-FBzNa] within the ranges of $0.0\text{--}0.005$ M at

(15) Lu, T.; Huang, J.; Li, Z.; Jia, S.; Fu, H. *J. Phys. Chem. B* **2008**, *112*, 2909–2914.

(16) Raghavan, S. R.; Kaler, E. W. *Langmuir* **2001**, *17*, 300–306 and references therein.

(17) Lin, Y.; Han, X.; Huang, J.; Fu, H.; Yu, C. *J. Colloid Interface Sci.* **2009**, *330*, 449–455.

(18) Shrestha, R. G.; Aramaki, K. *J. Nepal Chem. Soc.* **2008/2009**, *23*, 65–73.

(19) Clausen, T. M.; Vinson, P. K.; Minter, J. R.; Davis, H. T.; Talmon, Y. K.; Miller, W. G. *J. Phys. Chem.* **1992**, *96*, 474–484.

(20) (a) Shubert, B. A.; Wagner, N. J.; Kaler, E. W. *Langmuir* **2004**, *20*, 3564–3573. (b) Ali, A. A.; Makhloufi, R. *Colloid Polym. Sci.* **1999**, *277*, 270–275. (c) Hoffmann, H. In *Structure and Flow in Surfactant Solutions*; Herb, C. A., Prudhomme, R., Eds.; ACS Symposium Series 578; American Chemical Society: Washington, DC, 1994; pp 2–31. (d) Magid, L. J. *J. Phys. Chem.* **1998**, *102*, 4064–4074. (e) Aswal, V. K.; Goyal, P. S.; Thiyagarajan, P. *J. Phys. Chem. B* **1998**, *102*, 2469–2473. (f) Ali, A. A.; Makhloufi, R. *Phys. Rev. E* **1997**, *56*, 4474–4478.

(21) Khan, M. N.; Ismail, E. *Indian J. Chem.* **2009**, *48A*, 781–787 and references cited therein.

(22) Khan, M. N.; Ariffin, Z.; Ismail, E.; Ali, S. F. M. *J. Org. Chem.* **2000**, *65*, 1331–1334.

(23) Khan, M. N.; Ismail, E. *Prog. React. Kinet. Mech.* **2006**, *31*, 205–219.

Table 1. Kinetic Parameters k_{obs} , δ_{ob} , and A_{∞} Calculated from Equation ² for the Reaction of Pip with PS⁻ in the Presence of MX and the Absence of CTABr^a

[MX] = 10 ² [MX] M	3-FC ₆ H ₄ CO ₂ Na			4-FC ₆ H ₄ CO ₂ Na		
	10 ⁴ k_{obs} s ⁻¹	10 ⁻¹ δ_{ob} M ⁻¹ cm ⁻¹	10 ² A_{∞}	10 ⁴ k_{obs} s ⁻¹	10 ⁻¹ δ_{ob} M ⁻¹ cm ⁻¹	10 ² A_{∞}
0.0	340 ± 1.0 ^b	671 ± 1	1.8 ± 0	340 ± 0.4 ^b	705 ± 1	1.9 ± 0.1
0.2	338 ± 1.8	682 ± 2	1.6 ± 0.1	329 ± 0.3	695 ± 2	1.9 ± 0.3
0.5	342 ± 1.7	671 ± 2	1.6 ± 0.1	305 ± 0.9	707 ± 3	2.2 ± 0.2
0.8	324 ± 1.7	678 ± 5	1.1 ± 0.3	334 ± 0.8	708 ± 2	2.1 ± 0.1
1.0	345 ± 1.6	679 ± 2	1.9 ± 0.1	332 ± 0.7	717 ± 7	2.5 ± 0.3
1.5	332 ± 1.5	675 ± 2	1.6 ± 0.1	310 ± 1.0	697 ± 3	4.5 ± 0.8
2.0	333 ± 1.8	671 ± 2	1.7 ± 0.1	313 ± 0.8	701 ± 2	5.2 ± 0.3
2.5	317 ± 1.2	666 ± 1	2.1 ± 0.1	318 ± 0.3	711 ± 2	5.9 ± 0.8
3.0	329 ± 1.3	669 ± 1	1.9 ± 0.1	340 ± 0.9	699 ± 7	6.7 ± 0.9
4.0	322 ± 1.2	671 ± 1	1.7 ± 0.1	327 ± 1.0	682 ± 9	8.9 ± 0.3
5.0	321 ± 1.3	675 ± 1	2.0 ± 0.1	333 ± 0.1	712 ± 1	11 ± 0.1
7.0	305 ± 1.1	675 ± 1	1.9 ± 0.1	323 ± 0.8	702 ± 1	16 ± 0.3
10	304 ± 1.6	679 ± 2	2.1 ± 0.1	314 ± 0.5	702 ± 1	23 ± 0.1
15	278 ± 1.2	687 ± 1	2.6 ± 0.1	313 ± 1.4	711 ± 1	27 ± 0.1
20	340 ± 1.0	671 ± 1	1.8 ± 0.0	294 ± 0.4	704 ± 1	35 ± 0.1
30	338 ± 1.8	682 ± 2	1.6 ± 0.1	285 ± 0.9	706 ± 2	43 ± 0.2

^a[Phenyl salicylate]₀ = 2 × 10⁻⁴ M, 35 °C, λ = 350 nm and [piperidine]_T = 0.1 M, where []_T represents the total concentration and the aqueous reaction mixture for each kinetic run contained 2% v/v CH₃CN. The required amounts of 3- or 4-FC₆H₄CO₂Na ([MX]) were generated in the reaction mixture by using the stock solution (wM) of 3- or 4-FC₆H₄CO₂H prepared in (w + 0.05) M aqueous NaOH. The stock solution of NaOH was used to produce a fixed known concentration (0.03 M) of NaOH in the reaction mixture for each kinetic run. Thus, the maximum concentration of added NaOH was 0.06 M. ^bError limits are standard deviations.

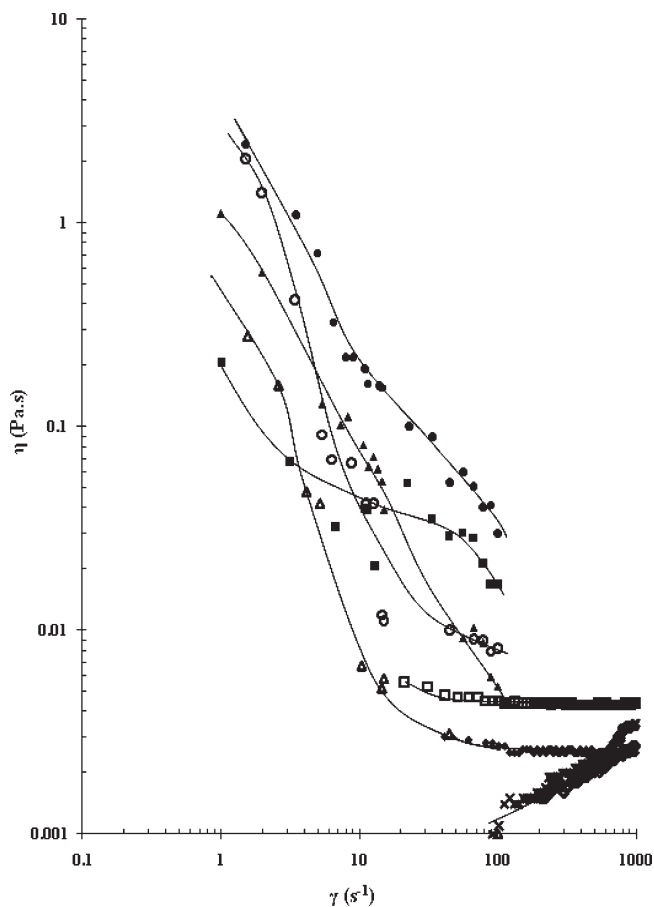


Figure 3. Plot showing the dependence of shear viscosity (η) upon shear rate (γ) for samples where [PSL] = 2.0 × 10⁻⁴ M, [NaOH] = 0.03 M, [Pip] = 0.1 M, [CTABr] = 0.015 M, and [3-FBzNa] = 0.0 (◇), 0.20 (×), 0.03 (◆), 0.05 (■), 0.06 (Δ), 0.07 (●), 0.08 (○), 0.10 (▲), and 0.15 M (□).

0.005, 0.006, and 0.007 M CTABr; 0.0–0.01 at 0.010 M CTABr; and 0.0–0.015 at 0.015 M CTABr. A further increase in [3-FBzNa] at 0.010 M 3-FBzNa and 0.005–0.007 M CTABr, 0.015 M 3-FBzNa and 0.010 M CTABr, and 0.020 M 3-FBzNa and

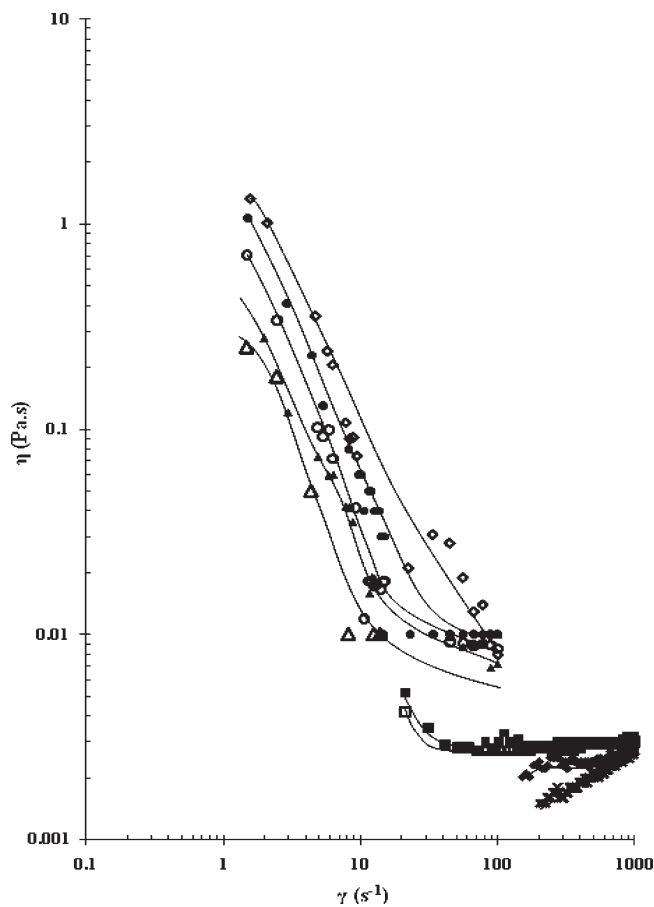


Figure 4. Plot showing the dependence of shear viscosity (η) upon shear rate (γ) for samples where [PSL] = 2.0 × 10⁻⁴ M, [NaOH] = 0.03 M, [Pip] = 0.1 M, [CTABr] = 0.015 M, and [4-FBzNa] = 0.0 (×), 0.02 (□), 0.04 (■), 0.06 (Δ), 0.07 (◇), 0.08 (●), 0.10 (○), 0.15 (▲), and 0.20 M (◆).

0.015 M CTABr has caused a nonlinear increase in k_{obs} with the increase in [3-FBzNa]. Similarly, Figures 2 as well as Tables III and IV reveal that the values of k_{obs} are independent of [4-FBzNa] within its ranges of 0.0–0.002 M at 0.005 and 0.006 M CTABr,

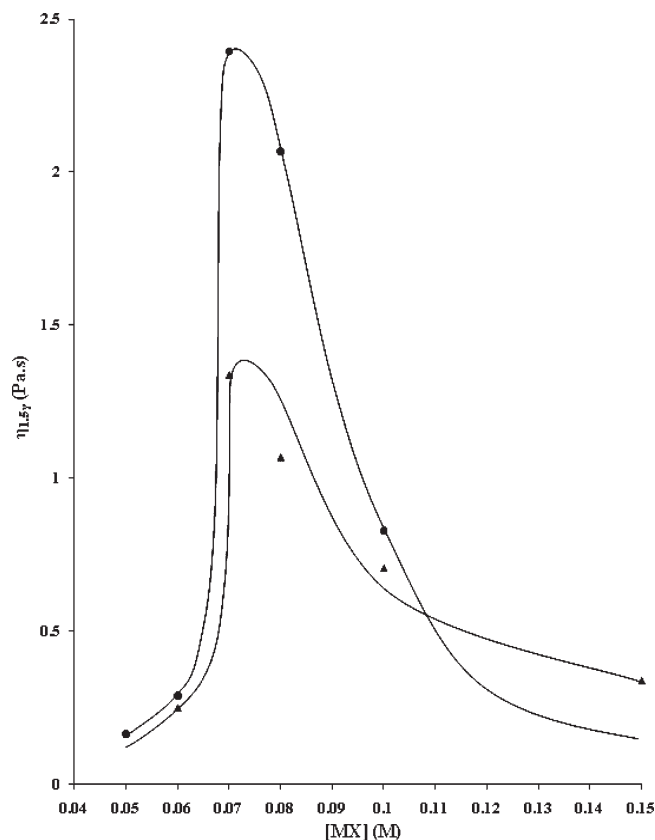


Figure 5. Plot of shear viscosity (η) at $\gamma = 1.5 \text{ s}^{-1}$ vs [MX] ([MX] = [3-FBzNa] (●) and [4-FBzNa] (▲)) at 0.015 M CTABr, 2.0×10^{-4} PS⁻, 0.03 M NaOH, 0.1 M Pip, and $\sim 35^\circ\text{C}$.

0.0–0.005 M at 0.007 and 0.010 M CTABr, and 0.0–0.008 M at 0.015 M CTABr. As the values of [4-FBzNa] increase from 0.005 M at 0.005 and 0.006 M CTABr, from 0.008 M at 0.007 and 0.010 M CTABr, and from 0.010 M at 0.015 M CTABr, the values of k_{obs} also increase nonlinearly. These observations cannot be attributed to merely an inert salt effect because the values of k_{obs} are almost independent of [3-FBzNa] and [4-FBzNa] within its range of 0.0–0.3 M (Table I). Similar observations have been obtained for 3-ClC₆H₄CO₂Na (a viscoelastic salt additive for CTABr micelles¹²).¹³ As described earlier in the text, the rate of piperidinolysis of PS⁻ is >10-fold larger in the aqueous phase than in the CTABr micellar pseudophase. Thus, the most obvious source of the nonlinear increase in k_{obs} with the increase in [MX] (Figures 1 and 2 as well as Tables I–IV) is the transfer of micellized PSL (PS⁻_M) to the aqueous phase through the X⁻/PS⁻ ion exchange. All possible ion exchange processes, in the present reaction system, are X⁻/PS⁻, X⁻/Br⁻, X⁻/HO⁻, HO⁻/Br⁻, HO⁻/PS⁻, and Br⁻/PS⁻. But in view of the explanations described elsewhere,^{9,11} the most effective ion exchange that could significantly affect k_{obs} is X⁻/PS⁻ under the experimental conditions of this study.

We attempted to fit the observed data (k_{obs} vs [MX]), shown graphically in Figures 1 and 2 as well as in Tables I–IV, to an empirical equation (eq 3)

$$k_{\text{obs}} = \frac{k_0 + \theta K^{X/S} [\text{MX}]}{1 + K^{X/S} [\text{MX}]} \quad (3)$$

where θ and $K^{X/S}$ are empirical constants, $k_0 = k_{\text{obs}}$ at [MX] = 0, and [micelles] $\neq 0$. Equation 3 has been found to explain satisfactorily the effects of various inert inorganic and organic salts on pseudo-first-order rate constants (k_{obs}) for alkaline hydrolysis

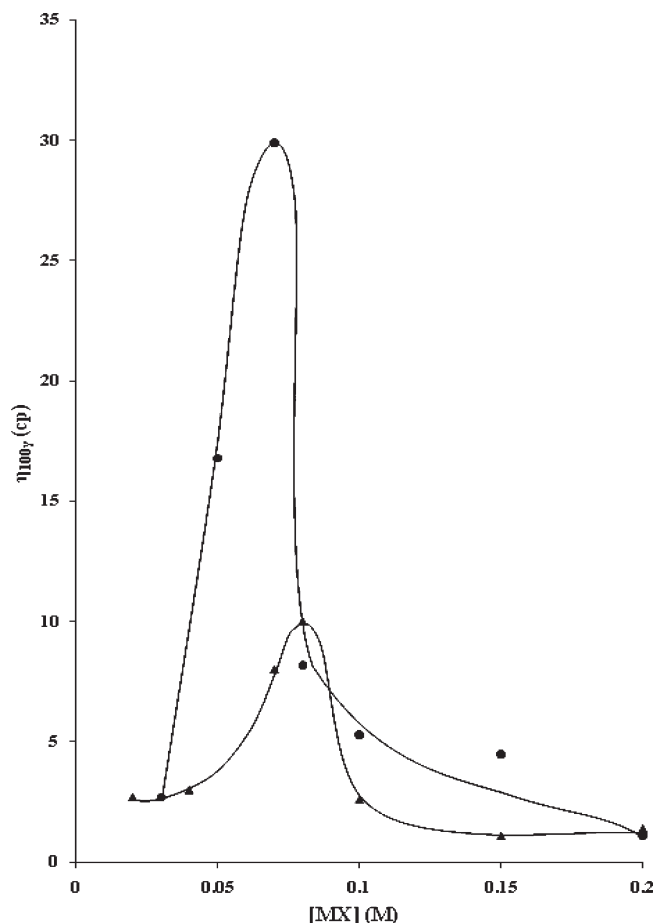
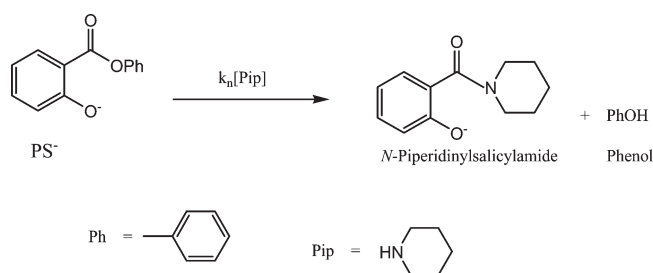


Figure 6. Plot of shear viscosity (η) at $\gamma = 100 \text{ s}^{-1}$ vs [MX] ([MX] = [3-FBzNa] (●) and [4-FBzNa] (▲)) at 0.015 M CTABr, 2.0×10^{-4} PS⁻, 0.03 M NaOH, 0.1 M Pip, and $\sim 35^\circ\text{C}$.

Scheme 1



and the aminolysis of phthalimide, phenyl salicylate, phenyl benzoate, and *N*-benzylphthalimide obtained at a constant concentration of cationic micelles, amine nucleophiles (such as piperidine, Pip), and NaOH.^{9,11,24} The nonlinear least-squares technique was used to calculate unknown parameters θ and $K^{X/S}$ as well as least-squares $\sum d_i^2$, (where $d_i = k_{\text{obs}i} - k_{\text{calc}i}$, with $k_{\text{obs}i}$ and $k_{\text{calc}i}$ representing respective experimentally determined and least-squares-calculated rate constants at the i th value of [MX]) from eq 3 by the use of an experimentally determined value of k_0 at [MX] = 0. These results are summarized in Table 2. The extent of reliability of the observed data fit to eq 3 is evident from the standard deviations associated with least-squares-calculated parameters θ and $K^{X/S}$, as shown in Table 2 and in Figures 1

(24) Khan, M. N.; Cheong, M. Y.; Ariffin, A. *AIP Conf. Proc.* **2009**, *1136*, 380–384.

Table 2. Values of Empirical Constants θ and $K^{X/S}$ Calculated from Equation 3 (Where $[MX] = [MX]_S^{ef}$ with Zero and Nonzero $[MX]_0^{op}$ Values) for Different MX in CTABr Micelles^a

$[CTABr]_T$ mM ^b	$10^4 k_o s^{-1c}$	$[MX]_0^{op}$ mM	$10^4 \theta s^{-1}$	$K^{X/S} M^{-1}$	$K_{X/S} M^{-1}$	$F_{X/S}$	$K_{X/S}^n M^{-1}$	K_X^{Br}	$10^8 \sum d^2$
MX = 3-FC ₆ H ₄ CO ₂ Na									
5.0	29.5	5.9	254 ± 8 ^d	12.8 ± 1.1 ^d	461 ^e	0.78 ^f	358 ^g	14.3 ^h	219.5
5.0	29.5	0	275 ± 14	9.37 ± 1.15	337	0.84	284	11.3	579.3
6.0	28.8	7.3	229 ± 6	10.1 ± 0.6	434	0.70	304	12.2	74.68
6.0	28.8	0	256 ± 16	6.92 ± 0.95	298	0.78	233	9.32	385.9
7.0	27.9	9.4	241 ± 7	8.18 ± 0.53	409	0.74	301	12.1	63.09
7.0	27.9	0	283 ± 24	5.09 ± 0.87	255	0.87	220	8.81	460.4
10.0	27.4	13.1	219 ± 6	6.76 ± 0.38	480	0.67	321	12.9	24.98
10.0	27.4	0	284 ± 37	3.47 ± 0.80	246	0.87	214	8.56	411.9
15.0	26.0	18.8	209 ± 23	4.59 ± 0.91	487	0.64	311	12.4	40.91
15.0	26.0	0	897 ± 1280	0.54 ± 0.86	57.2	2.74	157	6.28	255.2
MX = 4-FC ₆ H ₄ CO ₂ Na									
5.0	29.9	4.5	269 ± 6	11.9 ± 0.7	428	0.82	352	14.1	154.6
5.0	29.9	0	289 ± 12	9.15 ± 0.92	329	0.88	291	11.6	507.6
6.0	29.1	4.7	266 ± 3	9.76 ± 0.26	420	0.81	341	13.7	26.80
6.0	29.1	0	289 ± 11	7.44 ± 0.64	320	0.88	283	11.3	285.2
7.0	28.5	5.2	263 ± 9	8.28 ± 0.63	414	0.80	333	13.3	155.6
7.0	28.5	0	288 ± 17	6.25 ± 0.76	313	0.88	275	11.0	433.4
10.0	26.6	7.3	253 ± 10	6.23 ± 0.53	442	0.77	342	13.7	109.2
10.0	26.6	0	294 ± 24	4.23 ± 0.64	300	0.90	270	10.8	362.8
15.0	25.2	9.8	254 ± 27	3.76 ± 0.65	399	0.78	310	12.4	60.57
15.0	25.2	0	472 ± 191	1.39 ± 0.71	147	1.44	213	8.51	224.8

^a $[MX] = 3\text{-FBzNa}$ and 4-FBzNa . ^b Total concentration of CTABr. ^c $k_o = k_{obs}$ at $[MX] = 0$. ^d Error limits are standard deviations. ^e $K_{X/S} = K^{X/S} (1 + K_S^o [CTABr]_T)$ where $K_S^o = 7000 M^{-1}$. ^f $F_{X/S} = \theta/k_w$ where $k_w = k_{obs}$ at $[CTABr]_T = 0$, $[Pip]_T = 0.1 M$, and the value of k_w under such conditions is $32.7 \times 10^{-3} s^{-1}$ at $35^\circ C$. ^g $K_{X/S}^n = F_{X/S} K_{X/S}$. ^h $K_X^{Br} = K_{X/S}^n / K_{Br/S}^n$, where $K_{Br/S}^n = 25 M^{-1}$.

and 2 where dashed lines are drawn through the least-squares-calculated rate constants obtained from eq 3, with the calculated parameters listed in Table 2.

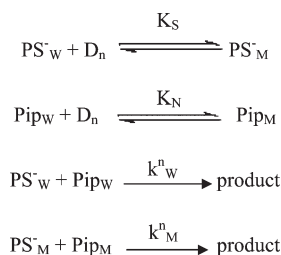
Significant negative deviations of the observed data points from the corresponding calculated data points with the decrease in $[MX]$ at its extreme lower values as well as higher values of $[CTABr]_T$ may be explained as follows. The addition of X^- to the reaction mixture containing CTABr micelles causes the most hydrophilic counterions HO^- to move first from the cationic micellar pseudophase to the bulk aqueous phase. Once such decreasing effects of $[MX]$ upon $[HO^-]_M$ and $[Br^-]_M$ at the respective $[MX]_{OH}^{op}$ and $[MX]_{Br}^{op}$ (where $[MX]_{OH}^{op}$ and $[MX]_{Br}^{op}$ represent the optimum/critical values of $[MX]$ at which a further increase in $[MX]$ has no effect on ion exchange X^-/HO^- and X^-/Br^- , respectively) are attained, a further increase in $[MX]$ at $[MX] = [MX]_S^{ef}$ (where $[MX]_S^{ef}$ is the effective value of $[MX]$ affecting the X^-/S^- ion exchange) causes the expulsion of S^- ions from cationic micelles into the aqueous phase. Thus,

$$[MX]_S^{ef} = [MX] - ([MX]_{OH}^{op} + [MX]_{Br}^{op}) \quad (4)$$

and eq 4 predicts that $[MX]_S^{ef} \approx [MX]$ when $[MX] \gg [MX]_0^{op} (= [MX]_{OH}^{op} + [MBr]_{Br}^{op})$. The increasing negative deviations of the observed data points from dashed lines in Figures 1 and 2 with decreasing values of $[MX]$ at the lower end of the $[MX]$ range show that the magnitudes of $[MX]_0^{op}$ are no longer negligible compared to $[MX]$ at $[MX] \leq [MX]_S^{ef}$.

The values of $[MX]_0^{op}$ were estimated as follows. The nonlinear least-squares technique was used to calculate unknown parameters θ and $K^{X/S}$ as well as the least-squares $\sum d^2$ from eq 3 (with the replacement of $[MX]$ by $[MX]_S^{ef} = [MX] - [MX]_0^{op}$) at a given (presumed) value of $[MX]_0^{op}$. The values of $\sum d^2$ were determined at different given (presumed) values of $[MX]_0^{op}$, and the typical $[MX]_0^{op}$ value, at which the value of $\sum d^2$ turned out to be minimum or nearly a minimum, was considered to be the most reliable kinetic value of $[MX]_0^{op}$. Such $[MX]_0^{op}$ values as well as calculated

Scheme 2



values of θ and $K^{X/S}$ (at these $[MX]_0^{op}$ values) at different $[CTABr]_T$ for MX = 3-FBz and 4-FBz are shown in Table 2. It is evident from the plots (solid lines) of Figures 1 and 2 as well as Tables I–IV that the values of $\sum d^2$ and $RE_2 (= 100 \times (k_{obs} - k_{calcd2})/k_{obs})$, where k_{calcd2} represents the least-squares-calculated rate constant obtained from eq 3 with $[MX] = [MX]_S^{ef}$ and parameters θ and $K^{X/S}$ listed in Table 2) are more reliable compared to the corresponding values of $\sum d^2$, k_{calcd1} , and RE_1 especially at lower and higher values of $[MX]$ and $[CTABr]_T$, respectively. Thus, the calculated values of θ and $K^{X/S}$ are more reliable when the data treatment with eq 3 was carried out by considering $[MX] = [MX]_S^{ef}$ at $[MX]_0^{op} \neq 0$.

The effects of CTABr micelles on the rate of reaction of Pip with PS^- in the absence and presence of an inert salt have been explained in terms of the pseudophase micellar (PM) model of micelles (Scheme 2).^{10b,25,26}

In Scheme 2, D_n represents a CTABr micelle and K_S and K_N are the CTABr micellar binding constants of PS^- and Pip, respectively. Symbols k^n_W and k^n_M represent nucleophilic second-order rate constants for the reactions of Pip with PS^- in the respective aqueous phase and micellar pseudophase. Subscripts W and M stand for water and the micellar pseudophase, respectively. The observed rate law ($\text{rate} = k_{obs}[S]_T$ where $[S]_T = [PS^-_W] + [PS^-_M]$)

(25) Khan, M. N.; Yusoff, M. R. *J. Phys. Org. Chem.* **2001**, *14*, 74–80.

(26) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698–4703.

at nearly zero concentration of nonionized phenyl salicylate and Scheme 2 can lead to eq 5

$$k_{\text{obs}} = \frac{(k_{\text{w}}^{\text{n}} + k_{\text{M}}^{\text{mr}} K_{\text{N}} K_{\text{S}} [D_{\text{n}}]) [\text{Pip}]_{\text{T}}}{(1 + K_{\text{S}} [D_{\text{n}}]) (1 + K_{\text{N}} [D_{\text{n}}])} \quad (5)$$

where $k_{\text{M}}^{\text{mr}} = k_{\text{M}}^{\text{n}} / V_{\text{M}}$ (V_{M} is the micellar molar volume⁹), $[D_{\text{n}}] = [\text{CTABr}]_{\text{T}} - \text{cmc}$ (cmc is the critical micelle concentration), and $[\text{Pip}]_{\text{T}} = [\text{Pip}_{\text{w}}] + [\text{Pip}_{\text{M}}]$ under the typical reaction conditions where the total concentration of protonated piperidine ($[\text{PipH}^+]_{\text{T}}$) is approximately zero. The reported value of the cmc is $< 1 \times 10^{-4}$ M in the presence of 2×10^{-4} M PS^- and in the absence of any inert salt.^{10b,27} The presence of an inert salt is expected to decrease the cmc, and thus under the present experimental conditions, the value of the cmc must be significantly lower than 1×10^{-4} M. It is therefore apparent that $[D_{\text{n}}] \approx [\text{CTABr}]_{\text{T}}$ under the experimental conditions of the present study.

The reported value of K_{N} (for N = Pip) for a tetradecyltrimethylammonium bromide (TTABr) micelle is $\sim 0.3 \text{ M}^{-1}$.^{28,29} The value of K_{N} for a CTABr micelle should not be significantly different from the K_{N} for TTABr.³⁰ The value of K_{N} would not be expected to change appreciably in the presence of varying concentrations of MX because piperidine is a nonionic, highly hydrophilic molecule. The value of the cetyltrimethylammonium chloride (CTACl) micellar binding constant of nonionic benzimidazole, a relatively much more hydrophobic molecule compared with Pip, increased from 43 to 68 M^{-1} with the increase in $[\text{NaCl}]$ from 0.0 to 1.0 at 0.01 M CTACl.³¹ Thus, it is apparent that $1 \gg K_{\text{N}} [D_{\text{n}}]$ at $[\text{CTABr}]_{\text{T}} \leq 0.02$ M, and under such conditions, eq 5 can be reduced to eq 6, where $[D_{\text{n}}] \approx [\text{CTABr}]_{\text{T}}$.

$$k_{\text{obs}} = \frac{(k_{\text{w}}^{\text{n}} + k_{\text{M}}^{\text{mr}} K_{\text{N}} K_{\text{S}} [D_{\text{n}}]) [\text{Pip}]_{\text{T}}}{1 + K_{\text{S}} [D_{\text{n}}]} \quad (6)$$

As concluded earlier in the text, the occurrence of the X^- / PS^- ion exchange (where $\text{X}^- = 3\text{-FBz}^-$ and 4-FBz^-) is the most effective cause of the nonlinear increase in k_{obs} with the increase of $[\text{MX}]$ at constant $[\text{CTABr}]_{\text{T}}$ and $[\text{PS}^-]_{\text{T}}$. The effect of $[\text{MX}]$ on the distribution of PS^- between the aqueous phase and the micellar pseudophase (due to X^- / PS^- ion exchange) is expected to be represented by eq 1. If this conclusion is correct, then eqs 1 and 6 can lead to eq 3 with

$$k_{\text{o}} = \frac{(k_{\text{w}}^{\text{n}} + k_{\text{M}}^{\text{mr}} K_{\text{N}} K_{\text{S}}^{\text{o}} [D_{\text{n}}]) [\text{Pip}]_{\text{T}}}{1 + K_{\text{S}}^{\text{o}} [D_{\text{n}}]} \quad (7)$$

where $k_{\text{w}}^{\text{n}} [\text{Pip}]_{\text{T}} = k_{\text{obs}}$ at $[D_{\text{n}}] = [\text{MX}] = 0$ and K_{N} is assumed to be independent of $[\text{MX}]$

$$\theta = \frac{F_{\text{X/S}} k_{\text{w}}^{\text{MX}} [\text{Pip}]_{\text{T}}}{1 + K_{\text{N}} [D_{\text{n}}]} \quad (8)$$

where $k_{\text{w}}^{\text{MX}} [\text{Pip}]_{\text{T}} = k_{\text{obs}}$ at a typical value of $[\text{MX}]$ and $[D_{\text{n}}] = 0$ and $F_{\text{X/S}} (= \theta / (k_{\text{w}}^{\text{MX}} [\text{Pip}]_{\text{T}}))$ under the condition $1 \gg K_{\text{N}} [D_{\text{n}}]$ are empirical constants whose magnitude should vary from ≤ 1.0 to $>$ and

$$K^{\text{X/S}} = \frac{K_{\text{X/S}}}{1 + K_{\text{S}}^{\text{o}} [D_{\text{n}}]} \quad (9)$$

Perhaps it is noteworthy that in a strict mathematical sense $\theta = k_{\text{w}}^{\text{MX}} [\text{Pip}]_{\text{T}}$ provided that $1 \gg K_{\text{N}} [D_{\text{n}}]$, but in view of the

physical reality, this relationship is true only if the limiting concentration of X^- can cause 100% transfer of S^- micellized counterions (i.e., PS^-_{M}) from the micellar pseudophase to the aqueous phase. The limiting concentration of a salt MX is defined as the optimum/critical value of $[\text{MX}]$ at which the values of k_{obs} become independent of $[\text{MX}]$ (i.e., at the optimum value of $[\text{MX}]$, $K^{\text{X/S}} [\text{MX}] \gg 1$ and $\theta K^{\text{X/S}} [\text{MX}] \gg k_{\text{o}}$ in eq 3). However, a moderately hydrophilic counterion (such as HO^- or Br^-) cannot be expected to expel a moderately hydrophobic counterion (such as PS^-) completely from the micellar pseudophase to the aqueous phase even if the values of $[\text{HO}^-]_{\text{T}} / [\text{PS}^-]_{\text{T}}$ and $[\text{Br}^-]_{\text{T}} / [\text{PS}^-]_{\text{T}}$ are very large. Thus, the value of empirical constant $F_{\text{X/S}}$ in eq 7 must be within the range of ≤ 1.0 to > 0 . The value of $F_{\text{X/S}}$ should measure the fraction of the micellized counterions PS^-_{M} transferred to the aqueous phase by the optimum concentration of MX through ion exchange X^- / PS^- provided that $1 \gg K_{\text{N}} [D_{\text{n}}]$. In another words, the value of $F_{\text{X/S}}$, obtained under the condition $1 \gg K_{\text{N}} [D_{\text{n}}]$, may be considered to be the measure of the micellar penetration of X^- relative to that of PS^- where the hydrophobicity of PS^- is larger than that of X^- .

It is evident from eq 8 that the values of θ should be independent of $[D_{\text{n}}]$ or $[\text{CTABr}]_{\text{T}}$ because $1 \gg K_{\text{N}} [D_{\text{n}}]$ under the experimental conditions of the present study. The calculated values of θ (Table 2) are almost independent of $[\text{CTABr}]_{\text{T}}$ for MX (= 3-FBzNa and 4-FBzNa).

It has been almost certain by direct/indirect experiments of a diverse nature that the micellar environment of micellized solubilizes of different hydrophobicity and steric requirements is not homogeneous in terms of water concentration, polarity, relative permittivity, and perhaps molecular fluidity. The respective hydrophobicity and hydrophilicity of the micellar environment increases and decrease continuously from the exterior regions of the headgroups to the interior of the core of a micelle. In view of the energy requirements, a solubilize molecule is expected to acquire a micellar location where various hydrophilic, electrostatic (in the case of an ionic micelle only), hydrophobic and steric interactions between the solubilize molecule and the micellar environment give the most stable state. Thus, the value of $F_{\text{X/S}}$ may be considered to be a measure of the cationic micellar penetration of X^- relative to that of S^- (i.e., PS^-), where the hydrophobicity of S^- is larger than that of X^- (= 3-FBz⁻ and 4-FBz⁻).

A satisfactory fit of the observed data to eq 3 with $[\text{MX}]$ replaced by $([\text{MX}] - [\text{MX}]_{\text{o}}^{\text{op}})$ reveals that θ is kinetically independent of $[\text{MX}]$ and hence $k_{\text{w}}^{\text{MX}} = k_{\text{w}}^{\text{n}}$ under such conditions. The values of $F_{\text{X/S}}$ were calculated from eq 8 where $1 \gg K_{\text{N}} [D_{\text{n}}]$, $k_{\text{w}}^{\text{n}} = 32.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$,¹³ and $[\text{Pip}]_{\text{T}} = 0.1$ M, and these results, at different $[\text{CTABr}]_{\text{T}}$, are summarized in Table 2. The average values of $F_{\text{X/S}}$, as shown in Table 3, reveal that CTABr micellar penetration of 3-FBz⁻ ($F_{\text{X/S}} = 0.70$) is only slightly ($\sim 12\%$) lower than that of 4-FBz⁻ ($F_{\text{X/S}} = 0.80$). These observations are supported by the study on investigations of monofluoro-substituted benzoates at the TTA⁺ (tetradecyltrimethylammonium ion) micellar interface where ¹H NMR measurements suggest both 3-FBz⁻ and 4-FBz⁻ localize in the Stern layer and are intercalated among the micellar $(\text{CH}_3)_3\text{N}^+$ headgroups.³² The values of $F_{\text{X/S}}$ for X = 3-FBz⁻ and 4-FBz⁻ are larger than those for X = 3-CH₃Bz⁻ and 4-CH₃Bz⁻ by respective 0.2 and 0.3 units.³³ Considerably low depths of CTABr micellar penetration of 3-CH₃Bz⁻ and 4-CH₃Bz⁻ compared with those of 3-FBz⁻ and 4-FBz⁻ may be attributed to the hydrophobicity and steric requirements of micellized 3-CH₃Bz⁻/4-CH₃Bz⁻ and

(27) Khan, M. N.; Arifin, Z. *J. Colloid Interface Sci.* **1996**, *180*, 9–14.

(28) Iglesias, E.; Leis, J. R.; Pefia, M. E. *Langmuir* **1994**, *10*, 662–669.

(29) Fernandez, A.; Iglesias, E.; Garcia-Rio, L.; Leis, J. R. *Langmuir* **1995**, *11*, 1917–1924.

(30) Bravo, C.; Herves, P.; Leis, J. R.; Pena, M. E. *J. Colloid Interface Sci.* **1992**, *153*, 529–536.

(31) Romsted, L. S. *J. Phys. Chem.* **1985**, *89*, 5113–5118.

(32) Vermathen, M.; Stiles, P.; Bachofer, S. J.; Simonis, U. *Langmuir* **2002**, *18*, 1030–1042.

(33) Khan, M. N.; Kun, S. Y. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1325–1330.

Table 3. Average Values of $F_{X/S}$ and K_X^{Br} for Different MX in the Presence of CTABr Micelles^a

X	[MX] _o ^{op}	10 ² $F_{X/S}$	K_X^{Br}	cmc ₂
3-FC ₆ H ₄ CO ₂ ⁻ (3-FBz ⁻)	nonzero	71 ± 6 ^b	12.8 ± 0.9 ^b	~12.9 mM ^c
	zero	122 ± 85	8.85 ± 1.80	
4-FC ₆ H ₄ CO ₂ ⁻ (4-FBz ⁻)	nonzero	80 ± 2	13.4 ± 0.6	~13.8 mM ^c
	zero	100 ± 25	10.6 ± 0.4	
C ₆ H ₅ CO ₂ ⁻ (Bz ⁻)	zero	70	5.8 ^d	200 mM CTACl + ≥ 50 mM BzK ^e
	nonzero	72	4.0 ^f	
2-ClBz ⁻			50 ^g	
3-ClBz ⁻			5.0 ^h	
2,6-Cl ₂ Bz ⁻			4.9 ⁱ	
2-CH ₃ Bz ⁻	nonzero	43	17.7 ⁱ	
3-CH ₃ Bz ⁻	nonzero	50	16.7 ⁱ	
4-CH ₃ Bz ⁻	nonzero	48		

^a Unless otherwise noted, cationic micelles are CTABr. ^b Error limits are standard deviations. ^c Reference 32; cmc₂ values are for TTAX micelles. ^d Reference 34. ^e Reference 20b. ^f Reference 25. ^g Reference 13. ^h Reference 7. ⁱ The values of K_X^{Br} were recalculated from the observed data published as ref 11.

3-FBz⁻/4-FBz⁻ where the hydrophobicity and molecular size of substituent CH₃ is significantly larger than those of F. The value of $F_{X/S}$ (= 0.70) for X = 3-FBz⁻ is comparable with those for X = 3-ClBz⁻ ($F_{X/S}$ = 0.72)¹³ and X = H ($F_{X/S}$ = 0.70).³⁴ This similarity may be explained qualitatively in terms of polarity, size and polarizability of these counterions (3-FBz⁻ and 3-ClBz⁻) where the effects of polarity/steric requirements and size/polarizability of counterions on their ionic micellar penetration are expected to oppose each other.

The values of $K_{X/S}$ were calculated from eq 9 with K_S^0 = 7.0 × 10³ M^{-19,35} and $[D_n] \approx [\text{CTABr}]_T$ (as concluded earlier in the text). These calculated values of $K_{X/S}$ at different $[\text{CTABr}]_T$ for 3-FBz⁻ and 4-FBz⁻ are summarized in Table 2. The values of $K_{X/S}$ are almost independent of $[\text{CTABr}]_T$ within its range 5–15 mM (Table 2).

The empirical definition of $K_{X/S}$ implies that the value of $K_{X/S}$ is proportional to the value of K_X (ionic micellar binding constant of counterion X) and inversely proportional to the value of K_S (ionic micellar binding constant of another counterions S). Thus, $K_{X/S} = \Omega_S K_X / K_S$ where Ω_S represents proportionality constant. The magnitude of Ω_S is assumed to depend only upon the molecular characteristics of counterion S (the counterion which is expelled by another counterion X from the ionic micellar pseudophase to the aqueous phase at a constant $[S]_T$ and [ionic micelle] and it is independent of the molecular characteristics of counterion X (the counterion which expels the counterion S from the ionic micellar pseudophase to the aqueous phase at a constant $[S]_T$, [ionic micelle] and varying $[X]_T$). Similarly, for another counterion Y (i.e., for another ion exchange Y⁻/S⁻), $K_{Y/S} = \Omega_S K_Y / K_S$. The relationships: $K_{X/S} = \Omega_S K_X / K_S$ and $K_{Y/S} = \Omega_S K_Y / K_S$ lead to eq 10

$$\frac{K_{X/S}}{K_{Y/S}} = \frac{K_X}{K_Y} \quad (10)$$

where K_X/K_Y ($\equiv K_X^Y$) represents usual ion exchange constant for ion exchange process X⁻/Y⁻ occurring at cationic micellar surface, i.e. $K_X^Y = ([X_M][Y_W])/([X_W][Y_M])$.

It is, perhaps, noteworthy that the use of eq 10 is correct only if $K_{X/S}$ and $K_{Y/S}$ have been determined experimentally from eq 1 where optimum concentration of counterions X or Y has caused > 90% expulsion of counterions S from micellar pseudophase to aqueous phase. If the values of $K_{X/S}$ and $K_{Y/S}$ have been determined experimentally by the use of eq 3, then these values

should be normalized, i.e. $K_{X/S}^n = F_{X/S} K_{X/S}$ and $K_{Y/S}^n = F_{Y/S} K_{Y/S}$ where $F_{X/S} = \theta/k^n w^{\text{MX}} [\text{Pip}]_T$ and $F_{Y/S} = \theta/k^n w^{\text{MY}}$ with $1 \gg K_N [D_n]$ (where $N = \text{Pip}$). Thus, under such conditions, the ratio $K_{X/S}/K_{Y/S}$ should be replaced by the ratio $K_{X/S}^n/K_{Y/S}^n$ in eq 10.

Because the values of $K_{X/S}$, listed in Table 2, were derived by the use of eq 3, these $K_{X/S}$ values have been normalized (i.e., $K_{X/S}^n = F_{X/S} K_{X/S}$) so that $K_{X/S}^n$ values could be used to calculate ion exchange constants (K_X^Y) from eq 10. The calculated values of $K_{X/S}^n$ (= $F_{X/S} K_{X/S}$, Table 2) and the reported value of 25 M⁻¹ for $K_{\text{Br}/S}^n$ with S = PS⁻ give the values of K_X^{Br} (by the use of eq 10 with Y = Br) for different X species. These calculated values of K_X^{Br} for X = 3-FBz⁻ and 4-FBz⁻ at different $[\text{CTABr}]_T$ are also shown in Table 2. The average values of K_X^{Br} (obtained at different $[\text{CTABr}]_T$ for a typical MX) for X = 3-FBz⁻ and 4-FBz⁻ are summarized in Table 3.

The cationic micellar growth has been found to cause an increase in the degree of counterion binding, β (= 1 - α).³⁶ However, the reported values of α are 0.16, 0.15, and 0.16 for respective counterions 2-FBz⁻, 3-FBz⁻, and 4-FBz⁻ of the TTA⁺ micellar surface. Similar observations were also obtained with TTA⁺/2-CH₃Bz⁻, TTA⁺/3-CH₃Bz⁻, and TTA⁺/4-CH₃Bz⁻ micellar systems.³² Although these values are nearly the same, various physical techniques such as conductometric and ¹H NMR measurements revealed the first cmc (cmc₁) and second cmc (cmc₂) for TTA⁺/3-FBz, TTA⁺/3-CH₃Bz⁻, TTA⁺/4-FBz⁻, and TTA⁺/4-CH₃Bz⁻ micelles whereas cmc₂ was not detected for either TTA⁺/2-FBz⁻ or TTA⁺/2-CH₃Bz⁻.³² These observations show that, perhaps, the values of α and β are not the true indicators of micellar structural transitions where the counterions are moderately hydrophobic.

The values of K_X^{Br} for X = Bz⁻, 2-ClBz⁻, 3-CH₃Bz⁻, and the 2,6-dichlorobenzoate ion (2,6-ClBz⁻) are not appreciably different from each other (Table 3), and these counterions of CTA⁺ micelles are known to produce only spherical micelles at ≤ 20 mM CTABr.^{7,12,37,38} However, the values of K_X^{Br} for X = 3-ClBz⁻ and 4-ClBz⁻ are nearly 10-fold larger than those for X = 2-ClBz⁻ and 2,6-dichlorobenzoate. Counterions 3-ClBz⁻, 4-ClBz⁻, and 3,5-dichlorobenzoate result in viscoelastic surfactant solutions when mixed with CTABr at ≤ 20 mM CTABr and ≤ 0.3 M inert salt for these counterions.^{7,12,37,38} The value of K_X^{Br} for X = 2-FBz⁻ could not be determined because of experimental complications caused by the moderate reactivity of 2-FBz⁻ toward

(36) (a) Abdel-Rahem, R. *Adv. Colloid Interface Sci.* **2008**, *141*, 24–36 and references cited therein. (b) Rodriguez, A.; Graciani, M. M.; Bitterman, K.; Carmona, A. J.; Moya, M. L. *J. Colloid Interface Sci.* **2007**, *313*, 542–550.

(37) Gravholt, S. *J. Colloid Interface Sci.* **1976**, *57*, 575–577.

(38) Rao, U. R. K.; Manohar, C.; Valaulikar, B. S.; Iyer, R. M. *J. Phys. Chem.* **1987**, *91*, 3286–3291.

(34) Khan, M. N.; Ismail, E. *J. Dispersion Sci. Technol.*, in press.

(35) (a) Khan, M. N.; Ismail, E. *Int. J. Chem. Kinet.* **2001**, *33*, 288–294. (b) Khan, M. N.; Arifin, Z.; Wahab, I. A.; Ali, S. F. M.; Ismail, E. *Colloids Surf., A* **2000**, *163*, 271–281.

PS^- and other unresolved degradation paths of 2-FBz^- under the reaction kinetic condition. However, the value of K_X^{Br} for $X = 2\text{-FBz}^-$ may not be significantly different from K_X^{Br} for $X = 2\text{-ClBz}^-$ and $2\text{-CH}_3\text{Bz}^-$. Thus, nearly 3-fold larger values of K_X^{Br} for $X = 3\text{-FBz}^-$ and 4-FBz^- than those for $X = \text{Bz}^-$, 2-ClBz^- , and $2\text{-CH}_3\text{Bz}^-$ are in favor of the respective presence and absence of cmc_2 for $\text{TTA}^+ / 3\text{-FBz}^-$, $\text{TTA}^+ / 4\text{-FBz}^-$, and $\text{TTA}^+ / 2\text{-FBz}^-$ micelles provided that TTA^+ and CTA^+ do not differ significantly in their effects on micellar growth. The value of K_X^{Br} ($= 50$) for $X = 3\text{-ClBz}^-$ is nearly 3-fold larger than those for 3-FBz^- and 4-FBz^- , which may be attributed to the relative polarity/hydrophobicity of Cl and F.

Viscosity maxima as a function of the concentration of the counterionic salt are known as the characteristic features of the wormlike micellar solutions.^{16,19,20} The maxima in Figures 3 and 4 occur at $[\text{MX}]/[\text{CTABr}]_{\text{T}} \approx 5$, where the value of $[\text{CTABr}]_{\text{T}}$ was kept constant at 15 mM. Similarly, a viscosity maximum was found to occur at $[\text{BzK}]/[\text{CTACl}]_{\text{T}} = 1$ with constant $[\text{CTACl}]_{\text{T}} = 200$ mM.^{20b} The cationic surfactant solutions containing 200 mM CTACl as well as $< \sim 50$ mM and $> \sim 50$ mM BzK behave like nonviscoelastic and viscoelastic solutions, respectively,^{20b} but the aqueous micellar solutions containing 10 mM CTABr, ≤ 0.08 M NaOH, 0.1 M Pip, 2×10^{-4} M PS^- , and BzNa within the concentration range of 0.0–500 mM remained essentially spherical at 35 °C.³⁴ The reasons for the maxima, such as those in Figures 3 and 4, are not yet clearly understood, but the possibilities include (a) a transition from linear to branched micelles or a maximum in micellar contour length¹⁶ and (b) the viscosity increase before a maximum can be attributed to the 1D micellar growth and increased density in the network structure whereas the viscosity decrease after the maximum is due to a decrease in the rigidity of the network structure (i.e., micellar breaking).¹⁸

Recently, Ge and co-workers³⁹ have reported the cryo-TEM images of the CTACl/4-FBzNa system at 5 mM CTACl and 3–20

mM [4-FBzNa]. These images show the presence of only spherical micelles at 3 mM 4-FBzNa but only mixed spherical and short threadlike micelles (TLM) at 20 mM 4-FBzNa. The shear viscosity of the aqueous solutions containing 5 mM CTACl and 3–20 mM 4-FBzNa remained 1 cP at shear rates of 10 and 1000 s^{-1} . In the present study, the shear viscosity of the aqueous solutions containing 15 mM CTABr and 20 mM 4-FBzNa changes from 4.2 to 3.0 cP with the change in shear rate from 21 to 1000 s^{-1} . Similarly, shear viscosity changes from 5.2 to 3.2 cP with the change in the shear rate from 21 to 1000 s^{-1} at 15 mM CTABr and 40 mM 4-FBzNa.

V. Conclusions

Nearly 3-fold larger values of K_X^{Br} for $X = 3\text{-FBz}^-$ and 4-FBz^- than for $X = 2\text{-ClBz}^-$ may be attributed to the presence of a second cmc (i.e., cmc_2) at ~ 13 mM $\text{TTA}^+ / 3\text{-FBz}^-$ and ~ 14 mM $\text{TTA}^+ / 4\text{-FBz}^-$ as reported elsewhere.³² The values of K_X^{Br} for $X = 3\text{-FBz}^-$ and 4-FBz^- give quantitative evidence of the perception that the strong micellar binding of certain counterions is the cause of the micellar structural transition from spherical to cylindrical to wormlike entangled micelles. The observed shear viscosity maxima as a function of the concentration of 3-FBzNa and 4-FBzNa (Figures 5 and 6) may be attributed to the possible presence of the viscoelastic behavior of these surfactant solutions.^{16,19,20}

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Supporting Information Available: Pseudo-first-order rate constants (k_{obs}) for the reaction of piperidine with anionic phenyl salicylate (PS^-) at a constant $[\text{CTABr}]_{\text{T}}$ and different [3- $\text{FC}_6\text{H}_4\text{CO}_2\text{Na}$] and [4- $\text{FC}_6\text{H}_4\text{CO}_2\text{Na}$]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(39) Ge, W.; Kesselman, E.; Talmon, Y.; Hart, D. J.; Zakin, J. L. *Non-Newtonian Fluid Mech.* **2008**, *154*, 1–12.