Research Article

Kinetics and Mechanism of Nanoparticles-Catalyzed Piperidinolysis of Anionic Phenyl Salicylate

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The values of the relative counterion (X) binding constant \( R_{Bx} = K_{X}/K_{Br} \), where \( K_{X} \) and \( K_{Br} \) represent cetyltrimethylammonium bromide, CTABr, micellar binding constants of \( X^{-} \) (in non-spherical micelles), \( V = 1, 2 \), and \( Br^{-} \) (in spherical micelles) are 58, 68, 127, and 125 for \( X^{-} = \text{Na}^{+}, \text{Na}_{2}^{+}, \text{Na}_{2}^{2-}, \) and \( 2^{2-} \), respectively. The values of 15 mM CTABr/[Na\_X] nanoparticles-catalyzed apparent second-order rate constants for piperidinolysis of ionized phenyl salicylate at 35°C are 0.417, 0.488, 0.926, and 0.891 M\(^{-1}\) s\(^{-1}\) for Na\_X = Na\_1, Na\_2, and Na\_2\_2, respectively. Almost entire catalytic effect of nanoparticles catalyst is due to the ability of nonreactive counterions, \( X^{-} \), to expel reactive counterions, \( 3^{-} \), from nanoparticles to the bulk water phase.

1. Introduction

Research on nanoparticles has now become a cutting-edge area of chemical research [1]. Mono- and bilayer surfactant aggregates are nanoparticles which have been known for their characteristic physicochemical properties for more than 100 years [2]. The effects of surfactant aggregates/nanoparticles of different structural features on reaction rates have been extensively studied for the past nearly six decades [3–5]. These studies reveal very complex mechanistic aspects of micellar/nanoparticles catalysis of reaction rates [4–6]. Effects of counterionic salts on ionic surfactant as well as biomolecular structural transitions have been under extensive study since 1887 when Hofmeister first reported specific salt effects on the salting-out proteins [7]. But the mechanistic aspects of these specific salt effects are not yet fully understood [8–10].

Effects of inert salts of moderately hydrophobic counterions, such as benzoate and substituted benzoate ions, on ionic surfactant micellar growth have become very important for various industrial applications [9–11]. However, mechanistic details of such inert salt effects on ionic micellar growth are almost nonexistent. Effects of inert counterionic salts on pseudo-first-order rate constants (\( k_{obs} \)) for the ionic surfactant nanoparticle-catalyzed semi-ionic bimolecular reactions, where ionic reactant is also a counterion, have been explained quantitatively by the use of pseudophase ion-exchange (PIE) model. But the use of PIE model involves mostly counterionic salts of highly and moderately hydrophilic counterions [12]. However, some inherent weaknesses of PIE model have been also realized [13, 14]. The increase in [MX] (MX = 3- and 4-FBzNa with Bz\(^- = C_{6}H_{4}CO_{2}^{-}\)) has caused nonlinear increase in \( k_{obs} \) for piperidinolysis of anionic phenyl salicylate (PSa\(^-\)) at a constant [CTABr]\(_{T} \gg \text{cmc where [CTABr]}\(_{T} \) and cmc represent total concentration of cetyltrimethylammonium bromide and critical micelle concentration of CTABr, respectively [15]. The magnitudes of the gradient of the plot of \( k_{obs} \) versus [MX] show continuous decrease with increasing [MX] [15]. The values of \( k_{obs} \) remained almost independent of [MX] within its range where the presence of 5 mM CTABr resulted in more than 10-fold increase in \( k_{obs} \). Thus, 5 mM CTABr/[MX] nanoparticles act as catalyst because, in the absence of CTABr, the values of \( k_{obs} \) remained independent of [MX] within its range covered in the study [15]. More than 10-fold catalytic effects of CTABr/MX nanoparticles were not emphasized and discussed in the report [15]. The catalytic effects of CTABr/MX/H\(_{2}O\) nanoparticles catalyst (MX = 4-methoxy and 4-methyl salicylates) on \( k_{obs} \) for piperidinolysis...
of Psal\(^-\) have been studied in the present study. The results and their probable explanations are described in this paper.

2. Materials and Methods

2.1. Materials. Reagent-grade 4-methoxysalicylic acid (1H), 4-methylsalicylic acid (2H), cetyltrimethylammonium bromide (CTABr), phenyl salicylate (3H), and piperidine (4) (Figure 1) were commercial products of highest available purity. Other common chemicals used were also of reagent grade. The stock solutions of 0.50M M with Na\(^+\) were prepared by adding 0.52 and 1.25M NaOH to the corresponding 0.50M solutions of 1H or 2H. The stock solutions of 0.01M 3H were prepared in acetonitrile. Throughout the text, the symbol [X]\(_T\) represents the total concentration of X.

2.2. Kinetic Measurements. The rate of CTABr/Na\(^+\) nanoparticles-catalyzed nucleophilic substitution reaction of 4 with Na3 was studied spectrophotometrically at 35\(^\circ\)C by monitoring the disappearance of Na3 at 365 or 370 nm. The products of the reaction of 4 with Na3 are sodium N-piperidinyl salicylate (Na5) and phenol (6) (Figure 1). The details of the kinetic procedure and product characterization have been described elsewhere [16]. Absorbance values (A\(_{obs}\)) at different reaction time (t) were found to fit to (1) for 8 half-lives of the reactions. In (1), [R\(_0\)] represents the initial concentration of 3H, \(\delta_{sp}\) is the apparent molar absorptivity of the mixture, \(k_{obs}\) is the pseudo-first-order rate constant, and A\(_{co}\) = A\(_{obs}\) at \(t = \infty\). Throughout the study, the initial concentrations of 3H or Na3 were kept constant at 0.2 mM. The choice of this specific concentration was governed by the need to keep it sufficiently low so that it is less than the other salicylate counterions but high enough to measure the absorption spectrophotometrically.

3. Results

3.1. Effects of [Na\(_x\)X] (\(v = 1, 2\)) on \(k_{obs}\) for the Reaction of 4 with Na3 at a Constant [CTABr]\(_T\) and 35\(^\circ\)C. A series of kinetic runs was carried out at the constant 15mM CTABr, 0.2mM 3H, 0.1 M 4, and varying values of [Na\(_x\)X] (v = 1, 2) within the range 0 \(\leq [Na_x X] \leq 0.30\) M for Na\(_x\)X = Na\(_1\) (v = 1, 2). The values of \(k_{obs}\) versus [Na\(_1\)] at [NaOH]/[1H] = 1.04 are shown in Figure 2. Similar plot of \(k_{obs}\) versus [Na\(_1\)] was also obtained at [NaOH]/[1H] = 2.50. The plot of Figure 2 shows initial segment where the values of \(k_{obs}\) are almost independent of [Na\(_1\)] at the initial low values of [Na\(_1\)] followed by the segment where the values of \(k_{obs}\) reveal monotonic increase of more than 7-fold with the increase in [Na\(_1\)].

The values of \(k_{obs}\) were also obtained at constant 15 mM CTABr, 35\(^\circ\)C, 0.2 mM 3H, 0.1M 4, and different values of [Na\(_2\)] (v = 1, 2) within the range 0 \(\leq [Na_2] \leq 0.30\) M. The values of \(k_{obs}\) versus [Na\(_2\)], at [NaOH]/[2H] = 1.04, are

![Figure 1: Molecular structures of compounds 1H, Na1, Na2, 1H, Na2, 2H, Na3, 3H, Na3, 4, Na5, and 6.](image-url)

![Figure 2: Plots showing the dependence of \(k_{obs}\) upon [Na1] for piperidinolysis of 3H at 0.2mM 3H, 0.1M 4, 0.03M NaOH, and 35\(^\circ\)C. The solid line is drawn through the calculated data points using (2) with kinetic parameters (\(k_{cat}\) and \(k_{X/Y}\)), listed in Table 2. The dotted line is drawn through the predicted data points assuming the presence of WM at [Na1]\(^{60}\) < [Na1] \(\leq 300\) mM.](image-url)
shown in Figure 3. Similar plot of \( k_{\text{obs}} \) versus \([Na,2] \) (not shown) was also obtained at \([NaOH]/[2H] = 2.5 \). The values of \([NaOH] \) were varied from 0.030 to \( \leq 0.18 \) M under the experimental conditions of entire kinetic runs for both \(Na,1\) and \(Na,2\). The shape of the plot of Figure 3 is similar to that of Figure 2 when \([Na,2] \leq ~20 \) mM. The increase in \([Na,2] \) at \( \sim 20 \) mM \(Na,2\) reveals a mild increase followed by a decrease and then increase again in the values of \(k_{\text{obs}}\) (Figure 3). Similar break in the plot (not shown) of \(k_{\text{obs}}\) versus \([Na,2] \) was also obtained at \([NaOH]/[2H] = 2.5 \). These observations may be attributed to the change in the structure of \(Na,X/\text{CTABr} \) nanoparticles to some higher interfacial curvature structures such as curved bilayer structures at \( \sim 20 \) mM \(Na,2\) [17].

The absence and presence of break in the monotonic plot of respective Figures 2 and 3 are indirectly supported by the following observations. The values of \( \delta_{ap} \), obtained for piperidinolysis of \( 3^- \) at \( 10 \) mM NaOH, \( 100 \) mM Pip, \( 0.2 \) mM \(3H\), \( 35^\circ\) C, and \( 370 \) nm, increase nonlinearly from \( 1750 \) to \( 4350 \) \(M^{-1} \) \(cm^{-1}\) with the increase in CH\(_3\)CN content from 2 to \( 92\%\) v/v in mixed aqueous solvents (Table 1). The values of \( \delta_{ap} \), obtained for piperidinolysis of \( 3^- \) at \( 30 \) mM NaOH, \( 100 \) mM Pip, \( 0.2 \) mM \(3H\), \( 35^\circ\) C, \( 370 \) nm, and different values of \([Na,X] \), for \(Na,1\) and \(Na,2\) \((\nu = 1, 2)\), are also summarized in Table 1. It is evident from Table 1 (a) that the values of \( \delta_{ap} \) are almost independent of \([Na,X] \) within its range \( 0 \sim \sim 15 \) mM for \(X = 1^-\) and \( 0 \sim \sim 50 \) mM for \(X = 2^-\) and (b) the values of \( \delta_{ap} \) reveal a monotonic decrease with increasing \([Na,1] \), \(\nu = 1, 2\), within its range \( \sim \sim 30 \sim 300 \) mM. But the values of \( \delta_{ap} \) show a sharp decrease with the increase in \([Na,2] \), \(\nu = 1, 2\), from \(50 \) to \(70 \) mM and then become almost independent of \([Na,2] \) within its range \( \sim \sim 70 \sim 300 \) mM. These observations simply demonstrate that \(Na,X\)-induced \(\text{CTABr}/Na,X\) nanoparticles structural transition, within \([Na,X] \) range of \( 50 \sim 300 \) mM, is not the same for \(Na,1\) and \(Na,2\) \((\nu = 1, 2)\).

### Table 1: The values of \( \delta_{ap} \), calculated from (1) for the piperidinolysis of \( 3^- \) under the variety of experimental conditions.

| [Na,X] \(^{b}\) (mM) | Na\(^{a}\) | \(10^{-1}\delta_{ap} \) (M\(^{-1}\) cm\(^{-1}\)) | \(Na,1\) | \( Na,2\) | CH\(_3\)CN (%v/v) | \(10^{-1}\delta_{ap} \) (M\(^{-1}\) cm\(^{-1}\)) \(^{c}\) |
|---------------------|---------|-----------------|--------|--------|-------------|-----------------|
| 0                   | 373 \pm 2 \(^{d}\) | 369 \pm 1 \(^{d}\) | 366 \pm 2 \(^{d}\) | 3372 \pm 1 \(^{d}\) | 2 | 372 \pm 1 \(^{d}\) | 2 | 175 \pm 1 \(^{d}\) |
| 10                  | 380 \pm 2 | 379 \pm 1 | 407 \pm 3 | 386 \pm 1 | 25 | 215 \pm 1 |
| 20                  | 356 \pm 1 | 362 \pm 1 | 341 \pm 1 | 343 \pm 1 | 50 | 250 \pm 1 |
| 30                  | 323 \pm 1 | 330 \pm 1 | 403 \pm 8 | 395 \pm 15 | 60 | 265 \pm 2 |
| 50                  | 286 \pm 1 | 292 \pm 2 | 457 \pm 5 | 364 \pm 6 | 70 | 288 \pm 1 |
| 100                 | 276 \pm 2 | 275 \pm 2 | 236 \pm 1 | 250 \pm 1 | 84 | 300 \pm 3 |
| 150                 | 251 \pm 1 | 276 \pm 1 | 240 \pm 1 | 230 \pm 4 | 90 | 367 \pm 3 |
| 200                 | 239 \pm 1 | 257 \pm 1 | 222 \pm 1 | 227 \pm 1 | 92 | 435 \pm 3 |
| 300                 | 219 \pm 1 | 251 \pm 1 | 222 \pm 2 | 226 \pm 1 | 92 | 438 \pm 2 |

\(^{a}\)[3H] = 0.2 mM, \(\lambda = 370 \) nm, \(35^\circ\) C, \(30 \) mM NaOH, \(100 \) mM Pip, and \(15 \) mM CTABr. \(^{b}\)[Na,X] = \([Na,1] \) and \([Na,2] \), \(\nu = 1, 2\). \(^{c}\)[NaOH]/[XH] = 1.04. \(^{d}\)[NaOH]/[XH] = 2.50. \(^{e}\)Calculated from (1) by the use of observed data (\(A_{obs} \) versus reaction time \(t\)) obtained for the kinetic runs at 0.2 mM \(3H\), 10 mM NaOH, 100 mM Pip, 370 nm, and 35\(^\circ\) C and within CH\(_3\)CN content range of 2–92\% v/v in mixed aqueous solvents. \(^{f}\)Error limits are standard deviations.

### Figure 3: Plot showing the dependence of \( k_{\text{obs}} \) upon \([Na,2] \), for piperidinolysis of \(3H\) at 0.2 mM PS\(^{+}\), 0.1 M \(4\), 0.03 M NaOH, and \(35^\circ\) C. The solid line is drawn through the calculated data points using (2) with kinetic parameters \(k_{\text{cat}} \) and \(K^{X=0} \). The dotted line is drawn through the predicted data points assuming the presence of WM at \([Na,2]_{0} ^{\sim} < [Na,2] < 300 \) mM.
Table 2: The values of empirical constants, $k_{cat}$ and $K^{X/S}$, for Na$_1$ and Na$_2$ ($\nu = 1, 2$), at 35°C in the presence of CTABr/Na$_X$ nanoparticles.

| Na$_X$ | [NaOH]/[XH] | [Na$_X$]$_{00}$ (mM) | [Na$_X$]$_{0}$ (mM) | $10^3 K_{MX}^{WS}$ (s$^{-1}$) | $10^4 k_{act}$ (s$^{-1}$) | $10^4 k_{cat}$ (M$^{-1}$s$^{-1}$) | $K^{X/S}$ (M$^{-1}$) | $F_{X/S}$ | $K^{X/S}_H$ (M$^{-1}$) | $K^{X/S}_R$ (M$^{-1}$) | $R^S_X$ (mM) | [Na$_X$]$_{range}$ (mM) |
|--------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|---------|----------------|----------------|--------------|----------------|----------------|
| Na1    | 1.04         | 11.7           | 10.6           | 30.7 ± 0.5    | 2.20 ± 0.03   | 417 ± 12      | 177 ± 0.9     | 0.77    | 1876           | 1444           | 58           | 12–100         |
| Na$_1$ | 2.50         | 13.0           | 11.6           | 30.5 ± 0.2    | 2.26 ± 0.04   | 488 ± 18      | 23.5 ± 1.3    | 0.68    | 2491           | 1694           | 68           | 15–120         |
| Na2    | 1.04         | 12.2           | 10.8           | 30.3 ± 0.1    | 2.20 ± 0.03   | 926 ± 70      | 30.0 ± 2.6    | 1.0     | 3180           | 3180           | 127          | 13–21          |
| Na$_2$ | 2.50         | 10.0           | 9.6            | 30.3 ± 0.6    | 2.20 ± 0.03   | 891 ± 103     | 30.4 ± 4.2    | 0.97    | 3222           | 3125           | 125          | 12–21          |

$[3H]_0 = 0.2$ mM, $\lambda = 365$ and $370$ nm for Na$_1$ and Na$_2$, respectively, 30 mM NaOH, 100 mM Pip, and 15 mM CTABr and aqueous reaction mixture for each kinetic run contains 2%v/v CH$_3$CN. $^a$Calculated by an iterative technique as mentioned in the text. $^b$Obtained by graphical technique as mentioned in the text. $^c$The value of $k_{MX}^{WS}$ is the mean value of $k_{obs}$ obtained within [Na$_X$] range where $k_{obs}$ values remained independent of [Na$_X$] at [CTABr]$_T = 0$. $^d$The value of $k_0$ is the mean value of $k_{obs}$ values obtained within [Na$_X$] range 0.0–[$[Na_X]_{00}$ at [CTABr]$_T = 15$ mM. $^e$F$_{X/S} = k_{cat}/(k_{MX}^{WS} \times K^{X/S})$. $^f$K$_{X/S} = K^{X/S} \times (1 + K^S_0 \times [CTABr]_T)$ where $K^S_0 = 7 \times 10^3$ M$^{-1}$ and [CTABr]$_T = 15$ mM. $^g$K$_{X/S} = F_{X/S} \times K_{X/S}$. $^h$R$^S_X = K^{X/S}_H/K_{Br/S}$ with K$_{Br/S} = 25$ M$^{-1}$. $^i$Total concentration range of Na$_X$ used in the data analysis. $^j$Error limits are standard deviations.
The experimental data ($k_{\text{obs}}$ versus $[\text{Na}_X]$) exhibited by Figures 2 and 3 (at $[\text{Na}_X] < -21 \text{ mM}$) were found to fit to empirical equation:

$$k_{\text{obs}} = \frac{k_0 + k_{\text{cat}}([\text{Na}_X] - [\text{Na}_X]_0^{\text{op}})}{1 + K_X^{\text{IS}}([\text{Na}_X] - [\text{Na}_X]_0^{\text{op}})},$$  

(2)

where $k_{\text{cat}}$ and $K_X^{\text{IS}}$ are empirical constants, $k_0 = k_{\text{obs}}$ at $[\text{Na}_X] = [\text{Na}_X]_0^{\text{op}} = 0$, and $[\text{Na}_X]_0^{\text{op}}$ represents the optimum concentration of Na$_X$ below which the values of $k_{\text{obs}}$ are independent of $[\text{Na}_X]$. The empirical constant $k_{\text{cat}}$ represents 15 mM CTABr/[Na]$\text{_X}$ nanoparticles-catalyzed apparent second-order rate constant for piperidinolysis of Na3. The values of $[\text{Na}_X]_0^{\text{op}}$ were calculated using an iterative technique as described elsewhere [15]. These values of $[\text{Na}_X]_0^{\text{op}}$ (Table 2) are comparable with the corresponding values of $[\text{Na}_X]_0^{\text{op}}$ obtained by the graphical technique [5]. As described in detail elsewhere [15, 18], the value of $[\text{Na}_X]_0^{\text{op}}$ represents the optimum value of $[\text{Na}_X]$ required for the occurrence of ion exchange processes $X^-/OH^-$ and $X^-/Br^-$. Equation (2), with replacement of $k_{\text{cat}}$ by $\theta K_X^{\text{IS}}$ where $\theta$ is an empirical constant, has been found to explain quantitatively similar observed data ($k_{\text{obs}}$ versus $[\text{Na}_X]$), for different Na$_X$ [5]. The nonlinear least-squares technique was used to calculate $k_{\text{cat}}$ and $K_X^{\text{IS}}$ from (2) by considering $k_0$ as a known parameter. The least-squares calculated values of $k_{\text{cat}}$ and $K_X^{\text{IS}}$ and experimentally determined values of $k_0$, at [NaOH]/[XH] = 1.04 and 2.50, are shown in Table 2. The statistical reliability of the observed data fit to (2) is evident from the standard deviations associated with the calculated values of $k_{\text{cat}}$ and $K_X^{\text{IS}}$ as well as from the solid line plots of Figures 2 and 3 which were drawn through the least-squares calculated data points.

It has been described in detail elsewhere [5, 15, 18] that the nonlinear increase in $k_{\text{obs}}$ with the increase of $[\text{Na}_X]$ at a constant CTABr$_T$ is due to the transfer of micellized 3$^-$ (i.e., 3$^-_M$ with subscript $M$ indicating micellar pseudophase) to aqueous phase (i.e., 3$^-_W$ with subscript $W$ indicating bulk water phase) through the occurrence of ion exchange process $X^-/3^-$. This is due to the reason that the value of $k_{\text{obs}}$ is more than 10-fold larger in the bulk water phase than that in the micellar pseudophase as evident from the listed values of $k_{\text{cat}}^n$ and $k_0$ in Table 2. The occurrence of ion exchange $X^-/3^-$ in the related reaction systems [5] has been found to decrease the CTABr micellar binding constant ($K_S$) of 3$^-$ with the increasing [Na$_X$] through an empirical relationship:

$$K_S = \frac{K_S^0}{(1 + K_X^{\text{IS}}[\text{Na}_X])},$$  

(3)

where $K_S^0 = K_S$ at $[\text{Na}_X] = 0$ and $K_X^{\text{IS}}$ represents an empirical constant whose magnitude is the measure of the ability of counterion $X^-$ to expel another counterion $S^-$ from the cationic micellar pseudophase to the bulk aqueous phase through the occurrence of ion exchange process $X^-/3^-/S^-/X^-$. It can be easily shown that the reaction mechanism for nucleophilic reaction of 4 with 3$^-$, expressed in terms of pseudophase micellar (PM) model and (3), can lead to (2) [18] with $k_{\text{cat}}$ and $K_X^{\text{IS}}$ expressed by (4) and (5), respectively. As shown in the following equation, $k_{\text{MX}}^{\text{IS}} = k_{\text{obs}}[\text{Na}_X] k_{\text{obs}}[\text{Na}_X] F_{\text{X}/\text{IS}}$ is an

$$k_{\text{cat}} = F_{\text{X}/\text{IS}} k_{\text{MX}}^{\text{IS}} K_X^{\text{IS}},$$  

(4)

$F_{\text{X}/\text{IS}}$ is valid only under the experimental conditions where [CTABr]$_T$ - cmc = [CTABr]$_T$ with cmc representing critical micelle concentration of CTABr. Perhaps, it is worth mentioning that the value of cmc of CTABr, at 0.2 mM 3$^-$ and [Na$_X$] = 0, was kinetically determined as 0.09 mM which became 0.04 mM at 0.1 M NaBr. The value of cmc became ~0 at ≥0.5 M NaBr [19]. These observations demonstrate that the value of cmc is negligible compared with [CTABr]$_T$ at its value of ≥5 mM.

The value of $F_{\text{X}/\text{IS}}$ measures the fraction of the micellized counterions ($3^-_M$) transferred to aqueous phase by the optimum concentration of Na$_X$ through ion exchange $X^-/3^-/3^-$ [18]. The value of $F_{\text{X}/\text{IS}}$ was calculated from (4) by the use of listed values of $k_{\text{cat}}$, $k_{\text{MX}}^{\text{IS}}$, and $K_X^{\text{IS}}$ in Table 2 and these calculated values of $F_{\text{X}/\text{IS}}$ for Na1, Na2, and Na3 are also listed in Table 2. The value of $K_X^{\text{IS}}$ was calculated from (5) with the reported value of $K_S^0$ (=7 × 10$^{-3}$ M$^{-1}$ [5, 15]). The calculated values of $K_X^{\text{IS}}$ for Na$_X$ with $\nu$ = 1, 2 and $X$ = 1, 2 are shown in Table 2. It has been concluded elsewhere [5, 18] that the normalized $K_X^{\text{IS}}$ (= $F_{\text{X}/\text{IS}}/K_X^{\text{IS}}$) values are empirically related to the ratio $K_X^{\text{IS}}/K_Y^{\text{IS}}$ through the relationship $R^n_Z = K_X^{\text{IS}}/K_Y^{\text{IS}}$ where $X = [X_M]/([X_W][D_n])$ and $Y = [Y_M]/([Y_W][D_n])$. The symbols $K_X^{\text{IS}}$ and $K_Y^{\text{IS}}$ represent CTABr micellar binding constants of counterions $X^-$ and $Y^-$, respectively, and $[D_n]$ is the concentration of CTABr micelles with each micelle containing n number of monomers. The values of $K_X^{\text{IS}}$ (Table 2) and the reported value of 25 M$^{-1}$ [15, 18] for $K_Y^{\text{BR}/\text{IS}}$ (with $Br^- = Y^-$) gives the values of $R^n_{\text{Br}/\text{IS}}$ for $X = 1^-$, 2$^-$ with $\nu = 1$ and 2. These results are also shown in Table 2. It is relevant to note that the value of $K_Y^{\text{BR}/\text{IS}}$ (=25 M$^{-1}$) is derived from kinetic parameters obtained in the presence of spherical CTABr micelles (SM). But the values of $K_X^{\text{IS}}$ may be derived in the presence of either SM or nonspherical micelles (NSM such as wormlike micelles, WM, or vesicles, V). Thus, $K_X^{\text{BR}/\text{IS}}$ becomes conventional ion exchange constant ($K_X^{\text{BR}}$) if the value of $K_X^{\text{IS}}$ is also obtained in the presence of SM. The value of $R^n_{\text{Br}/\text{IS}}$ (=89) for $X = 1^-$ may be compared with the $R^n_{\text{Br}^-}$ (=89) obtained at [NaOH]/[XH] = 2.1 for X representing 5-methoxysalicylate dianion [20]. The reported values of $R^n_{X}$ for $X = \text{salicylate dianion, benzoate ion, and}$
4-methoxybenzoate ion are 44, 5.6, and 5.2, respectively [20]. It is evident from the literature that the aqueous solutions of CTABr/M, X containing ≤15 mM CTABr and 12 mM ≤ [M, X] ≤ 22 mM exhibited the presence of SM for M, X = sodium benzoate [21] and WM for M, X = sodium salicylate [22], sodium 3-, 4-, and 5-methyl salicylate [23], and NaI, Na2 where ν = 1, 2. These observations cannot be explained in terms of Hamnett substituent constants (σ̄m, σ̄4 cat). These observations reveal that the shapes and sizes of the aqueous CTABr/M, X nanoparticles depend apparently upon the magnitudes of R^Br_X. The magnitude of R^Br_X is apparently governed by the combined effects of steric requirements and hydrophilic and hydrophobic interactions of counterion X^- with cationic headgroup. Hydrophilic interaction includes ion-ion, ion-dipole, dipole-dipole, and inter- and intramolecular hydrogen-bonding interactions.

The values of k_cat versus R^Br_X (Table 2) reveal a linear relationship with intercept = 0 and slope = (7.20 ± 0.07) × 10^-3 M^-1 s^-1. This observation implies that almost entire catalytic effect of CTABr/NaX nanoparticles catalyst is due to the ability of nonreactive counterions X^- to expel the reactive counterions 3^- from CTABr/NaX nanoparticles to the bulk water phase. Apparent maximum catalytic constant (µap) of 15 mM CTABr/[NaX] nanoparticle catalyst may be obtained from the relationship: 

µap = k_cat/k0 and such calculated values of µap are 190, (216), 421, and (405 M^-1) for respective NaI, Na2, and Na2 where parenthesized values represent at [NaOH]/[XH] = 2.5 (i.e., for Na2 and Na2). The estimated value of the second-order rate constant (k^2_M) for the reaction of 4 with 3^- in the CTABr micellar pseudophase (i.e., aqueous CTABr nanoparticles), at [NaX] = 0, is 3.4 × 10^-3 M^-1 s^-1 [19]. Thus, the real maximum catalytic constants (µreal) may be obtained from the relationship: 

µreal = k_cat' k^2_M where k_cat' = k_cat/[Pip] (with [Pip] = 0.1 M). The calculated values of µreal are 1230, (1440), 2720, and (2620 M^-1) for respective NaI, NaI, Na2, and Na2 where parenthesized values represent at [NaOH]/[XH] = 2.5.

The values of k_cat and R^Br_X for NaX are not significantly different from the corresponding values for Na2 for X = 1 and 2 (Table 2). These results reveal that energetically favorable electrostatic interaction is apparently insignificant compared with hydrophobic interaction between counterions, X^- and, and aqueous cationic interface of CTABr/NaX nanoparticles. Perhaps, this is the first qualitative explanation of the earlier qualitative experimental observation that sodium salicylate and salicylic acid are equally effective in driving the micellar structural transition SM-to-WM at a constant temperature [23]. The aqueous structure of CTABr/NaX nanoparticles remains WM at 35°C, ≤15 mM CTABr and 12 mM ≤ [NaX] ≤ ~22 mM for NaX = Na2 and Na2 (ν = 1, 2). But the values of k_cat are ~2-fold larger for Na2 than those for Na1 (Table 2). Thus, it is apparent that a quantitative correlation between k_cat and R^Br_X is better than that between k_cat and the aqueous structures of CTABr/NaX nanoparticles where rheologically assigned structures remain the same (WM) for both NaI, Na2 at <22 mM NaX.

5. Conclusions

The linear plot of k_cat versus R^Br_X with essentially zero intercept reveals indirectly that the catalytic efficiency of CTABr/NaX/H2O nanoparticles catalyst is almost entirely due to the ability of nonreactive counterions, X^- to expel reactive counterions, 3^- from nanoparticles to the bulk water phase. Binding affinity of counterions, X^- and X^2- with CTABr/NaX/H2O nanoparticles (measured by the magnitude of R^Br_X) remains nearly unchanged for X = 1 and 2. The polarity of the CTABr/NaX/H2O nanoparticles-bound 3^- is not the same for X^- = 1^- and 2^-, ν = 1, 2, within [NaX] range of ~70–300 mM.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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