# Iterative Calculation Method for Determining the Effect of Counterions on Acetylsalicylate Ester Hydrolysis in Cationic Micelles

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The fraction of micellar surface neutralized is calculated from kinetic results considering independent distribution equilibria between aqueous and micellar pseudophases for different ions in solution. The new model explains the kinetic results for the basic hydrolysis of acetylsalicylic acid in cetyltrimethylammonium bromide, chloride, and hydroxide (CTABr, CTACI, and CTAOH, respectively), and the basic hydrolysis of 3-acetoxy-2-naphthoic acid in CTAOH and CTABr.

#### Introduction

The effect of ionic micelles on the rates of bimolecular reactions is determined by increase in concentration of reactants within the small volume of the micellar Stern layer.<sup>1</sup> The apparent rate constants in micellar solutions may be either larger<sup>2</sup> or smaller<sup>3</sup> than the rate constants in water, showing both important catalytic or inhibition effects by these micellar systems. Most of the kinetic results can be explained by means of the pseudophase kinetic model proposed by Menger<sup>4</sup> and developed by Bunton<sup>5</sup> and Romsted<sup>6</sup> by assuming that the counterion of the micelle and the ionic reactant compete for the ionic head groups of the micellar surface, with the restriction that the fraction of these head groups neutralized,  $\beta$ , is a constant independent of the surfactant concentration. However, measurements by light scattering suggest that  $\beta$  increases on addition of counterions in solution<sup>7,8</sup> and even for ions that bind very strongly to the micelle to consider it as a constant is only an approximation.9

In this paper we have developed a new model that permits one to estimate the variation of  $\beta$  with surfactant concentration as a function of the distribution equilibria constants of the ions in solution between aqueous and micellar pseudophases at different surfactant concentrations. We applied the model to explain the basic hydrolysis of acetylsalicylic acid in CTABr, CTACl, and CTAOH and 3-acetoxy-2-naphthoic acid in CTABr and CTAOH.

## **Theoretical Approach**

The pseudophase kinetic model<sup>4,5,6,10,11</sup> considers the total volume of the micelles as a separate phase uniformly distributed in the aqueous phase, the reaction occurring in both phases according to Scheme I, where the subscripts M and W denote the micellar and aqueous phases, respectively, S is the substrate, Dn is the micellized surfactant whose concentration is given by [Dn] = [D]- cmc, cmc is the critical micelle concentration, and  $K_{\rm S}$  is the binding constant of the substrate to the micelle written in terms of micellized surfactant:

 $K_{\rm S} = [S_{\rm M}]/([S_{\rm W}][{\rm Dn}])$ 

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Scheme I

$$S_W + Dn \stackrel{K_S}{\underset{w'}{\longleftarrow}} S_M$$

 $k_{\rm W}'$  and  $k_{\rm M}'$  are the pseudo-first-order rate constants in aqueous and micellar pseudophases, respectively, given by

$$k_{W'} = k_{W}[OH_{W}]$$
  
 $k_{M'} = k_{M}[OH_{M}]/[Dn]$ 

where  $k_{\rm M}$  is written in terms of the mole ratio of micellar OHbound to the micellar head groups. The pseudo-first-order rate constant can be easily derived as

$$k_{\Psi} = \frac{k_{\rm W}[\rm OH_T^{-}] + (k_{\rm M}K_{\rm S} - k_{\rm W})m_{\rm OH}[\rm Dn]}{1 + K_{\rm S}[\rm Dn]}$$
(1)

where  $[OH_{T}^{-}] = [OH_{W}^{-}] + [OH_{M}^{-}]$  and  $m_{OH} = [OH_{M}^{-}]/[Dn]$ .

For a reaction with a reactive ion OH<sup>-</sup> as the micelle counterion, the distribution of this ion between aqueous and micellar pseudophases can be fitted to a mass-action model<sup>12</sup> as

$$K_{OH}' = [OH_{M}^{-}] / \{[OH_{W}^{-}]([Dn] - [OH_{M}^{-}])\}$$
 (2)

and the fraction of micellar head groups neutralized  $\beta$  will be  $\beta$ =  $[OH_{M}]/[Dn]$ . Equation 2 predicts that  $\beta$  increases with surfactant concentration.

When two ions compete for the micellar head groups, it is possible to define independent equilibria for each of them, so that for OH<sup>-</sup> as the reactive ion and X<sup>-</sup> as the micelle counterion, the equilibrium constants  $K_{OH}$  and  $K_{X}$  can be written as

$$\begin{split} K_{\rm OH'} &= [\rm OH_M^-] / \{[\rm OH_W^-]([\rm Dn] - [\rm OH_M^-] - [X_M^-])\} \\ K_{\rm X'} &= [\rm X_M^-] / \{[\rm X_W^-]([\rm Dn] - [\rm OH_M^-] - [X_M^-])\} \end{split}$$

which reduce to

$$K_{\text{OH}'}[\text{OH}_{\text{M}}^{-}]^{2} - (K_{\text{OH}'}[\text{Dn}] - K_{\text{OH}'}[\text{X}_{\text{M}}^{-}] + K_{\text{OH}'}[\text{OH}_{\text{T}}^{-}] + (1)[\text{OH}_{\text{M}}^{-}] + (1)[\text{OH}_{\text{M}}^{-}] - (1)[\text{OH}_{\text{M}}^{-}] = 0 \quad (3)$$

$$K_{X}'[X_{M}^{-}]^{2} - (K_{X}'[Dn] - K_{X}'[OH_{M}^{-}] + K_{X}'[X_{T}^{-}] + 1) \times [X_{M}^{-}] + ([Dn] - [OH_{M}^{-}])K_{X}'[X_{T}^{-}] = 0$$
(4)

These two equations can be solved simultaneously with an iterative calculation method to give the values of  $[OH_M]$  and  $[X_M]$  as a function of  $K_{OH}$  and  $K_{X}$  for each surfactant concentration. In our case we start the calculation setting  $[OH_M]$  as 0.000001 M and calculating iteratively the best values of micellar hydroxide and halide concentrations with a computer program. In this case the fraction of micellar head groups neutralized will be  $\beta$  =

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Figure 1. Variation of the pseudo-first-order rate constant  $k_{\Psi}$  with CTABr concentration for acetylsalicylic acid: ( $\odot$ ) [NaOH] =  $10^{-2}$  M, ( $\odot$ ) [NaOH] =  $3 \times 10^{-2}$  M, ( $\odot$ ) [NaOH] =  $5 \times 10^{-2}$  M, ( $\odot$ ) [NaOH] =  $8 \times 10^{-2}$  M. Lines are predicted values with different models.

 $([OH_M^-] + [X_M^-])/[Dn]$ . This value of  $\beta$  will depend on surfactant, total hydroxide, and halide concentrations and on the values of  $K_{OH}$  and  $K_{X}$ .

#### **Experimental Section**

Materials. Acetylsalicylic acid and other reactants from Merck were used without further purification. The 3-acetoxy-2-naphthoic acid was prepared from 3-hydroxy-2-naphthoic acid and acetic anhydride at room temperature and the product recrystallized from MeOH/Et<sub>2</sub>O. The surfactants CTACl and CTAOH were prepared by ion exchange of CTABr with anionic resin Amberlita 21 K. The CTAOH was prepared and kept under N<sub>2</sub> and it was used only the following day after preparation. The absence of Br<sup>-</sup> in CTACl and CTAOH was tested with fluorescein and silver ion, respectively.

Kinetics. All the reactions were run at  $25 \pm 0.1$  °C in a thermostated Spectronic 2000 Bausch and Lomb spectrophotometer. Both substrates were completely dissociated under our experimental conditions and the reactions were followed at 296.5 nm (isosbestic point) for the salicylic acid and 350 nm for the 3-hydroxy-2-naphthoic acid with its  $\lambda_{max}$  shifted slightly by surfactants. To the mixture of CTAX and NaOH at a given concentration in the thermostated cuvettes, 0.1 mL of acetylsalicylic acid or 3-acetoxy-2-naphthoic acid stock solution  $(3 \times 10^{-3} \text{ M})$ in acetonitrile) was added so that the amount of CH<sub>3</sub>CN in the reaction mixture was 3%. The concentrations were as follows: NaOH,  $10^{-2}$ -8 ×  $10^{-2}$  M; CTAX, 2 ×  $10^{-3}$ -6 ×  $10^{-2}$  M; and for both substrates  $10^{-4}$  M in all experiments. The hydroxide ion concentration was always in large excess over both substrates. Values of pseudo-first-order rate constants were obtained by least-squares fit with correlation coefficients greater than 0.999.

### **Results and Discussion**

The second-order rate constant,  $k_{\rm W}$ , for the basic hydrolysis of acetylsalicylic acid in water is 7.45  $M^{-1}$  min<sup>-1</sup>, which agrees with the literature value.<sup>13</sup> The experimental pseudo-first-order rate constants  $k_{\Psi}$  for the reaction in micellar solutions of CTABr, CTACl, and CTAOH are shown in Figures 1-3, respectively, at different hydroxide ion and surfactant concentrations. The variations of pseudo-first-order rate constants with hydroxide ion concentration at fixed concentrations of CTABr and CTACl are shown in Figure 4.

The kinetic results for the reaction in CTABr and CTACl can be adapted to the model proposed by  $Bunton^5$  and  $Romsted^{6,14}$  as already reported.<sup>15</sup> This model considers that ions bind to micelles according to the exchange model developed for resins and



Figure 2. Variation of the pseudo-first-order rate constant  $k_{\Psi}$  with CTACl concentration for acetylsalicylic acid: ( $\odot$ ) [NaOH] =  $10^{-2}$  M, (**0**)  $[NaOH] = 3 \times 10^{-2} M$ , (**0**)  $[NaOH] = 5 \times 10^{-2} M$ , (**0**) [NaOH]=  $8 \times 10^{-2}$  M. Lines are predicted values with different models.



Figure 3. Variation of the pseudo-first-order rate constant  $k_{\Psi}$  with CTAOH concentration for acetylsalicylic acid: (•) only CTAOH, (0)  $[NaOH] = 10^{-2} M$ , ( $\bullet$ )  $[NaOH] = 3 \times 10^{-2} M$ . Lines are predicted values



Figure 4. Variation of the pseudo-first-order rate constant  $k_{\Psi}$  with NaOH at a fixed surfactant concentrations for acetylsalicylic acid: (a)  $[CTABr] = 10^{-2} M$ , (b)  $[CTACl] = 10^{-2} M$ .

that  $\beta$  can be taken as a constant when one of the ions in solution binds very strongly to micelles.<sup>3</sup> For OH<sup>-</sup> reactive ion and X<sup>-</sup> as micelle counterion the ion-exchange equilibria can be expressed bν

$$OH_M^- + X_W^- \rightleftharpoons OH_W^- + X_M^-$$

with an equilibrium constant

 $K_{\rm Br}^{\rm OH} = [\rm OH_W^{-}][X_M^{-}]/[\rm OH_M^{-}][X_W^{-}]$ 

and the following expression for  $m_{OH}$  can be easily deduced:

$$m_{\text{OH}}^{2} + m_{\text{OH}} \left[ \frac{[\text{OH}_{\text{T}}^{-}] + K_{\text{Br}}^{\text{OH}}[\text{X}_{\text{T}}^{-}]}{(K_{\text{Br}}^{\text{OH}} - 1)[\text{Dn}]} - \beta \right] - \frac{\beta[\text{OH}_{\text{T}}^{-}]}{(K_{\text{Br}}^{\text{OH}} - 1)[\text{Dn}]} = 0 \quad (5)$$

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TABLE I: Parameters That Best Fit the Kinetic Results for Acetylsalicylic Acid in CTABr and CTACl, with  $\beta$  as a Constant

	CTABr				СТ	ACl		
[OH <sub>T</sub> <sup>-</sup> / M	$\frac{k_{\rm M}}{{ m min}^{-1}}$	<i>K</i> <sub>S</sub> / M <sup>-1</sup>	K <sub>Br</sub> OH	β	$\frac{k_{\rm M}}{{ m min}^{-1}}$	<i>K</i> <sub>S</sub> / Μ <sup>-1</sup>	K <sub>Cl</sub> OH	β
0.01	0.54	120	2	0.8	0.95	120	1.3	0.71
0.03	0.53	120	2	0.8	0.94	120	1.3	0.71
0.05	0.68	200	2	0.8	0.91	130	1.3	0.71
0.08	0.73	270	2	0.8	0.96	160	1.3	0.71

TABLE II: Parameters That Best Fit the Results for Acetylsalicylic Acid in CTAOH

[NaOH]/M	$k_{\rm M}/{\rm min^{-1}}$	$K_{\rm S}/{\rm M}^{-1}$	$K_{\rm OH}'/{\rm M}^{-1}$	
0.00	0.60	350	380	
0.01	0.60	350	380	
0.03	0.60	350	380	

TABLE III: Variation of  $\beta$  in CTAOH at Different NaOH **Concentrations for Acetylsalicylic Acid** 

	$oldsymbol{eta}$					
10 <sup>3</sup> [CTAOH]/M	0 M NaOH	0.01 M NaOH	0.03 M NaOH			
2	0.374	0.808	0.921			
4	0.484	0.813	0.921			
6	0.547	0.817	0.922			
10	0.621	0.825	0.923			
20	0.709	0.840	0.924			
40	0.781	0.860	0.927			
60	0.816	0.874	0.930			

The experimental rate constants can be adapted to eq 1 and 5 at different surfactant and NaOH concentrations by simulation techniques with a computer program, using  $k_W = 7.45 \text{ M}^{-1} \text{ min}^{-1}$ , cmc(CTABr) = 9 × 10<sup>-4</sup> M, cmc(CTACl) = 1.3 × 10<sup>-3</sup> M,<sup>16</sup>  $\beta$ (CTABr) = 0.8,  $\beta$ (CTACl) = 0.71,<sup>3,6</sup> and  $k_M$ ,  $K_S$ , and  $K_X^{OH}$ as adjustable parameters. The main problem is to fix the exact value of each of the parameters, because small variations in them also give acceptable fits of the experimental results, as already reported.<sup>3</sup> Table I gives the values of parameters that best fit the experimental results in CTABr and CTACl at constant  $\beta$ , but to fit them  $k_{\rm M}$  and  $K_{\rm S}$  must be allowed to vary. In figures 1 and 2 dashed lines represent the calculated values of  $k_{\Psi}$  for CTABr and CTACl, respectively. The variation of the pseudo-first-order rate constants at fixed CTABr and CTACl amounts with hydroxide ion concentrations (dashed lines in Figure 4) can only be fitted up, with this model, to  $[OH^-] = 0.05 \text{ M}$ .

To fit all the kinetic results, we used the new model proposed above, which allows  $\beta$  to vary with hydroxide and surfactant concentrations. The reaction was studied in micelles of CTAOH and the experimental results were fitted to eq 1 and 2 by using cmc(CTAOH) =  $8.4 \times 10^{-4} \text{ M}^{12}$  and  $k_{\text{W}} = 7.45 \text{ M}^{-1} \text{ min}^{-1}$  as fixed parameters, and determining  $K_{\rm S}$ ,  $K_{\rm OH}'$ , and and  $k_{\rm M}$  by simulation techniques. Table II gives the values of parameters that best fit the experimental results and Figure 3, solid lines, shows the values of  $k_{\Psi}$  so calculated. As can be seen, the fraction of micellar head groups neutralized  $\beta$  changes with surfactant and hydroxide ion concentration (Table III) and it is not possible to consider it as a constant for this hydrophilic ion.

The experimental results in CTABr and CTACl can be adapted to the new model proposed by using the values of  $K_{OH}$  and  $k_M$ obtained for CTAOH and  $K_S$  and  $K_X'$  as adjustable parameters. The values of them that best fit the results are given in Table IV and the pseudo-first-order rate constants so calculated are represented, by solid lines, in Figures 1 and 2 for CTABr and CTACl, respectively. The changes of  $\beta$  with surfactant and hydroxide concentrations for the estimated values of  $K_{OH}$  and  $K_{X}$  are plotted in Figure 5. As we can see,  $\beta$  is variable at small OH<sup>-</sup> concentrations, while for increasing it  $\beta$  becomes nearly constant with

TABLE IV: Parameters That Best Fit the Results for Acetylsalicylic Acid in CTABr and CTACl with the Iterative Calculation Method

	CTABr				CTACl	
$[OH_T]/M^{-1}$	$\frac{k_{\rm M}}{\rm min^{-1}}$	<i>K</i> s/ M <sup>-1</sup>	K <sub>Br</sub> '/ M <sup>-1</sup>	$\frac{k_{\rm M}}{{\rm min}^{-1}}$	K <sub>S</sub> / M <sup>-1</sup>	$\frac{K_{Cl}'/}{M^{-1}}$
0.01	0.60	110	760	0.61	150	494
0.03	0.59	110	760	0.62	150	494
0.05	0.60	110	760	0.61	150	494
0.08	0.60	110	760	0.62	150	494
1.0-				<b>8</b> }[	NaOH]=	0.08 M
				\$[	NaOH]=	0.03 M
0.9			-0	}[	NaOH] =	0.01 M
0.8						

Figure 5. Variation of  $\beta$  with [CTAX] at different NaOH concentrations for acetylsalicylic acid: (•) CTABr, (0) CTACl.



Figure 6. Variation of pseudo-first-order rate constant  $k_{\Psi}$  with CTAOH concentration for 3-acetoxy-2-naphthoic acid: (•) only CTAOH, (0)  $[NaOH] = 10^{-2} M$ . Lines are predicted values.

values higher than 0.9. It is important to notice that with this treatment, which considers  $\beta$  variable,  $k_{\rm M}$  becomes constant independent of surfactant and hydroxide ion concentrations as it should be and with the same value for the three studied surfactants CTAOH, CTABr, and CTACl, while  $K_S$  is different for each of them. The values of  $K_{\rm Br}$  and  $K_{\rm Cl}$  agree that  $\rm Cl^-$  binds to micelles less strongly than Br<sup>-10,17,18</sup>

In Figure 4 we plot the calculated results for  $k_{\Psi}$  at different OH<sup>-</sup> concentrations and fixed CTABr and CTACl amounts, using the parameters  $K_X'$  and  $k_M$  as determined before and the values of  $K_S$  of 150 and 110 M<sup>-1</sup> for CTACl and CTABr, respectively (solid lines). As we can see, the results fit very well until [OH<sup>-</sup>] = 0.15 M. In this case it is not possible to force the data to fit through an empirical increase of  $K_{\rm S}$ , as it has been done in the literature for other reactions, <sup>19,20</sup> because increasing  $K_S$  decreases the calculated value of pseudo-first-order rate constant. Some

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Figure 7. Variation of the pseudo-first-order rate constant  $k_{\Psi}$  with CTABr concentration for 3-acetoxy-2-naphthoic acid: ( $\odot$ ) [NaOH] =  $10^{-2}$  M, ( $\bullet$ ) [NaOH] =  $3 \times 10^{-2}$  M, ( $\circ$ ) [NaOH] =  $5 \times 10^{-2}$  M, ( $\circ$ ) [NaOH] =  $8 \times 10^{-2}$  M. Lines are predicted values with different models.

TABLE V: Parameters That Best Fit the Kinetic Results for 3-Acetoxy-2-naphthoic Acid in CTABr, with  $\beta$  as a Constant

[OH <sub>T</sub> <sup>-</sup> ]/M	$k_{\rm M}/{\rm min^{-1}}$	$K_{\rm S}/{\rm M}^{-1}$	K <sub>Br</sub> OH	β	
0.01	0.81	500	5	0.8	
0.03	0.85	400	5	0.8	
0.05	0.90	500	5	0.8	
0.08	0.88	500	5	0.8	

authors explain the results at high ion concentration considering an additional pathway across the micellar boundary, in which hydroxide ion in the aqueous phase would be able to react with the organic substrates,<sup>21</sup> although there is also some evidence that at high ion concentration there is a breakdown of the pseudophase model.<sup>22</sup>

In order to test the new model we have studied the basic hydrolysis of a more hydrophobic substrate, 3-acetoxy-2-naphthoic acid. The second-rate constant in pure aqueous solution  $k_W$  is 9.63 M<sup>-1</sup> min<sup>-1</sup>. The experimental pseudo-first-order rate constants for the reaction in CTAOH and CTABr are represented by dots in Figures 6 and 7, respectively, for different OH<sup>-</sup> and surfactant concentrations. The kinetics results for the reaction in CTABr can be adapted to the pseudophase kinetic model, Table V gives the values of parameters that best fit the experimental results, and in Figure 7 dashed lines represent the calculated values of  $k_{\Psi}$ . The results in CTAOH can be fitted to eq 1 and 2 by using

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 $K_{\rm S} = 800 \text{ M}^{-1}$ ,  $k_{\rm M} = 0.67 \text{ min}^{-1}$ ,  $K_{\rm OH}' = 380 \text{ M}^{-1}$ , and the calculated values of the pseudo-first-order rate constant are the solid lines in Figure 6. The new model, which considers  $\beta$  variable, also explains the experimental results in CTABr, and the parameters that give the best fit are  $K_{\rm S} = 600 \text{ M}^{-1}$ ,  $k_{\rm M} = 0.67 \text{ min}^{-1}$ , and  $K_{\rm Br}' = 1900 \text{ M}^{-1}$ , and in Figure 7 solid lines represent the calculated values of  $k_{\Psi}$ .

We note that the value of  $k_{\rm M}$  is nearly the same for both substrates, while the value of  $K_{\rm S}$  is higher for 3-acetoxy-2naphthoic acid as expected for a more hydrophobic substrate. The  $K_{\rm OH}'$  is also the same for both substrates, but the best value of  $K_{\rm Br}'$  is different for each of them, corresponding to exchange constant values  $K_{\rm Br}^{\rm OH}$  of 2 and 5 for acetylsalicylic acid and 3-acetoxy-2-naphthoic acid, respectively, but as we have pointed out earlier, it is possible to obtain acceptable fitting of the experimental results for both substrates by using some other values of  $K_{\rm Br}^{\rm OH}$  in the range 2–5.

Both substrates, acetylsalicylic acid and 3-acetoxy-2-naphthoic acid, are completely dissociated under our kinetic conditions and can be treated as exchangeable micelle counterions whose distribution will depend upon the concentrations of other counterions in solution,<sup>10</sup> but although the interaction between one ionic substrate with the micelle both electrostatic and hydrophobic forces will contribute, from the formal point of view the ionic substrate model does not improve the adjustment of the experimental results.

The results for the basic hydrolysis of acetylsalicylic acid and 3-acetoxy-2-naphthoic acid are important because independent of the model used the second-order rate constant in the micellar pseudophase  $k_2^m$ ,  $M^{-1} \min^{-1}$ , given by  $k_2^m = 0.14k_M$ , is about 100 times smaller than the second-order rate constant in water for both substrates. That means that binding of the substrate to cationic micelles stabilizes the ground state much more than the transition state, accounting for the small catalysis observed for these reactions.<sup>23</sup>

It can be concluded that by consideration of independent equilibrium distribution for ions in solution between aqueous and micellar pseudophases it is possible to explain the experimental results of the basic hydrolysis of acetylsalicylic acid and 3-acetoxy-2-naphthoic acid and, from the best fit of the results, to calculate the fraction of micellar head groups neutralized  $\beta$ , which depends on the values of the equilibrium distribution constants of different ions. This is only an approach to the real distribution of ions between aqueous and micellar pseudophases, although we are sure this is not the final solution for the treatment of kinetic data for reactions in micellar systems.

**Registry No.** CTAB, 57-09-0; CTAC, 112-02-7; CTAOH, 505-86-2; acetylsalicylic acid, 50-78-2; 3-acetoxy-2-naphthoic acid, 5464-07-3.

<sup>(23)</sup> Romsted, L. S., personal communication.