Influences of Micelle Formation and Added Salts on the Hydrolysis Reaction Rate of *p*-Nitrophenyl Benzoate in Aqueous Buffered Media

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ABSTRACT: The hydrolysis reaction rate of *p*-nitrophenyl benzoate (*p*-NPB) has been examined in aqueous buffer media of pH 9.18, containing surfactants, cetyltrimethylammonium bromide (CTAB) and chloride (CTAC), or sodium dodecyl sulfate (SDS) at 35°C. Although the rate constant [log (k/s^{-1})] of *p*-NPB hydrolysis has once decreased slightly below the critical micelle concentration (CMC) value for CTAB and CTAC, it has begun to increase drastically with micellar formation. With increasing concentrations larger than the CMC value, the log (k/s^{-1}) value has reached the optimal value, i.e., a 140- and 200-fold rate acceleration for CTAB and CTAC, respectively, compared to that without a surfactant. Whereas the anionic surfactant, SDS, has caused only a gradual rate deceleration in the whole concentration range (up to 0.03 mol dm^{-3}). Increases in pH of the buffer have resulted in increases of the hydrolysis rate. In the CTAB micellar solution, the remarkably enhanced rate has been retarded significantly by the addition of only 0.10 mol dm^{-3} bromide salts. The effects of rate retardation caused by the added salts follows in the order of NaBr > Me_4NBr > Et_4NBr > Pr_4NBr > *n*-Bu_4NBr. In the absence of surfactant, however, the addition of the bromide salts has accelerated the hydrolysis rate, except for the metallic salt of NaBr, with the order of Me_4NBr < Et_4NBr < Pr_4NBr < *n*-Bu_4NBr. In the CTAC micellar solution, similar rate retardation effects have been observed in the presence of chloride salts (NaCl, Et_4NCl, and *n*-Bu_4NCl). The effects of added salts have

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been interpreted from the viewpoints of the changes in activity of the OH^- ion and/or the nucleophilicities of the anions from the added salts. Int J Chem Kinet 49: 71–82, 2017

INTRODUCTION

Micelles are simple spherical supramolecules, which are formed by surfactants in water or media similar to water above the concentration of the surfactants called critical micelle concentration (CMC) at which micelles start to form [1]. A micellar system appears to be homogeneous since these aggregates are of the colloidal size; however, in reality, the absorbed reactants exist in a micro-heterogeneous two-phase system [2]. These systems have been recognized as potentially useful model matrices to study the processes that occur in complex plasma or cell membrane of living cells and also play a vital role in pharmaceutical industry and other industrial systems [3]. The feature that makes a micelle special with respect to its functioning as a micro- or nanoreactor is the proximity of extremely polar and nonpolar regions [1]. They provide microenvironments different from bulk water, and besides they may exert a concentration effect as they can shift equilibrium position.

The effect of micelles on reactions, according to Brown et al. [4], is ascribed to a combination of the following factors: First, the dielectric constant in the micelle is lower than in water. Second, the transition state of the reaction can be stabilized by interaction with the polar head groups, and the third is the reactants are concentrated, relative to the surrounding water phase, through interactions with the micelle surface or through insertion into the micelle itself, thus leading to an increased rate of bimolecular reactions. The concentration effect can be considered as dominant in many cases.

In the frame of the pseudophase model, the micelle is considered as a phase different from aqueous medium, where reaction rates and solubilities of the substrates can vary considerably. In reactions with ionic species, an important fact is the charge of the surfactant head groups and counterions. In this way, it is expected that the hydrolysis rates of hydrophobic esters with OH^- ions will be enhanced by cationic micelles, which can include the ester in their core and also attract reactive ions of opposite sign, that is, OH^-. Basically, these rate effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregate and in some cases to alterations in the structure of the surrounding water [5].

The solvolysis/hydrolysis of esters and related nucleophilic reactions in micellar system has been extensively investigated. Enzymatic and enzyme-analogous systems including micelles have a practical significance for the hydrolytic detoxifications of organic compounds [6–9] and even for treatment of waste water [10–12]. Micelles can cause an acceleration or inhibition of a given chemical reaction rate relative to the equivalent reaction in an aqueous medium, depending upon the type of surfactants used for micelle formation [13–20].

Reactivity maxima have been frequently found for substrates of a certain chain length in reactions in micellar aggregates, which leads to the conclusion that there must be an optimal reaction site for the reactions. The proximity of the reaction partners (hydroxide ions and the carbonyl group of the ester in the case of alkaline ester hydrolysis) in the Stern layer determines the higher rate of reaction relative to that in aqueous media [1,13–16,18–20].

The effects of added salts on the hydrolysis reaction rates of esters in both aqueous and binary solvent media have been extensively studied. Mabey and Mill [21] have reported the effects of solvent composition as well as added salt effects on the hydrolysis of organic compounds. The added salt can potentially lead to either rate acceleration or retardation depending upon the substrate, types of the salt, and their concentrations as well as the reaction mechanisms. We [22–27] have reported the significant changes in the hydrolysis (solvolysis) reaction rates of various organic compounds (S_N1, S_N2, and S_N1–S_N2 intermediate substrates) in binary solvent media containing added salts. Several factors potentially contribute to the changes in the hydrolysis rates. These includes the changes in "normal" water structure [22,28,29], the increase in the hydroxide ion (OH^-) activity [22,23], and coordination interaction between alkali metal or alkaline earth metal ions and the anion left from a substrate in the "modified" reaction media [22–27,30].

We [30] have proposed fascinatingly that water may lose its properties as the bulk water to get that of a nonaqueous solvent, such as an alcohol (R–O–H) or even an ether (R–O–R) when the highly "self-assembled structure" of bulk water is disturbed by salts at higher concentrations. Such water can be "reduced" to authentic singular H_2O molecules ["dihydrogen ether," (H)–O–(H)]. Reichardt et al. [31] have concisely

interpreted "dihydrogen ether" that, at high salt concentrations [c(salt) > 5 mol dm^{-3}], region C, according to the solvation model of Frank and Wen [32], can be abolished and only regions A and B survive, resulting in an aqueous solvent called "dihydrogen ether." In other words, the presence of electrolytes at higher concentration influences the properties (hydration strength) of water.

As noted above, there are a huge line of information on the effects of reaction rates of organic compounds in micellar media just like the reactions in aqueous media. However, as far as our knowledge, the detail information on the effects of added salts (especially, alkali metal or alkaline earth metal salts and nonmetallic salts) on the (hydrolysis) reaction rates of organic compounds in micellar media, compared with that of in aqueous or binary solvent media, is lacking or limited. There are some evidences on the effects of transition metal ions on the hydrolysis rate of esters [33–36] in micellar media.

In the present study, as the part of our interest in studying the true "medium effects" on the reaction rates of organic compounds, we extend our study to the salt effects on the hydrolysis rates of *p*-nitrophenyl benzoate (*p*-NPB) in micellar media. The micellar effects of cetyltrimethylammonium bromide (CTAB) and chloride (CTAC), or sodium dodecyl sulfate (SDS) are examined in the absence and presence of added salts.

Scheme 1 shows the simplified form of primary mechanism for the hydrolysis reaction of the substrate. The attack by the OH^- ion (the prominent nucleophile) and/or the H_2O molecule is expected to be on the carbonyl carbon center. We would like to explain experimental results based on not only micellar catalysis but also the changes in the OH^- activity or the nucleophilicities of anions with the addition of various salts.

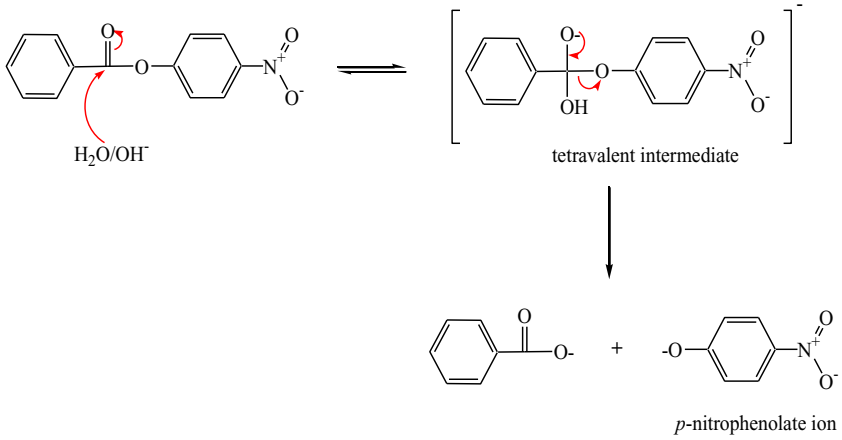
EXPERIMENTAL

Materials and Equipment

All chemicals and salts utilized were commercially available and used as received. The target compound, *p*-NPB (>97.0%) was obtained from Alfa Aesar, and *p*-nitrophenol (>99.0%) was from TCI (Tokyo). CTAB (>98.0) and CTAC (>95.0%) were both purchased from Wako (Osaka), and SDS (≥99.0%) was obtained from Aldrich. Salts of NaCl (99.5%), NaBr (99.5%), Et_4NBr (≥98.0%), Et_4NCl (≥98.0%), n-Bu_4NBr (≥98.0%), $Na_2B_4O_7{\cdot}10H_2O$ (≥99.6), and acetonitrile (of the GR grade) were all obtained from Wako. HCl and NaOH were also obtained from Wako. Other salts of Me_4NBr (≥98.0%), Pr_4NBr (≥98.0%), and n-Bu_4NCl (>97%) were all obtained from Aldrich. Instead of the commercially available buffer solution, we used the carefully prepared (in laboratory) borate buffer solutions of pH ranging from 8.50 to 10.0 to avoid the influences of NaN_3, contained as the stabilizer in the commercial borate buffer. The buffer solutions other than pH 9.18 were adjusted by adding appropriate volumes of 0.1 mol dm^{-3} HCl or NaOH to the borate buffer solution. Distilled water purified by the MilliQ System was used in all the experiments. A Horiba F-51 digital pH meter was used for measuring the apparent pH of the reaction solutions.

Kinetic Procedure

Kinetic measurements were performed using a Shimadzu UV–vis spectrophotometer (model UV-2550)



Scheme 1 Proposed mechanism for alkaline hydrolysis of *p*-NPB.

equipped with a thermostated cell holder whose temperature was controlled within 25 ± 0.1°C, in a 1.0-cm quartz cuvette. Reaction solutions were prepared by combining the appropriate amounts of water, a surfactant [CTAB and CTAC, or SDS], the borate buffer of pH 9.18 (with a final concentration of 5.0 mmol dm^{-3}), and a salt (such as NaBr) and then were left to stand for about 30 min in a Taitec constant temperature water bath at 35 ± 0.1°C to reach the thermal equilibrium.

Prior to the beginning of the reaction, the 5.0 × 10^{-3} mol dm^{-3} stock solution of the substrate (*p*-NPB) was prepared in acetonitrile (as the substrate is sparingly soluble in pure water). Then, reactions were initiated by transferring a 1.0-mL of the stock solution into a reaction vessel (50 mL) to reach the final substrate concentration of 1.0 × 10^{-4} mol dm^{-3}. The samplings of 3–4 mL were carried out from the reaction vessel at certain time intervals, and the sampled solutions were immediately dipped into an ice water bath.

The reaction progress was followed spectrophotometrically by monitoring the liberation of *p*-nitrophenolate ion at λ_{max} = ca. 400 nm as a function of time. The "pseudo"–first-order rate constants were obtained from the slopes of ln $(A_\infty - A_t)$ versus time (s), where A_∞ and A_t are the values of absorbance at the final of the reaction and at time *t*, respectively. All rate constants were evaluated from the linear curves with correlation coefficients (R^2) of normally 0.999 or better and the uncertainties for log (k/s^{-1}) are generally less than ±0.01.

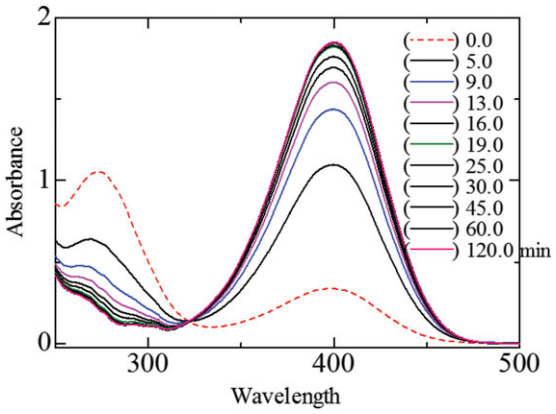


Figure 1 Generation of *p*-nitrophenolate ion with time as the hydrolysis product from *p*-NPB (1.0 × 10^{-4} mol dm^{-3}) in aqueous borate buffer media of pH 9.18 containing 2.0 × 10^{-3} mol dm^{-3} CTAB at 35°C.

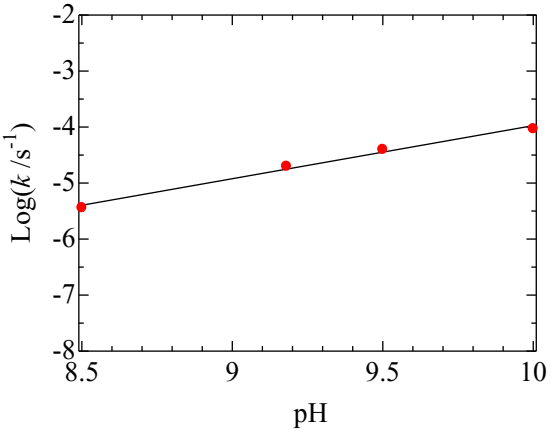


Figure 2 Changes in log (k/s^{-1}) with pH of the buffer for the hydrolysis of *p*-NPB in aqueous solution without surfactant at 35°C.

RESULTS AND DISCUSSION

Generation of *p*-Nitrophenolate Ion with Time

At 35ºC, we have evaluated the rates of hydrolysis reactions of *p*-NPB in the presence of 2.0 × 10^{-3} mol dm^{-3} CTAB, the cationic surfactant. The increase in absorbance at λ_{max} (400 nm) of UV–visible spectra with time has been followed, as shown in Fig. 1. The isosbestic point given at 320 nm should indicate the coexistence between the original substrate and the released *p*-nitrophenolate ion.

Effects of pH in the Absence of Surfactants

The effects of change in pH of the buffer on the hydrolysis reactions rate of *p*-NPB in aqueous media without surfactant are examined. Figure 2 shows that the rate constant [log (k/s^{-1})] increases linearly as –5.44, –4.74, –4.40, and –4.03 with increasing pH of the buffer as 8.50, 9.18, 9.50, and 10.0, respectively. The increase in the hydrolysis reaction rate with increasing pH of the buffer is a normal and expected phenomenon, which is attributed to an increase in the activity of the prominent nucleophile, OH^-.

Determination of CMC in a Buffered Solution

The spectroscopic method developed by Small and Carey [37] has been employed to determine the CMC values of all the surfactants, CTAB, CTAC, and SDS. The plots of wavelength (λ_{max}) or the absorbance (A) at λ_{max} versus the surfactant concentration may give two straight lines with different slopes. The intersection of these two lines is taken as the CMC value of the surfactant.

Figure 3 shows changes of the slope in the plots of the λ_{max} value versus the logarithm of surfactant

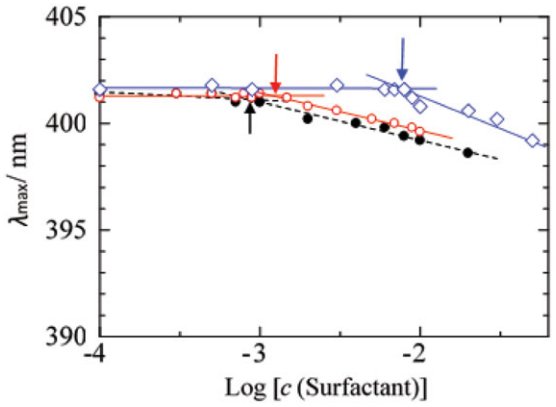


Figure 3 Variation of λ_{max} versus the logarithm of surfactant concentration for surfactants in solution containing 5.0 mmol dm^{-3} borate buffer (pH 9.18) at 35°C: (●) CTAB; (○) CTAC; (◇) SDS. *p*-Nitrophenol (1.0×10^{-4} mol dm^{-3}) is used as the probe, and the arrows indicate the intersection points of the slopes.

Table I CMC Values Determined by the Spectrophotometric Method Using *p*-Nitrophenol as the Probe in Aqueous Solution Containing 5.0 × 10^{-3} mol dm^{-3} Borate Buffer of pH 9.18 at 35°C

Surfactant	$\times 10^3$ CMC (mol dm^{-3})	
CTAB	0.91	0.98[a]
CTAC	1.26	1.30 (at 30°C)[b]
SDS	8.1	8.60 (at 40°C)[b]

[a]From [38].
[b]From [3].

concentration for CTAB, CTAC, and SDS in aqueous buffer of pH 9.18 media, making use of *p*-nitrophenol (1.0×10^{-4} mol dm^{-3}) as the probe at 35°C. The CMC values determined in the buffered media are summarized in Table I, and the values are consistent with the values already reported [3,38]. We have noticed that no significant changes of the CMC values are caused in buffered media. The variation of CMC values of surfactants with the types of probes is due to the interactions between the surfactant monomers and probes, which alters the micellization process, as stated by Fuguet et al. [39] and others [40,41].

Effects of CTAB, CTAC, and SDS Surfactants on the Hydrolysis Rate

Figure 4 shows the effects of CTAB, CTAC, and SDS surfactants on the alkaline hydrolysis rate of *p*-NPB in aqueous buffer media of pH 9.18 at 35°C. It has been found that the reaction rate decelerates slightly upon the addition of small concentrations up to 5.0×10^{-4} mol dm^{-3} for CTAB or CTAC (cf. Table II). This rate

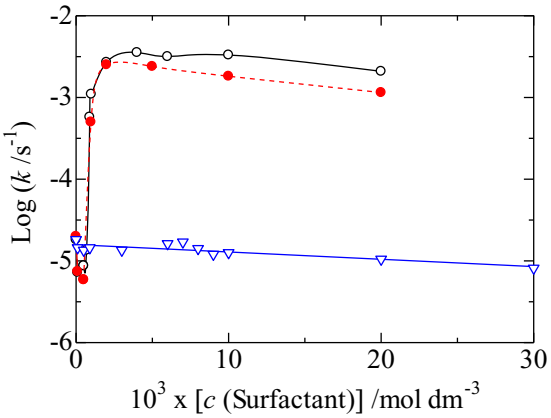


Figure 4 Changes in log (k/s^{-1}) values with the surfactant concentration for the hydrolysis of *p*-NPB in aqueous buffer solution of pH 9.18 at 35°C: (○) CTAC; (●) CTAB; (▽) SDS.

deceleration may be attributed to the decrease in water activity due to the added surfactant. However, the rate is sharply promoted by further increasing concentration of the surfactants and reaches the maximum values at 2.0×10^{-3} and 4.0×10^{-3} mol dm^{-3} for CTAB and CTAC, respectively. We may mention that the CMC values are 9.12×10^{-4} and 1.26×10^{-3} mol dm^{-3} for CTAB and CTAC in the buffer media (cf. Table I).

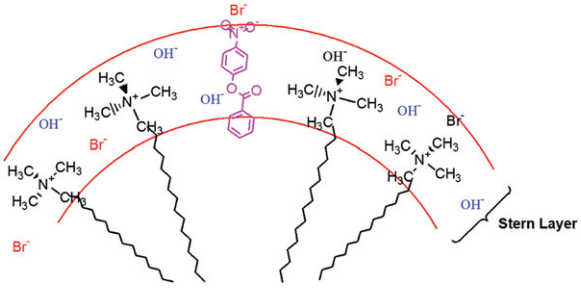
At the optimal point, a 140-fold rate acceleration is caused by CTAB, compared to the rate constant without CTAB. Similarly, about 200-fold rate acceleration is observed for CTAC at its optimal point, compared to the rate value without CTAC. A gradual decrease in the hydrolysis rate has been caused by the further increase in the CTAB or CTAC concentration. This type of rate profile, i.e. the appearance of a rate maximum, for the hydrolysis reactions of various organic compounds in the presence of cationic surfactants, is well documented [8,13–18,20,42–45]. These studies have suggested strongly that, in micellar media, most reactions take place on the surface of micelle at or near the highly charged double layer, commonly called, the Stern layer (Scheme 2).

At any rate, Fig. 4 shows that the enhancement in the reaction rates is originated by the presence of the cationic surfactants, CTAB and CTAC. The following two factors should explain the enhancement in reaction rate: (1) The *p*-NPB substrate is hydrophobic in nature and tends to associate with the micelles by mainly hydrophobic effect. (2) The anion, OH^-, is attracted as the counterion of the cetyltrimethylammonium cation in the micelle. This supramolecular assembly plays as a microreactor and causes the increased concentrations of the two reactants (*p*-NPB and OH^-) in the medium.

The gradual decreases in the reaction rates at higher surfactant concentrations are well-known phenomena

Table II Effects of Surfactant Concentrations upon the Hydrolysis Rate of 1.0×10^{-4} mol dm^{-3} *p*-NPB in Aqueous Buffer Solution of pH 9.18 at 35°C

$\times 10^3$ *c* (surfactant) (mol dm^{-3})	CTAB		CTAC		SDS	
	k (s^{-1})	log (*k*/s^{-1})	*k* (s^{-1})	log (*k*/s^{-1})	*k* (s^{-1})	log (*k*/s^{-1})
0.0	1.82×10^{-5}	–4.74	1.82×10^{-5}	–4.74	1.82×10^{-5}	–4.74
0.1	7.42×10^{-6}	–5.13	7.10×10^{-6}	–5.14	1.45×10^{-5}	–4.84
0.5	5.90×10^{-6}	–5.23	8.64×10^{-6}	–5.06	1.07×10^{-5}	–4.97
0.7	–	–	1.34×10^{-4}	–4.87	–	–
0.9	–	–	5.75×10^{-4}	–3.24	1.45×10^{-5}	–4.84
0.98	5.04×10^{-4}	–3.30	–	–		–
1	–	–	1.10×10^{-3}	–2.96		–
2	2.49×10^{-3}	–2.60	2.68×10^{-3}	–2.57		–
3	–	–	–	–	1.35×10^{-5}	–4.87
4	–	–	3.56×10^{-3}	–2.45		–
5	2.41×10^{-3}	–2.62	3.39×10^{-3}	–2.47		–
6	–	–	3.13×10^{-3}	–2.50	1.62×10^{-5}	–4.79
7	–	–	–	–	1.70×10^{-5}	–4.77
8	–	–	–	–	1.41×10^{-5}	–4.85
9	–	–	–	–	1.20×10^{-5}	–4.92
10	1.80×10^{-3}	–2.74	3.28×10^{-3}	–2.48	1.26×10^{-5}	–4.90
20	1.15×10^{-3}	–2.94	2.11×10^{-3}	–2.68	1.05×10^{-5}	–4.98
30	–	–	–	–	8.13×10^{-6}	–5.09
50	–	–	–	–	5.37×10^{-6}	–5.27

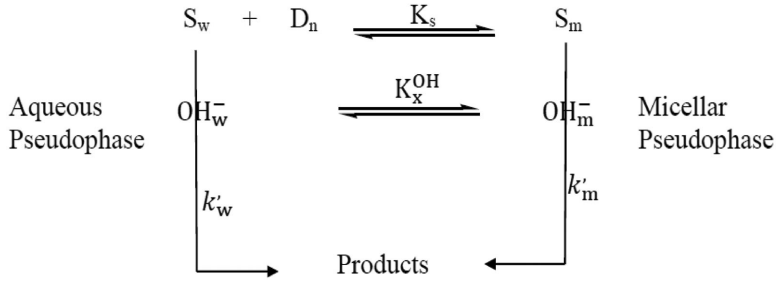


Scheme 2 A hypothetical orientation of *p*-NPB bound to micelles of CTAB.

in most of the micelle-catalyzed bimolecular reactions. In the presence of a surfactant much higher than the CMC concentration, the total population of micelles is increased; therefore, the local molarities of the organic substrate and the OH^- ion in and around Stern layer of micellar surface should decrease. That is, the net concentrations of reactants are diluted with the increasing concentrations of surfactants (after the CMC values), which results in the deceleration of the reaction.

The anionic surfactant SDS, however, has caused only a gradual rate deceleration in its whole concentration range up to 0.03 mol dm^{-3} (cf. 8.1×10^{-3} mol dm^{-3} of the CMC in Table I). As noted by Cordes and Dunlap [19], the most dramatic change in surfactant structure, and the easiest to interpret, in terms of influence on the kinetics of reactions in micellar phases, is change in the charge type of the head group. The inhibitive effect of SDS micelles on the hydrolysis rates of *p*-NPB can be explained by applying the Berezin's pseudophase model [46]. The inhibition in the observed reaction rate can be attributed to the selective partitioning of reactants in the micellar region. According to the model, one of the reactants (usually organic) is preferentially bound with the micelles while the other is repelled, due to bearing the similar charges, on the micellar surface. In the present study, the inhibition in the rate of alkaline hydrolysis of *p*-NPB should also be due to its preferential binding with the SDS micelles. At the same time, the negatively charged OH^- ions are being repelled by the negatively charged surface of the micelles. Thus, the distribution of the two reactive species in the different localities provides less chance for interaction between them and therefore, causes deceleration in the reaction.

A kinetic treatment of micellar effects on the hydrolysis reaction rates of organic compounds requires some approximations. From a purely formal approach, the Michaelis–Menten methods known from enzyme chemistry can be recognized [1]. Kinetic considerations are most frequently based on the pseudophase model [46], in which the aqueous medium and



Scheme 3 Pseudophase ion exchange model for the hydrolysis reaction in aqueous and micellar media.

the micelle are viewed as separated phases with which the substrate is in thermodynamic equilibrium as hypothetically shown in Scheme 3. The reactive organic molecule, for instance *p*-NPB in this particular case, is considered to be distributed in both the aqueous and micellar phases in accordance with their hydrophilic or hydrophobic characteristics.

In Scheme 3, S_w and S_m represent substrates in aqueous and micellar media, respectively. k'_w and k'_m are pseudo–first-order rate constants in aqueous and micellar pseudophases, respectively. K_s is the binding constant of the substrate to the micelle and mathematically given by Eq. (1):

$$K_s = \frac{[S_m]}{[S_w]\,[D_n]} \tag{1}$$

where D_n is the micellized surfactant (D_n = [D] – cmc, where D is the total surfactant concentrations) and cmc is the CMC. The observed rate constant can be described mathematically as Eq. (2), a derivation of the Michaelis–Menten equation.

$$k_{obs} = \frac{k'_w + k'_m K_s\,[D_n]}{1 + K_s[D_n]} \tag{2}$$

The rate constants in the respective pseudophases (k'_w and k'_m) are given by Eqs. (3) and (4), respectively,

$$k'_w = k_w\left[OH_w^-\right] \tag{3}$$

$$k'_m = \frac{k_m\left[OH_m^-\right]}{D_n} \tag{4}$$

Competition of the nucleophile with the counterion of the surfactant must be taken into account in the case of bimolecular reactions with an uncharged hydrophobic substrate and an ionic nucleophile in a cationic micelle. This is possible by the introduction of an ion-exchange equilibrium [Eq. (5)], with which the ionic concentrations in the aqueous and the micellar pseudophase can be calculated.

$$OH_m^- + X_w^- \rightleftharpoons OH_w^- + X_m^- \tag{5}$$

and K_x^{OH} is given as Eq. (6)

$$K_x^{OH} = \frac{\left[OH_w^-\right][X_m^-]}{\left[OH_m^-\right]\left[X_w^-\right]} \tag{6}$$

where K_x^{OH} is equilibrium constant for the binding of the counterion, X^-, and hydroxide ions (OH^-) to the micellar surface. In this expression, X_m^- and X_w^- are surfactant counterions existing in the micellar and aqueous phases, respectively.

For OH^- as a reactive ion and Br^- as a nonreactive micelle counterions, the ion-exchange equilibrium can be expressed as Eq. (7):

$$OH_m^- + Br_w^- \rightleftharpoons OH_w^- + Br_m^- \tag{7}$$

And equilibrium constant for the binding of the counterion, Br^-, and hydroxide ions (OH^-) to the micellar surface is given as Eq. (8)

$$K_{Br}^{OH} = \frac{\left[OH_w^-\right][Br_m^-]}{\left[OH_m^-\right]\left[Br_w^-\right]} \tag{8}$$

In the present study, unfortunately, we are not able to determine many parameters in Scheme 3 with reliable assumptions.

Effects of Bromide Salts in the Absence and Presence of CTAB Surfactant

Figure 5 shows influences of added bromide salts on the first-order rate constants [log (k/s^{-1})] for the hydrolysis of *p*-NPB in aqueous media containing 5.0 mmol dm^{-3} of borate buffer of pH 9.18 in the presence of 5.0 × 10^{-3} mol dm^{-3} CTAB (cf. Table III). The promoted rate constant with the micelle formation has been retarded by the addition of a metal

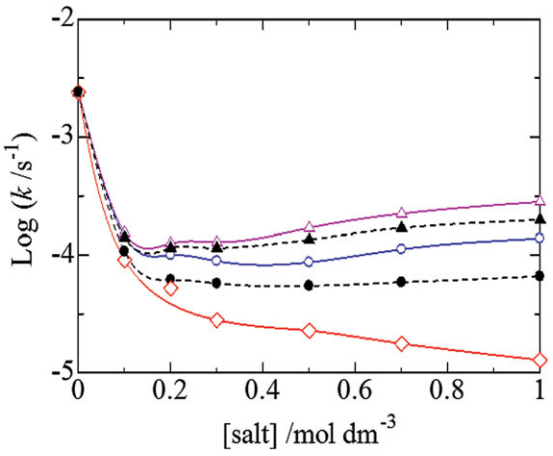


Figure 5 Changes in the log (k/s^{-1}) value with bromide salt concentration for the hydrolysis of *p*-NPB in aqueous buffered solution of pH 9.18 containing 5.0 × 10^{-3} mol dm^{-3} CTAB at 35°C: (◇) NaBr; (●) Me_4NBr; (○) Et_4NBr, (▲) Pr_4NBr, (△) *n*-Bu_4NBr.

Table III Effects of Added Bromide Salts on the Hydrolysis Rate of *p*-NPB (1.0 × 10^{-4} mol dm^{-3}) in Aqueous Buffer Solution of pH 9.18 Containing 5.0 × 10^{-3} mol dm^{-3} CTAB at 35°C

c (salt) (mol dm^{-3})	log (k/s^{-1})				
	NaBr	Me_4NBr	Et_4NBr	Pr_4NBr	*n*-Bu_4NBr
0.0	–2.62	–2.62	–2.62	–2.62	–2.62
0.1	–4.04	–3.97	–3.84	–3.85	–3.81
0.2	–4.28	–4.21	–4.00	–3.94	–3.90
0.3	–4.55	–4.24	–4.05	–3.94	–3.89
0.5	–4.64	–4.26	–4.06	–3.87	–3.77
0.7	–4.75	-4.23	–3.95	–3.77	–3.65
1.0	–4.89	–4.18	–3.86	–3.60	–3.55

bromide, NaBr. For instance, 0.10 mol dm^{-3} of NaBr causes a sudden decrease in log (k/s^{-1}) from –2.62 to –4.04 and the further increasing NaBr concentration results in the further gradual deceleration.

Nonmetallic bromide salts, such as Me_4NBr, also have caused significant rate retardation upon the addition of 0.1 mol dm^{-3} salt. However, with increasing salt concentration (>0.2 mol dm^{-3}), the rate retardation seems to be gradually diverted (though not so significant) and, finally, even a slight but obvious rate acceleration is observed (cf. Fig. 5 and Table III).

The rate retardation caused by all the added salts can be attributed to the competition between the reactant (OH^-) and the abundant anions from the electrolytes (e.g., NaBr) for the "binding site" on or in the micelle. The abundant Br^- ion from added salts, which is also the counterion of the cationic surfactant, should compete with the prominent nucleophile, the OH^- ion, for the micellar surface. Accordingly, with the increased bromide salt concentration, the Br^- ion displaces the OH^- ion from the micellar surface and hence results in the abrupt rate deceleration. Interestingly, the rate retardation seems to depend upon the hydrophobicity of the salt cations. The remarkable rate retardation caused by the added salts follows the order of NaBr > Me_4NBr > Et_4NBr > Pr_4NBr > *n*-Bu_4NBr.

However, a further increase in the nonmetallic bromide concentration, especially, in the higher concentration range of 0.30–1.0 mol dm^{-3}, has caused the reversal rate acceleration. This reversed acceleration may be attributed to some changes in micellar structure, or more substantially speaking, to the increase in activities of the OH^- ion which should be brought by the destruction of bulk water structure with the added high concentration of the nonmetallic salts. In addition, the nucleophilicity of the Br^- ion (vide infra), which is basically available in large quantities in the media, could possibly contribute to the small reversal acceleration.

The further rate deceleration caused by the added NaBr can be justified by the apparent pH of the reaction solution. The apparent pH of the reaction solution measured after the completion of the hydrolysis reaction have shown some decrement with increasing NaBr concentration. This decrement phenomenon can be attributed to the possible interaction between Na^+ and OH^- ions, as discussed previously [23]. The nonmetallic salts, however, have caused no significant change in apparent pH especially in the presence of up to 0.3 mol dm^{-3}, after which, increases in apparent pH are observed (cf. Fig. 6). The increases in pH value with increasing concentration of nonmetallic salts should be caused by the decrease of water activity, or the destruction of bulk water structure through hydrogen bonding, with the added salts.

We have tried to keep the ionic strength with $LiClO_4$ or $NaClO_4$; however, the catalytic effects by cationic surfactants have been completely inhibited on the addition of the salt. The addition of the neutral salts, such as NaBr or Et_4NBr, should not bring any H^+ or OH^- directly. The decrease in (apparent) pH by the addition of NaBr may be caused by weak interaction between Na^+ and OH^- in H_2O (or hydrolysis) (as mentioned above) and/or by the increase in the ionic strength.

The observed pH increase in the presence of R_4NX should be caused by the decrease in the water activity, or in other words, the increased OH^- ion activity coefficient. We have explained the increase in OH^- activity (the pH increase) in terms of changes of water activity. The decrease in water activity, at last, causes the increase of OH^- activity through the poor solvation

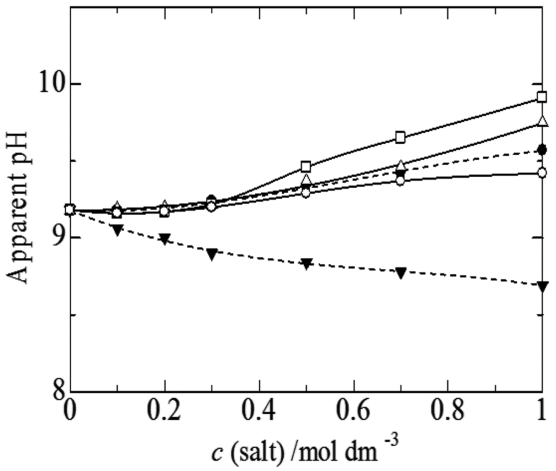


Figure 6 Changes in the apparent pH value of the reaction solution with salt concentration for the hydrolysis of *p*-NPB in aqueous buffer media of pH 9.18 containing 5.0×10^{-3} mol dm^{-3} CTAB at 35°C: (▼) NaBr; (○) Me_4NBr; (●) Et_4NBr, (△) Pr_4NBr, (□) *n*-Bu_4NBr.

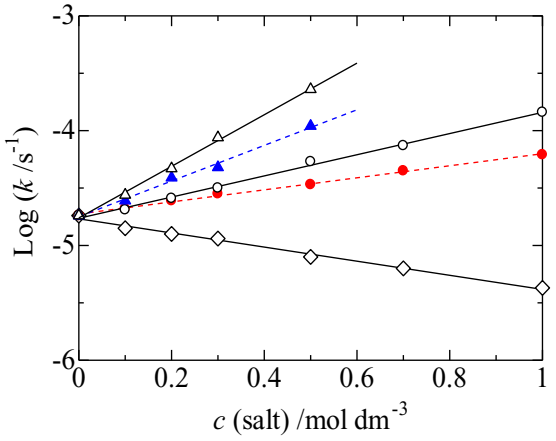


Figure 7 Changes in log (k/s^{-1}) values with the bromide salt concentration for the hydrolysis of *p*-NPB in aqueous buffered solution of pH 9.18 in the absence of surfactant at 35°C: (◇) NaBr; (●) Me_4NBr; (○) Et_4NBr, (▲) Pr_4NBr, (△) *n*-Bu_4NBr.

(hydration) toward ions. The above discussion would be valid in micelle as well as bulk water systems. At any rate, the changes of rate observed in Fig. 5 are in good correlation with the (apparent) pH changes shown in Fig 6.

Without the CTAB surfactant, the influences of these bromide salts on the hydrolysis reaction rates of *p*-NPB in aqueous buffer media of pH 9.18 have been also examined (Fig. 7). In the absence of CTAB, the NaBr salt once again decelerates linearly the hydrolysis rate of *p*-NPB. The log (k/s^{-1}) value decrease from –4.74 to –4.85, –4.90, –4.94, –5.10, –5.20, and –5.37 with increasing NaBr concentration of 0.10, 0.20, 0.30, 0.50, 0.70, and 1.0 mol dm^{-3}, respectively (Table IV). However, nonmetallic bromide salts have accelerated the hydrolysis rate linearly (in solution containing no surfactant). In the presence of Et_4NBr, for instance, the log (k/s^{-1}) value has increased as –4.69, –4.59, –4.50, –4.27, –4.13, and –3.94 with its concentrations of 0.10, 0.20, 0.30, 0.50, 0.70, and 1.0 mol dm^{-3}, respectively. Generally, the rate acceleration effect imposed by the bromide salts has increased with increasing hydrophobicity (size) of the nonmetallic cations in the order of $Me_4NBr < Et_4NBr < Pr_4NBr <$ *n*-Bu_4NBr. The larger the cation of the nonmetallic salt, the more it distracts the water structure/or activity, which lead to an increase in the activity of the prominent nucleophile, the OH^- ion. We may mention that the Br^- ion is also an excellent nucleophile toward an S_N2 substrate [24,25,27].

Table IV Effects of Added Bromide Salts on the Hydrolysis Rate of *p*-NPB (1.0×10^{-4} mol dm^{-3}) in Aqueous Buffer Solution of pH 9.18 in the Absence of CTAB at 35°C

c (salt) (mol dm^{-3})	log (k / s^{-1})				
	NaBr	Me_4NBr	Et_4NBr	Pr_4NBr	*n*-Bu_4NBr
0.0	–4.74	–4.74	–4.74	–4.74	–4.74
0.1	–4.85	–4.68	–4.69	–4.61	–4.56
0.2	–4.90	–4.61	–4.59	–4.41	–4.33
0.3	–4.94	–4.55	–4.50	–4.32	–4.06
0.5	–5.10	–4.47	–4.27	–3.96	–3.64
0.7	–5.20	–4.35	–4.13	–3.54	–3.60
1.0	–5.37	–4.21	–3.84	–3.44	–3.54

We can notice that the positive influences of added bromide salts in media without the surfactant are similar to those in the CTAB micellar media (for >0.3 mol dm^{-3} of added salts). It is suspected that similar mechanisms are operating in both systems, regardless of the micellar effect by surfactant and the retardation by ~0.1 mol dm^{-3} added salts. The rate acceleration caused by the added bromide salts, except NaBr, should be attributed to the increase of the OH^-activity in the media where water structure is distorted by the added salts. In addition to the OH^- ion, the attack by the Br^- ion (a nucleophile) toward the target compound, the *p*-NPB, should also contribute to the rate acceleration.

The observed micellar effect (increase of the rate with cationic surfactants and decrease with anionic one) may be related with some degree of stabilization or instabilization of the transition state of the reaction. However, this point is not discussed further in the present paper.

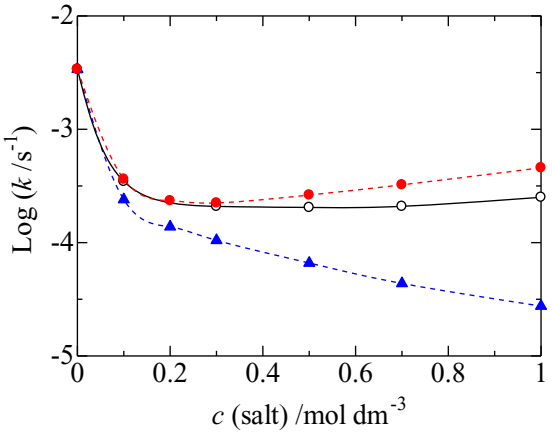


Figure 8 Changes in log (k/s^{-1}) values with the chloride salt concentration for the hydrolysis of *p*-NPB in aqueous buffered solution of pH 9.18 containing 5.0 × 10^{-3} mol dm^{-3} CTAC at 35°C: (▲) NaCl; (○) Et_4NCl, (●) *n*-Bu_4NCl.

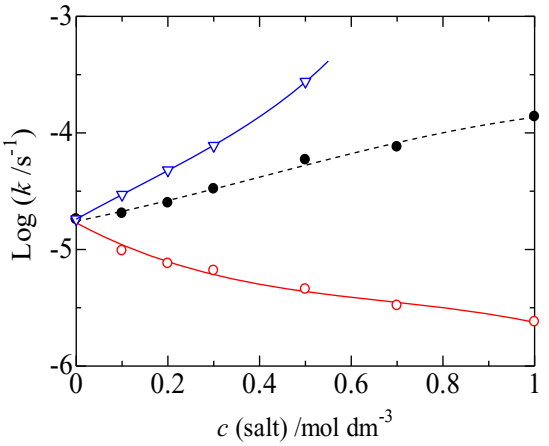


Figure 9 Changes in log (k/s^{-1}) values with chloride salt concentration for the hydrolysis of *p*-NPB in aqueous buffered solution of pH 9.18 in the absence of surfactant at 35°C: (○) NaCl; (●) Et_4NCl; (△) *n*-Bu_4NCl.

Table V Effects of Added Chloride Salts on the Hydrolysis Rate of *p*-NPB (1.0 × 10^{-4} mol dm^{-3}) in Aqueous Buffer Solution of pH 9.18 Containing 5.0 × 10^{-3} mol dm^{-3} CTAC at 35°C

c (salt) (mol dm^{-3})	log (k/s^{-1})		
	NaCl	Et_4NCl	*n*-Bu_4NCl
0.0	–2.47	–2.47	–2.47
0.1	–3.62	–3.46	–3.44
0.2	–3.86	–	–3.63
0.3	–3.98	–3.68	–3.65
0.5	–4.18	–3.69	–3.58
0.7	–4.36	–3.68	–3.49
1.0	–4.56	–3.60	–3.34

Effects of Chloride Salts in the Absence and Presence of CTAC Surfactant

The influences of chloride salts, NaCl, Et_4NCl, and *n*-Bu_4NCl, on the hydrolysis reaction rates of *p*-NPB have been examined in aqueous buffer media of pH 9.18 containing 5.0 × 10^{-3} mol dm^{-3} CTAC surfactant at 35°C (Fig. 8). The CMC value with CTAC in the buffered media has been found to be 1.26 × 10^{-3} mol dm^{-3} (cf. Table I). All the added salts up to 0.20 mol dm^{-3} have retarded remarkably the hydrolysis rate. The NaCl salt has caused a continuous rate deceleration with further increasing concentration of NaCl (cf. Table V). However, nonmetallic salts, Et_4NCl and *n*-Bu_4NCl, of higher concentrations (>0.3 mol dm^{-3}) have managed to recover the retarded reaction rate to some extent. The rate deceleration caused by the chloride salts follow the order of NaCl > Et_4NCl > *n*-Bu_4NCl, for > 0.3 mol dm^{-3}.

Cordes and Dunlap [19] have reported the rate retardation upon addition of foreign salts for the hydrolysis of *p*-nitrophenyl hexanoate in the presence of CTAC in aqueous buffer media of pH 10.15. They have indicated that all the added salts are inhibitors and that specially 0.1 mol dm^{-3} bromide, and nitrate ions are sufficient to convert the surfactant-catalyzed reaction to uncatalyzed (inhibited) one. We have examined the detailed effects of various salts (with the wide concentration range up to 1.0 mol dm^{-3}) on the hydrolysis rates of *p*-NPB in the absence and presence of CTAB and CTAC surfactants. It has been found that the retarded (inhibited) reaction rate of *p*-NPB hydrolysis by 0.10 mol dm^{-3} salts is partially recovered with increasing concentrations of the nonmetallic bromide and chloride salts of >0.3 mol dm^{-3} (excluding the metal salts of NaBr and NaCl).

In the absence of CTAC, the NaCl salt has only decelerated the hydrolysis rate of *p*-NPB (Fig. 9). The log(k/s^{-1}) value decreases to –4.74, –5.01, –5.12, –5.18, –5.34, –5.48, and –5.65 with increasing NaCl concentrations of 0.0, 0.10, 0.20, 0.30, 0.50, 0.70, and 1.0 mol dm^{-3}, respectively (cf. Table VI). The rate deceleration caused by NaCl is slightly stronger than that caused NaBr. This difference may be caused by the ion size difference between the anions.

The nonmetallic salts, Et_4NCl and *n*-Bu_4NCl, however, have caused considerable rate accelerations in their respective concentrations. The acceleration can be attributed mainly to the nucleophilicity of the Cl^- ion toward the substrate compound. The rate acceleration caused by Et_4NCl and *n*-Bu_4NCl salts is slightly weaker than the corresponding bromide salts. It is well known that the nucleophilicty of Br^- is stronger

Table VI Effects of Added Chloride Salts on the Hydrolysis Rate of *p*-NPB (1.0×10^{-4} mol dm^{-3}) in Aqueous Buffer Solution of pH 9.18 in the Absence of CTAC at 35°C

	log (k / s^{-1})		
c (salt) (mol dm^{-3})	NaCl	Et_4NCl	n-Bu_4NCl
0.0	–4.74	–4.74	–4.74
0.1	–5.01	–4.69	–4.53
0.2	–5.12	–4.60	–4.32
0.3	–5.18	–4.48	–4.11
0.5	–5.34	–4.23	–3.56
0.7	–5.48	–4.12	–
1.0	–5.65	–3.86	–

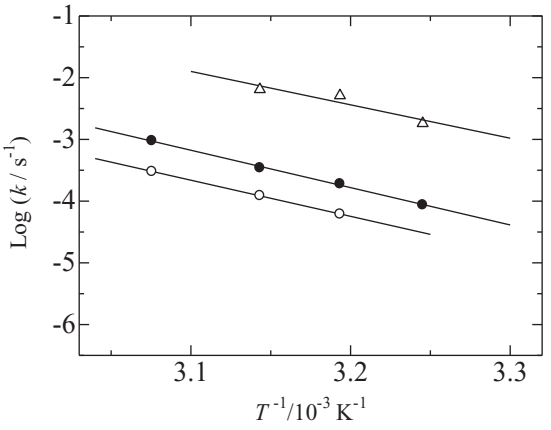


Figure 10 Arrhenius plots of log (k/s^{-1}) for the *p*-NPB hydrolysis in aqueous buffer of pH 9.18 media: (○) no surfactant; (●) 5.0×10^{-3} mol dm^{-3} CTAB + 0.50 mol dm^{-3} Et_4NBr; (△) 10.0×10^{-3} mol dm^{-3} CTAB.

than Cl^- in aqueous solution. The following overall nucleophilicity order for the S_N2 mechanism (in protic solvents) has been reported: $I^- > CN^- > OH^- > N_3^- > Br^- > ArO^- > Cl^-$ > pyridine > $AcO^- > H_2O$ [47]. In the previous paper [22], we have reported that tetraalkylammonium chloride and bromide accelerate the hydrolysis reaction of *p*-nitrophenyl anthranilate (2-aminobenzoate) in aqueous and binary MeCN-H_2O mixed solutions. In addition, it has been established that anion exchange reactions between Cl^- and Br^- from a substrate or added salts cause remarkable rate changes (acceleration and deceleration) in solvolyis reactions of organic halides in binary solvents between water and organic solvents [24,25,27].

Temperature Dependency

Figure 10 shows the Arrhenius plots for hydrolysis of the substrate in aqueous buffered media in the presence of the CTAB surfactant. All the systems examined have given a good linearity in the range from 35 to 50ºC. The observed activation energy (E_a) values are 112.6, 115.8, and 103.6 kJ mol^{-1} for no surfactant, 5.0×10^{-3} mol dm^{-3} CTAB + 0.50 mol dm^{-3} Et_4NBr, and 10.0×10^{-3} mol dm^{-3} CTAB (without added salt), respectively. The good linearity in the plots and those large E_a values suggest that the hydrolysis reactions in the presence and/or absence of surfactant and salts are controlled by the normal temperature-dependent mechanism. We may mention that the rate constant obtained for the solution without surfactant nor added salt at 35ºC has a slight deviation from the straight line with other temperatures.

CONCLUSIONS

We have observed the micellar effects on the alkali hydrolysis rate of *p*-NPB with CTAB, CTAC, and SDS surfactants in pH buffered media. The cationic surfactants, CTAB and CTAC, promote the reaction rate significantly with micelle formation, while no acceleration for the anionic surfactant, SDS, even with the micellization. The promoted reaction rates with the micellization of CTAB and CTAC surfactants have been inhibited or retarded by only 0.1 mol dm^{-3} salts added to the micellar solutions. Alkali metal salts (NaBr and NaCl) have caused further gradual decrease in the reaction rate with increasing salt concentration. However, nonmetallic salts of more than 0.2 or 0.3 mol dm^{-3} have managed to recover the retardation to some extent. The rate recovering has followed in the order of $Me_4NBr <$ $Et_4NBr < Pr_4NBr <$ n-Bu_4NBr or $Et_4NCl <$ n-Bu_4NCl in CTAB or CTAC micellar media, respectively. In the absence of surfactants, all the added salts, except for NaBr and NaCl, have accelerated linearly the hydrolysis rate of *p*-NPB in the order of $Me_4NBr < Et_4NBr$ $< Pr_4NBr <$ n-Bu_4NBr or $Et_4NCl <$ n-Bu_4NCl. We may propose that the increases in the rate constants in the absence and presence of surfactants (regardless of micellization) are caused not only by the increase of OH^- activity with further distortion of the bulk water structure but also the activity increase of another nucleophile, X^- (X = Br or Cl), with increasing concentration of the bulky nonmetallic salts.

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