Colloid Polym Sci 279:813–818 (2001)

SHORT COMMUNICATION

K. Ruan
Z. Zhao
J. Ma

Effect of bromide salts on cationic micellar catalysis

Received: 1 August 2000
Accepted: 31 January 2001

K. Ruan · Z. Zhao (✉) · J. Ma
Department of Chemistry
Peking University
Beijing 100871, China
e-mail: rank@263.net
Tel.: 86-10-62762309
Fax: +86-10-62751708

Abstract The effect of bromide salts, MBr [M = Na, $(CH_3)_4N$, $(C_2H_5)_4N$, $(C_4H_9)_4N$, $C_8H_{17}N(CH_3)_3$], on the first-order rate constant, k_1, of basic hydrolysis of 2,4-dinitrochlorobenzene in micelle solutions of cetyltrimethylammonium bromide has been studied. The main results are as follows. The molar ratio concentrations of OH^-, m_{OH}^S, on the micelle surface in the presence of different concentrations of Br^- ions, were calculated on the basis of the pseudophase ion-exchange model, and there is a linear relation between k_1 and m_{OH}^S. The relation between k_1 and the concentrations of various bromides could be presented with a single curve, and the cations of the bromides have little effect on k_1. Under the experimental conditions, there is a linear relation between $1/k_1$ and the concentrations of Br^-; thereby a new method calculating the competition binding constant between OH^- and Br^- from dynamic data is proposed. The hydrodynamic radii of the micelles increase with the addition of bromide salts.

Key words Micellar catalysis · 2,4-Dinitrocholorobenzene · Cetyltrimethylammonium bromide · Hydrolysis · Bromide salts

Introduction

Micellar catalysis and microemulsion catalysis are one of the current active fields in the physical chemistry of surfactant [1–3]. Generally, cationic micelles assist reactions of anions with nonionic organic substrates, while anionic micelles inhibit such reactions, and vice versa. Nonionic micelles usually have a weak effect on the chemical reaction. On the other hand, 1,000–2,000-fold, even 10^6-fold, overall rate constant enhancement has been observed in some reactions catalyzed by cationic micelles [4].

The pseudophase ion-exchange (PIE) model is applied most widely in micellar catalysis. The basic assumptions of PIE are as follows:

1. Micelles act as a separate phase from water, all reactants are distributed quickly between water and micellar phase, and the reaction rate can be considered as the sum of that in two phases.
2. The reaction in the micellar pseudophase occurs mainly at the micelle surface.
3. The reaction ions and inert ions compete at the charged micellar surface.

The PIE model has been applied to explain qualitatively and quantitatively many experimental phenomena and results [5].

There are many factors that affect micellar catalysis, for example, the properties and structure of the surfactant, the concentrations of the surfactants and the reaction substrate, temperature, the properties and concentrations of additives, etc. [6–8]. Especially the effects of reaction ions on micellar catalysis have been studied extensively and thoroughly [5, 9, 10], and the PIE model has been used to explain the results, although the effect of hydroxide ions does not fit the model very well. However the effects of inert ions, especially coions, have been little studied [9, 11]. Most work has focused on the inhibition effects of various counterions, and the results are not explained quantitatively.

This work is focused on the effect of various bromides on the basic hydrolysis reaction rate of 2,4-dinitrochlorobenzene (DNCB). Some linear equations are derived from the PIE model, so some parameters of the model can be derived from the kinetic data. The PIE model is applied to explain quantitatively and qualitatively the effects of bromide ions and various coions.

Experimental

Materials

Cetyltrimethylammonium bromide (CTAB, Shan Dong Jining Chemical, China, AR grade) was recrystallized twice from an acetone and ethanol mixture. $(C_2H_5)_4NBr$ (Et_4NBr, Beijing Chemical, AR grade) was recrystallized twice from butanol. $(C_4H_9)_4NBr$ (Bu_4NBr, Shan Dong Jining Chemical, AR grade) was recrystallized twice from acetone. DNCB (Beijing Chemical, CP grade) was recrystallized from ethanol. NaBr, $(CH_3)_4NBr$ (Me_4NBr), octatrimethylammonium bromide (OTAB) and NaOH are all AR grade (Beijing Chemical). All solutions were prepared in doubly distilled water.

Determination of the rate constant of hydrolysis of DNCB

At 25 °C, the solutions of CTAB, DNCB, NaOH, and bromide were mixed rapidly. The concentration of the hydrolysate, 2,4-dinitrophenol, was determined by UV absorption at 358 nm [7]. A solution of NaOH, CTAB, and bromide with the same concentrations as they are in the reaction mixture was used as a reference. In all the experiments the concentrations of DNCB were about 9.5×10^{-5} moll^{-1} and the concentrations of NaOH were about 0.05 moll^{-1}. The hydrolysate (2,4-dinitrophenol) concentration corresponding to the different absorbance could be checked from the standard curve, which was made by determining the absorbances of a series of 2,4-dintrophenol solutions with known concentrations. At time t, the concentration of DNCB in the reaction system was c_0–c_t, where c_0 is the original concentration of DNCB and c_t is the product concentration at time t. The first-order rate constant, k_1, was determined by the slope of the plot $\ln(c_0 - c_t)$ against t.

Determination of hydrodynamic radii of the micelles

The hydrodynamic radii of the micelles were determined by dynamic light scattering. The experimental conditions were wavelength, 514.5 nm; power, 200 or 300 mW; temperature, 30 °C; scattering angle, 90°.

Result and discussion

Characteristics of the basic hydrolysis of DNCB in CTAB micelle solutions

It is well known that the basic hydrolysis of DNCB is a second-order reaction of nucleophilic substitution by OH^- ions [7]. It could be considered as a pseudo-first-order one if the OH^- ions are in large excess,

$$-\mathrm{d}c_{\mathrm{DNCB}}/\mathrm{d}t = k_2 c_{\mathrm{DNCB}} c_{\mathrm{NaOH}} = k_1 c_{\mathrm{DNCB}} \ ,$$

where c_{DNCB} and c_{NaOH} are the concentrations of DNCB and NaOH in molarity, and k_2 and k_1 are second-order and pseudo-first-order rate constants, respectively.

The relationship between k_1 and concentrations of CTAB is shown in Fig. 1, when the concentration of NaOH is 0.046 moll^{-1}, and the original concentration of DNCB is 0.095 mmol · l^{-1}. It can be seen from Fig. 1 that the hydrolysis of DNCB is catalyzed by the CTAB micelles and that the maximum second-order rate constant, k_2, is 100 times higher than that in pure water, which is 1.42×10^{-4} lmol^{-1}s^{-1} [12]. A maximum appears in the k_1–CTAB concentration curve at a CTAB concentration of about 7 mmoll^{-1}, which is an ordinary phenomenon when the surfactant concentration exceeds the critical micelle concentration (cmc), since the high concentration of the surfactant may lead to the appearance of some "blank" micelles containing no substrates, and correspondingly, the decrease of the substrate concentration in the micellar pseudophase. On the other hand, the increase in the micelle concentration dilutes the second reactant OH^- within the micellar pseudophase, causing a decrease in k_1. When the concentration of CTAB is very low, the curve of k_1 with concentration does not show an apparent S-type change [12]. This may due to the fact that the CTAB concentration used in this work is far larger than the cmc of CTAB, which is 3.2×10^{-4} moll^{-1} in the presence of 0.05 moll^{-1} NaOH, making the S-type change not apparent.

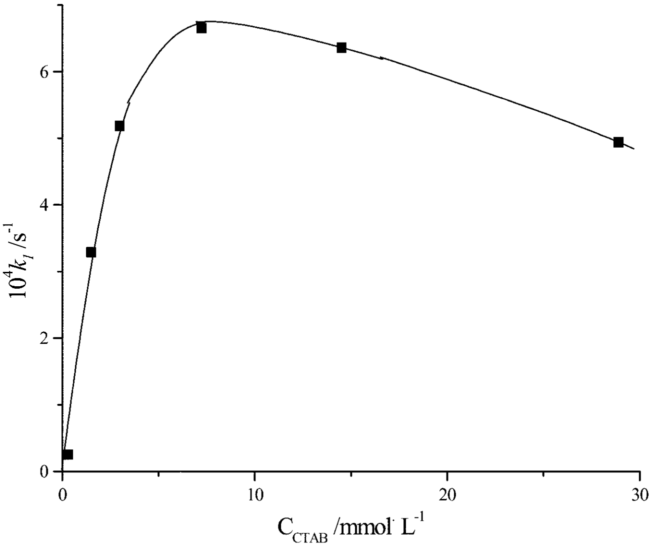

Fig. 1 Relation between k_1 and the concentrations of cetyltrimethylammonium bromide

Effect of small molecule bromides on the rate constant k_1

Effect of Br^- on the concentrations of OH^- at the micelle surface

OH^- ions are the reacting ions in the hydrolysis of DNCB. As described in the mass action law, k_1 should increase with the concentration of NaOH [12]. The addition of Br^- ions inhibits the catalytic effect of the CTAB micelles by excluding OH^- ions from the micelle surface and decreasing the effective concentration of OH^- at the micelle surface as a result of ionic competition for micelle head groups.

According to the PIE model, the chemical reaction takes place separately in the micellar pseudophase and the aqueous phase; therefore the overall reaction rate is the sum of the reaction rates in the two phases. In the micellar pseudophase, the reaction takes place mainly at the Stern layer and depends on the concentrations of reactants at the micelle surface. In the micelle solutions of cationic surfactant, D, the reaction rate constant, k_1, of the basic hydrolysis of DNCB is as follows [13]:

$$k_1 = \frac{k_2^W[OH_T] + (k_2^M K_S - k_2^W)[D_n]m_{OH}^S}{1 + K_S[D_n]} \ , \qquad (1)$$

where K_S is the binding constant of substrate S with the micelle and has the value of 67 $lmol^{-1}$ for DNCB [14]. $[OH_T]$ is the total concentrations of OH^- in the solution. $[D_n]$ is the concentration of micellized surfactants, i.e., $[D_n] = [D]$–cmc, where [D] is the total concentration of the surfactant in the solution and cmc is the cmc of the surfactant. k_2^W and k_2^M are the second-order rate constants in water and the micellar phases, respectively; however, k_2^M is described in terms of the molar ratio concentration, so its unit is reciprocal seconds.

The effective concentration of OH^- in the micellar phase is generally described by m_{OH}^s, which is the mole fraction of OH^- in the micellar pseudophase, i.e., the ratio of the molarity of OH^- in micellar pseudophase to $[D_n]$ [13]:

$$\left(m_{OH}^S\right)^2 + m_{OH}^S\left(\frac{[OH_T] + K_{Br}^{OH}[Br_T]}{(K_{Br}^{OH} - 1)[D_n]} - \beta\right) - \frac{\beta[OH_T]}{(K_{Br}^{OH} - 1)[D_n]} = 0 \ , \qquad (2)$$

where $[Br_T]$ is the total concentration of Br^- in solution. β is the degree of binding of the counterion with micelles, i.e., the average counterion number bound to each micellized surfactant ion. In the present work, the concentration of NaOH is much higher than that of bromides, so β can be considered as constant. K_{Br}^{OH} is the competition binding constant between OH^- and Br^- and describes the relative degree of binding of those ions with the micelle surface. The experimental values of K_{Br}^{OH} are mostly between 10 and 20, and K_{Br}^{OH} is often taken as 12.5 [15]. In the present work, the known variables are $K_{Br}^{OH} = 12.5$, $\beta = 0.8$, $K_S = 67\ lmol^{-1}$, $[OH_T] = 0.046 moll^{-1}$, $[D] = [CTAB] = 1.49\ mmoll^{-1}$, and cmc = 0.3 $mmoll^{-1}$ (the cmc for simple CTAB micelles is 0.9 $mmoll^{-1}$ and the value is correlated to be 0.3 $mmoll^{-1}$, considering the effect of OH^- and Br^- on the cmc [16]). From the previously mentioned data and concentrations of bromides, m_{OH}^s at different concentration of bromides could be calculated from Eq. (2).

The relationship between k_1 determined at different Br^- concentrations and the calculated m_{OH}^s is shown in Fig. 2. From Fig. 2 it can be seen that:

1. The value of k_1 increases with increasing m_{OH}^s in a linear relation. Since the increase in the concentration of Br^- ions will decrease m_{OH}^s at the micelle surface, the Br^- ions play a role of inhibiting the catalytic effect of the CTAB micelles.
2. From Eq. (1), the intercept for the line of k_1 versus m_{OH}^s should be $k_2^W[OH_T]/(1 + K_S[D_n])$. From the line intercept of Fig. 2 and the previously mentioned data, k_2^W was calculated to be about $7.5 \times 10^{-5}\ lmol^{-1}s^{-1}$. In consideration of the experimental error and the small value of the intercept in Fig. 2, the calculated k_2^W value is quite close to the rate constant $1.42 \times 10^{-4}\ lmol^{-1}s^{-1}$ obtained in pure water by Bunton and Robinson [12].
3. From the line slope in Fig. 2 and Eq. (1), k_2^M was calculated to be 0.0072 s^{-1}, which is the second-order rate constant in the micellar phase described by the molar ratio concentration as previously.

Because the reaction occurs mainly in the Stern layer at the micelle surface, and the mole volume, V_m, of the Stern layer for spherical micelles is about 0.14 $lmol^{-1}$ [5],

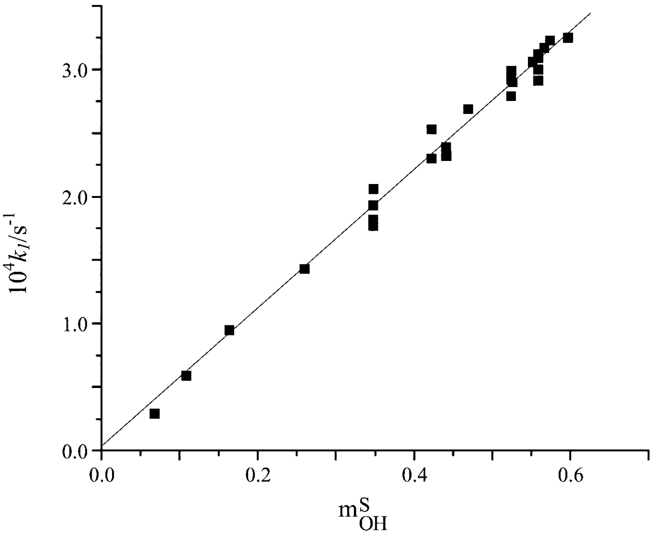

Fig. 2 Relations between k_1 of the 2,4-dinitrochlorobenzene hydrolysis reaction and the molar ratio concentrations, m_{OH}^s, at the micelle surface

$k_2^{\mathrm{m}} = k_2^{\mathrm{M}} \mathrm{V_m} = 1.0 \times 10^{-3}\ \mathrm{lmol^{-1}s^{-1}}$, where k_2^{m} is the second-order rate constant in the micellar pseudophase in terms of the molarity. $k_2^{\mathrm{m}}/k_2^{\mathrm{w}} = 7.1(k_2^{\mathrm{w}} = 1.42 \times 10^{-4}\ \mathrm{lmol^{-1}s^{-1}}$ [12]), and it is in accordance with the result, $1 < k_2^{\mathrm{m}}/k_2^{\mathrm{w}} < 10$, which was reported in the references about the aromatic nucleophilic substitution reactions [5]. The negatively charged σ-complex compound is formed as a transition state in the aromatic nucleophilic substitution reaction and it interacts easily with the positively charged end group of cationic surfactants. So the rate constant is larger in the micellar phase than in water, i.e., the hydrolysis of DNCB is catalyzed in the cationic micellar solutions.

The relation between the concentrations of bromides and k_1 and the calculation of $K_{\mathrm{Br}}^{\mathrm{OH}}$

The relation between k_1 of the DNCB basic hydrolysis reaction and the concentrations of bromides (NaBr, $\mathrm{Me_4NBr}$, $\mathrm{Et_4NBr}$, $\mathrm{Bu_4NBr}$, and OTAB) at constant concentration of CTAB ($1.49\ \mathrm{mmoll^{-1}}$) and NaOH ($0.046\ \mathrm{moll^{-1}}$) is shown in Fig. 3. In the Fig. 3, k_1 decreases with increasing concentrations of bromides, and the experimental data of the five kinds of bromides fall on the same curve. That is to say, the main factor affecting k_1 is the concentration of the counterion $\mathrm{Br^-}$ of the $\mathrm{CTA^+}$ micelle, and k_1 has little relation with the properties of the bromine cations.

The main reasons for the inhibiting effect of the added bromide on the micellar catalysis of the DNCB basic hydrolysis reaction are as follows.

1. The competition between $\mathrm{Br^-}$ ions and $\mathrm{OH^-}$ ions at the micelle surface decreases the concentration of $\mathrm{OH^-}$ ions at the micelle surface.
2. $\mathrm{Br^-}$ has a stronger affinity for the cationic micelle than $\mathrm{OH^-}$; therefore, it could compress the electrical double layer around the micelle surface to a greater extent and, hence, increase the aggregation number of the micelles and the size of the micelles. Consequently, the organic substrate tends to enter the interior of the micelles more deeply, which is not favorable for the reaction at the micelle surface region.

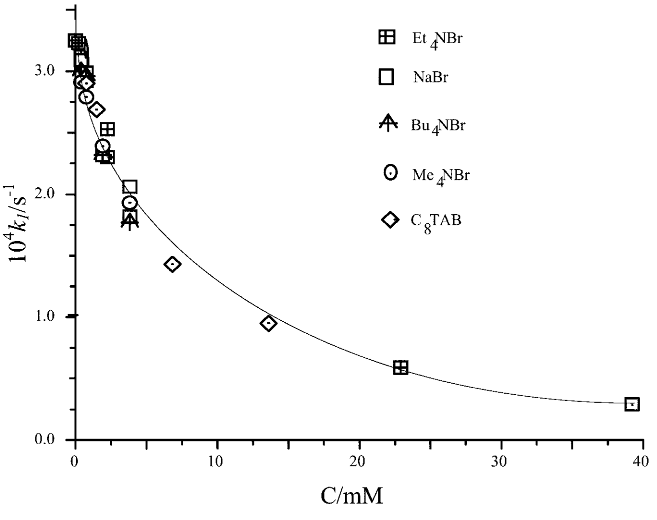

Fig. 3 Relation between k_1 and concentrations of bromide salts

Under the previously mentioned experimental conditions, assuming that the value of $K_{\mathrm{Br}}^{\mathrm{OH}}$ is 10–20 in Eq. (2),

$$\frac{[\mathrm{OH_T}] + K_{\mathrm{Br}}^{\mathrm{OH}}[\mathrm{Br_T}]}{(K_{\mathrm{Br}}^{\mathrm{OH}} - 1)[\mathrm{D_n}]} \gg \beta \tag{3}$$

and when $[\mathrm{Br^-}]$ is large

$$\left(\frac{[\mathrm{OH_T}] + K_{\mathrm{Br}}^{\mathrm{OH}}[\mathrm{Br_T}]}{(K_{\mathrm{Br}}^{\mathrm{OH}} - 1)[\mathrm{D_n}]}\right)^2 \gg \frac{4\beta[\mathrm{OH_T}]}{(K_{\mathrm{Br}}^{\mathrm{OH}} - 1)[\mathrm{D_n}]} \ . \tag{4}$$

The approximate value of $m_{\mathrm{OH}}^{\mathrm{s}}$ can be obtained by solving Eq. (2), where the items on the right of Eqs. (3) and (4) are omitted.

$$m_{\mathrm{OH}}^{\mathrm{S}} \approx \frac{\beta[\mathrm{OH_T}]}{[\mathrm{OH_T}] + K_{\mathrm{Br}}^{\mathrm{OH}}[\mathrm{Br_T}]} \tag{5}$$

Because $k_2^{\mathrm{m}} \gg k_2^{\mathrm{W}}$, Eq. (6) can be obtained by substituting Eq. (5) in Eq. (1),

$$\frac{1}{k_1} = \frac{1 + K_{\mathrm{S}}[\mathrm{D_n}]}{k_2^{\mathrm{M}} K_{\mathrm{S}}[\mathrm{D_n}]\beta} + \frac{(1 + K_{\mathrm{S}}[\mathrm{D_n}])K_{\mathrm{Br}}^{\mathrm{OH}}}{k_2^{\mathrm{M}} K_{\mathrm{S}}[\mathrm{D_n}][\mathrm{OH_T}]}[\mathrm{Br_T}] \ . \tag{6}$$

Equation (6) suggests a plot of $1/k_1$ against $[\mathrm{Br_T}]$ should yield a straight line; from the ratio of the slope to the intercept of the line ($K_{\mathrm{Br}}^{\mathrm{OH}}/[\mathrm{OH_T}]$), the value of $K_{\mathrm{Br}}^{\mathrm{OH}}$ was calculated to be 9.2, which is close to the value of 12.5 reported in Ref. [15]. The previous discussion provides a method for calculating $K_{\mathrm{Br}}^{\mathrm{OH}}$ from dynamic data, and the value obtained can be confirmed by other methods [15].

From the intercept of the line in Fig. 4 and corresponding known data, k_2^{M} was calculated to be $0.0056\ \mathrm{s^{-1}}$, quite close to the value of $0.0072\ \mathrm{s^{-1}}$ obtained from the slope of k_1 versus $m_{\mathrm{OH}}^{\mathrm{s}}$ in Fig. 2.

Effect of bromides on the structure of the micelle

The degree of counterion binding, β, shows the affinity between the counterions and the micelles, and the larger the β value, the larger the affinity. In the literature, the value of β of the $\mathrm{Br^-}$ ion was reported to be about 0.8, and β of $\mathrm{OH^-}$ is about 0.5 for $\mathrm{CTA^+}$ micelles [13]. That is to say, for $\mathrm{CTA^+}$ micelles, $\mathrm{Br^-}$ has a stronger affinity than $\mathrm{OH^-}$, and thus $\mathrm{Br^-}$ ions can decrease the activity of the micellar catalysis of the hydrolysis of DNCB by excluding ionic reactant $\mathrm{OH^-}$ from the micelle surfaces.

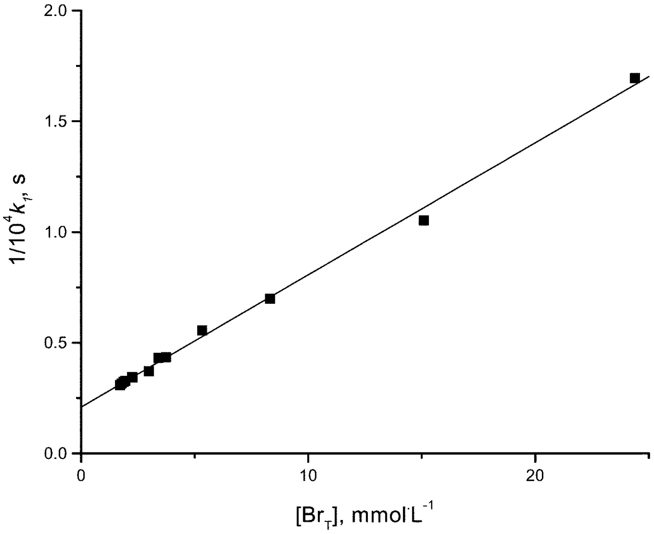

Fig. 4 Relation between $1/k_1$ and [Br_T]

Meanwhile, as the value of β increases, the repulsion interaction between the end groups of the cationic ions of the surfactant becomes weak, and hence the aggregation number and the size of the micelles increase. The hydrodynamic radii of CTAB micelles under different conditions were determined by dynamic light scattering, and the values are listed in Table 1. From the table, it can be seen that the hydrodynamic radii of CTAB micelles increase remarkably in the presence of additive bromides. The increase in the micellar radius could lead to two results:

1. The positive charge density of the cationic micelle surface decreased inversely with the square of the micelle radius, so the concentration of OH^- decreased at the micelle surface region.
2. The hydrophobic hydrocarbon chains of the surfactants became extended, with the increase in the micelle radius, making the substrate (DNCB) enter the interior of the micelles easily, which is disadvantageous for its contact and reaction with OH^- at the micelle surface region.

It should be pointed out that, according to Eq. (2), the concentrations of Br^- and OH^- at the micelle surface are not inversely proportional to each other, i.e., there are other factors affecting the interaction between Br^- and the micelle surface besides the electrostatic interaction, for example, the difference in the hydrated radius of different counterions, etc.

Table 1 Effect of additive bromide salts on cetyltrimethylammonium bromide (*CTAB*) micelle size (c_{CTAB} = 0.0149 moll^{-1}, c_{NaOH} = 0.046 moll^{-1})

Concentrations of bromide salts (moll^{-1})	Micelle hydrodynamic radius (nm)
None	2.11
NaBr (0.0204)	2.54
Octatrimethylammonium bromide (0.0204)	2.64

Up to now, only a few works studied the effect of the ions carrying the same sign of charge with micelles on the micellar catalysis. The result in Fig. 3 shows that, Na^+, Me_4N^+, Et_4N^+, Bu_4N^+, and OTA^+ ions of the five kinds of bromides increase sequentially in their size and hydrophobicity, but their effect on the rate constant is almost the same, probably because the concentrations of the coions are very low in the Stern layer where the reaction takes place, which is also one assumption of the PIE model. Even if the OTA^+ ions, with a relatively long hydrophobic group, could take part in the formation of micelles, the mole fraction of OTA^+ in the micelles is very low, because its cmc is much larger than that of CTAB. Meanwhile, from Table 1, the size of the micelles having OTA^+ as an additive shows little difference from the micelles when the same amount of NaBr is added. All these factors make cations have a weak effect on the rate constant of the DNCB basic hydrolysis.

The effect of mixed micelles, CTAB and cetyl pyridine bromide (CPB), has also been studied; the results show that the effect of CPB on micellar catalysis is different from that of the low-molecular-weight bromides. The reaction rate is greatly increased with the addition of CPB, and the size of the micelles having CPB as an additive is also larger than that of the micelles when the same amount of bromides is added. Therefore it can be conclude that CPB has taken part in the formation of the micelles, but more work is needed to explain the results of mixed micellar catalysis by the PIE model.

Acknowledgement The support from the National Science Foundation of China (project 29733110) is gratefully acknowledged.

References

1. Fendler JH, Fendler EJ (1975) In: Catalysis in micellar and macromolecular systems. Academic, New York, pp 98, 220
2. Broxton TJ, Nasser A (1997) Can J Chem 75:202
3. Broxton TJ (1998) Aust J Chem 51:541
4. Fendler JH (1976) Acc Chem Res 9:153
5. Bunton CA (1991) In: Rubingh DN, Holland PM (eds) Cationic surfactants: physical chemistry. Dekker, New York, pp 323–405
6. Tascioglu S (1996) Tetrahedron 52:11113
7. Shen JJ, Zhao ZG, Ma JM (1997) Chem J Chin Univ 18:1527
8. Zhao ZG, Jiao TS (1999) Chem J Chin Univ 20:281

9. Buist GJ, Bunton CA, Robinson L, Sepulveda L, Stam M (1970) J Am Chem Soc 92:4072
10. Broxton TJ (1981) Aust J Chem 34:2313
11. Broxton TJ, Sango DB (1983) Aust J Chem 36:711
12. Bunton CA, Robinson L (1968) J Am Chem Soc 90:5972
13. Blasko A, Bunton CA, Cerichelli G, McKenzie DC (1993) J Phys Chem 97:11324
14. Bunton CA, Moffat JR, Rodenas E (1982) J Am Chem Soc 104:2653
15. Broxon TJ, Christic JR, Sango X (1987) J Org Chem 52:4814
16. Valiente M, Rodenas E (1989) J Colloid Interface Sci 127:522