# Metallomicelle Catalysis: Hydrolysis of *p*-Nitrophenyl Picolinate Induced by Schiff Base Co(II) Complexes in a Gemini Surfactant Micellar Solution

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ABSTRACT: Two Schiff base cobalt(II) complexes containing crowned substituents have been synthesized and employed to promote the hydrolysis of *p*-nitrophenyl picolinate (PNPP) in a buffered micellar solution formed by a cationic Gemini surfactant, bis(hexadecyldimethylammonium)hexane bromide (G(hex)C16, $2Br^-$) over a pH range of 6.50–8.50. In comparison, the reactivity of PNPP hydrolysis catalyzed by the same catalysts in the other micellar system, formed by a conventional single-chain analogue, that is, hexadecyltrimethylammonium bromide (CTAB), has also been evaluated under a selected condition. The results clearly reveal that the two metallomicelles made of the aforementioned Co(II) complexes and the G(hex)C16 are both efficient for catalyzing PNPP hydrolysis with about 3 orders of magnitude in rate acceleration compared with the background rate of PNPP spontaneous hydrolysis. Moreover, the rates of PNPP hydrolysis catalyzed by

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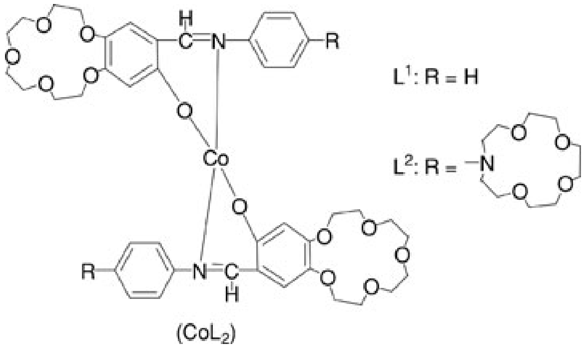
the two cobalt(II) complexes in G(hex)C16 micelles are about 2 times higher than in CTAB micelles, correspondingly. In addition, observations show that steric hindrance of substituents of the two complexes is also one of the major influencing factors in the PNPP hydrolytic reaction. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 672–680, 2007

## INTRODUCTION

As we know, hydrolysis of carboxylic acid esters plays an important role in chemistry and biochemistry [1,2]. In the past two decades, many groups [3–9] have focused on the hydrolysis of carboxylic acid esters, promoted by a variety of catalytic systems, and these researches provided highly important insights into the catalytic reaction mechanism of carboxylic acid esters. However, it is undoubtedly a big challenge that the activity of an artificial hydrolase can approach to that of natural enzymes. We have also devoted our attention to study the hydrolysis of carboxylic acid esters and found some satified catalytic systems [10–13]. In the last 2 years, we began to explore the catalytic property of Schiff base complexes in esters hydrolysis, and surprisingly found that Schiff base complexes not only accelerate the rate of some oxidation reactions effectively [14,15] but also promote the hydrolytic process of carboxylic acid esters and phosphate diesteres notably [16,17].

Moreover, it is worthy of pointing out that metallomicellar systems, which exhibit similar structural and kinetic properties to natural enzymes, have been extensively investigated as effective biomimetic systems for the catalytic hydrolysis of *p*-nitrophenyl picolinate (PNPP) [18–21]. Many insights have been gained about the importance of a suitable microenvironment provided by varied micelles for the ester hydrolysis, for example, the solubilization of substrate in micelles and electrostatic interaction. Nevertheless, in previous studies, conventional surfactants frequently acted as reaction media for PNPP hydrolysis. On the contrary, few Gemini surfactants were applied in the hydrolysis of esters [22–29].

Gemini surfactants [30–35], which have lower critical micelle concentrations (CMC), greater propensity of lowering the oil–water interfacial tension, better rheological behavior, and better wetting property, will displace many conventional surfactants in a multitude of scientific, industrial, and household applications [36–37]. However, most previous studies on Gemini surfactants have mainly focused on their specific aggregation behavior and structural properties, with very limited investigations on the effects of Gemini media on the reaction rates [38]. As a result, a combination of the crowned Schiff base complexes and Gemini surfactant should provide us important information on the catalytic hydrolysis of esters. To the best of our knowledge, there is no description that crowned Schiff base Co(II) complexes catalyze the hydrolysis of PNPP in Gemini surfactant micellar solution so far.



(CoL$_2$)

**Figure 1** Schematic depiction of structures of Schiff base Co(II) complexes (CoL$^1_2$ and CoL$^2_2$).

On the basis of the above discussion, we have synthesized two Co(II) complexes (Fig. 1) and elucidated their reactivity toward PNPP hydrolysis in the presence of micelles formed by a cationic Gemini surfactant G(hex)C16 (bis(hexadecyldimethylammonium)-hexane bromide) over a pH range of 6.50–8.50. In addition, with the goal of understanding the structural effects of Gemini surfactant G(hex)C16 on the PNPP hydrolysis, control experiments were carried out in other catalytic systems made up of Cobalt (II) complexes mentioned above and CTAB (hexadecyltrimethylammonium bromide), a single-chained analogue of G(hex)C16. The present observation indicates that the cationic Gemini G(hex)C16 is a better medium for PNPP hydrolysis compared with CTAB. We believe this is a good attempt that the hydrolysis of PNPP was catalyzed by metallomicellar systems, which were formed by crowned Schiff base complexes and Gemini surfactants.

## EXPERIMENTAL

### Instruments and Materials

The acidity of the buffers was measured at 25°C using a radiometer PHM 26 pH meter fitted with G202C glass and K4122 calomel electrodes. Kinetic runs were conducted on a GBC 916 UV–vis spectrophotometer

(GBC Co., Melbourne, Australia) equipped with a thermostatic cell holder.

All reagents were of analytical grade and used as received unless otherwise noted. The buffer reagent Tris (tris(hydroxymethyl)aminomethane) and cationic surfactant CTAB were the commercial products of Sigma-Aldrich Co. (St. Louis, MO, USA). Potassium chloride (KCl), ethanol, and methanol were purchased from the Chengdu Kelong Chemical Co. (Sichuan Chengdu, China). All buffers were made of standardized hydrochloric acid. Water used for kinetic measurements was redistilled deionized water. Other reagents were prepared by using the published methods: Schiff base complexes $CoL^1_2$ [39], $CoL^2_2$ [15], *p*-nitrophenyl picolinate (PNPP) [40], and Gemini surfactant G(hex)C16 [41]. Ionic strength ($I$) was maintained at 0.1 M KCl. The PNPP stock solution for kinetics was prepared in distilled acetonitrile. Owing to the small solubility of the title complexes in water, we first dissolved them in ethanol, and then mixed the Co(II) complex ethanol solution and buffered micellar solution, according to a calculated dosage to obtain the buffered metallomicelle.

### Kinetic Measurements

Pseudo-first-order rate constants ($k_{obs}$) of PNPP hydrolysis reaction were obtained based on the initial rate method, that is, according to the following equations: $(\text{rate})_0 = -(dC/dt)_0 = -(dA/dt)_0/\varepsilon$ and $(\text{rate})_0 = k_{obs}[\text{ML}]_0$, where $(\text{rate})_0$ is the initial rate of PNPP hydrolysis and $[\text{ML}]_0$ is the initial concentration of the complex. Hence, $k_{obs}$ was obtained from the slopes of the linear plots of $(\text{rate})_0$ against $[\text{ML}]_0$.

Each kinetic run was started by injecting the desired PNPP stock solution into a 1-cm cuvette filling 3 mL buffered mixture of Schiff base Mn(III) complex solution and Gemini surfactant G(hex)C16 with the desired concentration at 25 ± 0.1°C. The final concentration of the catalyst was $1.0 \times 10^{-5}$ mol dm$^{-3}$. The final concentration of substrate was a series of values, that is, $2.00 \times 10^{-4}$ mol dm$^{-3}$, $2.67 \times 10^{-4}$ mol dm$^{-3}$, $3.33 \times 10^{-4}$ mol dm$^{-3}$, $4.00 \times 10^{-4}$ mol dm$^{-3}$, and $4.67 \times 10^{-4}$ mol dm$^{-3}$. The CMC of Gemini surfactant G(hex)C16 at 25 ± 0.1°C is about $4.3 \times 10^{-5}$ mol dm$^{-3}$ [41], and the CMC of CTAB is $9.20 \times 10^{-4}$ mol dm$^{-3}$ [10]. The ionic strength of the catalytic system was 0.1 M KCl in overall experiments. The release of *p*-nitrophenolate ions was measured at 400 nm on a GBC 916 UV–vis spectrophotometer under the conditions of the about 20–47-fold excess of substrate over the concentration of complex. The listed data are the average of two or three runs with uncertainty of less than 3%.

## RESULTS AND DISCUSSION

### Pseudo-First-Order Rate Constants ($k_{obs}$) of PNPP Catalytic Hydrolysis

To study the reactive properties of PNPP hydrolysis in G(hex)C16 and CTAB micellar solutions, the concentration of each surfactant solution for kinetic runs must be higher than its CMC to ensure formation of micelles in Tris–TrisH$^+$ buffer.

All $k_{obs}$ obtained values are presented in Table I. From the values given in Table I, we can obtain important correlative information. First, the $CoL_2$ ($L = L^1, L^2$)/G(hex)C16 metallomicelle is a predominant system for promoting PNPP hydrolysis compared to the metallomicellar systems formed by $CoL_2$ ($L = L^1, L^2$)

**Table I** Pseudo-First-Order Rate Constants ($k_{obs}$) for PNPP Hydrolysis Promoted by $CoL_2$ ($L = L^1, L^2$) in Gemini Surfactant G(hex)C16 and CTAB[a]

| | $10^3$[S] (mol dm$^{-3}$) | | | | | $10^3$[S] (mol dm$^{-3}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0.200 | 0.267 | 0.333 | 0.400 | 0.467 | 0.200 | 0.267 | 0.333 | 0.400 | 0.467 |
| pH | $10^3 k_{obs}$ (s$^{-1}$) for $CoL^1_2$/G(hex)C16[b] | | | | | $10^3 k_{obs}$ (s$^{-1}$) for $CoL^2_2$/G(hex)C16[b] | | | | |
| 6.50 | 3.617 | 4.131 | 5.287 | 5.760 | 6.334 | 1.681 | 2.210 | 2.398 | 2.550 | 3.058 |
| 7.00 | 13.93 | 16.38 | 19.47 | 21.08 | 23.67 | 7.675 | 9.230 | 10.25 | 11.09 | 13.10 |
| 7.50 | 14.24 | 17.64 | 20.40 | 22.60 | 28.07 | 8.396 | 9.978 | 11.84 | 13.21 | 15.35 |
| 8.00 | 37.90 | 53.13 | 60.84 | 71.63 | 82.43 | 23.93 | 30.91 | 37.09 | 45.13 | 49.32 |
| 8.50 | 60.06 | 80.02 | 99.88 | 114.6 | 126.3 | 52.18 | 63.24 | 78.17 | 95.89 | 111.7 |
| 7.00[c] | $7.8 \times 10^{-3}$ | | | | | | | | | |
| 7.00[d] | 7.370 | 8.809 | 9.614 | 10.40 | 11.71 | 4.137 | 4.969 | 5.468 | 5.665 | 6.161 |

[a] 25 ± 0.1°C, [G(hex)C16] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, [CTAB] = $1.0 \times 10^{-2}$ mol dm$^{-3}$, [$CoL_2$] = $1.0 \times 10^{-5}$ mol dm$^{-3}$.

[b] All runs were carried out in Gemini G(hex)C16 micelle over the pH range of 6.50–8.50.

[c] Pseudo-first-order rate constant ($k_0$) of PNPP spontaneous hydrolysis under the conditions of pH 7.00 and 25 ± 0.1°C.

[d] Data listed in this line show $k_{obs}$ values of PNPP catalytic hydrolysis by the title complexes in the CTAB micellar solution at pH 7.00.

and CTAB, correspondingly. Second, the catalytic activity of $\mathrm{CoL}_2^1$/G(hex)C16 is about 2 times higher than that of $\mathrm{CoL}_2^2$/G(hex)C16 system in a rate enhancement. Comparing with the rate ($k_0$) of PNPP spontaneous hydrolysis, the hydrolytic rates of PNPP mediated by the two Schiff base cobalt(II) complexes in the Gemini G(hex)C16 micellar solution increased by a factor of about $1.8 \times 10^3$ for $\mathrm{CoL}_2^1$ and $9.9 \times 10^2$ for $\mathrm{CoL}_2^2$, respectively, at pH 7.00 and $[\mathrm{PNPP}] = 2.0 \times 10^{-4}$ mol $\mathrm{dm}^{-3}$. Furthermore, under the same experimental conditions, the reactivity of PNPP hydrolysis catalyzed by the same catalyst in the two surfactant micelles follows in the order of CTAB < G(hex)C16. This is possibly due to the intrinsic difference in their structures. Moreover, these observations show that the rates of the PNPP catalytic hydrolysis increase with the increase in both pH values and the concentration of substrate ([S]).

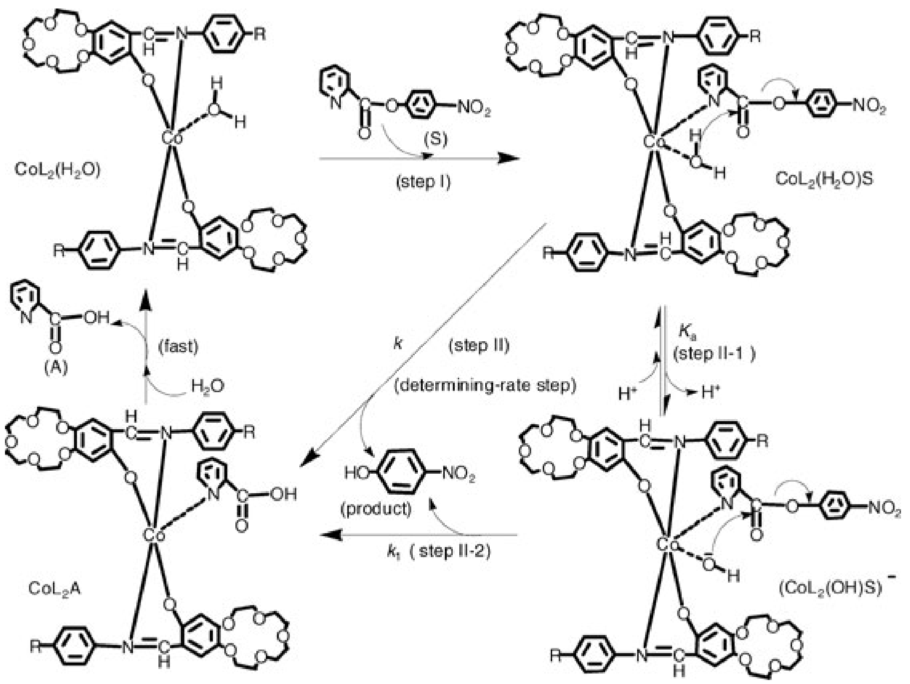
## Proposed Mechanism of PNPP Catalytic Hydrolysis

Herein, a metal-hydroxide activation mechanism is proposed to analyze the possible processes of PNPP cleavage induced by the two Co(II) complexes in micellar solutions. The catalytic hydrolysis of the majority of common esters occurs through a nucleophilic attack of the metal-coordinated hydroxide ion at the carbonyl carbon of carboxylic acid esters [42].

Scheme 1 shows the proposed pathway of PNPP catalytic hydrolysis promoted by the title complexes in micellar solutions. Details are as follows. Step I: The nitrogen of a pyridine ring in a substrate molecule coordinates to the Co(II) ion in the hydrate complex ($\mathrm{CoL_2(H_2O)}$), which results in formation of the catalyst–substrate complex [$\mathrm{CoL_2(H_2O)S}$]. As we know, the catalyst–substrate complex indeed benefits the conversion of an intermolecular reaction to a pseudo-intramolecular one [43,44]. This will reduce the activation energy of the reaction, and ultimately accelerate the hydrolysis of PNPP. Step II: A metal-bound hydroxide acts as an actual nucleophile to attack the positive carbon atom of the carbonyl group easily and also promotes the departure of the*p*-nitrophenyl group from PNPP with the first-order-rate constant ($k$). This step is the rate-determining step of the total reaction concerning an acid–base equilibrium (step II-1). Step III: Another water molecule is coordinated with the Co(II) ion to accelerate the release of picoline acid; eventually, the next catalytic cycle is induced by a regenerated catalyst.

## pH Dependence of $\mathrm{CoL_2}$/G(hex)C16 Activity

The rates of all enzymatic reactions are sensitive to pH [45]. To ascertain the pH dependence of PNPP catalytic hydrolysis, kinetic experiments were performed over a series of pH values, ranging from 6.50 to 8.50 in the present study.



Scheme 1

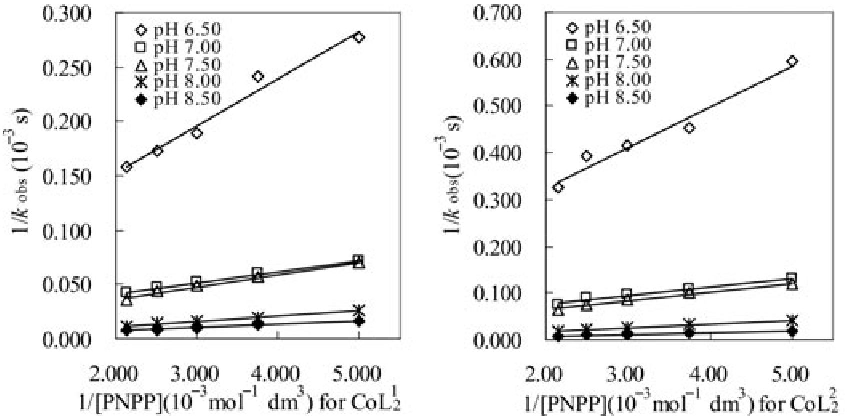


**Figure 2** Plots of $1/k_{obs}$ versus 1/[PNPP] for PNPP hydrolysis promoted by $CoL_2$ ($L = L^1, L^2$) in Gemini G(hex)C16 micellar solutions over a pH range of 6.50–8.50. Conditions: pH 7.00, 25 ± 0.1°C, [G(hex)C16] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, [$CoL_2$] = $1.0 \times 10^{-5}$ mol dm$^{-3}$.

Combining the previous report [11] with the theory of initial rate method, we can have

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \frac{1}{Kk[\text{S}]} \tag{1}$$

In Eq. (1), [S] denotes the free PNPP concentration and can be displaced by the initial concentration of PNPP on the basis of the initial rate method, $K$ is the association constant between the substrate and $CoL_2$ in the micellar solution, $k$ is the apparent first-order rate constant for the intracomplex nucleophilic reaction in the catalyst–substrate compound and is pH dependent.

The values of $k$ can be evaluated from the intercepts of the plots of $1/k_{obs}$ versus 1/[S] for the $CoL_2$/G(hex)C16 system by the linear regression method, as shown in Fig. 2. For comparison, $1/k_{obs}$ 1/[S] plots for $CoL_2$/CTAB are given in Fig. 3. All plots in Fig. 2 show a good linear relationship ($r \geq 0.98$), which suggests that the proposed mechanism for PNPP hydrolysis in this paper is reasonable. Each $k$ of PNPP catalytic hydrolysis in $CoL_2$/G(hex)C16 and $CoL_2$/CTAB systems is shown in Table II.

As shown in Tables I and II, both $k_{obs}$ and $k$ values increase as a function of pH from 6.50 to 8.50. This hints that the hydrolytic reaction possibly undergoes a deprotonated process (step II-1 in Scheme 1) at the determining-rate step, and the hydrolysis of PNPP catalyzed by Co(II) complexes is characteristic of the acid–base catalysis. In addition, the $k$ values of PNPP catalytic hydrolysis in the two buffered micellar solutions follow an increasing order of CTAB < G(hex)C16 at pH 7.00.

In step II-1, $K_a$ signifies the acidic ionization constant of $H_2O$ molecule coordinated to Co(II) ion, and $k_1$ displays the pH independent first-order rate

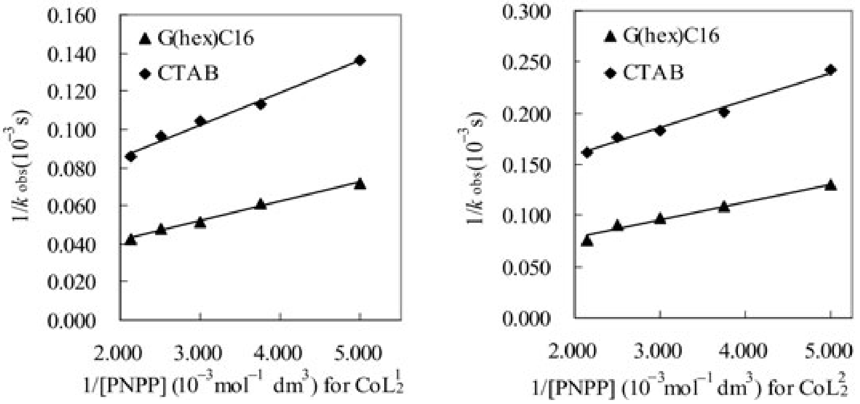


**Figure 3** Plots of $1/k_{obs}$ versus 1/[PNPP] for PNPP catalytic hydrolysis by Schiff base Co(II) complexes in G(hex)C16 and CTAB micellar solution. Conditions: pH 7.00, 25 ± 0.1°C, [G(hex)C16] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, [$CoL_2$] = $1.0 \times 10^{-5}$ mol dm$^{-3}$. Symbols: ▲, G(hex)C16; ◆, CTAB.

**Table II** The *k* Values of PNPP Catalytic Hydrolysis by $CoL_2$/G(hex)C16 and $CoL_2$/CTAB at 25 ± 0.1°C[a]

| | pH | | | | |
|---|---|---|---|---|---|
| | 6.50 | 7.00 | 7.50 | 8.00 | 8.50 |
| $10^3k(CoL_2^1/CTAB)$ | | 19.19 | | | |
| $10^3k(CoL_2^2/CTAB)$ | | 9.524 | | | |
| $10^3k(CoL_2^1/G(hex)C16)$ | 15.11 | 47.62 | 73.53 | 625.0 | 1000 |
| $10^3k(CoL_2^2/G(hex)C16)$ | 6.489 | 23.47 | 35.59 | 270.3 | 625.0 |

[a] Conditions are the same as in Table I.

constant of the hydrolysis reaction in the metallomicellar system. The deprotonation of the intermediate $CoL_2(H_2O)S$ first gives a more catalytically active species $(CoL_2(OH)S)^-$, and *p*-nitrophenol is subsequently released from the PNPP molecule by $k_1$ step. According to the principles of the chemical equilibration, it is obvious that the rate of PNPP hydrolysis increases with the increase in pH values in the current study.

From the results presented in Tables I and II, it is found that the $k_{obs}$ and $k$ values in the presence of $CoL_2$/G(hex)C16 increased sharply at pH >7.50. The pH–$k$ curve (Fig. 4) displays a sigmoid tendency even if the $k$ values do not level off obviously at the higher pH range. The sigmoidal pH–$k$ profile can be fitted to a single-proton ionization process by considering that the deprotonated form is the active species. The $pK_a$ value of Co-bound $H_2O$ can be determined with the inflection points, that is, 7.9 for $CoL_2^1$ and 8.3 for $CoL_2^2$, respectively. In the same way, we attempt to obtain the $pK_a$ values of the metal-coordinated water by the following method.

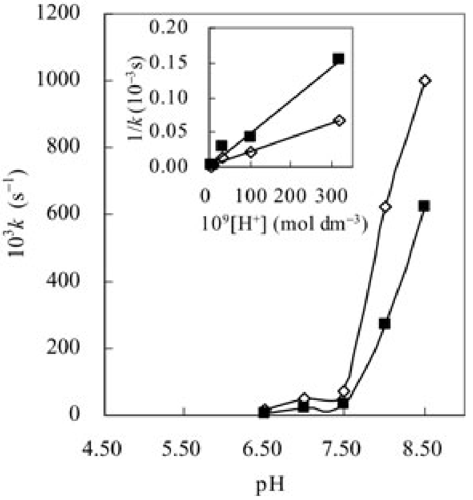


**Figure 4** Plots of $10^3k$ versus pH for the PNPP hydrolytic reaction at various pH in Gemini G(hex)C16 micellar solution. Conditions: pH 7.00, 25 ± 0.1°C, [G(hex)C16] = 1.0 × $10^{-4}$ mol dm$^{-3}$, $[CoL_2] = 1.0 \times 10^{-5}$ mol dm$^{-3}$. Symbols: ◇, $CoL_2^1$; ■, $CoL_2^2$; (insert) ◇, $CoL_2^1$; ■, $CoL_2^2$.

According to the literature [10,45], we cite a typical equation as follows:

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_1 K_a}[H^+] \qquad (2)$$

On the basis of Eq. (2), we can calculate the $k_1$ and $K_a$ values through the slope and the intercept of the plot of 1/*k* versus $[H^+]$ (see the insert in Fig. 4). The results show that $k_1$ and $pK_a$ values are 0.53 mol$^{-1}$ dm$^3$ s$^{-1}$ and 8.02 for $CoL_2^1$, whereas they are 0.48 mol$^{-1}$ dm$^3$ s$^{-1}$ and 8.38 for $CoL_2^2$, respectively. The obtained $pK_a$ values by this method are consistent with those estimated for $pK_a$ values on the basis of pH–$k$ profiles as shown in Fig. 4. The smaller $pK_a$ value of $CoL_2^1$ indicates that the generation of the active Co-$OH^-$ moiety species in $CoL_2^1$/16-6-16 system is easier than that in $CoL_2^2$/G(hex)C16 system, and then the nucleophilic attack of a negative metal-bound hydroxide on the substrate takes place handily. Thus, $CoL_2^1$ with the lower $pK_a$ (8.02) holds the predominance of speeding up the process of PNPP hydrolysis under the same experimental conditions.

## Structural Effects of the Complexes on the Hydrolytic Rate of PNPP

Usually, the catalytic activity of enzyme is correlative with the enzymatic structure [46,47]. From Table I, it can be seen that both $CoL_2$ ($L = L^1, L^2$)/G(hex)C16 (or CTAB) system exhibit higher activity for the PNPP hydrolysis reaction at pH 7.00, [PNPP] = 2.0 × $10^{-4}$ mol dm$^{-3}$. However, the rates of PNPP hydrolysis catalyzed by $CoL_2^1$ are 1.8 times greater than that of $CoL_2^2$ in the same micellar solution, that is, in G(hex)C16 or CTAB system. The above-mentioned results adequately demonstrate that the difference in their activities is dependent on the intrinsic structure of the two Co(II) complexes.

A variety of studies [48–50] confirmed that the nucleophilic attack is very sensitive to the size of both the reactants and catalyst. In the present case, the geometrical size of the two Co(II) complexes may be one important factor influencing their catalytic activity. An opening catalytic center is required to benefit the coordination between the PNPP molecule and the catalytic center. The active site is blocked primarily by outer bulky substituents due to the closeness of local rigid framework to the Co(II) center in $CoL_2$, and this results in the hindrance of the PNPP molecule binding to the Co(II); therefore, it limits the rate acceleration of the reaction. In $CoL_2^1$, no big para-substituent connects to the benzene ring linked to the nitrogen atom of C=N bond, which constructs an open environment for the PNPP molecule approaching the Co(II) ion. This will be favorable for the formation of the productive catalyst–substrate complex [43,44], and then the hydrolytic rate of PNPP is accelerated notably. In contrast, the active site of $CoL_2^2$ is very steric hindered due to the link of the aza-15-crown-5 as a larger substituent to the benzene ring in $CoL_2^2$. Consequently, $CoL_2^2$ does not provide more coordinated directions for the PNPP molecule to the Co(II) center, which results in a smaller concentration of catalyst–substrate complex. For this reason, the catalytic activity of $CoL_2^2$ is lower than that of $CoL_2^1$.

Furthermore, Choi et al. [51] have once mentioned that smaller molecule easily solubilizes in micellar solutions. As a result, more small $CoL_2^1$ molecules penetrate into Gemini G(hex)C16 micelles expediently, which are in favor of the hydrolytic process of PNPP. In a word, the difference in catalytic behavior of the two complexes highlights that the presence of aza-15-crown-5 moiety in $CoL_2^2$ is an essential structural element, influencing the hydrolytic rate of PNPP in the same micelles. That is to say, bulky substituents closer to the active site of catalyst may play a negative role in catalyzing the hydrolysis of PNPP.

### Roles of G(hex)C16 Micelle in the PNPP Hydrolysis Reaction

Gemini surfactant [52] is a new class of amphiphilic molecule, containing two headgroups and two aliphatic chains. They have physicochemical properties that are different from those of comparable conventional surfactants (single chain, single headgroup) [30].

Figure 5 shows the metal-promoted PNPP hydrolysis in the interfacial region of G(hex)C16 micelles. From the obtained results, the hydrolytic rate of PNPP mediated by the two Schiff base Co(II) complexes in G(hex)C16 micellar solutions is approximately twofold greater than that in CTAB micellar solutions. This confirms that Gemini surfactant has more surface activity over its conventional counterpart does, though the shape of the G(hex)C16 micelle is closer to that assumed by a CTAB micelle (spherical micelle) [31]. On the one hand, Gemini micelles are superior to conventional single-tailed surfactants in solubilizing hydrophobic reactants in water [53]. In our study, there is a supereminent solubilization of the hydrophobic reactants (including substrate and catalyst) in the Stem layer of G(hex)C16 micelles, in which the dimethylammonium headgroup exists, associated with bromide counterions and water molecules, spacer methylene groups, and the hydrated portion of the *n*-hexadecyl chain [54]. Therefore, the increase in local concentrations of PNPP and the catalyst in the G(hex)C16 micelle phase enhances the collision frequency of the reactants, and this will remarkably accelerate the rate of PNPP hydrolytic reaction compared with in CTAB micelles. On the other hand, a cooperative effect of positive Co(II) ion [13] and headgroups of Gemini G(hex)C16 markedly stabilized the negative transition state, which gives the additional rate enhancement of the PNPP hydrolysis reaction. By comparison, a similar function of CTAB is weaker than that of G(hex)C16 due to the small charge density of headgroups of CTAB. Consequently, the synergic effect of aforementioned factors leads to the higher hydrolytic rate of PNPP in G(hex)C16 micelles than that in CTAB.

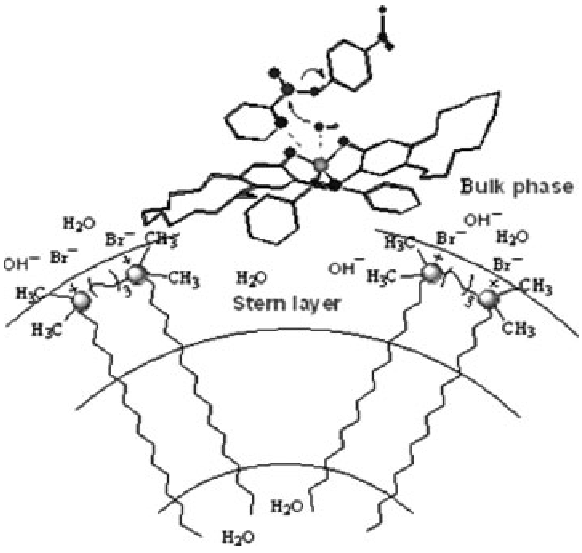


**Figure 5** Proposed hydrolytic process of PNPP promoted by the title complex in the Stern layer of G(hex)C16 micelles at 25 ± 0.1°C.

## CONCLUSIONS

In this paper, the hydrolysis of PNPP promoted by the crowned Schiff base Co(II) complexes in Gemini surfactant G(hex)C16 and CTAB micellar solution has been studied. The results obtained show that the hydrolytic rates of PNPP, induced by each Co(II) complex in G(hex)C16 micellar solution, are greater than that in the CTAB micellar solution. This may be contributed to the unique surface property of Gemini G(hex)C16. In addition, $\mathrm{CoL}_2^1$ possesses better catalytic activity when compared with $\mathrm{CoL}_2^2$ in the identical micelles, which is most probably due to the smaller steric hindrance of substituent groups residing in the former complex. Experimental results also imply that Gemini surfactant will likely be a class of potential and excellent substitutes for conventional surfactants in artificial enzyme research fields.

In view of the fact that there have been few studies of structural effects of different Gemini surfactants on the hydrolysis of esters, there is a tendency to introduce Gemini surfactants with distinct spacers in the catalytic hydrolysis of esters.

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