

Editor choice paper

# Gemini metallomicellar catalysis: Hydrolysis of *p*-nitrophenyl picolinate catalyzed by Cu(II) and Ni(II) complexes of macrocyclic ligands in gemini surfactant micelles

Ling-Guang Qiu\*, Xia Jiang, Li-Na Gu, Gang Hu

*School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, China*

Received 15 May 2007; received in revised form 14 July 2007; accepted 16 July 2007

Available online 21 July 2007

## Abstract

Cu(II) and Ni(II) complexes of two hexaaza macrocyclic ligands with and without pendant hydroxyl groups, 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane (**1**) and 3,10-bis(2-ethyl)-1,3,5,8,10,12-hexaazacyclotetradecane (**2**), were synthesized. Effects of these complexes on the hydrolysis of *p*-nitrophenyl picolinate (PNPP) in micelles of cationic gemini surfactants with different spacer lengths, alkanediyl- $\alpha,\omega$ -bis(dimethyl dodecylammonium bromide) (designated as 12-*s*-12, *s* = 2, 3 and 6), have been investigated at 25 °C. The results showed that metallomicelle systems containing gemini surfactants exhibited more efficient activities for hydrolysis of PNPP than those containing the corresponding single-chained conventional surfactant dodecyltrimethyl-ammonium bromide (DTAB). For gemini surfactants, it was found that catalytic activity of the metallomicellar systems containing the surfactant 12-2-12 was lower than those of surfactants 12-3-12 and 12-6-12. In addition, metal complexes of macrocyclic ligand **1** bearing pendant hydroxyl groups showed higher catalytic activities than corresponding metal complexes of **2** without hydroxyl group, indicating that ligand hydroxyl groups play an important role for catalyzed hydrolysis of PNPP in metallomicellar systems.

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**Keywords:** Metallomicelle; Micellar catalysis; Gemini surfactant; Macrocyclic ligand; Hydrolysis

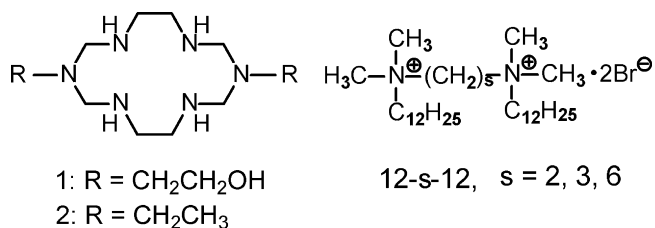
## 1. Introduction

As an effective biomimetic system for hydrolytic metalloenzymes, metallomicelle made up of functionalized surfactant or co-surfactant capable of effective chelation of metal ions has been extensively investigated in the past few decades [1–6]. It has been demonstrated in metallomicellar catalysis that ligands containing one or more hydroxyl groups are very significant for catalyzed hydrolysis of carboxylate or phosphate esters [4,7–10]. The hydroxyl group of the ligand, being activated by transition metal ion, acts as a more effective nucleophile than the chelating water molecule. In recent years, the use of macrocyclic metal complexes as biomimetic models of hydrolytic metalloenzymes has attracted considerable attention due to their similarities to the macrocyclic metal complexes found in biological systems, such as metal-porphin complexes, and the results

revealed that some macrocyclic metal complexes performed great catalytic activities for hydrolysis of some esters [11,12].

Recently, a new generation of surfactants, gemini surfactants, have attracted great interest [13–15]. These surfactants have been demonstrated to possess many unique properties, such as lower critical micelle concentration (cmc), greater efficiency in lowering the surface tension of water, lower Krafft temperature and better solubilization in comparison with conventional surfactants. However, most investigations on gemini surfactants have focused on their unusual physicochemical properties [16–22]. Micellar- [23–27] or metallomicellar-catalyzed [28] reaction using gemini surfactants to mimic enzymes or metalloenzymes is rarely studied. In previous study, we have clearly demonstrated that metallomicellar system containing gemini surfactant 12-2-12 and metal complexes of some triazole-based ligands behavior as an effective catalyst for cleavage of *p*-nitrophenol picolinate [28], and the gemini surfactant 12-2-12 shows higher catalytic activity for hydrolysis of some organic substrate in comparison with the corresponding conventional single-chained surfactants [26,27].

\* Corresponding author. Tel.: +86 551 5107304; fax: +86 551 5107342.  
E-mail address: [lgqiu@ahu.edu.cn](mailto:lgqiu@ahu.edu.cn) (L.-G. Qiu).



Scheme 1.

In the present work, Cu(II) and Ni(II) complexes of a hexaaza macrocyclic ligand with pendant hydroxyl groups, 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane (**1**), were synthesized, and effects of these complexes on the hydrolysis of *p*-nitrophenyl picolinate (PNPP) in micelles of a series of cationic gemini surfactants with different spacer lengths, alkanediyl- $\alpha,\omega$ -bis(dimethyl dodecylammonium bromide) (designated as 12-*s*-12, *s* = 2, 3 and 6) (Scheme 1), and the corresponding single-chained conventional surfactant dodecyl-trimethylammonium bromide (DTAB) have been investigated at 25 °C, respectively. In order to investigate effects of ligand hydroxyl groups on the hydrolysis reaction, Cu(II) and Ni(II) complexes of another ligand having no functional hydroxyl group, 3,10-bis(2-ethyl)-1,3,5,8,10,12-hexaazacyclotetradecane (**2**), were also synthesized and investigated. Some kinetic parameters of reactions were obtained by employing the ternary complex kinetic model for metallomicellar catalysis. Effects of molecular structure of the ligand and spacer length of the gemini surfactant on the catalytic hydrolysis of PNPP were discussed. To the best of our knowledge, this is the first example of gemini metallomicellar catalysis using macrocyclic metal complexes.

## 2. Experimental

### 2.1. Materials

*p*-Nitrophenyl picolinate (PNPP) was synthesized according to literature procedure [29]. Gemini surfactant 12-2-12 was prepared from *N,N,N',N'*-tetramethylethylenediamine and dodecyl bromide. Surfactants 12-3-12 and 12-6-12 were synthesized by the reactions of 1,3-dibromopropane and 1,6-dibromohexane, respectively, with *N,N*-dimethyldodecylamine in absolute ethanol as reported previously [30]. Critical micelle concentrations of the surfactants were determined to be  $8.9 \times 10^{-4}$ ,  $9.7 \times 10^{-4}$  and  $1.21 \times 10^{-3}$  mol L<sup>-1</sup> for 12-2-12, 12-3-12 and 12-6-12, respectively, by electric conductivity method at 25 °C [30].

Chloride salts of Cu(II) and Ni(II) complexes of macrocyclic ligands **1** and **2** were synthesized by the template reaction of corresponding metal salt with ethylenediamine, formaldehyde, and appropriate primary amine (ethanolamine for complexes of **1**, and ethylamine for complexes of **2**) according to the procedure reported previously [31]. Double distilled water was used for preparing test solutions for all measurements. PNPP stock solution (0.005 mol L<sup>-1</sup>) for kinetic study was prepared in acetonitrile. Tris–TrisH<sup>+</sup> buffer system was used in all cases and its

pH was adjusted by adding nitric acid in all runs according to literature procedures [9].

### 2.2. Kinetic measurements

Kinetic measurements of hydrolysis of PNPP were carried out spectrophotometrically at 25 °C, employing a Puxi TU-1901 UV–vis spectrophotometer. Reactions were initiated by injecting 30  $\mu$ l of PNPP stock solution into a 1-cm cuvette containing 3 ml of desired reagents, whose pH was adjusted beforehand to desired value with variation of 0.02 unit and the ion strength was maintained at 0.2 with KNO<sub>3</sub>. The reaction rate was followed by monitoring the liberation of *p*-nitrophenyl at 400 nm, and the apparent first-order rate constant was determined from slope of the plots  $\ln(A_t - A_\infty)$  versus time ( $A_t$  is the absorbance at time  $t$ , and  $A_\infty$  is the absorbance at equilibrium). The reaction followed apparent first-order rate kinetics for at least three half-lives. Rate constants are means of three measurements, and its average relative standard deviation is less than 3.5%.

## 3. Results and discussion

### 3.1. General survey of apparent rate constants for hydrolysis of PNPP in different systems at pH 7.0, 25 °C

The rates of catalytic reactions at pH 7.0 and 25 °C under the condition of excess macrocyclic metal complex over the substrate PNPP in DTAB and 12-*s*-12 micelles, respectively, were determined, and the apparent first-order rate constants are summarized in Table 1. It was found that both the gemini surfactants 12-*s*-12 and the conventional surfactant DTAB showed almost no rate enhancement effect on hydrolysis of PNPP. However, great rate enhancement was observed for macrocyclic metal complexes in buffer solutions (*ca.* 298-fold for **1**-Cu<sup>2+</sup>, 215-fold for **1**-Ni<sup>2+</sup>, 170-fold for **2**-Cu<sup>2+</sup>, and 121-fold for **2**-Ni<sup>2+</sup>), and more obvious enhancement was observed for macrocyclic metal complexes in micellar solutions of both conventional surfactant DTAB and the gemini surfactants 12-*s*-12. In addition, metal complexes of macrocyclic ligand **1** with pendant hydroxyl groups were found to be more active to catalyze the hydrolysis of PNPP than corresponding complexes of ligand **2** having no hydroxyl group under the same conditions, indicating that pendant hydroxyl groups of the ligand play an important

Table 1  
Apparent first-order rate constants ( $10^3 \times k_{\text{obsd}}/s^{-1}$ ) for the hydrolysis of PNPP<sup>a</sup>

complex	Buffer	DTAB <sup>b</sup>	12-2-12 <sup>c</sup>	12-3-12 <sup>d</sup>	12-6-12 <sup>d</sup>
Buffer	0.011	0.017	0.028	0.034	0.039
<b>1</b> -Cu <sup>2+</sup>	3.28	10.41	13.78	17.17	19.43
<b>1</b> -Ni <sup>2+</sup>	2.36	7.36	11.57	14.73	16.27
<b>2</b> -Cu <sup>2+</sup>	1.87	5.01	7.50	9.69	11.81
<b>2</b> -Ni <sup>2+</sup>	1.33	2.96	5.05	6.76	7.91

<sup>a</sup> Conditions: 0.1 M Tris–TrisH<sup>+</sup> buffer, pH 7.00,  $\mu = 0.2$  (KNO<sub>3</sub>), 25 °C, [PNPP] =  $5 \times 10^{-5}$  M, and [ML] =  $6 \times 10^{-4}$  M.

<sup>b</sup> [Surfactant] = 0.075 M.

<sup>c</sup> [Surfactant] =  $3 \times 10^{-3}$  M.

<sup>d</sup> [Surfactant] =  $5 \times 10^{-3}$  M.

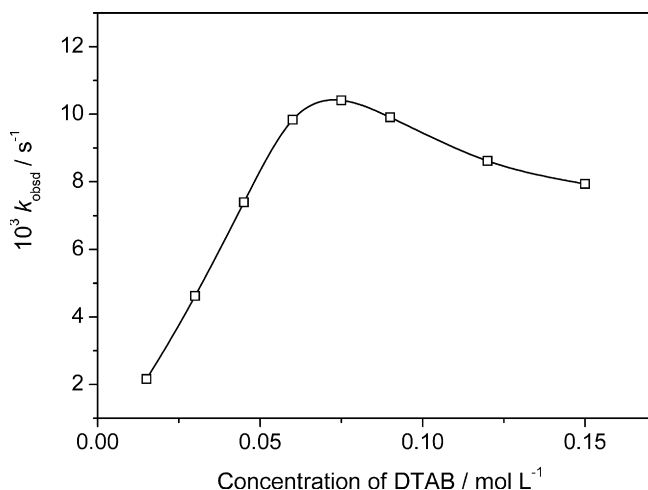


Fig. 1. Effect of concentration of surfactant DTAB on catalysis of PNPP catalyzed by Cu(II) complex of **1** at pH 7.00, 25 °C. [PNPP] =  $5 \times 10^{-5}$  mol L<sup>-1</sup>; [Cu<sup>2+</sup>-**1**] =  $6 \times 10^{-4}$  mol L<sup>-1</sup>.

role for the catalytic catalysis of PNPP as will be discussed below.

### 3.2. Effect of surfactant concentration

In metallomicellar catalysis, the reaction rate may be dependent on the surfactant concentration, as well as catalyst concentration and pH value. To obtain the optimum surfactant concentration, a series of measurements were carried out at pH 7.0 and at 25 °C for **1**-Cu<sup>2+</sup> in the presence of DTAB or 12-*s*-12 at various surfactant concentrations. The results are shown in Figs. 1 and 2. Saturation kinetics was observed for both conventional surfactant DTAB and the gemini surfactants 12-*s*-12, i.e. the rate constants increased with increasing surfactant concentration up to the saturation level. For micellar- or metallomicellar-catalysis reactions, such the rate saturation effect could be attributed to the saturation of substrate incor-

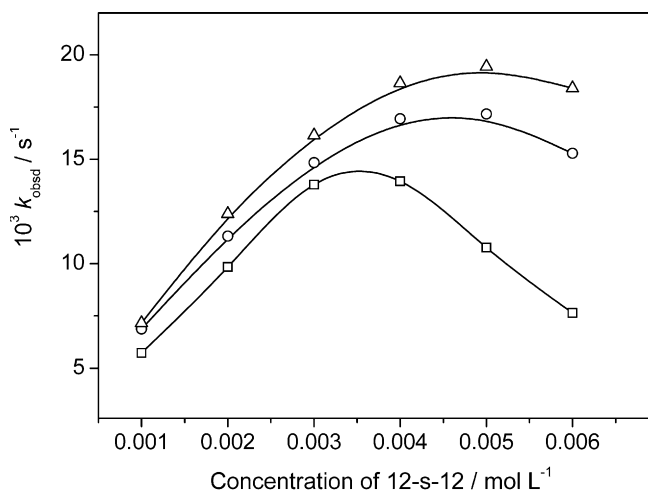


Fig. 2. Effect of concentration of surfactants 12-2-12 (□), 12-3-12 (○), and 12-6-12 (Δ) on catalysis of PNPP catalyzed by Cu(II) complex of **1** at pH 7.00, 25 °C. [PNPP] =  $5 \times 10^{-5}$  mol L<sup>-1</sup>; [Cu<sup>2+</sup>-**1**] =  $6 \times 10^{-4}$  mol L<sup>-1</sup>.

poration into the micelles as reported previously [10,26–28]. As can be seen from Figs. 1 and 2, surfactant concentrations corresponding to the maximum rate constant are *ca.* 0.07 M for DTAB, 3.5 mM for 12-2-12, 4.5 mM for 12-3-12 and 5 mM for 12-6-12. Consequently, kinetic studies in this study on the catalyzed hydrolysis of PNPP were carried out at surfactant concentration near these concentrations (see footnotes of Table 1) for corresponding systems to obtain the best catalytic efficiency. Also, it can be found that gemini surfactants 12-2-12, 12-3-12 and 12-6-12 are more efficient for catalytic hydrolysis of PNPP in comparison with the conventional surfactant DTAB under the same conditions. This phenomenon can be easily explained in view of unique molecular structure of the gemini surfactant and great ability to form micelles at a relatively low surfactant concentration.

In addition, a difference of saturation behavior was found between gemini surfactant 12-2-12 and the other three surfactants. For DTAB, 12-3-12 and 12-6-12, when the saturation point is reached, further increases in surfactant concentration result in a gradual decrease of the rate constant for the catalyzed hydrolysis of PNPP. However, a significant decrease of the rate constant was observed for metallomicellar system containing gemini surfactant 12-2-12. Also, for surfactant 12-2-12, the corresponding surfactant concentration to the saturation point is lower than those of 12-3-12 and 12-6-12, although these three gemini surfactants have a similar molecular structure and very close critical micelle concentrations (0.89, 0.97 and 1.21 mM for 12-2-12, 12-3-12 and 12-6-12, respectively). In our previous studies, it was found that high microviscosity of the gemini surfactant 12-2-12 and 18-triazole-18 at high surfactant concentrations may cause a decrease in diffusion coefficient of reactants in aqueous solution of the gemini surfactant, which is due to a strong tendency to micelle growth with an increase in concentration of 12-2-12 [19], thus resulting in a decrease in reaction rate of the hydrolysis reaction [26–28]. In addition, a decrease in micellar reactivity is also ascribed to a change from globular to cylindrical micelles, as previously found by Melhado and Gutsche [32], which is due to low catalytic activity of cylindrical micelles with a larger aggregation number. For gemini surfactant 12-2-12, significant changes of micelle shape were found from spherical micelles to worm-like micelles, branched thread-like micelles as well as closed ring cylindrical micelles, while micelles of gemini surfactants 12-3-12 and 12-6-12, and conventional surfactant DTAB remained spherical even at fairly high concentration [18,19].

### 3.3. Kinetic analysis of metallomicellar catalytic hydrolysis of PNPP

Based on phase-separation model of the micelle [33], a ternary complex kinetic model for metallomicellar catalysis has been established [8–10]. So kinetic results can be quantitatively treated with the model, and some kinetic and thermodynamic parameters may be obtained to get a better understanding of the catalytic mechanism. The hydrolytic of PNPP (S) catalyzed by metal complex (ML) can be supposed to take place in the bulk phase and the metallomicellar phase simultaneously to afford

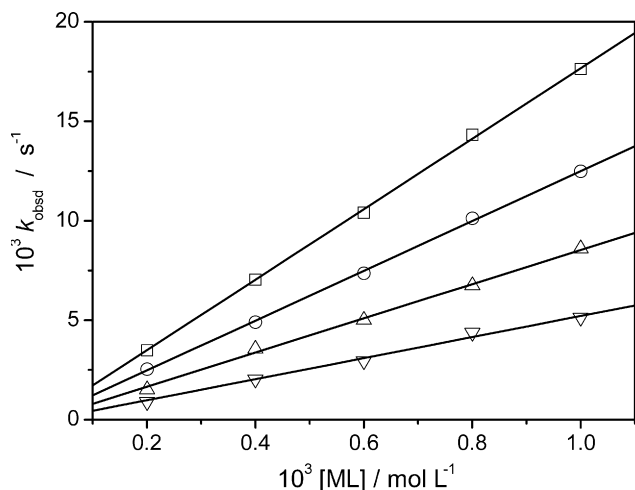
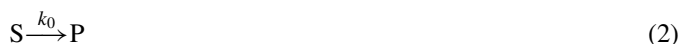


Fig. 3. Plot of  $k_{\text{obsd}}$  vs.  $[\text{ML}]$  for the hydrolysis of PNPP catalyzed by macrocyclic metal complexes  $\text{Cu}^{2+}\text{-1}$  ( $\square$ ),  $\text{Ni}^{2+}\text{-1}$  ( $\circ$ ),  $\text{Cu}^{2+}\text{-2}$  ( $\triangle$ ), and  $\text{Ni}^{2+}\text{-2}$  ( $\nabla$ ) in DTAB micelles at pH 7.00, 25 °C.

the products (P):



where  $k_c$  is the catalytic second-order-rate constant for the complex with substrate and  $k_0$  is the pseudo-first-order rate constant of reaction in bulk phase without the complex. Accordingly, kinetic equations can be obtained as

$$\text{Rate} = k_{\text{obsd}}[\text{S}] = (k_c[\text{ML}] + k_0)[\text{S}] \quad (3)$$

$$k_{\text{obsd}} = k_c[\text{ML}] + k_0 \quad (4)$$

where  $k_{\text{obsd}}$  is the pseudo-first-order rate constant for hydrolysis of PNPP catalyzed by macrocyclic metal complex in micellar solution. As a result, the plots of  $k_{\text{obsd}}$  versus  $[\text{ML}]$  would allow the evaluation of values of  $k_c$  for different metallomicelle systems (Figs. 3–6). No saturation kinetics was observed, indicating

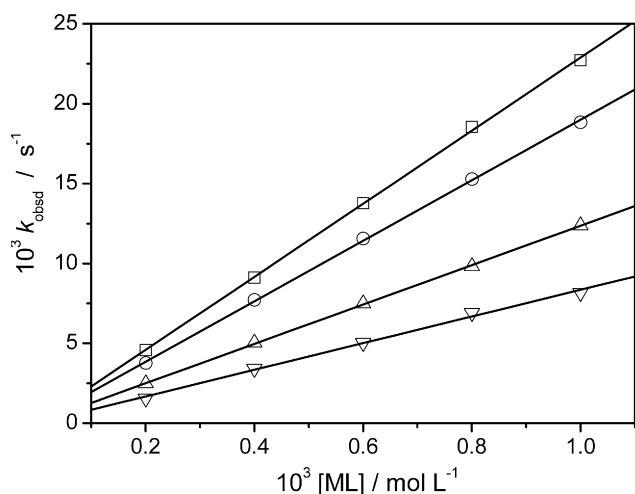


Fig. 4. Plot of  $k_{\text{obsd}}$  vs.  $[\text{ML}]$  for the hydrolysis of PNPP catalyzed by Cu(II) and Ni(II) complexes of macrocyclic ligands **1** and **2** in 12-2-12 micelles at pH 7.00, 25 °C. Symbols as in Fig. 3.

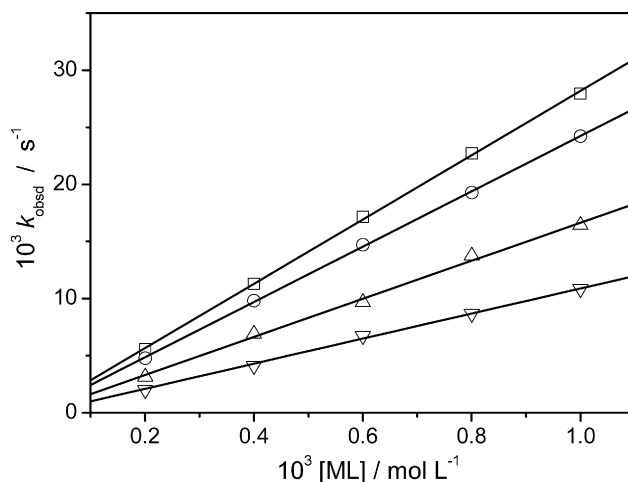


Fig. 5. Plot of  $k_{\text{obsd}}$  vs.  $[\text{ML}]$  for the hydrolysis of PNPP catalyzed by Cu(II) and Ni(II) complexes of macrocyclic ligands **1** and **2** in 12-3-12 micelles at pH 7.00, 25 °C. Symbols as in Fig. 3.

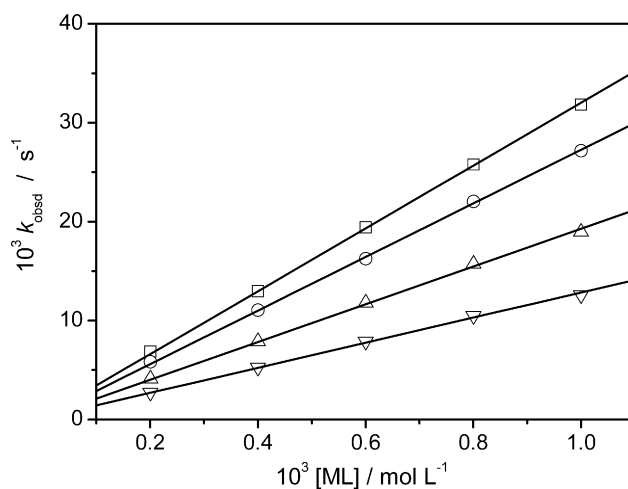


Fig. 6. Plot of  $k_{\text{obsd}}$  vs.  $[\text{ML}]$  for the hydrolysis of PNPP catalyzed by Cu(II) and Ni(II) complexes of macrocyclic ligands **1** and **2** in 12-6-12 micelles at pH 7.00, 25 °C. Symbols as in Fig. 3.

that the binding constants of substrate PNPP to macrocyclic complexes were low [34].  $k_c$  values for different metallomicellar systems are summarized in Table 2.

It can be found that  $k_c$  values for different macrocyclic metal complexes in the same micellar system follows the order

Table 2  
Apparent second-order rate constants  $k_c$  of the hydrolysis of PNPP in different metallomicellar systems<sup>a</sup>

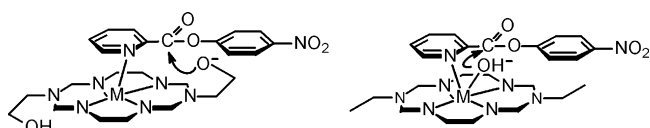
Complex	DTAB <sup>b</sup>	12-2-12 <sup>c</sup>	12-3-12 <sup>d</sup>	12-6-12 <sup>d</sup>
1-Cu <sup>2+</sup>	17.70	22.86	28.13	31.73
1-Ni <sup>2+</sup>	12.51	18.93	24.20	27.07
2-Cu <sup>2+</sup>	8.58	12.32	16.66	19.05
2-Ni <sup>2+</sup>	5.29	8.34	10.97	12.67

<sup>a</sup> Conditions: 0.1 M Tris–TrisH<sup>+</sup> buffer, pH 7.00,  $\mu = 0.2$  (KNO<sub>3</sub>), 25 °C, and  $[\text{PNPP}] = 5 \times 10^{-5}$  M.

<sup>b</sup>  $[\text{Surfactant}] = 0.075$  M.

<sup>c</sup>  $[\text{Surfactant}] = 3 \times 10^{-3}$  M.

<sup>d</sup>  $[\text{Surfactant}] = 5 \times 10^{-3}$  M.



Scheme 2.

complex  $\text{Cu}^{2+}\text{-1} > \text{Ni}^{2+}\text{-1}$  and  $\text{Cu}^{2+}\text{-2} > \text{Ni}^{2+}\text{-2}$ , which indicates obvious effect of metal ion species of the complexes on catalyzed hydrolysis of PNPP in cationic metallomicellar systems. In addition, although ligands **1** and **2** have the same molecular structure except that **1** contains two hydroxyl groups,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  complexes of **1** exhibited higher kinetic activity to catalyze the hydrolysis of PNPP in micelles than the corresponding metal complexes of **2** under the same conditions. It has been demonstrated that ligands bearing hydroxyl groups showed high catalytic activity in metallomicellar systems, because deprotonated ligand hydroxyl groups activated by metal ion are more effective to catalyze the nucleophilic reactions than hydroxide through deprotonation of water molecule coordinated to metal ion in micellar systems [4,7–10]. As can be seen in Scheme 2, for metallomicellar systems containing metal complexes of ligand **2**, the water molecule coordinated to the ligand is firstly deprotonated to form the catalytically active species  $\text{ML-OH}^-$ ; then the metal ion in  $\text{ML-OH}^-$  holds the substrate through the coordination of the pyridine moiety of the substrate to yield reactive ternary complex. Finally,  $\text{OH}^-$  in  $\text{ML-OH}^-$  attacks the carbonyl of the substrate to cause the intramolecular nucleophilic reaction. However, for metallomicellar system containing complexes of ligand **1**, the ligand hydroxyl group activated by the metal ion acts as a nucleophile more effectively than the activated water molecule coordinated to the metal ion.

On the other hand, the molecular structure and micellar aggregation behavior of the surfactants were also found to remarkably affect catalyzed hydrolysis of PNPP in metallomicellar systems. As can be seen from Table 2,  $k_c$  values for the same macrocyclic metal complex in different micellar system follows the order surfactant 12-6-12 > 12-3-12 > 12-2-12 > DTAB. This indicates that gemini surfactants 12-*s*-12 in metallomicelle systems are more effective for hydrolysis of PNPP than conventional surfactant DTAB. Similar results were also found in micellar catalyzed reactions in the presence of gemini cationic surfactants and corresponding conventional single-chain surfactant, and such the high catalytic activities of gemini surfactants were ascribed to higher solubility of substrates in gemini micelles and higher binding constant of catalysts to the gemini micelles in comparison with corresponding single-chain surfactants [23,24,26–28]. It can be also found that gemini surfactants 12-3-12 and 12-6-12 with longer spacer group exhibited higher activity in metallomicelle systems than 12-2-12. This may be attributed to higher microviscosity and less active worm-like micelles of 12-2-12 at higher concentrations as described above.

### 3.4. pH-rate profile

Series of pseudo-first-order rate constants of catalyzed hydrolysis of PNPP were determined in 12-6-12 micelles within

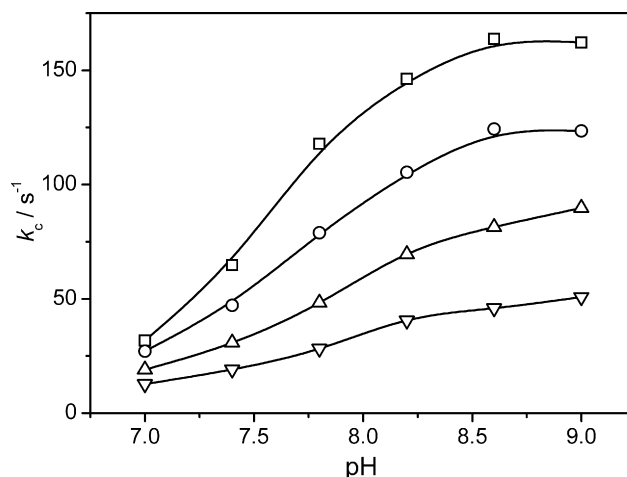


Fig. 7. Plot of  $k_c$  vs. pH for the hydrolysis of PNPP catalyzed by macrocyclic metal complexes  $\text{Cu}^{2+}\text{-1}$  (□),  $\text{Ni}^{2+}\text{-1}$  (○),  $\text{Cu}^{2+}\text{-2}$  (△), and  $\text{Ni}^{2+}\text{-2}$  (▽) in 12-6-12 micelles at 25 °C.

pH range 7.0–9.0 for macrocyclic complexes  $\text{Cu}^{2+}\text{-1}$ ,  $\text{Ni}^{2+}\text{-1}$ ,  $\text{Cu}^{2+}\text{-2}$ , and  $\text{Ni}^{2+}\text{-2}$ , respectively, and corresponding apparent second-order rate constants were obtained. Fig. 7 shows the plots of  $k_c$  versus pH for Cu(II) and Ni(II) complexes of macrocyclic ligands **1** and **2** in 12-6-12 micelles. It can be found that  $k_c$  increases with an increase in pH value for hydrolysis of PNPP catalyzed by both metal complex of ligand **1** and **2**, and the curves show a characteristic of acid-base catalytic processes [35]. This result also suggests that the deprotonated ligand hydroxyl groups or hydroxide through deprotonation of water molecule coordinated to metal ion in macrocyclic complex acts as the nucleophiles for the hydrolytic reaction of PNPP.

Based on experimental data,  $\text{p}K_a$  values of the metal complexes were obtained from pH at which the reflection of the plot of  $\log k_c$  versus pH occurs. Compared with Cu(II) and Ni(II) complexes of ligands **2** in gemini micelles, corresponding metal complexes of **1** show lower  $\text{p}K_a$ 's (7.87 for  $\text{Cu}^{2+}\text{-1}$ , 8.05 for  $\text{Ni}^{2+}\text{-1}$ , 8.18 for  $\text{Cu}^{2+}\text{-2}$ , and 8.29 for  $\text{Ni}^{2+}\text{-2}$ ). Also,  $\text{p}K_a$  values of metal complexes of ligand **1** and **2** are much lower than those of corresponding metal hydrates [36], which indicates that the metal ions may make ligand hydroxyl group or the water molecule coordinating to metal ion in the ternary complex change into more nucleophilic group  $\text{O}^-$  (for complexes of ligand **1**) or  $\text{OH}^-$  (for ligands **2**, see Scheme 2) and then the nucleophilic attack on the substrate takes place easily, which increases the rate of the hydrolysis of PNPP.

## 4. Conclusions

Cu(II) and Ni(II) complexes of two hexaaza macrocyclic ligands with and without pendant hydroxyl groups were synthesized, and effects of these complexes on the hydrolysis of PNPP in micelles of cationic gemini surfactants 12-*s*-12 with different spacer lengths and the corresponding single-chained surfactant DTAB have been investigated at 25 °C, respectively. It was found that metallomicellar catalytic systems containing gemini surfactants showed more efficient activities for hydrolysis of PNPP than those containing conventional surfactant DTAB,

and catalytic activity of the micelles of gemini surfactants 12-*s*-12 increased with increasing spacer length owing to different micellar aggregation structures between the surfactant 12-2-12 and the surfactant 12-3-12 or 12-6-12. In addition, metal complexes of microcyclic ligand bearing pendant hydroxyl groups showed higher catalytic activities than those of ligand without hydroxyl group, which indicates that hydroxyl groups of the ligand play an important role for catalyzed hydrolysis of PNPP in metallomicellar systems.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (20501001), the Key Project of Natural Science Foundation from Education Bureau of Anhui Province (kj2007A078), and the Science Foundation for Excellent Young Teachers of Universities of Anhui Province (2005jq1028).

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