# The Metallomicelle of Lanthanide Metal (Ce, La) Aza-Macrocyclic Complexes with a Carboxyl Branch: The Catalytic Activity and Mechanism in the Hydrolysis of a Phosphate Diester

Fang-zhen Li · Famei Feng · Lan Yu · Jia-qing Xie

Received: 19 January 2014/Accepted: 12 May 2014/Published online: 6 August 2014 © Springer Science+Business Media New York 2014

Abstract An aza-macrocyclic ligand, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-N'- acetic acid (L), was synthesized and characterized. The chemical composition of the complexes (CeL and LaL) was determined by a UV-Vis spectrophotometric method and kinetic Job plot. Two metallomicellar systems made of an lanthanide metal complex and *n*-lauroylsarcosine (LSS) micelle were used as catalyst in the hydrolysis of bis(4-nitrophenyl) phosphate ester (BNPP), and their catalytic activity was studied by the comparative method. The interaction between the complex and BNPP in the metallomicelle was studied by its fluorescent spectroscopy. The catalytic rate of BNPP hydrolysis was measured kinetically by UV–Vis spectrophotometry. The results indicate that CeL systems (aqueous solution and metallomicelle) exhibit higher catalytic activity than those of the LaL systems in BNPP hydrolysis, and the micelle provides an effective catalytic environment in the catalytic reaction. A reaction mechanism was also proposed on the basis of the results.

**Keywords** Metallomicelle · Lanthanide complex · Carboxyl branch · Catalytic activity · BNPP hydrolysis

# 1 Introduction

Phosphate ester specific hydrolysis plays an important role in the metabolic processes of living organisms. Research on artificial phosphate diesterases is an important subject in the

F. Feng

F. Li  $\cdot$  L. Yu  $\cdot$  J. Xie ( $\boxtimes$ )

College of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing 400054, People's Republic of China e-mail: xjq8686@163.com

College of Chemistry & Pharmaceutical Engineering, Sichuan University of Science & Engineering, Zigong 643000, Sichuan, People's Republic of China

fields of molecular biological technology and drug development. Many researchers have been working hard to develop biomimetic models of metalloenzyme with high efficiency and selectivity [1–4]. A variety of different synthetic catalysts for hydrolysis of DNA and the phosphate diester have been reported, usually based on lanthanide or transition metal ions [5–9].

The investigations indicate that lanthanide complexes are generally more active than other transition metal complexes due to the extremely strong Lewis acidity of a lanthanide cation [10, 11]. Previous studies revealed that the active species was the specific hydroxo-lanthanum(III) complex in alkali solution [10, 12]. Many lanthanide(III) complexes are highly active at catalyzing phosphodiester hydrolysis in alkali solution, but not in acidic solution [12]. These results were also obtained in our experiments. The major drawback of the hydroxo lanthanum(III) complex system is its very low stability in alkaline solution. A possible solution to this problem would be to use a lanthanum(III) complex with appropriate ligands as catalyst. The investigation also indicated that the structure of the ligand of the complex plays a key role in designing the mimetic model of the phosphate hydrolase [13–18]. The aza-macrocyclic ligand is considered as a potential mimetic enzyme because of its recognition of guests and hosts.

On the other hand, as an enzymatic model, we consider not only the structure of the active center, but also the microenvironment around the active center [19]. X-ray crystallographic studies showed that the structures of micelles and globular proteins and the substrate-binding capability of micelle and enzyme are similar [20], so micelles have often been employed to simulate the microenvironment of enzymes [21]. Based on the factors above, two lanthanide metal aza-macrocyclic complexes with a carboxyl branch were chosen as the catalytic activity center, and the metallomicellar system made of the lan-thanide(III) complex and LSS micelle was designed as a mimetic model of the phosphate hydrolase for the hydrolytic cleavage of bis(4-nitrophenyl)phosphate (BNPP). The primary goals of this work are to explore the relation between the catalytic activity of the metallomicellar system and the complex structure, pH of the system, and micelle, and to find better catalytic systems and catalytic conditions for the mimetic phosphate hydrolases.

## 2 Experimental

#### 2.1 Instrumentation and Materials

Fluorescence spectra were measured using a Cary Eclipse spectrofluorophotometer (Agilent Technologies Co. USA.). The elemental analysis was performed on a Carlo Erba 1106 elemental analyzer (Carlo-Erba Co. Italy). The pH of the solution was determined by using a Radiometer PHM 26 pH meter with G202C glass and K4122 calomel electrodes (Shanghai Photics Apparatus Co. China). The melting point was determined on a Yanaco MP-500 micro-melting point apparatus (Yanaco-Mat Co. USA.) and is uncorrected. The kinetic study was carried out and UV–Vis absorption spectra were recorded using a GBC 916 UV–Vis spectrophotometer equipped with a temperature holder (Australia).

The *n*-lauroylsarcosine (LSS, purity  $\geq 95.0$  %), trishydroxy-methylaminomethane (Tris, purity  $\geq 99.5$  %), and bis(*p*-nitrophenyl) phosphate (BNPP, purity > 98.0 %) were purchased from Sigma Chemical Co. Other reagents used in the experiments, unless otherwise indicated, were of analytical grade (purity  $\geq 99.0$  %), and were purchased from Chongqing Chemical Co. The water used for kinetic experiments was doubly distilled.

macrocyclic ligand



2.2 Synthesis of the Ligand (L)

An aza-macrocyclic ligand, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-N<sup>-</sup>acetic (L), was synthesized according to the literature method [22]. Melting point: 235–236 °C. IR (KBr, cm<sup>-I</sup>): 3400 (OH); 3200 (NH); 2650–2900 (NH<sub>2</sub><sup>+</sup>); 1730 (COOH). 'H NMR (D<sub>2</sub>O):  $\delta$  0.95–1.04 (3H, d, CH<sub>3</sub>-C–N), 1.13–1.20 (3H, d, CH<sub>3</sub>-C–N), 1.30–1.41 (12 H, t, CH<sub>3</sub>-C–N), 1.72–1.93 (4 H, m, C–CH<sub>2</sub>-C), 2.85 (2H, **s**, CH<sub>2</sub>COOH), 2.90–3.20 (8 H, m, CH<sub>2</sub>-N), 3.64 (1 H, s, C–CH-N), 3.85 (1 H, s, C-CH-N). Analysis, calculated for C<sub>18</sub>H<sub>42</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>3</sub>(H<sub>2</sub>O): C, 41.39; H, 8.10; N, 10.73. Found: C, 41.38; H, 8.09; N, 10.57. The structure of the ligand (L) is shown in Fig. 1.

# 2.3 Preparation of the Solutions and Metallomicelle of the Lanthanide Metal Aza-Macrocyclic Complex

A concentrated solution  $(5 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3})$  of lanthanide metal nitrate and the ligand was prepared at pH = 8.0. The lanthanide metal aza-macrocyclic complex solution of  $5 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$  was prepared by mixing the concentrated lanthanide metal nitrate (10 mL) and the concentrated ligand solution (10 mL) at 100 °C and stirring for 10 h. Then the mixture solution was transferred to a volumetric flask of 100 mL, and diluted with trishydroxy-methylaminomethane (Tris) buffer solution of pH = 8.0.

The concentrated surfactant LSS solution of  $4.6 \times 10^{-2}$  mol·dm<sup>-3</sup> was prepared in Tris buffer solution of pH = 8.0. The surfactant LSS of the desired concentration was prepared by adding the concentrated surfactant LSS solution to the buffer solution of pH = 8 with stirring. The metallo-micellar system of  $5 \times 10^{-5}$  mol·dm<sup>-3</sup> was prepared by adding the lanthanide metal aza-macrocyclic complex solution of  $5 \times 10^{-3}$  mol·dm<sup>-3</sup> (1 mL) to LSS solution of the desired concentration (100 mL) and pH = 8 with stirring.

Stock solutions of BNPP and *p*-nitrophenyl phosphate (NPP) were prepared at  $5.0 \times 10^{-2}$  mol·dm<sup>-3</sup> in water. The final concentration of the substrate (BNPP and NPP) was  $5.0 \times 10^{-4}$  mol·dm<sup>-3</sup> in the kinetic experiments of hydrolysis of phosphate ester.

## 2.4 Analysis of the Characteristic Spectrum

The UV–Vis spectra of the aza-macrocyclic ligand and the mixture solution (Ln(NO<sub>3</sub>)<sub>3</sub> and the ligand) were examined by UV–Vis absorption spectrophotometry in the wavelength range 190–500 nm and at pH = 8.0, 25 °C. Tris buffer solution (3 cm<sup>3</sup>) of pH = 8.0 was

added to the reaction cuvette and the reference cuvette, respectively, and then the absorbance of the solution was set to zero. The absorbance measurement of the solution was initiated by injecting 30 µL of the ligand or the mixture solution ( $5.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ) into the reaction cuvette. The fluorescence change of the metallomicelle system upon addition of BNPP was monitored at pH = 8.0, 25 °C, [complex] =  $5.0 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ , [BNPP] =  $5.0 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ ,  $\lambda_{ex} = 254 \text{ nm}$ ,  $\lambda_{em} = 290\text{-}490 \text{ nm}$ , voltage = 650 V, and slit width = 5 nm.

## 2.5 Kinetic Measurement Method

Kinetic studies were carried out using a GBC 916 UV–Vis spectrophotometer equipped with a temperature controlled cell holder. The metallomicellar solution (3 cm<sup>3</sup>, 5 × 10<sup>-5</sup> mol·dm<sup>-3</sup>) was added to the reaction cuvette and reference cuvette (4 cm<sup>3</sup>), respectively, and then the absorbance of the solution was set to zero. The reaction was initiated by injecting 30 µL of the substrate (BNPP and NPP) stock solution ( $5.0 \times 10^{-2} \text{ mol·dm}^{-3}$ ) into the reaction cuvette. The characteristic spectrum of *p*-nitrophenol (the product of BNPP and NPP hydrolysis) was detected at the wavelength of 400 nm. Therefore, the kinetics of the substrate cleavage was monitored by the absorbance change of the *p*nitrophenol at 400 nm. To obtain reliable trends of BNPP and NPP catalytic hydrolysis, the testing was performed on one day with the same reaction cuvette and stock solutions. The catalytic hydrolysis was observed to be a first-order reaction. The observed first-order rate constant ( $k_{obs}$ ) of BNPP catalytic hydrolysis was obtained by the mapping method with the equation  $\ln(A_{\infty} - A_t) = k_{obs} t + \ln(A_{\infty} - A_0)$ .  $A_0$ ,  $A_t$  and  $A_{\infty}$  are the initial absorbance, absorbance at time t and final absorbance of the product at 400 nm. The data were obtained from the kinetic curves followed up to 95 % or higher conversion of the substrate.

## **3** Results and Discussion

#### 3.1 Composition of the Binary Complex in the Metallomicelle

The UV–Vis spectra of the aza-macrocyclic ligand and the mixture solution (Ln(NO<sub>3</sub>)<sub>3</sub> and the ligand) are shown in Fig. 2. From this figure, it can be seen that the characteristic peak ( $\lambda = 201$  nm) of the ligand is lower in the mixture solution than in the ligand solution. Generally, the change of UV–Vis absorption intensity in the mixture solution can be used to confirm the binding between metal ions and ligands. This may be ascribed to the energy transfer between metal ions and ligand. Apparently, the results in Fig. 2 indicate the formation of new complex Ln<sub>x</sub>L<sub>y</sub> between lanthanide metal ions and the ligand in the mixture solution.

To determine the chelating stoichiometry of metal complex,  $k_{obs}$  (s<sup>-1</sup>) of BNPP catalytic hydrolysis on different the mole fraction (*x*) of metal ion was examined and is shown in Table 1. The relationship (kinetic Job's plot) between the observed rate constants ( $k_{obs}$ ) and the mole fraction (*x*) is plotted at constant total concentration of the metal ion and ligand [23] and the results are shown in Fig. 3. It be seen that the *x* value corresponding to the maximum  $k_{obs}$  is about 0.5 for the two metal complexes investigated at the desired pH, which indicates that the 1:1 complex (x:y = 1:1 in complex  $Ln_xL_y$ ) is the active species, and this result also verifies the presence of the metal complex. Because the coordination number of a lanthanide metal ion is usually 8 or 9, and one molecule of the ligand bromide can supply only 7 donor atoms to the lanthanide metal ion, the binary complex contains at



**Fig. 2** Absorption spectra of ligand with increasing amounts of Ce<sup>3+.</sup> 25.00 °C, pH = 8.0,  $[La^{3+}] = [Ce^{3+}] = [ligand] = 5 \times 10^{-5} \text{ mol·dm}^{-3}$ 

least two water molecules directly coordinated to the lanthanide metal ion. Therefore, the complex LnL in the metallomicellar system as catalyst can coordinate water molecules and then form the hydrated complex LnLBr<sub>2</sub>(OH)(H<sub>2</sub>O) or LnLBr<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub> or LnLBr<sub>2</sub> (OH)<sub>2</sub> at different acidities.

### 3.2 The Comparison of the Catalytic Activity of Different Systems

To analyze the product of BNPP catalytic hydrolysis, the spectra of the standard sample of *p*-nitrophenol and the product of BNPP were measured in the metallomicelle of CeL; these are shown in Fig. 4. The experimental results show that the standard *p*-nitrophenol has a strong absorption peak at 400 nm in the metallomicelle. From Fig. 4, it can also be seen that the absorbency of  $\lambda_{max}$  (290 nm) of BNPP decreased and the absorbency of  $\lambda_{max}$  (400 nm) of hydrolytic product increased with passage of time. The results indicate that one of the products of BNPP is *p*-nitrophenol.

The catalytic activity of different systems is shown in Table 2. The experimental results show that the ligand and LSS have no activity. From Table 2, it can be seen that the rate of BNPP catalytic hydrolysis is accelerated by about  $2 \times 10^7$  or  $2 \times 10^6$  times those for CeL or LaL aqueous solution and by about  $1 \times 10^9$  or  $1 \times 10^8$  times in CeL or LaL metallomicelles, respectively, when compared with the rate of BNPP spontaneous hydrolysis [24]. Obviously, the catalytic activity of the CeL system is higher than that of the LaL system. This can be attributed to differences of the central metal ion radius in the two systems. Although the ligands of the complexes are the same in the two catalytic systems, the metal ions are different and then the Pauling radius of the metal ion Ce(III) is smaller than that of the metal ion radius is, the stronger is the interaction between the metal ion and BNPP molecule in the reaction, which is conducive to stability of the intermediate containing BNPP and the complex molecule. Therefore, the catalytic efficacy of the CeL system is higher than that of LaL system.

Moreover, the experimental results also indicate that the rate of BNPP hydrolysis catalyzed by LnL complex in the metallomicelle system is about fifty times faster than that in

<b>Table 1</b> $k_{obs} (s^{-1})$	of BNPP catalyt	ic hydrolysis on c	lifferent the mole	fractions $(x)$ of 1	metal ion				
x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$k_{\rm obs}~({\rm s}^{-1})$ in CeL	$8.68 \times 10^{-5}$	$5.32 \times 10^{-4}$	$1.36 \times 10^{-3}$	$6.08\times10^{-3}$	$1.16 \times 10^{-2}$	$8.25\times10^{-3}$	$5.36 \times 10^{-3}$	$9.75 \times 10^{-4}$	$6.28 \times 10^{-5}$
$k_{\rm obs}~({\rm s}^{-1})$ in LaL	$3.82 \times 10^{-5}$	$2.54 \times 10^{-4}$	$5.93 \times 10^{-4}$	$9.12 \times 10^{-4}$	$1.25 \times 10^{-3}$	$9.46 \times 10^{-4}$	$7.92 \times 10^{-4}$	$7.42 \times 10^{-5}$	$6.23 \times 10^{-6}$
$25.00  ^{\circ}\text{C},  \text{pH} = 8.0$	), [LSS] = 4.95	$\times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$	(BNPP] = 5.0 >	< 10 <sup>-4</sup> mol·dm <sup>-3</sup>	$^{3}, [L] + [Ln^{3+}] =$	$= 1 \times 10^{-4} \text{ mol}.$	$\mathrm{Im}^{-3}$		
$x = [Ln^{3+}]/[Ln^{3+}]$	+ [L]								

metal
of
X
fractions
mole
the
different
on
nydrolysis
catalytic 1
of BNPP
$s^{-1}$
$k_{\rm obs}$ (:
ble 1



**Table 2**  $k_{obs}$  (s<sup>-1</sup>) of BNPP hydrolysis catalyzed by the different systems

System	Ce complex	La complex	Ce complex + LSS	La complex + LSS	H <sub>2</sub> O
$k_{\rm obs}~({\rm s}^{-1})$	$2.72 \times 10^{-4}$	$2.35 \times 10^{-5}$	$1.16 \times 10^{-2}$	$1.25 \times 10^{-3}$	$1.2 \times 10^{-11}$ [24]
25.00 °C, [LnL] = 5.	pH = 8.0, [ $.0 \times 10^{-5} mol \cdot c$	$LSS] = 4.95 \times dm^{-3}$	$10^{-4}$ mol·dm <sup>-3</sup> ,	$[BNPP] = 5.0 \times 10^{-4}$	$mol \cdot dm^{-3}$ , and

the aqueous solution under the same conditions. It is well known that micelles play very important roles in the catalytic process owing to the effect of the high local concentration [25]. The zwitterionic surfactant LSS (isoelectronic point of 5.2 [26]) shows anionic characteristics in the range of pH investigated in this paper, so the complex is solubilized easily in the Stern layer of LSS micelles because of the electrostatic attraction between the electropositive complex and the anionic micelle (see Scheme 1). This will increase the local concentration and the collision frequency of the reaction molecules due to the solubilizing effect of the LSS micelle, and so facilitate the BNPP catalytic hydrolysis.

## 3.3 The Acid Effect and Real Active Species

The experimental results at various pH values are shown in Table 3 and Fig. 5. From this figure, it can be seen that the pH-rate curve presents a "bell–shape" profile with the acidity





change of the catalytic system from pH = 7.0 to 9.0, and the best pH values of the BNPP catalysis are 8.2 and 8.0 in the LaL and CeL metallomicelles, respectively. This indicates that the  $k_{obs}$  of BNPP catalytic hydrolysis is correlated to the acidity of the reaction system. The experiment results also show that the metallomicelle is remarkably stable over a week at pH = 8.0. Therefore, in spite of the optimal acidity for stabilization of the metallomicelle being at pH = 7.0 in the measured range of pH values, the major experiment of BNPP catalytic hydrolysis was performed at pH = 8.0 because the activity of the metallomicelle is much higher at pH = 8.0 than that at pH = 7.0.

From the structure of the lanthanide metal complex, the ionization of  $H_2O$  in the complex can be induced by the acidity of the metallomicelle system. Therefore, the complex exists in three different protonated states through the first and second acidic dissociation of  $H_2O$  molecules coordinated to lanthanum(III) ion in solution. The two-hydroxy complex LnLBr<sub>2</sub>(OH)<sub>2</sub> is easily generated in the strongly alkaline solution, and the hydrated complex LnLBr<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> is easily generated in the strongly acidic solution, but both are unfavorable for the formation and stabilization of the mono-hydroxy complex LnLBr<sub>2</sub>(H<sub>2</sub>O)(OH). So, the mono-hydroxy complex is most likely to be the active species in BNPP catalytic hydrolysis since the maximum  $k_{obs}$  of the pH-rate curve in Fig. 5 is at ca. pH = 8.0 or 8.2.

## 3.4 Mechanism of BNPP Hydrolysis Catalyzed by the Metallomicelle

To clarify the interaction between the complex and BNPP in the metallomicelle, the fluorescence spectra of the cerium complex was determined and analyzed in the presence and absence of BNPP. The fluorescence spectra of the cerium complex under different conditions are shown in Fig. 6. This figure shows that the emission intensities of the CeL complex decrease with increasing concentration of BNPP. The obvious decrease of fluorescence intensity of the complex caused by BNPP indicates strong binding between the complex and BNPP molecules, since the binding can lead to the photoelectron transfer from BNPP to the excited state of the complex [27] and then cause a configuration change of the complex.

Because one mole of BNPP can liberate two moles of p-nitrophenol, the catalytic hydrolysis rate of the p-nitrophenyl phosphate ester (NPP) is examined in the

<b>Table 3</b> $k_{obs} (s^{-1})$	of BNPP catalytic ł	hydrolysis at differe	nt acidities					
Hq	7.0	7.2	7.5	7.8	8.0	8.2	8.5	9.0
$k_{obs}$ (s <sup>-1</sup> ) in CeL $k_{obs}$ (s <sup>-1</sup> ) in LaL 25.00 °C, [LSS] = 4	$5.21 \times 10^{-3}$ 2.83 × 10^{-4} .95 × 10^{-4} mol·dm	$7.42 \times 10^{-3}$ 5.12 × 10^{-4} $n^{-3}$ , [BNPP] = 5.0	$9.67 \times 10^{-3}$ 7.53 × 10^{-4} × 10^{-4} mol·dm^{-3},	$1.06 \times 10^{-2}$ 9.33 × 10^{-4} [LnL] = 5.0 × 10	$1.16 \times 10^{-2}$ 1.25 × 10^{-2} $^{-5}$ mol·dm <sup>-3</sup>	$1.08 \times 10^{-2}$ $1.37 \times 10^{-2}$	$9.94 \times 10^{-3}$ $1.07 \times 10^{-3}$	$9.62 \times 10^{-3}$ $9.97 \times 10^{-4}$

aciditie
different
at
/sis
G
ýď
д.
ytic
catal
NPP
В
ē
_s
$k_{\rm obs}$
e
le



**Fig. 5** pH-rate profile for BNPP catalytic hydrolysis in the metallomicelle system: 25.00 °C,  $[LSS] = 4.95 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ,  $[BNPP] = 5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ,  $[LnL] = 5.0 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ 



metallomicelle of the lanthanide(III) metal complex. Fast hydrolysis of the monoester has been confirmed by a separate experiment on NPP hydrolysis. The experimental results show that hydrolysis rate of the *p*-nitrophenyl phosphate ester (NPP) is ten times higher than that of BNPP. Therefore, it may be deduced that the release of the first *p*-nitrophenol molecule of BNPP is the rate-determining step in BNPP catalytic hydrolysis.

According to the experimental results and the acid effect of BNPP catalytic hydrolysis above, the mechanism of BNPP hydrolysis catalyzed by the title complex is proposed as Scheme 2. This Scheme shows that the complex binds the phosphodiester through electrostatic interaction between lanthanide(III) metal ion center and the BNPP molecule, which is proved by the obvious change of fluorescence intensity of the complex in the fluorescence experiment, and this will facilitate the formation of the reaction intermediate containing BNPP and the complex LnLBr<sub>2</sub>(OH)(H<sub>2</sub>O) in the metallomicelle. In this process, the intermediate is stabilized and the negative charge of the substrate molecule is



Scheme 2 The reaction pathway of the BNPP catalytic hydrolysis

dispersed by the coordination of phosphoryl oxygen and lanthanide metal ion. Then the intramolecular Ln(III)-bound OH, as a nucleophile, attacks the electropositive P atom of the BNPP molecule, which is the rate-determining step of the whole reaction. Scheme 2 also shows that the second *p*-nitrophenol is released rapidly and the catalyst is rapidly regenerated in the BNPP catalytic hydrolysis cycle. Furthermore, the intermediate of the transition state of the reaction can also be stabilized by interaction with the polar head groups of the micelle [28], which is conducive to the stability of the intermediate.

The relationship between the  $k_{obs}$  and  $k_{cat}$  can be obtained by the method described previously [29]; that is  $1/k_{obs} = 1/k_{cat} + 1/K k_{cat}$  [LnL]. Here,  $k_{cat}$  is first order rate constant and is pH-dependent, K is the association constant between LnL and the BNPP molecule, and [LnL] is the concentration of the catalyst.

## 4 Conclusion

In summary, two metallomicellar systems made of the lanthanide metal complexes and *n*-lauroylsarcosine (LSS) micelle can promote BNPP cleavage, and exhibit high catalytic activity in the hydrolysis of BNPP at 25 °C; the catalytic efficiency of the metallomicellar system is dependent on the pH value of the reaction system, and the best catalyst acidity for the CeL and LaL metallomicellar systems are pH = 8.0 and 8.2, respectively; the LSS micelle palys two important roles in the BNPP catalytic hydrolysis, one is to promote the solubilization of the solute and the other is to stabilize the intermediate containing BNPP and the complex molecule.

**Acknowledgments** The authors gratefully acknowledge financial support from Chinese National Natural Science Foundation (21173274) and Major Science and Technology Project of Zigong city (2013X03), and the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of High Education (LYJ1303).

#### References

- Iranzo, O., Kovalecsky, A.Y., Morow, J.R.: Physical and kinetic analysis of the cooperative role of metal ions in catalysis of phosphodiester cleavage by a dinuclear Zn(II) complex. J. Am. Chem. Soc. 125, 1988–1993 (2003)
- Feng, F.M., Cai, S.L., Liu, F.A., Xie, J.Q.: Studies of DNA-binding and DNA-cutting mechanism of an azamacrocyclic cerium complex with carboxyl branch. Prog. Reac. Kin. Mech. 38, 283–294 (2013)
- Tonde, S.S., Kumbhar, A.S., Padhye, S.B.: Self-activating nuclease activity of copper (II) complexes of hydroxyl-rich ligands. J. Inorg. Biochem. 100, 51–57 (2006)
- Ferreira, D.E.C., Almeida, W.B.D., Neves, A.: Theoretical investigation of the reaction mechanism for the phosphate diester hydrolysis using an asymmetric dinuclear metal complex as a biomimetic model of the purple acid phosphatase enzyme. Phys. Chem. Chem. Phys. 10, 7039–7046 (2008)
- Katada, H., Seino, H., Mizobe, Y., Sumaoka, J., Komiyama, M.: Crystal structure of Ce((IV)/dipicolinate complex as catalyst for DNA hydrolysis. J. Biol. Inorg. Chem. 13, 249–255 (2008)
- Kuchma, M.H., Komanski, C., Colon, J., Teblum, A., Masunov, A.E., Alvarado, B., Babu, S., Seal, S., Summy, J., Baker, C.H.: Phosphate ester hydrolysis of biologically relevant molecules by cerium oxide nanoparticles. Nanomedicine: Nanotech. Biol. Med. 6, 738–744 (2010)
- Rossi, L.M., Neves, A., Horner, R.: Hydrolytic activity of a dinuclear copper(II, II) complex in phosphate diester and DNA cleavage. Inorg. Chim. Acta 337, 366–370 (2002)
- Jiang, W.D., Xu, B., Lin, Q., Li, J.Z., Liu, F., Zeng, X.C., Chen, H.: Metal-promoted hydrolysis of bis(*p*-nitrophenyl) phosphate by trivalent manganese complexes with Schiff base ligands in gemini micellar solution. Coll. Surf. A: Physicochem. Eng. Aspects **315**, 103–109 (2008)
- Gunnlaugsson, T., O'Brien, J.E., Mulready, S.: Glycine–alanine conjugated macrocyclic lanthanide ion complexes as artificial ribonucleases. Tet. Lett 43, 8493–8497 (2002)
- Maldonado, A.L., Yatsimirsky, A.K.: Kinetics of phosphodiester cleavage by differently generated cerium(IV) hydroxo species in neutral solutions. Org. Biomolec. Chem. 3, 2859–2867 (2005)
- Jurek, P.E., Jurek, A.M., Martell, A.E.: Phosphate diester hydrolysis by mono- and dinuclear lanthanum complexes with an unusual third-order dependence. Inorg. Chem. 39, 1016–1020 (2000)
- Penkova, L.V., Macia, A., Akimova, E.V.R.: Efficient catalytic phosphate ester cleavage by binuclear zinc(II) pyrazolate complexes as functional models of metallophosphatases. Inorg. Chem. 48, 6960–6971 (2009)
- Tjioet, L., Joshit, T., Forsytht, C.M.B., Murray, K.S., Brugger, J., Graham, B., Spiccia, L.: Phosphodiester cleavage properties of copper(II) complexes of 1,4,7-triazacyclononane ligands bearing single alkyl guanidine pendants. Inorg. Chem. 51, 939–953 (2012)
- Jurek, P., Martell, A.: Catalysis of hydrolysis of a phosphate diester by mono-and dinuclear macrocyclic zinc(II) complexes. Inorg. Chim. Acta 287, 47–51 (1999)
- Rawji, G.H., Yamada, M., Sadler, N.P., Milburn, R.M.: Cobalt(III)-promoted hydrolysis of 4-nitrophenyl phosphate: the role of dinuclear species. Inorg. Chim. Acta 303, 168–174 (2000)
- Mancin, F., Tecill, P.N.: Zinc(II) complexes as hydrolytic catalysts of phosphate diester cleavage: from model substrates to nucleic acids. New J. Chem. 31, 800–817 (2007)
- Ichikawa, K., Tarnai, M., Uddin, M.K., Nakata, K., Sato, S.: Hydrolysis of natural and artificial phosphoesters using zinc model compound with a histidine-containing pseudopeptide. J. Inorg. Biochem. 91, 437–450 (2002)
- Manseki, K., Nakamura, O., Horikawa, K., Sakamoto, M., Sakiyama, H., Nishida, Y., Sadaoka, Y., Okawa, H.: Synthesis of copper(II)–lanthanum(III) complex of a dinucleating macrocycle and its hydrolytic property for 4-nitrophenylphosphate. Inorg. Chem. Comm. 5, 56–58 (2002)
- Jiang, B.Y., Xiang, Y., Du, J., Xie, J.Q., Hu, C.W., Zeng, X.C.: Hydrolysis of *p*-nitrophenyl picolinate catalyzed by divalent metal ion complexes containing imidazole groups in micellar solution. Coll. Surf. A: Physicochem. Eng. Aspects 235, 145–151 (2004)
- Fendler, J.H.: Catalysis in Micellar and Macromolecular Systems, 3rd edn. 102. Academic Press, New York (1975)
- You, J.S., Yu, X.Q., Su, X.Y.: Hydrolytic metalloenzyme models enantioselective hydrolysis of long chain α-amino acid esters by chiral metallomicelles composed of lipophilic L-histidinol. J. Mol. Cat.A: Chem 202, 17–22 (2003)
- Xu, J.D., Ni, S.S., Lin, Y.J.: Syntheses and characterization of 5,5,7,12,12,14-hexamethyl1-, 4,8,11tetraazacyclotetradecane-N-acetic acid (H L1) and its transition-metal complexes: crystal structures of HL1.2HBr.H<sub>2</sub>O, [NiL1(H<sub>2</sub>O)]Br, and [NiL1(NCS)]H<sub>2</sub>O. Inorg. Chem. **27**, 4651–4657 (1988)
- Jiang, F.B., Jiang, B.Y., Chen, Y., Yu, X.Q., Zeng, X.C.: Metallomicellar catalysis: effects of bridgeconnecting ligands on the hydrolysis of PNPP catalyzed by Cu(II) complexes of ethoxyl-diamine ligands in micellar solution. J. Mol. Cat. A: Chem. 210, 9–16 (2004)

- Young, M.J., Wahnon, D., Hynes, R.C., Chin, J.: Reactivity of copper(II) hydroxides and copper(II) alkoxides for cleaving an activated phosphate diester. J. Am. Chem. Soc. 117, 9441–9447 (1995)
- Gruber, B., Kataev, E., Aschenbrenner, J., Stadlbauer, S., König, B.: Vesicles and micelles from amphiphilic zinc(II)-cyclen complexes as highly potent promoters of hydrolytic DNA cleavage. J. Am. Chem. Soc. 133, 20704–20707 (2011)
- Xiang, Y., Jiang, B.Y., Zeng, X.C., Xie, J.Q.: Metallomicellar catalysis: catalytic cleavage of *p*nitrophenyl picolinate by Cu<sup>2+</sup> complex of 4-chloride-2,6-bis(N-hydroxyethylaminomethyl)-benzophenol in micellar solution. J. Coll. Interface Sci. 247, 366–371 (2002)
- Rajendiran, V., Karthik, R., Palaniandavar, M., Stoeckli-Evans, H., Periasamy, V.S., Akbarsha, M.A., Srinag, B.S., Krishnamurthy, H.: Mixed-ligand copper(II)-phenolate complexes: effect of coligand on enhanced DNA and protein binding, DNA cleavage, and anticancer activity. Inorg. Chem. 46, 8208–8221 (2007)
- Dwars, T., Paetzold, E., Oehme, G.: Reactions in Micellar Systems. Angew. Chem. Int. Ed. 44, 7174–7199 (2005)
- Xie, J.Q., Xie, B., Feng, F.M., Zou, L.K., Feng, J.S.: Kinetic study on p-nitrophenyl picolinate hydrolysis promoted by the complex bis(0,0'-di(2-benzyl)dithiophosphato) nickel(II). Prog. React. Kin. Mech. 34, 249–260 (2009)