Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 202 (2003) 17–22

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Hydrolytic metalloenzyme models Enantioselective hydrolysis of long chain α-amino acid esters by chiral metallomicelles composed of lipophilic L-histidinol

Jing-Song You, Xiao-Qi Yu*, Xiao-Yu Su, Tao Wang, Qing-Xiang Xiang, Meng Yang, Ru-Gang Xie[1]

Sichuan Key Laboratory of Green Chemistry and Technology, Department of Chemistry, Sichuan University, Chengdu 610064, PR China

Received 17 September 2002; accepted 13 January 2003

Abstract

Chiral metallomicellar supramolecular systems composed of lipophilic L-histidinol have been investigated for their catalytic activities and enantioselectivities in the hydrolysis of N-protected α-amino acid esters. Kinetic evidence suggests that the mechanism of the deacylation promoted by ligand **4a** with a hydroxyl group and **2a** lacking a hydroxyl group is different. The apparent pK_a of Zn^{2+}-**4a** is 6.8 in the micelllar aggregate. The highest enantioselectivity in hydrolysis of *R*(*S*)-C_{12}-Leu-PNP ($k_S/k_R = 3.01$) was obtained with **4a**-Zn^{2+} as catalyst.

Keywords: Enantioselective hydrolysis; α-Amino acid esters; Chiral metallomicelles; L-Histidinol; Synthesis

1. Introduction

Metallomicelles are currently receiving considerable attention as new metalloenzyme models, which are made up of ligand surfactants chelating metal ions or lipophilic complexes and surfactants [1–3]. Of particular interest is the micellar models of hydrolytic metalloenzymes that are able to promote the cleavage of phosphoric and carboxylic esters or amides. Among these supramolecular systems, considerable attention has been paid to the imidazole-containing models because the imidazole residue of histidine is well recognized as the active sites of a lot of enzymes [4]. On the other hand, mimicing the enzyme-catalyzed stereoselectivity has proven much more challenging. In recent years, a few examples have been provided dealing with the enantioselective hydrolysis by chiral homo- and metallomicelles as models for hydrolytic metalloenzymes [5]. Inspecting the impressively long list of these imidazole-containing metallomicellar models, however, the chiral models are quite rare [6]. We have recently reported the enantioselective hydrolysis of α-amino acid esters by chiral metallomicelles composed of chiral lipophilic pyridyl-containing β-amino alcohol ligands [7] or the chiral sulfur-containing macrocyclic ligands [8]. In this paper, we report our work on the synthesis of lipophilic L-histidinol **4a** and the enantioselective hydrolysis of α-amino acid esters by their metal ion complexes in micelles. Ligands **2a** lacks the hydroxymethyl group with the aim of defining the role of the hydroxyl function in the complexes

* Corresponding author. Tel.: +86-28-85411684; fax: +86-28-85412285.
E-mail address: schemorg@mail.sc.cninfo.net (X.-Q. Yu).
[1] Co-corresponding author.

1381-1169/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1381-1169(03)00199-7

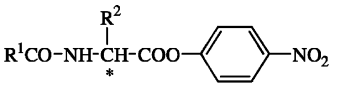
with ligands **4a**. The water-soluble ligands **2b** and **4b**, which do not contain a hydrophobic long chain, have also been investigated so that the catalytic activity of these compounds can be used for comparison.

2. Results and discussion

2.1. Ligands and substrates

The N^{α}-acyl-L-histidinols were synthesized according to the procedures outlined in Scheme 1 using L-histidine as a starting material. The acylated histidine **2a** could be obtained by a modified procedure in an excellent yield (>90%) when a mixed system consisting of aqueous KOH histidine and tetrahydrofuran was allowed to react with lauroyl chloride by vigorous stirring at 0–5 °C [9,10]. Subsequently, compound **2a** was smoothly esterified in a good yield in the presence of $SOCl_2$ at 0 °C, followed by reduction with $NaBH_4$ to afford the L-histidinol ligands **4a**. In a similar manner **2b** and **4b** were prepared. Their structures are supported by the data obtained from elemental analysis, MS and ^{1}H NMR. Compounds **2a** and **4a** can be soluble in MES buffer (0.05 M, pH 6.80) and form micellar aggregates: the critical micellar concentrations (cmc) are 5.0×10^{-5} and 6.4×10^{-5} M, respectively.

Scheme 2 shows the substrates investigated: they are all chiral, non-metallophilic substrates, i.e. the N-protected *p*-nitrophenyl esters of *R*(*S*)-phenylalanine, *R*(*S*)-leucine and *R*(*S*)-alanine.



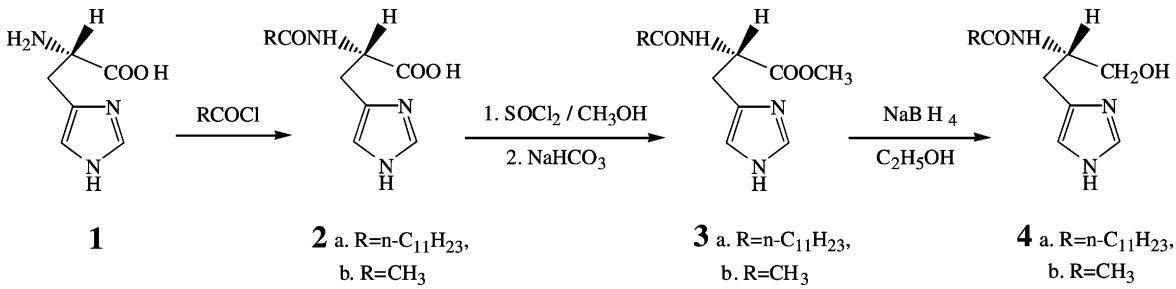
Substrate	R^1	R^2
R(S)-C_{12}-Phe-PNP	n-$C_{11}H_{23}$	CH_2Ph
R(S)-C_{12}-Leu-PNP	n-$C_{11}H_{23}$	$CH_2CH(CH_3)_2$
R(S)-C_{12}-Ala-PNP	n-$C_{11}H_{23}$	CH_3
R(S)-C_2-Ala-PNP	CH_3	CH_3

Scheme 2.

2.2. Kinetics

The rate of hydrolysis was followed by observing the release of *p*-nitrophenol spectrophotometrically under pseudo-first-order conditions. The pseudo-first-order rate constants (k_R and k_S) for the enantioselective cleavage of (*R*) and (*S*)-α-amino acid *p*-nitrophenyl esters promoted by metal ion complexes comicellized with Brij35 are summarized in Table 1, along with the enantioselectivity k_S/k_R. The results show that these chiral metallomicelles composed of the lipophilic L-histidinol ligands can effectively catalyze the enantioselective hydrolysis of (*R*) and (*S*)-α-amino acid esters with moderate enantioselectivities, and that the (*S*)-substrate is hydrolyzed faster than the corresponding (*R*)-isomer. Table 1 demonstrates that metal ions themselves show essentially no catalytic activity. Large rate enhancements are observed in the presence of both ligand and metal ion, and the enantioselectivities distinctly depend on the nature of the transition metal ion, in the order of $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Mn^{2+}$.

As shown in Table 1, the lipophilic metallocatalyst **4a**-Zn^{2+} containing a hydroxyl group gives the highest rate enhancement and enantioselectivity. Compared to ligand **4a**, **2a** lacks the hydroxyl group to lead to a decrease in the rate and enantioselectivity



Scheme 1.

Table 1
Pseudo-first-order constants (k_R and k_S, s^{-1}) and enantioselectivities (k_S/k_R) for the cleavage of α-amino acid esters by ligands **2–4** and M^{2+} comicellized with Brij35

Entry	Ligand	Substrate	M^{2+}	$k_S/10^{-5}$	$k_R/10^{-5}$	k_S/k_R
1	None	*R*(*S*)-C_{12}-Phe-PNP	None	9.01	9.02	1.00
2	None	*R*(*S*)-C_{12}-Phe-PNP	Zn^{2+}	18.9	19.2	0.98
3	**4a**	*R*(*S*)-C_{12}-Phe-PNP	Ni^{2+}	675	338	2.00
4	**4a**	*R*(*S*)-C_{12}-Phe-PNP	Co^{2+}	869	577	1.51
5	**4a**	*R*(*S*)-C_{12}-Phe-PNP	Mn^{2+}	814	689	1.18
6	**4a**	*R*(*S*)-C_{12}-Phe-PNP	Cu^{2+}	864	475	1.82
7	**4a**	*R*(*S*)-C_{12}-Phe-PNP	Zn^{2+}	1500	500	3.00
8	**4a**	*R*(*S*)-C_{12}-Leu-PNP	Zn^{2+}	1230	409	3.01
9	**4a**	*R*(*S*)-C_{12}-Ala-PNP	Zn^{2+}	256	151	1.70
10	**4a**	*R*(*S*)-C_{12}-Ala-PNP	Zn^{2+}	118	95.9	1.23
11	**2a**	*R*(*S*)-C_{12}-Phe-PNP	Zn^{2+}	1055	450	2.34
12	**2b**	*R*(*S*)-C_{12}-Phe-PNP	Zn^{2+}	23.0	17.3	1.33
13	**4b**	*R*(*S*)-C_{12}-Phe-PNP	Zn^{2+}	65.2	45.0	1.45

Conditions: 25 ± 0.1 °C, pH 6.80 [0.05 mol dm^{-3} 2-morpholinoethanesulfonic acid (MES) buffer], [ligand] = 3.33×10^{-4} mol dm^{-3}, [substrate] = 2.5×10^{-5} mol dm^{-3}, [M^{2+}] = 1.67×10^{-4} mol dm^{-3}, [Brij35] = 4.0×10^{-3} mol dm^{-3}.

(comparing entries 7 and 11). We also notice that the water-soluble **4b**-Zn^{2+} lacking a long chain is also less reactive and enantioselective than the lipophilic **4a**-Zn^{2+}, indicating that the hydrophobic interactions between substrate and metallocatalyst are favorable for both high rate acceleration and good enantioselectivity. A lipophilic long chain can introduce an extra orientation requirement in the supramolecular assembly between the metal ion complex and the lipophilic substrate coexisting in the micelle by the hydrophobic interations.

Structural effect of substrates on the hydrolysis catalyzed by comicelles composed of **4a**-Zn^{2+} and Brij35 is also depicted in Table 1. The increase in the size of the residue R^2 of the amino acid side chain from alanine to phenylalanine is accompanied by a rate increase (entries 7–9). Quite likely, the increase in the rate is due to an increased hydrophobically driven interaction between metallocatalyst and substrate. On the other hand, the extent of the enantioselectivity is in the order *R*(*S*)-C_{12}-Ala-PNP < R(*S*)-C_{12}-Leu-PNP ≈ R(*S*)-C_{12}-Phe-PNP. In the deacylation of *R*(*S*)-C_2-Ala-PNP, the extent of the enantioselectivity increase is negligibily small (k_S/k_R = 1.23) (entry 10), indicating that such ester substrates as *R*(*S*)-C_2-Ala-PNP lacking the hydrophobic long chain are likely to be absorbed onto the water–micelle interface and are hardly incorporated into the micellar phase, leading to insufficient substrate-metallocatalyst proximity.

2.3. Mechanism

2.3.1. Concentration effect of Zn^{2+} on the hydrolysis rate

Under fixed concentration of **2a** or **4a,** the effects of [Zn^{2+}] on the deacylation rate of (*S*)-C_{12}-Phe-PNP are shown in Fig. 1. Initial addition of Zn^{2+} to **4a** leads to a fast increase in the reaction rate until the ratio reaches a maximum when [Zn^{2+}]:[**4a**] is 1:2. With further

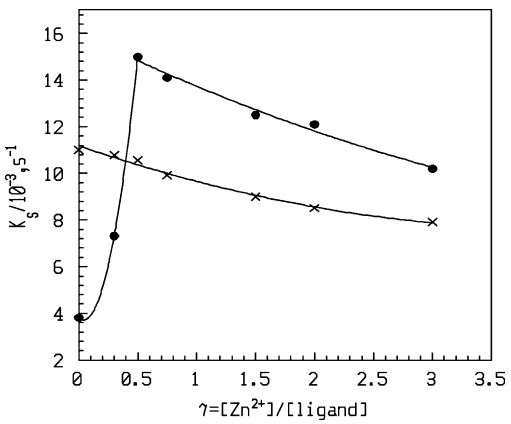


Fig. 1. Pseudo-first-order rate constants for the hydrolysis of (*S*)-C_{12}-Phe-PNP as a function of [Zn^{2+}] under fixed concentration of ligands **2a** (×) or **4a** (●) in Brij35 micelles, [ligand] = 3.33×10^{-4} mol dm^{-3}. See Table 1 for other conditions.

increase in the concentration of Zn^{2+}, a rate decrease is observed. Unlike **4a**, the **2a**-Zn^{2+}-catalyzed hydrolysis rate gradually decreases with increasing Zn^{2+} concentration, implying the mechanism of the deacylation is not the same as that catalyzed by **4a**-Zn^{2+}. The imidazolyl 3N-position of **2a** plays an important role in the transacylation process as a nucleophile. With addition of Zn^{2+}, the imidazolyl 3N-position is shielded to lead to a rate decrease. However, for **4a**, addition of Zn^{2+} may activate the hydroxyl group of ligand for nucleophilic attack to cause the rate enhancement.

2.3.2. Stoichiometry of the reactive complexes

To know the stoichiometry of the kinetically reactive complexes, the kinetic version of Job Plots was examined by plotting k_R and k_S as a function of molar fraction of ligand (γ), keeping the total concentrations of ligand and metal ion constant. The results shown in Fig. 2 indicate that in the case of Zn^{2+} and ligand **4a** the rate maxima are observed at $\gamma = 0.67$, which correspond to a stoichiometry of ligand: Zn^{2+} = 2:1. Ligand **4a** forms stable complex with Zn^{2+} as indicated by the sharp maxima in the Job Plots. We also obtained direct evidence for this complex by measuring the ESI mass and the peak at 710 shows the existence of complex formed by two ligand and Zn^{2+}. The **4a**-Zn^{2+}-substrate

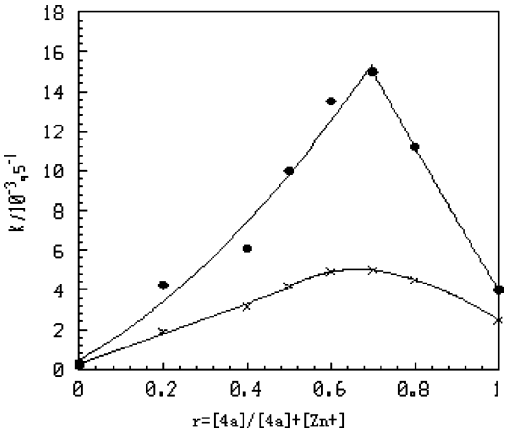
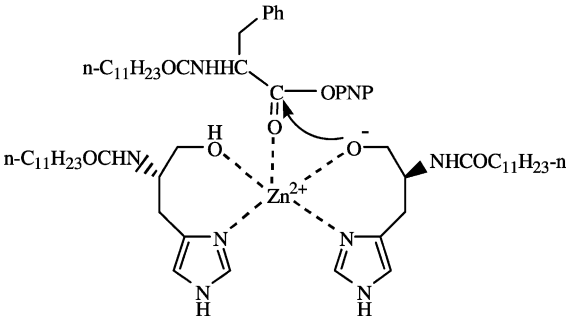


Fig. 2. Kinetic Job Plots for the cleavage of (*R*)-C_{12}-Phe-PNP (×) and (*S*)-C_{12}-Phe-PNP (●) by ligand **4a** and Zn^{2+} in MES buffer, pH 6.30, 25±0.1 °C. ([**4a**]+[Zn^{2+}]) = 5.0×10^{-4} mol dm^{-3}. See Table 1 for other conditions.



Scheme 3. The ternary complex of **4a**-Zn^{2+}-substrate.

formed ternary complex is indicated in Scheme 3 [6,11].

2.4. pH-Rate profile

As discussed above, from the analysis of Table 1, it is concluded that a free hydroxyl of ligand is of importance for high rate acceleration and good enantioselectivity in micelles. The pH-rate constant profiles were determined for reactions of (*S*)-C_{12}-Phe-PNP with catalyst **4a**-Zn^{2+}. The pH value was checked before and after any kinetic run and proved to be constant within ±0.05 pH unit. The inflections in the rate-pH profiles are diagnostic of an operative pK_a value of ca. 6.8 (Fig. 3). They are taken as the systematic pK_a of the hydroxyl bound to Zn^{2+} under our micellar reaction conditions.

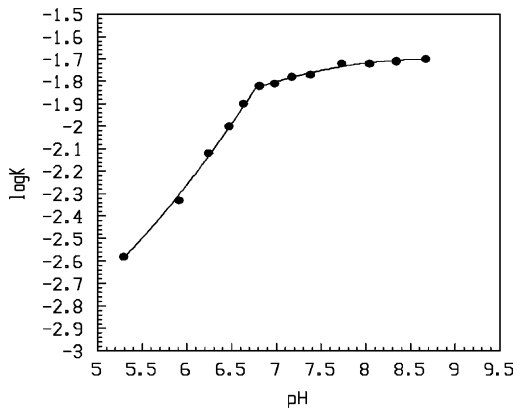


Fig. 3. Log *k* vs. pH for the cleavage of (*S*)-C_{12}-Phe-PNP by **4a**-Zn^{2+}. [Zn^{2+}] = 1.67×10^{-4} mol dm^{-3}. See Table 1 for other conditions.

3. Experimental

3.1. General methods and materials

Melting points were taken on a micro-melting apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz, and chemical shifts in ppm are reported relative to internal Me_4Si. Mass spectra data were recorded on a Finnigan MAT 4510 spectrometer. Elemental analyses were performed with a Carlo Erba 1106 instrument. Optical rotations were taken on a WZZ-1 polarimeter. Kinetic runs were conducted on a Shimadzu UV-265FW spectrophotometer equipped with a thermostated cell compartment. $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $MnCl_2$, N^{α}-Acetyl-L-histidine$\cdot H_2O$ and polyethylene glycol dodecyl ether (Brij35) were purchased from commercial sources and used without further purification. The buffers were 2-morpholinoethanesulfonic acid (MES) (pH = 5.0–6.8), 4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid (HEPES) (pH = 6.8–7.8), 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS) (pH = 7.7–9.0). The *p*-nitrophenyl esters of the N-protected α-amino acids were prepared according to literature procedures [12]. All other chemicals and reagents were obtained commercially and used without further purification.

3.2. General procedure of N^{α}-acyl-L-histidinol **4**

3.2.1. Synthesis of N^{α}-lauroyl-L-histidinol **4a**

*3.2.1.1. N^{α}-lauroyl-L-histidine **2a**.* To 5.0 g (32.3 mmol) of L-histidine and 2.0 g (32.3 mmol) of KOH in 250 ml of water and 50 ml of THF was added dropwise 6.6 g (30.0 mmol) of lauroyl chloride in 20 ml of THF over 1.5 h at 0–5 °C. This mixture was vigorously stirred during addition and for a further 3 h period. THF was then removed. The aqueous phase was acidified until pH = 5 with formic acid, and the precipitate was filtered and washed with water. The crude product was extracted with *n*-hexane (4 × 100 ml), and dried to give a white amorphous powder **2a** (90%), m.p. 158–160 °C. MS (*m*/*z*): 337 ($M^+ + 1$, 30).

*3.2.1.2. N^{α}-lauroyl-L-histidine methyl ester **3a**.* Compound **2a** (10.1 mmol) was suspended in 40 ml of methanol and cooled down to 0 °C in an ice bath. $SOCl_2$ (3.0 ml) was added dropwise with stirring over 0.5 h. After the addition was complete, the mixture was stirred at the same temperature for another 24 h. The solvent was then evaporated under reduced pressure. The mixture was treated with aqueous NH_3 until the pH was 8.0, and extracted with $CHCl_3$ (4 × 30 ml). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the histidine ester as a white solid in a 60% yield, m.p. 91–92 °C, $[\alpha]_D^{25} = -3.5$ (c = 1.0, CH_3OH). ^{1}H NMR (CDCl3): δ 0.86 (t, J = 6.7 Hz, 3H, $(CH_2)_9CH_3$), 1.23 (s, 18H, $(CH_2)_9CH_3$), 1.60 (t, J = 6.5 Hz, 2H, $CH_2(CH_2)_9$), 2.16 (dd, J = 5.8, 5.2 Hz, 1H, $ImCH_{2a}$ CHNH), 2.29 (dd, J = 5.8, 5.2 Hz, 1H, $ImCH_{2b}CHNH$), 3.67 (s, 3H, OCH_3), 4.79 (m, 1H, CH_2CHNH), 6.87 (s, 1H, Im5H), 7.12 (d, J = 7.6 Hz, 1H, Im2H), 7.77 (s, 1H, NHCO) ppm. MS (*m*/*z*): 352 ($M^+ + 1$, 30).

*3.2.1.3. N^{α}-lauroyl-L-histidinol **4a**.* To 2.85 mmol of compound **3a** in 30 ml of EtOH was added 0.3 g (7.9 mmol) of $NaBH_4$ at 0 °C in an ice bath. The mixture was stirred at this temperature for 1 h, and then refluxed for 4 h. The solvent was evaporated and the residue was treated with 15 ml of saturated Na_2CO_3 and extracted with $CHCl_3$ (5 × 30 ml). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica, $CHCl_3/CH_3OH$ 5:1), and then recrystallized from ethyl acetate and petroleum to give a white solid (yield 54%), m.p. 100–101 °C, $[\alpha]_D^{25} - 8.2$ (c = 1.0, CH_3OH). ^{1}H NMR (CDCl3): δ 0.85 (t, J = 6.6 Hz, 3H, $(CH_2)_9CH_3$), 1.23 (s, 18H, $(CH_2)_9CH_3$), 2.01 (t, J = 7.3 Hz, 2H, $CH_2(CH_2)_9$), 2.49 (dd, J = 5.2, 5.0 Hz, 1H, $ImCH_{2a}CHNH$), 2.68 (dd, J = 5.2, 5.0 Hz, 1H, $ImCH_{2b}CHNH$), 3.92 (br s, 2H, CH_2OH), 4.62 (m, 1H, CH_2CHNH), 6.54 (s, 1H, Im5H), 6.73 (s, 1H, Im2H), 7.60 (d, J = 8.8 Hz, 1H, NHCO) ppm. Anal. Calcd. for $C_{18}H_{33}O_2N_3$:C 66.83, H 10.28, N 12.99; found: C 66.56, H 10.37, N 12.77. MS (*m*/z): 324 ($M^+ + 1$, 100).

3.2.2. Synthesis of N^{α}-acetyl-L-histidinol **4b**

This compound was synthesized by following the same procedure as followed in the synthesis of **4a**. A white solid (yield 34%), m.p. 152–153 °C, $[\alpha]_D^{25} - 14.8$

($c = 0.8$, CH_3OH). ^1H NMR ($CDCl_3$): δ 1.78 (s, 3H, CH_3), 2.51 (d, 2H, $J = 5.9$ Hz, $ImCH_2CHNH$), 3.34 (m, 2H, CH_2OH), 3.87 (br s, 1H, CH_2OH), 4.67 (m, 1H, CH_2CHNH), 6.75 (s, 1H, Im5H), 7.54 (s, 1H, Im2H), 7.68 (d, $J = 8.1$ Hz, 1H, NHCO) ppm. Anal. Calcd. for $C_8H_{13}O_2N_3$:C 52.44, H 7.15, N 22.94; found: C 52.30, H 7.39, N 22.77. MS (*m*/*z*): 184 ($M^+ + 1$, 55).

3.3. Kinetic studies

Solutions of the ligands, metal ions and co-surfactants were prepared in the proper buffer (0.05 M). Reaction temperature was maintained at $25 \pm 1\,^{\circ}C$. Kinetics was typically started by injecting an acetonitrile solution (0.01 M) of substrate ester into a 1 cm cuvette containing 2.5 ml of buffered micellar solution and the desired concentration of metal ion and ligand. Pseudo-first-order rate constants (k_R and k_S) for the hydrolysis of substrate ester were determined by monitoring the release of *p*-nitrophenol at 320 nm (pH 5.0–6.3) or 400nm (pH 6.3–8.5) for at least five half-lives, and obtained by linear plots of $\mathrm{Ln}(A_\infty - A_t)$ versus time. The rate constants for each reaction were determined three times from three separate runs with an uncertainty of less than 5%.

Acknowledgements

We would like to thank National Natural Science Foundation of China (20132020) and Doctoral Foundation of National Educational Department of China for financial support.

References

[1] (a) X.Q. Yu, J.S. You, Q.X. Xiang, Q.S. Yan, R.G. Xie, Chin. Chem. Lett. 9 (1998) 731;
(b) Q.X. Xiang, X.Q. Yu, X.Y. Su, Q.S. Yan, T. Wang, J.S. You, R.G. Xie, J. Mol. Catal. A Chem. 187 (2002) 195;
(c) S. Bhattacharya, K. Snehalatha, S. George, J. Org. Chem. 63 (1998) 27;
(d) E. Kimura, H. Hashimoto, T. Koike, J. Am. Chem. Soc. 118 (1996) 10963;
(e) S. Taşcioğlu, Tetrahedron 52 (1996) 11113;
(f) T.J. Broxton, R.A. Cox, Can. J. Chem. 71 (1993) 670;
(g) Q.X. Xiang, X.Q. Yu, J.S. You, Q.S. Yan, R.G. Xie, Chin. J. Chem. 19 (2001) 158.

[2] (a) C.A. Bunton, P. Scrimin, P. Tecilla, J. Chem. Soc. Perkin Trans. 2 (1996) 419;
(b) P. Scrimin, P. Tecilla, U. Tonellato, J. Org. Chem. 59 (1994) 18;
(c) P. Scrimin, P. Tecilla, U. Tonellato, J. Org. Chem. 56 (1991) 161.

[3] (a) J.G.J. Weijnen, J.F.J. Engbersen, Recl. Trav. Chim. Pays-Bas (1993) 351;
(b) J.G.J. Weijnen, A. Koudijs, G.A. Schellenes, J.F.J. Engbersen, J. Chem. Soc. Perkin Trans. 2 (1992) 829.

[4] (a) H. Dugas, Bioorganic Chemistry, third ed., Springer-Verlag, New York, 1996;
(b) A. Neuberger, K. Brockiehurst (Eds.), Hydrolytic Enzymes, Elsevier Science, Amsterdam, 1987.

[5] (a) M.C. Cleij, F. Mancin, P. Scrimin, P. Tecilla, U. Tonellato, Tetrahedron 53 (1997) 357;
(b) M.C. Cleij, P. Scrimin, P. Tecilla, U. Tonellato, Langmuir 12 (1996) 2956;
(b) P. Scrimin, P. Tecilla, U. Tonellato, J. Org. Chem. 59 (1994) 4194.

[6] (a) K. Ogino, H. Yamamoto, T. Yoshida, W. Tagaki, J. Chem. Soc. Chem. Commun. (1995) 691;
(b) K. Ogino, N. Kashihara, T. Ueda, T. Isaka, T. Yoshida, W. Tagaki, Bull. Chem. Soc. Jpn. 65 (1992) 373;
(c) K. Ogino, K. Inoue, W. Tagaki, Tetrahedron Lett. 33 (1992) 4191;
(d) W. Tagaki, K. Ogino, O. Tanaka, K. Machiya, N. Kashihara, T. Yoshida, Bull. Chem. Soc. Jpn. 64 (1991) 74;
(e) J.H. Van Esch, M. Damen, M.C. Feiters, R.J.M. Nolte, Recl. Trav. Chim. Pays-Bas 113 (1994) 186.

[7] J.S. You, X.Q. Yu, K. Liu, L. Tao, Q.X. Xiang, R.G. Xie, Tetrahedron: Asymmetry 10 (1999) 243.

[8] J.S. You, X.Q. Yu, X.S. Li, Q.S. Yan, R.G. Xie, Tetrahedron: Asymmetry 9 (1998) 1197.

[9] (a) J.S. You, X.Q. Yu, C.L. Liu, R.G. Xie, Synth. Commun. 29 (1999) 2447;
(b) J.S. You, X.Q. Yu, G.L. Zhang, Q.X. Xiang, J.B. Lan, R.G. Xie, Chem. Commun. (2001) 1816.

[10] C. Gitler, A. Ochoa-Solano, J. Am. Chem. Soc. 90 (1968) 5004.

[11] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, third ed., Wiley, New York, 1972.

[12] (a) D.W. Ingles, J.R. Knowles, Biochem. J. 104 (1967) 369;
(b) M. Bodanszky, V.D. Vigneaud, J. Am. Chem. Soc. 81 (1959) 5688.