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Catalytic hydrolysis of carboxylic acid esters by Cu(II) and Zn(II) complexes containing a tetracoordinate macrocyclic Schiff base ligand in Brij35 micellar solution

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Abstract

The macrocyclic Schiff base complexes of Cu(II) and Zn(II) in Brij35 micellar solution are investigated kinetically for the catalytic hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl picolinate (PNPP) at 30 °C. The results indicate that different mechanisms are operative for the two complexes in the hydrolysis of PNPA and PNPP. The Cu(II) complex can only catalyze the hydrolysis of PNPP by the mechanism which involves the nucleophilic attack of external hydroxide ion on the carbonyl, while the Zn(II) complex can accelerate the hydrolysis of both PNPP and PNPA, by way of the intramolecular nucleophilic attack of zinc-bound hydroxide ion on carbonyl for PNPP and the less effective intermolecular nucleophilic attack of zinc-bound hydroxide ion on carbonyl for PNPA, respectively. The catalytic activity of Zn(II) complex is close to or even higher than that of Cu(II) complex. The reason is discussed in details.

Keywords: Macrocyclic Schiff base complex; Carboxylic acid ester hydrolysis; Metallomicelle; Catalysis; Kinetics

1. Introduction

The hydrolysis of carboxylic acid esters is of paramount importance in biological and industrial processes [1]. Therefore, we [2,3] and other groups [4–6] have developed the biomimetic models for metalloenzyme which catalyzes the hydrolysis of carboxylic acid esters in biological body. These biomimetic models provide insight into the mechanism by which metalloenzyme may operate and consequently provide a theoretical base for designing highly effective artificial metalloenzyme.

Metallomicelles, which exhibit similar structural and kinetic properties to enzyme, have been extensively investigated as effective biomimetic systems for hydrolytic metalloenzymes [7–9]. Examples are the metal-ion complexes of the lipophilic imidazoles [10] and pyridines [11] co-micellerized with surfactants. Other metal-ion complexes of the derivatives of hydroxylamine [12], *N*-ammoniocarboxyamidate [13] and *N*-alkylethylenediamine [14] were also examined on ester hydrolysis under micellar conditions. In all of these examples, the ligands are used to form metal-ion complexes, and the metal ion sites of the complexes are presumed to act as polar-head groups of surfactants.

In recent years, the use of macrocyclic metal complexes as biomimetic models of hydrolytic metalloenzymes [15–17] has attracted considerable attention because of their similarities to the macrocyclic metal complexes found in biological systems, such as those of porphin and corrin. However, the macrocyclic Schiff base complexes are seldom employed to catalyze the hydrolysis of carboxylic acid esters in metallomicellar system [18]. Therefore, in this report, we investigate the catalytic hydrolysis of carboxylic acid esters by macrocyclic Schiff base complexes of Cu(II) and Zn(II) in Brij35 micellar solution.

2. Experimental

2.1. Materials

Brij35($C_{12}H_{25}(OCH_2CH_2)_{23}OH$) is Sigma product and was used as received. Tris(trihydroxylmethyaminomethane),

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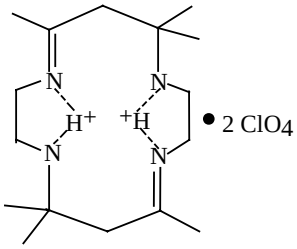

Scheme 1. The structure of L·2HClO$_4$.

HNO_3, KNO_3, acetonitrile are of analytical reagent grade. PNPA was obtained from Tokyo Kasei Kogyo Co. and used without further purification. PNPP was prepared and purified by the literature method [19]. The water used for kinetic experiment was obtained by distilling deionized water. The stock solutions of PNPA and PNPP were prepared in acetonitrile.

Macrocyclic Schiff base ligand, 5,7,7,12,14,14-hexamethyl - 1,4,8,11 - tetraazacycl -odeca-4,11-dienedihydrogen perchlorate, $C_{16}H_{32}N_4{\cdot}2HClO_4$ (L·2HClO$_4$, Scheme 1) was prepared according to the literature [20]. Ethylenediamine (0.2 mol) in 10 ml ethanol was cooled in an ice bath. Then, 0.2 mol of perchloric acid was slowly added to the ethylenediamine solution. After the perchloric acid was added, 30 ml of acetone was added and the solution was allowed to cool in an ice bath for several hours. A white precipitate crystallized from the solution. The precipitate was filtered, washed with acetone and recrystallized from hot methanol–water solution. Anal. Calcd. for $C_{16}H_{34}Cl_2N_4O_8$: C, 39.92; H, 7.12; N, 11.64. Found: C, 40.15; H, 7.21; N, 11.70. IR (KBr, cm^{-1}): 3154 (N-H, 3145 [21]); 2933 (C–H); 1668 (C=N, 1670 [21]); 1119, 1059 (ClO_4^-, 1090, 1070 [21]).

Complexes $[Cu(C_{16}H_{32}N_4)](ClO_4)_2$ (CuL) and $[Zn(C_{16}H_{32}N_4)(H_2O)](ClO_4)_2$ (ZnL-H$_2$O) was prepared by the method similar to that employed in the literature [22].

$[Cu(C_{16}H_{32}N_4)](ClO_4)_2$ Macrocyclic Schiff base ligand (5 mmol) was added to an equimolar amount of copper acetate monohydrate in 40 ml methanol and refluxed for 1 h. The resulting purplish red solution was filtered and concentrated on a hot water bath until crystals began to form. After cooled, the dark red crystal was filtered and recrystallized from hot ethanol–water mixture. Anal. Calcd. for $C_{16}H_{32}N_4O_8Cl_2Cu$: C, 35.39; H, 5.94; N, 10.32. Found: C, 35.24; H, 5.91; N, 10.18. IR (KBr, cm^{-1}): 3208 (N–H, 3205 [21]); 2984 (C–H, 2985 [21]); 1666 (C=N, 1675 [21]); 1096 (ClO_4^-, 1095 [21]).

$[Zn(C_{16}H_{32}N_4)(H_2O)](ClO_4)_2$ This complex was prepared by refluxing the equimolar mixture of macrocyclic Schiff base ligand and zinc acetate dihydrate as described above for the copper complex. Anal. Calcd. for $C_{16}H_{34}N_4O_9Cl_2Zn$: C, 34.15; H, 6.10; N,9.97. Found: C, 34.33; H, 6.27; N, 9.90. IR (KBr, cm^{-1}): 3495 (O–H, 3500 [21]); 3254 (N–H, 3260 [21]); 2964 (C–H, 2980 [21]); 1668(C=N, 1675 [21]); 1106 (ClO_4^-, 1110 [21]).

2.2. Method

A pHs-3A pH meter was used for the pH determination and control. Elemental analysis was performed on a MOD 1106 elemental analyzer. Infrared spectra were measured with a Perkin-Elmer 16PC FT-IR spectrophotometer. Kinetic runs were conducted by using a GBC 916 spectrophotometer equipped with a thermostatic cell compartment. Reaction temperature was maintained at 30 °C. Reaction was initiated by injecting 30 μl of acetonitrile solution of substrate into a 1 cm cuvette containing 3 ml of desired concentration of complex in micellar solution. Pseudo-first-order rate constants for the hydrolysis of substrate ester were determined by monitoring the release of *p*-nitrophenolate at 400 nm under the conditions of excess of catalyst over substrate. Reactions were generally followed for at least six half-lives. Pseudo-first-order rate constants were obtained by the initial rate method for PNPA and by using $\ln(A_\infty - A_t)$–$\ln(A_\infty - A_0) = -k_{obsd}t$ for PNPP. Kinetic runs carried out in triplicate gave rate constants with uncertainty of less than 3%.

3. Results and discussion

In order to avoid the influence of the components of the buffer on the hydrolysis of PNPA and PNPP, pH was varied by varying the ratio of Tris:HNO_3.

All experiments were carried out in the solution containing 5.00×10^{-3} mol dm^{-3} surfactant Brij35 concentration which is well above the reported [23] critical micelle concentration range of $6.00 \times 10^{-5} \sim 9.00 \times 10^{-5}$ mol dm^{-3}

3.1. General survey of rate for hydrolysis of PNPP and PNPA in different systems

Since the complexes are all water-soluble, the kinetic study was carried out in plain buffer and in buffered micelle, respectively. In Table 1 are shown the pseudo-first-order rate constants (k_{obsd}) of different systems obtained under the conditions of an excessive complex over the substrates.

From Table 1, we can see that the complex ZnL-H$_2$O can accelerate the hydrolysis of both PNPP and PNPA in plain

Table 1
Pseudo-first-order rate constants (k_{obsd}) for hydrolysis of PNPP and PNPA in different systems at pH = 7.15, 30 °C[a]

No.	System	$10^3 k_{obsd}$ (PNPP)/s^{-1}	$10^5 k_{obsd}$ (PNPA)/s^{-1}
1	Buffer	0.0442	1.82
2	Buffer + CuL	3.52	1.89
3	Buffer + ZnL-H$_2$O	2.35	16.8
4	Buffer + Brij35	0.0261	1.11
5	Buffer + Brij35 + CuL	2.61	1.13
6	Buffer + Brij35 + ZnL-H$_2$O	1.60	4.47

[a] In 0.1 mol dm^{-3} Tris–HNO_3 buffer, μ = 0.1 (KNO_3); [Brij35] = 5.00×10^{-3} mol dm^{-3}; [CuL] = [ZnL-H$_2$O] = 4.10×10^{-3} mol dm^{-3}; [PNPP] = [PNPA] = 5.00×10^{-5} mol dm^{-3}.

buffer or in buffered Brij35 micelle, while the complex CuL can only promoted hydrolysis of PNPP in plain buffer or in Brij35 micellar solution. Furthermore, at pH 7.15, the rate constant for CuL-mediated hydrolysis of PNPP is larger than that for ZnL-H_2O promoted hydrolysis of PNPP, but the reverse circumstances are observed at higher pHs, which is an indication of acid–base catalysis for ZnL-H_2O promoted hydrolysis. As described below, all above catalytic characteristics depend on the nature of complex and substrates.

From Table 1, it can be also found that both the pseudo-first-order rate constant for complex catalyzed hydrolysis in Brij35 micellar solution and that for spontaneous hydrolysis in Brij35 micellar solution is smaller than that in plain buffer, indicating that the inhibition for hydrolysis of PNPP and PNPA occurs in non-ionic surfactant Brij35 micellar solution.

According to the "phase-separation" model [24,25] for micellar catalysis, a homogeneous aqueous micellar solution may be treated as two pseudo-phases: bulk water phase and micellar phase, which is hydrophobic, and the reaction rates will depend upon the distribution of the reactants between these two pseudo-phases. Therefore, the reasons for the slower rates in micellar solution than those in plain buffer solution may be ascribed to the following: (1) the hydrophobic substrates are incorporated into the micellar pseudo-phase through hydrophobic interaction [26]; (2) the water-soluble metallocomplexes prefer to stay in the bulk water phase [27]; (3) the twined long polyoxyethylene chain hinders the movement of molecules of the reactants [28]. Accordingly, these results indicate that the Brij35 micellar microenvironment is not favorable for hydrolysis of carboxylic acid esters.

3.2. Kinetic investigation of CuL-mediated hydrolysis of PNPA and PNPP in Brij35 micellar solution

Figs. 1 and 2 show the variation of the pseudo-first-order rate constants with CuL concentration for the hydrolysis of PNPP and PNPA in Brij35 micellar solution at different pHs, respectively. From Fig. 1, it can be seen that the

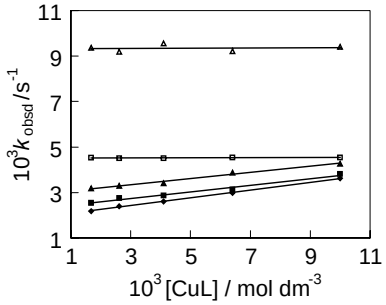

Fig. 1. Variation of the pseudo-first-order rate constant with CuL concentration for CuL-promoted hydrolysis of PNPP in Brij35 micellar solution at 30 °C. I = 0.1 (KNO_3); [Brij35] = 5.00×10^{-3} mol dm^{-3}; [PNPP] = 5.00×10^{-5} mol dm^{-3}; pH = 7.15 (◆), 7.51 (■), 7.80 (▲), 8.09 (□), 8.68 (△).

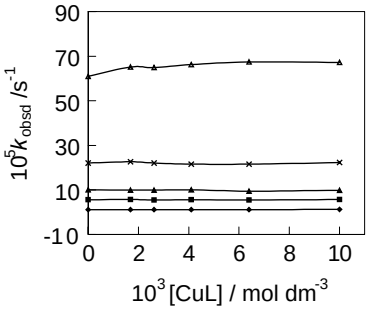

Fig. 2. Variation of the pseudo-first-order rate constant with CuL concentration for CuL-mediated hydrolysis of PNPA in Brij35 micellar solution at 30 °C. I = 0.1 (KNO_3); [Brij35] = 5.00×10^{-3} mol dm^{-3}; [PNPP] = 5.00×10^{-5} mol dm^{-3}; pH = 7.15 (◆), 7.51 (■), 7.80 (▲), 8.09 (×), 8.68 (△).

pseudo-first-order rate constants for the hydrolysis of PNPP increase with increasing CuL concentration at lower pHs. No saturation kinetics is observed, indicating that the binding constant of PNPP to CuL is low [27]. However, at higher pHs, the pseudo-first-order rate constants for the hydrolysis of PNPP almost keep constant irrespective of CuL concentration.

In CuL, no source, which forms the nucleophile for the hydrolysis of PNPP, can be found. Thus, the hydrolysis of PNPP catalyzed by CuL in Brij35 micellar solution may be caused by external OH^- acting as a nucleophile, while Cu(II) only act as a general Lewis acid holding the substrate for OH^- attack, as shown in Fig. 3. Similar Lewis acid mechanism has been proposed for divalent metal ion catalyzed hydrolysis of a series of picolinic acid esters including PNPP [29,30]. In these cases, as in ours, the picolinate nitrogen and carbonyl of picolinic acid esters act as the site of metal ion binding to coordinate with metal ion, which makes carbonyl more active, facilitating the nucleophilic attack of external hydroxide ion at carbonyl of picolinic acid esters.

For this mechanism, it is important for substrate PNPP to be bound to CuL. But at higher pHs, as previously reported [31], the complex CuL may form the dihydroxo complex, which makes cupric ion in CuL coordinatively saturated. No site of coordination is left for substrate PNPP, resulting in the loss of catalytic activity of CuL toward PNPP. Consequently, the pseudo-first-order rate constants for hydrolysis of PNPP in Brij35 micellar solution at higher pHs remain unchanged. Kenley and co-workers [32] observed analogous circumstances for cobalt(III) complex catalyzed hydrolysis of phosphorus esters, in which the

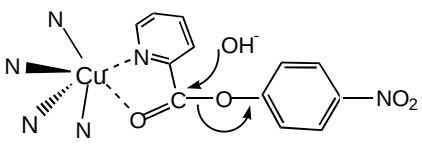

Fig. 3. The possible mechanism for hydrolysis of PNPP catalyzed by CuL in Brij35 micellar solution.

aquohydroxo(tetraamine)cobalt(III) complexes lost their catalytic activities when they are transformed into dihydroxo(tetraamine)cobalt(III) complexes. Accordingly, we think that the similar processes may proceed in the CuL-mediated hydrolysis of PNPP at higher pHs.

As for PNPA, from Fig. 2 it can be seen that at any pH, the pseudo-first-order rate constants for the hydrolysis of PNPA remain nearly constant irrespective of the CuL concentration and were almost equal to the corresponding rate constants for spontaneous hydrolysis of PNPA, that is, the CuL hardly influences the hydrolysis of PNPA. This can be attributed to the very weak polarization of carbonyl in PNPA by Cu(II) in CuL because of the weak coordination of carbonyl with Cu(II). No other coordination group in PNPA exists except carbonyl with weak coordinative ability, while a stronger coordination group (pyridine) co-exists with carbonyl in PNPP. The N atom in pyridine can coordinate more strongly with Cu(II) in the hydrolytic process of PNPP. Thus, PNPP can be held by Cu(II) in CuL and the carbonyl in PNPP is drawn close to Cu(II), resulting in a stronger polarization of carbonyl by Cu(II) and more effective activation compared with PNPA(see Fig. 3). Therefore, CuL can accelerate the hydrolysis of PNPP, but shows almost no catalytic activity toward PNPA.

3.3. Kinetic analysis of the effect of ZnL-H_2O on the hydrolysis of PNPA and PNPP in Brij35 micellar solution

The difference in the structure between ZnL-H_2O and CuL is that ZnL-H_2O coordinates a water molecule. This may cause the different mechanism for the catalytic hydrolysis of PNPA and PNPP. In Figs. 4 and 5 are presented respectively the variation of the pseudo-first-order rate constants with ZnL-H_2O concentration for the hydrolysis of PNPA and PNPP in Brij35 micellar solution at different pHs. From Figs. 4 and 5, it can be seen that the pseudo-first-order rate constants for the hydrolysis of PNPA and PNPP increase linearly with ZnL-H_2O concentration at any pH, which is different from the CuL-mediated hydrolysis of PNPA and PNPP.

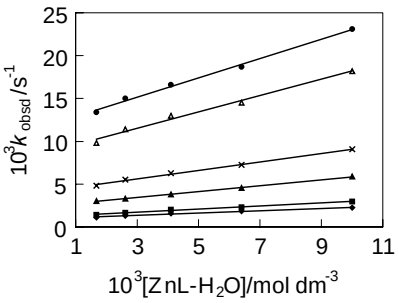

Fig. 4. Variation of the pseudo-first-order rate constant with ZnL-H_2O concentration for ZnL-H_2O promoted hydrolysis of PNPP in Brij35 micellar solution at 30 °C. $I = 0.1$ (KNO_3); [Brij35] $= 5.00 \times 10^{-3}$ mol dm^{-3}; [PNPP] $= 5.00 \times 10^{-5}$ mol dm^{-3}; pH = 7.15 (◆), 7.40 (■), 7.80 (▲), 8.09 (×), 8.68 (△), 9.00 (●).

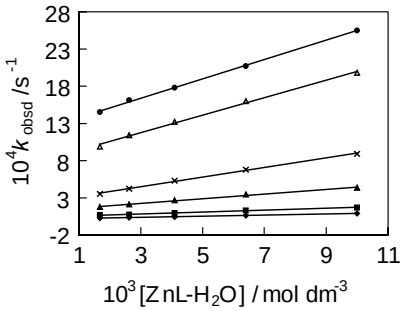

Fig. 5. Variation of the pseudo-first-order rate constant with ZnL-H_2O concentration for ZnL-H_2O promoted hydrolysis of PNPA in Brij35 micellar solution at 30 °C. $I = 0.1$ (KNO_3), [Brij35] $= 5.00 \times 10^{-3}$ mol dm^{-3}, [PNPP] $= 5.00 \times 10^{-5}$ mol dm^{-3}, pH = 7.15 (◆), 7.40 (■), 7.80 (▲), 8.09 (×), 8.68 (△), 9.00 (●).

The hydrolytic process can be expressed as Eqs. (1) and (2)

$$S + \text{ZnL-}H_2O \xrightarrow{k_c} \text{product} \quad (1)$$

$$S \xrightarrow{k_0} \text{product} \quad (2)$$

where S refers to the substrate (PNPP or PNPA), k_c is the apparent second-order rate constant due to the ZnL-H_2O alone and k_0 the first-order rate constant for spontaneous hydrolysis of substrate in plain buffer. From Eqs. (1) and (2), we have

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

$$k_{obsd} = k_c[\text{Znl-}H_2O] + k_0 \quad (4)$$

where k_{obsd} is the pseudo-first-order rate constant for hydrolysis of PNPP or PNPA catalyzed by ZnL-H_2O.

According to Eq. (4), the apparent second-order rate constants, k_c, can be derived from the slope of the plot of the k_{obsd} versus the concentration of ZnL-H_2O. The apparent second-order rate constants obtained are listed in Table 2.

Table 2
Apparent second-order rate constants for ZnL-H_2O promoted hydrolysis of PNPA and PNPP in Brij35 micellar solution at 30 °C[a]

Substrate	pH	k_c (mol^{-1} dm^3 s^{-1})
PNPP	7.15	0.135
	7.40	0.181
	7.80	0.344
	8.09	0.495
	8.68	0.956
	9.00	1.13
PNPA	7.15	0.00751
	7.40	0.0125
	7.80	0.0311
	8.09	0.0646
	8.68	0.118
	9.00	0.133

[a] [PNPP] = [PNPA] $= 5.00 \times 10^{-5}$ mol dm^{-3}, [Brij35] $= 5.00 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ (KNO_3).

From Table 2, it can be seen that k_c increases with the increase in pH. This indicates that ZnL-H_2O promoted hydrolysis of PNPP and PNPA are acid–base catalytic processes and the active species is the product of the dissociated complex, namely, ZnL-OH^- species. Based on this speculation, the Eq. (1) can be rewritten as

$$\text{ZnL-H}_2\text{O} \overset{K_a}{\rightleftharpoons} \text{ZnL-OH}^- + \text{H}^+ \quad (1a)$$

$$\text{S} + \text{ZnL-OH}^- \overset{k_S}{\rightarrow} \text{product} \quad (1b)$$

where k_a is the deprotonation constant of the ZnL-H_2O and k_s the second-order rate constant for the bimolecular reaction of the substrate and the catalytically active species ZnL-OH^-. From Eqs. (1b) and (2), we have

$$\text{Rate} = k_{obsd}[\text{S}] = (k_S[\text{ZnL-OH}^-] + k_0)[\text{S}] \quad (5)$$

Thus

$$k_{obsd} = k_S[\text{ZnL-OH}^-] + k_0 \quad (6)$$

Comparing Eqs. (6) and (4) gives

$$k_c[\text{ZnL-H}_2\text{O}] = K_S[\text{ZnL-OH}^-] \quad (7)$$

With Eq. (1a), the concentration of ZnL-OH^- can be obtained as follows

$$[\text{ZnL-OH}^-] = \frac{K_a}{[\text{H}^+] + K_a}[\text{ZnL-H}_2\text{O}] \quad (8)$$

Inserting Eq. (8) into Eq. (7) gives

$$k_c = k_s \frac{K_a}{[\text{H}^+] + K_a} \quad (9)$$

If ZnL-H_2O-mediated hydrolysis of PNPP and PNPA are acid–base processes, Eq. (9) suggests that the apparent second-order rate constant k_c may be expected to be a sigmoid function of pH [33]. In Figs. 6 and 7 are shown the plots of the apparent second-order rate constants k_c for the hydrolysis of PNPA or PNPP versus pH, which gives two sigmoid curves. This indicates that the hydrolysis of PNPP and PNPA catalyzed by ZnL-H_2O is characteristic of

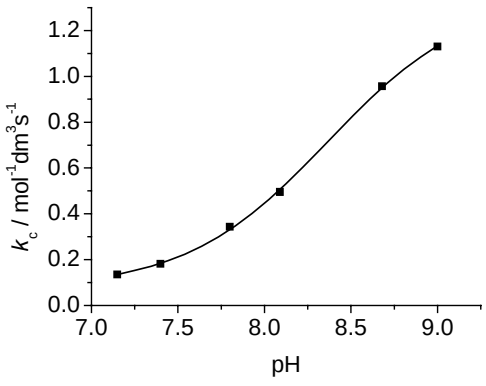

Fig. 6. Plot of second-order rate constant (k_c) vs. pH for ZnL-H_2O promoted hydrolysis of PNPP.

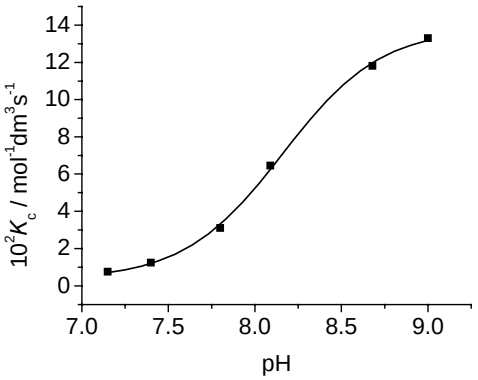

Fig. 7. Plot of second-order rate constant (k_c) vs. pH for ZnL-H_2O promoted hydrolysis of PNPA.

acid–base catalysis and that the catalytically active species in hydrolysis is ZnL-OH^- species, as proposed by Kimura et al. [34] for macrocyclic polyamine complex catalyzed methyl acetate hydrolysis and acetaldehyde hydration.

The deprotonation constant pK_a of ZnL-H_2O can be estimated from the pH value at which the inflection of sigmoid curve occurred. Figs. 6 and 7 show that the inflection points of two sigmoid curves are almost the same pH (8.3 for PNPP and 8.4 for PNPA, respectively). Thus the estimate of pK_a of ZnL-H_2O is 8.3–8.4, which is about two orders of magnitude lower than that of the water in the hydrated zinc ion, $[Zn(H_2O)_6]^{2+}$ [35]. This suggests that the concentration of the metal bound hydroxide ion ZnL-OH^-, which is an effective nucleophile [36,37], is much higher than that of hydroxide ion under neutral or mildly alkaline conditions. Consequently, the active species for ZnL-H_2O promoted hydrolysis of PNPP and PNPA is the metal bound hydroxide ion ZnL-OH^-other than hydroxide ion.

From the results above, obviously it can be seen that the active species for ZnL-H_2O promoted hydrolysis of both PNPA and PNPP are ZnL-OH^-. However, the same active species ZnL-OH^- exhibits different catalytic activities toward hydrolysis of PNPP and PNPA. The rate for the hydrolysis of PNPP is faster than that for PNPA(for example, at pH 7.15, the apparent second-order rate constants for hydrolysis of PNPP and PNPA are 0.135 mol^{-1} dm^3 s^{-1} and 7.51×10^{-3} mol^{-1} dm^3 s^{-1}, respectively). Apparently, the structural characteristics of the substrates must be a key factor that should be considered. The carbonyl in PNPA molecule is linked to methyl group which is electron-donating group, while in the PNPP molecule the carbonyl is linked to an aromatic (pyridine) ring group which is electron-withdrawing. In the hydrolytic process of carboxylic acid ester, the electron-withdrawing group linked to carbonyl can stabilize the negative charge of the tetrahedral transition state, resulting in a fast hydrolysis rate. This is why, in the absence of ZnL-H_2O (please see No. 4 in Table 1), PNPP is hydrolyzed faster than PNPA. But it should be noted that in the absence of ZnL-H_2O, the rate advantage of PNPP hydrolysis over PNPA is only ca.

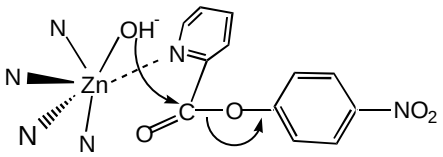

Fig. 8. The possible mechanism for ZnL-H_2O promoted hydrolysis of PNPP in Brij35 micellar solution.

1.3 times, while in the presence of ZnL-H_2O (please see No. 6 in Table 1), this rate advantage becomes ca. 35 times under the same conditions. Evidently, the larger rate constant for PNPP hydrolysis should have other reasons than the electron-withdrawing properties of the aromatic (pyridine) ring of PNPP, which would be the difference in the hydrolytic mechanisms between PNPP and PNPA. Since PNPP is a metallophilic substrate, the picolinate nitrogen is expected to orientate PNPP on the metal ion through the formation of reactive ternary complex [19]. Therefore, the mechanism for ZnL-H_2O promoted hydrolysis of PNPP may start with the deprotonation of ZnL-H_2O to form the catalytically active species ZnL-OH^-; then Zn(II) in ZnL-OH^- holds the substrate through the coordination of the pyridine moiety of the substrate to yield reactive ternary complex. In the ternary complex, the zinc ion-bound hydroxide ion, namely, OH^- in ZnL-OH^- attacks the carbonyl of substrate to cause the intramolecular nucleophilic reactions, as shown in Fig. 8. Breslow et al. [38] has proposed the analogous mechanism for zinc-catalyzed hydrolysis of anhydrides.

As widely accepted, in enzymatic catalysis enzymes generally bind their substrates and then use the action of two or more well-placed functional groups synergistically to achieve catalysis [39]. Thus, enzymatic reactions, being intramolecular reactions, often proceed much faster than their intermolecular counterparts [40].

Compared to PNPP, PNPA is unable to form any ternary complex with ZnL-H_2O because it has no functional group which can serve as an effective ligand to the metal ion [19]. Thus, the mechanism for ZnL-H_2O catalyzed hydrolysis of PNPA may involve the intermolecular nucleophilic attack of zinc-bound hydroxide ion on the carbonyl of PNPA, as shown in Fig. 9, which is less effective than the intramolecular reaction [38] for the ZnL-H_2O promoted hydrolysis of PNPP. Therefore, it is reasonable that the hydrolytic reaction of PNPA catalyzed by ZnL-H_2O proceeds slower than that of PNPP. From the discussion above, it could be concluded that the primary reason for the faster rate for ZnL-H_2O mediated hydrolysis of PNPP than that for PNPA is the difference in the reaction mechanisms and that the electron-withdrawing properties of the aromatic (pyridine) ring of PNPP is another reason.

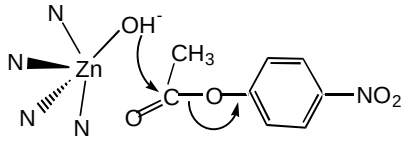

Fig. 9. The possible mechanism for ZnL-H_2O promoted hydrolysis of PNPA in Brij35 micellar solution.

Carboxylic acid ester hydrolysis promoted by Zn(II) complexes of substituted 1,10-phenanthrolines [7], substituted pyridines [11,41], substituted imidazoles [42] and macrocyclic polyamines [34,43] have been studied. For PNPP hydrolysis, similar mechanisms have been proposed, which involves the initial coordination of PNPP to Zn(II) assuming the formation of a reactive mixed chelate, followed by an intramolecular nucleophilic attack of the metal ion-bound hydroxide ion or activated hydroxyl group or by an intermolecular nucleophilic attack of the external hydroxide ion on the carbonyl of PNPP. For PNPA hydrolysis catalyzed by Zn(II) complexes of macrocyclic polyamines [34,43], the mechanisms all involve the intermolecular nucleophilic attack of metal ion-bound hydroxide ion on the carbonyl of ester, and the second-order rate constants are $1.1 \times 10^{-1}\,mol^{-1}\,L\,s^{-1}$ at pH 9.2, 25 °C for macrocyclic tetraamine zinc complex [43] and $4.1 \times 10^{-2}\,mol^{-1}\,L\,s^{-1}$ at pH 8.2, 25 °C for macrocyclic triamine zinc complex [34], respectively. In the case of PNPA hydrolysis promoted by ZnL-H_2O, the apparent second-order rate constant is $1.33 \times 10^{-1}\,mol^{-1}\,L\,s^{-1}$ at pH 9.0, 30 °C and in $5.00 \times 10^{-3}\,mol\,L^{-1}$ Brij35 micellar solution, which is larger than those for PNPA hydrolysis catalyzed by macrocyclic polyamine Zn(II) complexes [34,43].

Previous investigations [41,44,45] discovered that Cu(II) complex is generally more active than Zn(II) complex for the catalytic hydrolysis of carboxylic acid ester. However, we have found that ZnL-H_2O can accelerate the hydrolysis of not only PNPP but also PNPA in Brij35 micellar solution in neutral condition or in mildly alkaline condition and that the catalytic activity is close to or even higher than that of CuL. This may be explained in terms of the structural modes of two complexes. The four-coordinate macrocyclic Schiff base ligand chelates to Cu(II) to form a square planar complex or more possibly certain torsional form of the square planar one, similar to the structure of nickel(II) complex of the isomer of the same ligand [46] or the structure of copper(II) complex of an analogous macrocyclic Schiff base ligand [47]. ZnL-H_2O with a square cone structure is coordinatively less saturated and/or sterically more open for carboxylic acid ester substrate than CuL and the electrophilic coordination site is more available for carbonyl of substrate ester. This may further reveal why Zn(II) is widely used in natural hydrolytic metalloenzyme but not Cu(II).

4. Conclusion

The macrocyclic Schiff base complexes CuL and ZnL-H_2O show different catalytic activities and different mechanisms are operative for the hydrolysis of PNPA and PNPP in Brij35 micellar solution, which depends on the nature of the complex and substrate. CuL can catalyze the

hydrolysis of PNPP though the Lewis acid mechanism, which involves the nucleophilic attack of external hydroxide ion on the carbonyl polarized by cupric ion in CuL. But it cannot promote the hydrolysis of PNPA, presumably because PNPA could not be bound to CuL owing to lack of effective site for metal ion binding in PNPA. ZnL-H_2O can accelerate the hydrolysis of both PNPP and PNPA by different mechanisms, which involve the intramolecular nucleophilic attack of zinc-bound hydroxide ion for PNPP and the less effective intermolecular nucleophilic attack of zinc-bound hydroxide ion for PNPA, respectively.

The catalytic activities of macrocyclic Schiff base complexes of Cu(II) and Zn(II) in the Brij35 micellar system are lower than those in plain buffer. Thus, the macrocyclic Schiff base complexes of Cu(II) and Zn(II) in plain buffer system are better potential models for hydrolytic metalloenzyme than those in the Brij35 micellar system.

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