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Metallomicellar catalysis: Hydrolysis of *p*-nitrophenyl picolinate catalyzed by Cu(II) complexes of triazole-based ligands in cationic gemini surfactant micelles

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Abstract

A series of triazole-based ligands with hydroxyl groups, 3,5-bis(hydroxymethyl)-1,2,4-triazole (**L_1**) and *N*-alkyl(C_nH_{2n+1})-3,5-bis(hydroxymethyl)-1,2,4-triazole ($n = 1$ (**L_2**), 10 (**L_3**) and 12 (**L_4**)) were synthesized. Hydrolysis of *p*-nitrophenyl picolinate (PNPP) catalyzed by Cu(II) complexes of these ligands in micelles of a cationic gemini surfactant, 1,2-ethane bis(dimethyldodecylammonium bromide) (12-2-12), were investigated kinetically at 25 °C. It was found that Cu(II) complexes of these triazole-based ligands, especially ligands **L_3** and **L_4**, showed effective catalytic activity on the hydrolysis of PNPP. Possible catalytic mechanisms and the effect of molecular structure of the ligands on catalyzed hydrolysis of PNPP were discussed. A binuclear Cu(II) complex was found to be active species in 12-2-12 micelles for catalyzed hydrolysis of PNPP for **L_1**, while mononuclear complexes were found for **L_2**–**L_4** due to different structures of the ligands. Kinetic study showed that the apparent first-order rate constant for product formation in the metallomicellar phase (k'_N), the association constant between the substrate and the binary complex (K_T), and the association constant between the metal ion and the ligand (K_M) increased with an increase in pH value of the system. With an increase in the hydrocarbon chain length of the ligand, k'_N and K_T increased while K_M decreased at constant pH.

Keywords: Metallomicellar catalysis; Gemini surfactant; Hydrolysis; Triazole; Metal complex; Kinetics

1. Introduction

Metallomicelles made up of functionalized surfactants or co-surfactants capable of effective chelation of metal ions, which exhibit similar structural and kinetic properties to enzyme, have been extensively investigated as a simple model for hydrolytic metalloenzymes in recent years [1–6]. In these metallomicelle systems, many ligands contain one or more hydroxyl groups. When they form complexes with transition metal ion, one obvious feature is that the hydroxyl group of the ligand acts as a strong nucleophilic group activated by transition metal ion [4,7–10]. In addition, the location of the transition metal ions in active center plays a very important role in activating substrate, stabilizing the negative charge, and producing nucleophilic group OH^- under the near neutral conditions [11]. As a result, a large number of studies on mimicking hydrolytic metalloenzymes using metal ions such as Co(III), Cu(II), Ni(II), and Zn(II) as the active center have been reported, and complexes containing Cu(II) as the metalloenzymatic model are especially successful [7–15].

Recently, a new generation of surfactants, gemini surfactants, have attracted great interest [16]. They are constituted by two hydrophilic groups and two hydrophobic groups per molecular unit. These surfactants have been demonstrated to possess some unique properties, such as lower critical micelle concentration (cmc), greater efficiency in lowering the surface tension, lower Krafft temperature, and better solubilization in comparison with conventional surfactants, which is due to great difference of molecular structures between gemini surfactants and conventional surfactants. Many gemini surfactants have been synthesized, and a considerable number of investigations have been reported on their unusual physicochemical properties, including their high surface activity, unusual changes of viscosity, unusual micelle structure, and aberrant aggregation behavior [16–25].

Derivatives of imidazole and some triazoles have been found to play an important role in physiological activity [26]. As a

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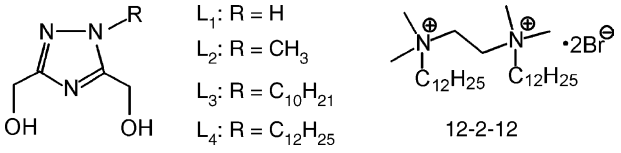


Scheme 1.

result, imidazole and triazole, as well as their derivatives and their metal complexes may be selected to mimic hydrolytic enzymes. Although some investigations have been reported on the imidazole derivatives as effective ligands for catalyzed hydrolysis of esters, and the results suggested that their metal complexes behaved as an effective catalyst [12,13], until now, few study on metallomicelles containing triazole ligands has been reported. Moreover, in most of the available literatures on micellar catalysis or metallomicellar catalysis, conventional surfactants with different molecular structures were selected, however, micellar- or metallomicellar-catalyzed reaction using gemini surfactants is rarely studied [27,28]. In the present work, a series of triazole-based ligands with hydroxyl groups, 3,5-bis(hydroxymethyl)-1,2,4-triazole (**L_1**), and *N*-alkyl(C_nH_{2n+1})-3,5-bis(hydroxymethyl)-1,2,4-triazole ($n = 1$ (**L_2**), 10 (**L_3**) and 12 (**L_4**), Scheme 1), were synthesized. Effects of their Cu(II) complexes on the hydrolysis of *p*-nitrophenyl picolinate (PNPP) in micelles of a cationic gemini surfactant, 1,2-ethane bis(dimethyldodecylammonium bromide) (12-2-12), were investigated kinetically at 25 °C. Some kinetic parameters of reactions were obtained by employing the ternary complex kinetic model for metallomicellar catalysis, and possible catalytic mechanism and the effect of molecular structure of the ligands on catalyzed hydrolysis of PNPP were also discussed.

2. Experimental

2.1. General

FT-IR spectra were recorded on a Nicolet NEXUS 870 spectrometer (KBr discs). Elemental microanalyses were performed on a Perkin-Elmer 240 analytical instrument. ^{1}H-NMR spectra in $CDCl_3$ were obtained on a Bruker Advanced DMX 500 spectrometer using TMS as internal standard. Glycolic acid was purchased from Shanghai Sihewei Chemicals Co., China. Methyl iodide, decyl bromide, dodecyl bromide, hydrazine hydrate, and $CuCl_2{\cdot}6H_2O$ were of analytical grade and were purchased from Shanghai Chemical Reagent Co., China, and all other chemicals were also of reagent grade and were commercially available. *p*-Nitrophenyl picolinate was synthesized according to literature [29]. Cu^{2+} stock solution was titrated against EDTA. PNPP stock solution (0.005 mol L^{-1}) for kinetic study was prepared in acetonitrile. Tris-TrisH^+ was used in all cases and its pH was adjusted by adding nitric acid in all runs according to literatures [9,10].

Gemini surfactant 12-2-12 was prepared from *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and dodecyl bromide, and the product was purified by repeated recrystallization. The purity was confirmed by elemental analysis and ^{1}H NMR [25]. Critical micelle concentration of the surfactant was determined to be 8.9×10^{-4} mol L^{-1} at 25 °C, according to the break point in plot of the specific conductance versus concentration of the gemini surfactant 12-2-12.

2.2. Synthesis of ligands

3,5-Bis(hydroxymethyl)-1,2,4-triazole (**L_1**) was prepared by the procedure reported previously [30]. *N*-Alkyl-3,5-bis(hydroxymethyl)-1,2,4-triazole (**L_2**–**L_4**) were synthesized from **L_1** and the corresponding alkyl halides (methyl iodide for **L_2** [31], and decyl bromide and dodecyl bromide for **L_3** and **L_4**, respectively). 3,5-Bis(hydroxymethyl)-1,2,4-triazole (6.45 g, 50 mmol) was added to a solution of potassium hydroxide (2.86 g, 50 mmol) in methanol (150 mL). The mixture was stirred for 1 h, and the alkyl halide (60 mmol) was added. The solution was refluxed for 48 h, and methanol was evaporated. The residue was recrystallized repeatedly from acetonitrile.

N-Methyl-3,5-bis-(hydroxymethyl)-1,2,4-triazole (**L_2**) (76% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3H, CH_3), 4.38 and 4.57 (2 d, $J = 6.2$ Hz, 4H, CH_2OH), 5.21 and 5.62 (2 t, $J = 6.2$ Hz, 2H, OH). Anal. Calcd for $C_5H_9N_3O_2$: C, 41.95; H, 6.34; N, 29.35%. Found: C, 41.81; H, 6.47; N, 29.16%. IR (KBr, cm^{-1}): 3325, 1639, 1573, 1471.

N-Decyl-3,5-bis-(hydroxymethyl)-1,2,4-triazole (**L_3**) (72% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, $J = 6.9$ Hz, 3H, CH_3), 1.21 (m, $J = 5.3$ Hz, 14H, $CH_3(CH_2)_7$–), 1.67 (m, $J = 7.1$ Hz, 4H, $C_8H_{17}(CH_2)_2$–), 4.62 (br, s, 4H, CH_2OH), 5.54 (br, s, 2H, OH). Anal. Calcd for $C_{14}H_{27}N_3O_2$: C, 62.42; H, 10.10; N, 15.60%. Found: C, 62.23; H, 10.17; N, 15.38%. IR (KBr, cm^{-1}): 3321, 2849, 1637, 1570, 1469.

N-Dodecyl-3,5-bis-(hydroxymethyl)-1,2,4-triazole (**L_4**) (67% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, $J = 6.7$ Hz, 3H, CH_3), 1.26 (m, $J = 5.1$ Hz, 18H, $CH_3(CH_2)_9$–), 1.63 (m, $J = 6.9$ Hz, 4H, $C_{10}H_{21}(CH_2)_2$–), 4.65 (br, s, 4H, CH_2OH), 5.61 (br, s, 2H, OH). Anal. Calcd for $C_{16}H_{31}N_3O_2$: C, 64.61; H, 10.50; N, 14.13%. Found: C, 64.41; H, 10.34; N, 13.96%. IR (KBr, cm^{-1}): 3323, 2850, 1635, 1571, 1469.

2.3. Kinetic measurements

Kinetic measurements of hydrolysis of PNPP were carried out spectrophotometrically at 25 °C, employing a TU-1901 UV–vis spectrophotometer. Reactions were initiated by injecting 30 μl of PNPP stock solution (0.005 mol L^{-1}) into a 1 cm cuvette containing 3 ml of desired reagents. The ion strength was maintained at 0.2 mol L^{-1} with KNO_3. The reaction rate was followed by monitoring the release 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_∞ is the absorbance at equilibrium). The reaction followed apparent first-order constant kinetics for at least three half-lives. Rate constants are means of three measurements, and its average relative standard deviation is smaller than 3.5%.

3. Results and discussion

3.1. Apparent rate constants for hydrolysis of PNPP at pH 7.0, 25 °C

Ligands **L$_3$** and **L$_4$** with long hydrocarbon chains were very weakly soluble in water, but could be solubilized (up to ca. 8×10^{-4} M) in 0.01 M gemini surfactant 12-2-12 micellar solution at room temperature. The rates of reactions under the condition of excess metal ion and ligand over the substrate at pH 7.0 and 25 °C were determined spectrophotometrically and the apparent first-rate constants were summarized in Table 1. It was noticed that uncatalyzed rate constant in buffer solution was 1.06×10^{-5} s^{-1} at pH 7.0 and 25 °C, which was in accordance with the results reported previously [10]. Neither the gemini surfactant 12-2-12 nor co-micelles of 12-2-12/**L$_1$** nor 12-2-12/**L$_2$** showed significant rate enhancement effect on hydrolysis of PNPP. However, both co-micelles of 12-2-12/**L$_3$** and 12-2-12/**L$_4$** showed obvious rate acceleration (ca. 27-fold for 12-2-12/**L$_3$** and 30-fold for 12-2-12/**L$_4$**). In addition, obvious rate acceleration was also observed for Cu^{2+} in buffer solution or in micellar solutions. However, the mixed system with Cu^{2+}, ligand, and 12-2-12 exhibited more remarkable rate acceleration, which indicated Cu(II) complexes were formed in 12-2-12 micellar solution, and it is those complexes that should be responsible for the large rate enhancement of hydrolysis of PNPP.

3.2. Effect of gemini surfactant concentration

To obtain the optimum surfactant concentration, a series of measurements were carried out for Cu^{2+}/**L$_4$**/12-2-12 catalytic system at pH 7.0 and 25 °C at various concentrations of the gemini surfactant 12-2-12, and the result was shown in Fig. 1. It was found that the rate constant for the catalyzed hydrolysis of PNPP increased sharply with increasing 12-2-12 concentration until a maximum point was reached, which corresponds to the optimum surfactant concentration range ca. 3×10^{-3} mol L^{-1} to 4×10^{-3} mol L^{-1}. Further increase in the surfactant concentration caused a significant decrease in the rate constants. Consequently, all kinetic studies on the catalyzed hydrolysis of PNPP were carried out at 3×10^{-3} mol L^{-1} of gemini surfactant 12-2-12 to obtain the best catalytic efficiency in the present study.

Table 1
Apparent first-order rate constants ($10^3 \times k_{obsd}$ (s^{-1})) for the hydrolysis of PNPP at pH 7.00, 25 °C[a]

System	Without Cu^{2+}	Cu^{2+}
–	0.0106	7.32
12-2-12	0.0282	12.7
L$_1$ + 12-2-12	0.0117	45.9
L$_2$ + 12-2-12	0.0129	27.2
L$_3$ + 12-2-12	0.281	195
L$_4$ + 12-2-12	0.323	249

[a] In 0.1 mol L^{-1} Tris-TrisH$^+$ buffer; μ = 0.2 mol L^{-1} (KNO_3); [12-2-12] = 3×10^{-3} mol L^{-1}; [PNPP] = 5×10^{-5} mol L^{-1}; [ligand] = [Cu^{2+}] = 1×10^{-4} mol L^{-1}.

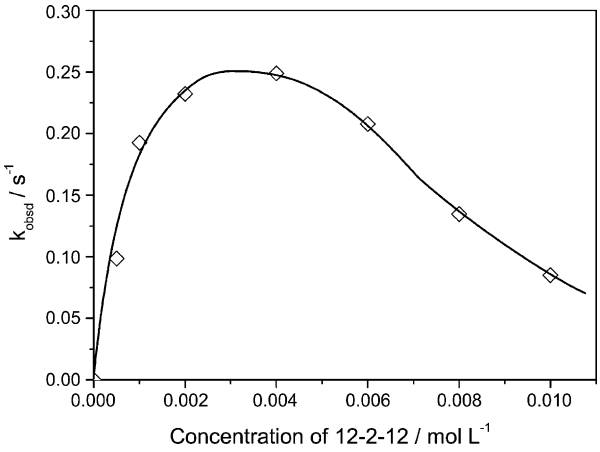


Fig. 1. Apparent first-order rate constant for the hydrolysis of PNPP as a function of concentration of gemini surfactant 12-2-12 for the Cu(II) complex of ligand **L$_4$** at pH 7.00, 25 °C. [PNPP] = 5×10^{-5} mol L^{-1}; [L_4] = [Cu^{2+}] = 1×10^{-4} mol L^{-1}.

The optimum surfactant concentration in micellar or metallomicellar catalysis can be attributed to the orientation effect and local concentration effect of micelles on reagent [15]. On the other hand, higher microviscosity of the gemini surfactant 12-2-12 at higher surfactant concentration may also be responsible for remarkable decreases of pseudo-first-order rate constant at higher surfactant concentration. The studies on gemini surfactants have demonstrated that the microviscosity increased strongly from the single-chained surfactant (monomer) to the gemini surfactant (dimer) [19,20]. Accordingly, higher microviscosity of the gemini surfactant will cause a decrease in diffusion coefficient of the reactants in aqueous solution of the gemini surfactant, thus resulting in a decrease in reaction rate of the hydrolysis reaction. In addition, with an increase in surfactant concentration, 12-2-12 exhibited a strong tendency to micelle growth [21,22]. A transmission electron microscope study at cryogenic temperature (cryo-TEM) showed dramatically the transition of micelle shape from spherical micelles to worm-like micelles, branched thread-like micelles and closed ring cylindrical micelles [22]. With an increase in micelle size, the hydrophobic substrate PNPP may enter the interior of the micelles, which is disadvantageous for the catalyzed hydrolysis reaction of the substrate in micellar medium.

3.3. Stoichiometry of metal complexes in reaction systems

A convenient method for determining the chelating stoichiometry of metal complexes is the kinetic version of Job plots, in which the apparent rate constants were plotted as a function of the mole fraction (r) of a ligand or metal ion, keeping their total concentration constant [4,9,10]. As shown in Fig. 2, for systems containing Cu^{2+}/**L$_2$**, Cu^{2+}/**L$_3$** and Cu^{2+}/**L$_4$** in the presence of 3×10^{-3} mol L^{-1} of 12-2-12, respectively, maximum rate constants were all obtained at r = 0.5, which corresponded to a stoichiometry of metal ion to ligand of 1:1 for kinetically active species in 12-2-12 micelles. However, for Cu^{2+}/**L$_1$**/12-2-12 system maximum rate constant was obtained at r = 0.35, which corresponded to a stoichiometry of metal ion to ligand of

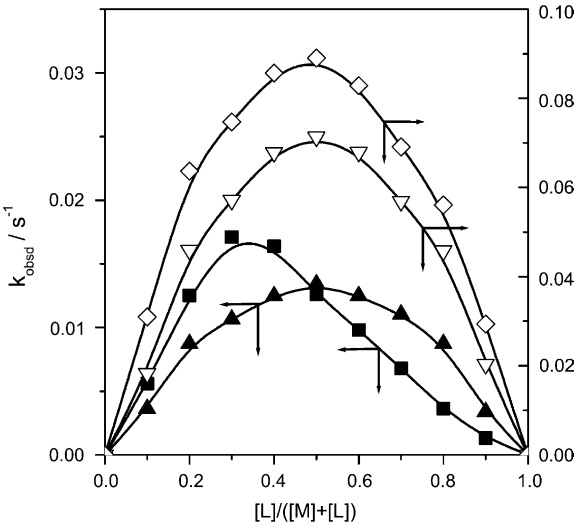


Fig. 2. Job plots for the Cu(II) complex of ligand **L₁** (■), **L₂** (▲), **L₃** (▽), and **L₄** (◊) in 3×10^{-3} mol L^{-1} of 12-2-12 at pH 7.00, 25 °C. [PNPP] = 5×10^{-5} mol L^{-1}; [ligand] + [Cu^{2+}] = 1×10^{-4} mol L^{-1}.

2:1 for kinetically active species. This result is probably due to the different molecular structures between ligand **L₁** and ligands **L₂**–**L₄** as discussed below.

3.4. The ternary complex kinetic model for metallomicellar catalysis

Based on phase-separation model of the micelle [32], a ternary complex kinetic model for metallomicellar catalysis has been well established [9,10,13–15]. To get a better understanding of the catalytic mechanism, some kinetic parameters can be obtained by fitting the kinetic data with the ternary complex model. As previously reported, kinetic model of metallomicellar catalytsis for metal complex M_mL_n can be expressed as [11,33]

$$\frac{1}{k_{\mathrm{obsd}} - k_0'} = \frac{1}{k_N' - k_0'} + \frac{m^2}{(k_N' - k_0')K_{\mathrm{T}}[M]_{\mathrm{T}}} + \frac{1}{(k_N' - k_0')K_{\mathrm{T}}K_{\mathrm{M}}[M]_{\mathrm{T}}^m[L]_{\mathrm{T}}^n} + \frac{n^2}{(k_N' - k_0')K_{\mathrm{T}}[L]_{\mathrm{T}}} \quad (1)$$

where k_N' and k_0' are the apparent first-order rate constants for product formation in the metallomicellar phase and in the bulk phase, respectively. k_0' is given by $k_0' = k_0 + k_{\mathrm{L}}[L] + k_{\mathrm{M}}[M]$, where $[L]$ and $[M]$ are concentrations of ligand and metal ion, respectively. K_{M} is the association constant between the metal ion and the ligand, and K_{T} is the association constant between the substrate and the binary complex (M_mL_n). $[M]_{\mathrm{T}}$ and $[L]_{\mathrm{T}}$ are the total concentrations of metal ion and ligand, respectively. According to Eq. (1), the plots of $1/(k_{\mathrm{obsd}} - k_0')$ versus $1/[L]_{\mathrm{T}}$ should give straight lines for 1:1 and 2:1 complexes (metal:ligand) in metallomicellar systems. The intercept, I, and the slope, Q, of the straight line for 2:1 complex are, respectively, expressed as

$$I = \frac{1}{k_N' - k_0'} + \frac{4}{(k_N' - k_0')K_{\mathrm{T}}}\frac{1}{[M]_{\mathrm{T}}}, \quad (2)$$

$$Q = \frac{1}{(k_N' - k_0')K_{\mathrm{T}}} + \frac{1}{(k_N' - k_0')K_{\mathrm{T}}K_{\mathrm{M}}}\frac{1}{[M]_{\mathrm{T}}^2}. \quad (3)$$

For 1:1 complex the intercept, I, and the slope, Q, of the straight line are, respectively, expressed as

$$I = \frac{1}{k_N' - k_0'} + \frac{1}{(k_N' - k_0')K_{\mathrm{T}}}\frac{1}{[M]_{\mathrm{T}}}, \quad (4)$$

$$Q = \frac{1}{(k_N' - k_0')K_{\mathrm{T}}} + \frac{1}{(k_N' - k_0')K_{\mathrm{T}}K_{\mathrm{M}}}\frac{1}{[M]_{\mathrm{T}}} \quad (5)$$

According to Eqs. (2)–(5), the plots of I versus $1/[M]_{\mathrm{T}}$ and Q versus $1/[M]_{\mathrm{T}}^2$ for 2:1 complex, and the plots of I versus $1/[M]_{\mathrm{T}}$ and Q versus $1/[M]_{\mathrm{T}}$ for 1:1 complexes would allow the evaluations of values of k_N', K_{T}, and K_{M}. Series of apparent first-order rate constants were determined for Cu^{2+} in the presence of the ligands **L₁**–**L₄**, respectively, in 12-2-12 micelles within pH range 6.0-8.0. k_N', K_{T}, and K_{M} were obtained by linear fitting the plots of I versus $1/[M]_{\mathrm{T}}$ and Q versus $1/[M]_{\mathrm{T}}^2$ (or Q versus $1/[M]_{\mathrm{T}}$) as shown in Figs. 3 and 4, respectively, and the results were summarized in Table 2. It was found that for the same ligand k_N', K_{S}, and K_{M} increased with an increase in pH value. This may be attributed to an increase in the nucleophilicity of the hydroxyl groups in the ligand or the electrophilicity of the substrate at higher pH, which leads to easier association of the substrate with Cu^{2+} to form a ternary complex and a much easier intermolecular nucleophilic reaction in this ternary complex.

Compared with system containing **L₂**, Cu^{2+} complex of **L₁** in 12-2-12 micelles showed larger k_{obsd} and k_N', although these two ligands had very similar structures. This result indicated that there might exist different catalysis mechanisms between Cu^{2+} complexes of **L₁** and that of **L₂** in 12-2-12 micelles. As described above, a 2:1 complex (metal:ligand) for kinetically active species in 12-2-12 micelles was formed for **L₁**, while a 1:1 complex was formed for **L₂** under similar conditions. As

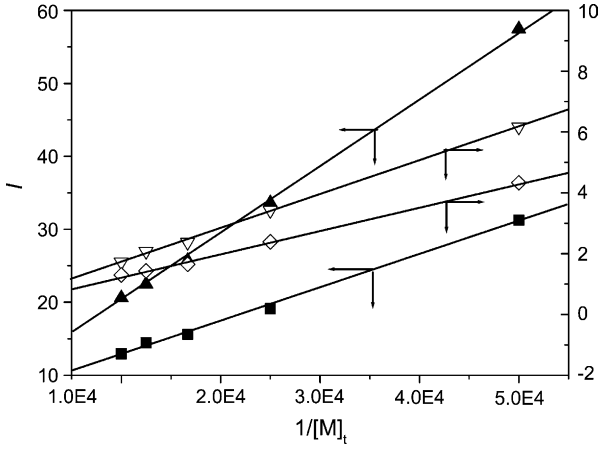


Fig. 3. Plot of I vs. $1/[M]_{\mathrm{T}}$ for the hydrolysis of PNPP catalyzed by Cu(II) complexes of ligands **L₁**–**L₄** in 12-2-12 micelles at pH 7.00, 25 °C. Symbols as in Fig. 2.

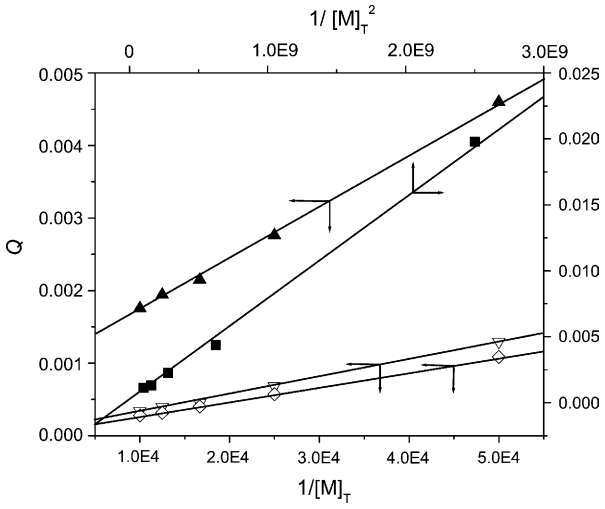
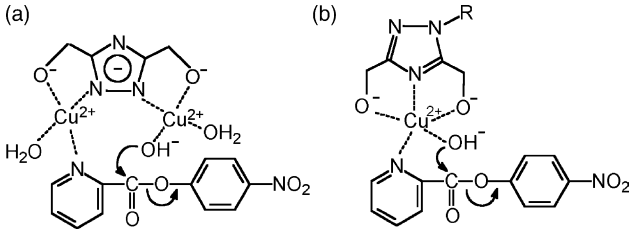


Fig. 4. Plot of Q vs. $1/[M]_T$ (Cu(II) complexes of **L_2**–**L_4**) or $1/[M]_T^2$ (Cu(II) complex of **L_1**) for catalyzed hydrolysis of PNPP in 12-2-12 micelles at pH 7.00, 25 °C. Symbols as in Fig. 2.

shown in Scheme 2, a dinuclear complex may have a quite different catalysis mechanism from a mononuclear complex. For dinuclear Cu(II) complex of **L_2**, one of the Cu^{2+} ions may coordinate with the nitrogen atom from pyridine of PNPP to control the substrate tightly, and then activate it. Next, the other Cu^{2+} ion acts as Lewis acid and then activates the coordinated water molecule to produce a nucleophile, OH^-, to complete the catalytic reaction (Scheme 2(a)). So these two metal ions in the dinuclear complex cooperate with each other to complete the catalytic process. As a result, the dinuclear Cu(II) complex of **L_1** showed more effective catalytic activity for hydrolysis of

Table 2
pH dependencies of k'_N, K_M, and K_T of the hydrolysis of PNPP in metallomicellar systems at 25 °C

Ligand	pH	k'_N (s^{-1})	$10^{-3}K_T$ ($L\,mol^{-1}$)	$10^{-3}K_M$ ($L\,mol^{-1}$)
L_1	6.0	0.019	47.95	3200
	6.5	0.052	62.98	7900
	7.0	0.118	76.48	14400
	7.5	0.196	89.51	21700
	8.0	0.249	108.62	32100
L_2	6.0	0.015	7.63	8.63
	6.5	0.041	9.76	10.72
	7.0	0.091	11.90	12.52
	7.5	0.150	19.35	16.73
	8.0	0.189	23.85	18.39
L_3	6.0	0.661	2.94	2.26
	6.5	1.239	4.19	3.84
	7.0	1.714	5.13	5.01
	7.5	1.949	6.84	6.73
	8.0	2.038	7.46	7.29
L_4	6.0	0.835	3.28	1.96
	6.5	1.539	4.83	3.17
	7.0	2.098	6.23	3.78
	7.5	2.371	7.18	4.13
	8.0	2.472	8.05	4.92



Scheme 2.

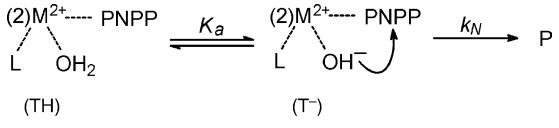
PNPP in 12-2-12 micelles than the mononuclear complex of **L_2** in the present work. It should be noted that, although Cu(II) complex of **L_1** showed a extremely larger k_M and a quite larger k_T than those of **L_2**, it showed only slightly larger k_{obsd}. This may be due to a larger solubility of the ligand **L_1** in aqueous solution in comparison with **L_2**, and the ligand **L_1** and its Cu(II) complex existed mainly in bulk phase but not in micellar phase, while the substrate was solubilized in the micellar phase or partitioned between the bulk phase and the micellar phase, which resulted in the separation of the reactants.

For ligands **L_2**–**L_4**, which have similar structures with different hydrocarbon chains, it was found that, at constant pH, k'_N and K_T increased with an increase in the hydrocarbon chain length of the ligands, while K_M decreased significantly. The increases in k'_N and K_T are probably due to the fact that the longer the hydrocarbon chain length of the ligand, the easier the ligand solubilized in 12-2-12 micelles. In addition, an increase in the hydrocarbon chain length of the ligand may result in a kind of addition hydrophobic bond energy on the micellar surface, which lowers the activation energy of the catalyzed reaction and stabilizes the activated complex, thus resulting in an increase in k'_N [33]. The decrease of K_M with increased hydrocarbon chain length can be easily explained by the fact that the ligand with longer hydrocarbon chain should be more hindered as it coordinates with the metal ion than the short one.

3.5. pH-rate profile

It was found that k'_N was pH-dependent as shown in Table 2, which indicated that k'_N might be related to the acid dissociation constant (K_a) of the ternary complex in the reaction system (Scheme 3) where TH is the undissociated complex, T^- the dissociated complex anion assumed to be the active species in metallomicellar phase and k_N the first-order rate constant which is pH-independent. Then the relationship of k'_N with k_N, K_a, and $[H^+]$ can be expressed as [10,13]

$$\frac{1}{k'_N} = \frac{1}{k_N} + \frac{1}{k_N K_a}[H^+] \quad (6)$$



Scheme 3.

Table 3
k_N and pK_a of the hydrolysis of PNPP in metallomicellar systems at 25 °C

Ligand	k_N (s^{-1})	pK_a
1	0.281	7.14
2	0.198	7.06
3	2.083	6.33
4	2.611	6.30

On the basis of Eq. (6), the values of k_N and K_a can be afforded from the slope and the intercept of the plot $1/k_N$ versus $[H^+]$. The results were shown in Table 3.

In enzymatic catalysis, the crucial factor determining the catalytic efficiency of acid–base catalyst is that, under certain conditions, whether catalyst presents effective (or proper) ionization state (protonated or deprotonated state) or not, i.e., acid acts as effective acid catalysis only when it is in acid-form, and base catalyst exhibits high catalytic efficacy when it is in base-form [13]. So, in micellar solution with relatively low pH value, the complex with low pK_a is more active on the catalytic hydrolysis of PNPP than that with high pK_a. In addition, the metal ions may make the water molecule coordinating with metal ion in the ternary complex change into more nucleophilic group OH^-, and then the nucleophilic attack on the substrate takes place easily, which increases the rate of the hydrolysis of PNPP. As a result, Cu(II) complex which has relatively low pK_a value should exhibit higher catalytic activity under the same experimental conditions, as shown in Table 3. However, Cu(II) complex of $\mathbf{L_1}$, which has a higher pK_a value than that of $\mathbf{L_2}$, showed higher catalytic activity for catalyzed hydrolysis of PNPP than Cu(II) complex of $\mathbf{L_2}$. This is due to different catalysis mechanism for these two complexes in the catalytic reaction as discussed above.

4. Conclusion

Copper(II) complexes of triazole-based ligands $\mathbf{L_1}$–$\mathbf{L_4}$, especially $\mathbf{L_3}$ and $\mathbf{L_4}$, showed effective catalytic activity on the hydrolysis of PNPP in micelles of gemini surfactant 12-2-12. Kinetic study showed that k'_N, K_T, and K_M increased with increased pH value. With an increase in the hydrocarbon chain length of the ligand, k'_N and K_T increased while K_M decreased at constant pH. Different mechanisms of catalyzed hydrolysis of PNPP were found between Cu(II) complexes of $\mathbf{L_1}$ and $\mathbf{L_2}$–$\mathbf{L_4}$ in 12-2-12 micelles. A binuclear Cu(II) complex was found to be active species for catalyzed hydrolysis of PNPP for $\mathbf{L_1}$, and mononuclear complexes were found for $\mathbf{L_2}$–$\mathbf{L_4}$ due to different structures of the ligands. Consequently, Cu(II) complex of $\mathbf{L_1}$ showed higher catalytic activity than that of $\mathbf{L_2}$, although these two ligands have very similar structure.

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