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Cent. Eur. J. Chem. • 7(3) • 2009 • 542-549
DOI: 10.2478/s11532-009-0043-x

Central European Journal of **Chemistry**

Hydrolysis kinetics of p-nitrophenylpicolinate catalyzed by schiff base Mn(III) complexes in Gemini 16-2-16 micellar solutiony

Research Article

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Received 10 October 2008; Accepted 22 February 2009

Abstract: Two mono-Schiff base Mn(III) complexes (MnL_2Cl, L=L^1 and L^2) were synthesized and employed as artificial hydrolases in catalyzing the hydrolysis of p-nitrophenylpicolinate (PNPP) in Gemini 16-2-16 micellar solution. The effect of different micelles and their complex structures on the catalytic hydrolysis of PNPP is discussed in detail. The observations showed that MnL^2_2Cl exhibited higher catalytic activity over MnL^1_2Cl under a comparable condition, which confirmed that an open active centre is essential for modulating the activities of the two enzyme mimics. Moreover, under the conditions employed, hydrolytic rates of PNPP induced by these Mn(III) complexes were faster in Gemini 16-2-16 micelles than that in the micellar solution of cetyltrimethylammonium bromide (CTAB), a conventional analogue of Gemini 16-2-16.

Keywords: *PNPP • Hydrolysis kinetics • Steric hindrance • Gemini 16-2-16 micelle • Schiff base Mn(III) complexes*

1. Introduction

Schiff base metal complexes as a type of artificial enzymes have already been applied in many fields [1-7]. However, Schiff base metal complexes were seldom used as artificial hydrolases in promoting hydrolysis of carboxylic esters and phosphate esters. Due to their convenient synthesis and modifications, we and other researchers have once before attempted to evaluate the hydrolytic reactivity of various Schiff base complexes towards the hydrolysis of carboxylic esters and phosphate esters [8-16]. In our previous studies, we found that Schiff base Mn(III) complexes with larger pendants led to their smaller catalytic activities, which implied that an open active site is very important in the metal-promoted ester hydrolysis.

As we know, functional micelles [17-20] and vesicles are investigated as effective catalytic systems which provide a hydrophobic environment for binding the substrate since, the hydrophobic cage of the enzyme is essential for the approach of hydrophobic substrate molecules [21, 22]. To mimic the hydrophobic environment of natural enzymes, metallomicelles [23-29] have widely been used as artificial hydrolases to catalyze the hydrolytic cleavage of various esters. In general, many conventional single-chain surfactants were employed as monomers for the formation of micellar aggregates. Besides our study, only a few reports [30-33] have

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studied the application of Gemini surfactants with high surface activity in the field of esterolysis [8,9,34].

In this study we detail the interaction between the substrate, *p*-nitrophenylpicolinate (PNPP) and two Schiff base Mn(III)complexes (Fig. 1) as catalysts towards the hydrolysis. PNPP is a classic substrate for studying the hydrolysis of carboxylic esters. It is well known that different micellar aggregates present their distinguishing effect during the reactive course of chemical reactions [35]. Therefore, we have determined kinetic behavior of PNPP hydrolysis in the presence of two kind of surfactants, namely, bis(hexadecyldimethylammonium)hexane bromide (16-2-16, $2Br^-$) and cetyltrimethylammonium bromide (CTAB), respectively. In addition, a blank run was also preformed in the absence of surfactant. The results obtained indicated that the MnL^1_2Cl containing a huge substituent (aza-15-crown-5) exhibited a lower catalytic activity in contrast with its analogue MnL^2_2Cl, suggesting that an open active site in the artificial enzyme is necessary for the linkage of substrate to enzyme. Moreover, micellar effects of the two kinds of surfactants are correlated to their native properties.

2. Experimental Procedures

2.1 Materials

All reagents were of analytical-grade and used without further purification, except where otherwise specified. Water used in kinetic measurements was obtained from distilled water treated with a water purification system, Nex Power 1000 (Human Corporation, Korea) to achieve a resistivity of at least 16 MΩ cm^{-1}. A series of buffer solutions were prepared to cover a pH range of 6.50 - 8.50. The ionic strength (I) of solutions was kept constant at 0.1 mol L^{-1} with KCl (a product of China Kelong Chemical Co.). CTAB was commercially available from Sigma. Tris (trishydroxymethyl aminomethane) was bought from Aldrich, and was used as received. PNPP stock solution (1.0×10^{-2} mol L^{-1}) was prepared in absolute acetonitrile. The two Schiff base manganese(III) complexes (metal:ligand=1:2), PNPP and Gemini surfactant 16-2-16 were synthesized using the following references: Schiff base manganese(III) complexes [1], PNPP [36], Gemini 16-2-16 [37].

2.2 Kinetics Methods

The acidities of buffer solutions were measured on a Radiometer PHM 26 pH meter (Shanghai Radiometer Equipment Ltd Co., China). All hydrolytic kinetics were performed in a 1 cm quartz cuvette, which was placed within a thermally equilibrated cell compartment of a GBC 916 UV-vis spectrophotometer (GBC Scientific Equipment Ltd., Vic. Australia), coupled to a water bath thermostat with a ±0.1°C error. The reaction was initiated by the addition of a stock solution of the required substrate by microsyringe, with continuous stirring, care must be taken to avoid the formation of air bubbles. Reference cell consisted of identical solutions without the added substrate. A series of 30 – 70 μL samples of PNPP stock solutions were individually injected to give final concentration range of 2.00×10^{-4} to 4.67×10^{-4} (mol L^{-1}). In each kinetic run, the final concentration of catalyst was maintained a constant at 1.0×10^{-5} mol L^{-1}. The rates of PNPP hydrolysis were determined by monitoring the increase in absorbance of *p*-nitrophenolate anion at 400 nm. The runs were conducted in triplicates for each reaction. The rate constant and standard deviation (*s.d.*) were reproducible within ±4%. Pseudo-first-order rate contants (k_{obs}) were calculated by an iterative nonlinear fit to the absorbance data Each data presented in this paper is the average of three runs.

3. Results and Discussion

Fig. 2 summarizes various pseudo-first-order rate constants (k_{obs}) for PNPP hydrolysis in different systems. From Fig. 2, it is seen that the hydrolysis rates increased linearly with increasing PNPP concentration. All correlative coefficients (r) are approximately 0.98. The linear increase in rate suggested that the hydrolysis

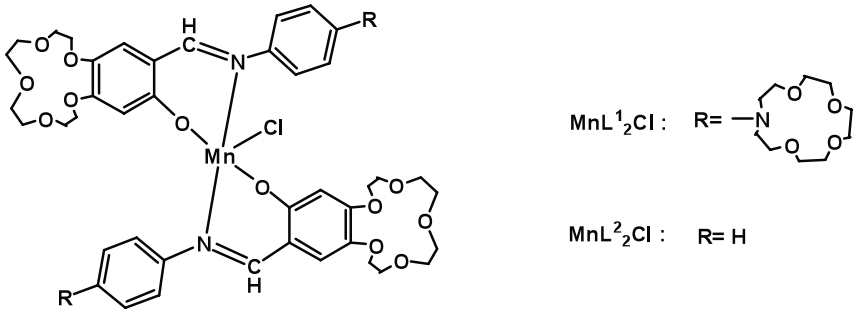


Figure 1. Chemical structures of the two Schiff base Mn(III) complexes

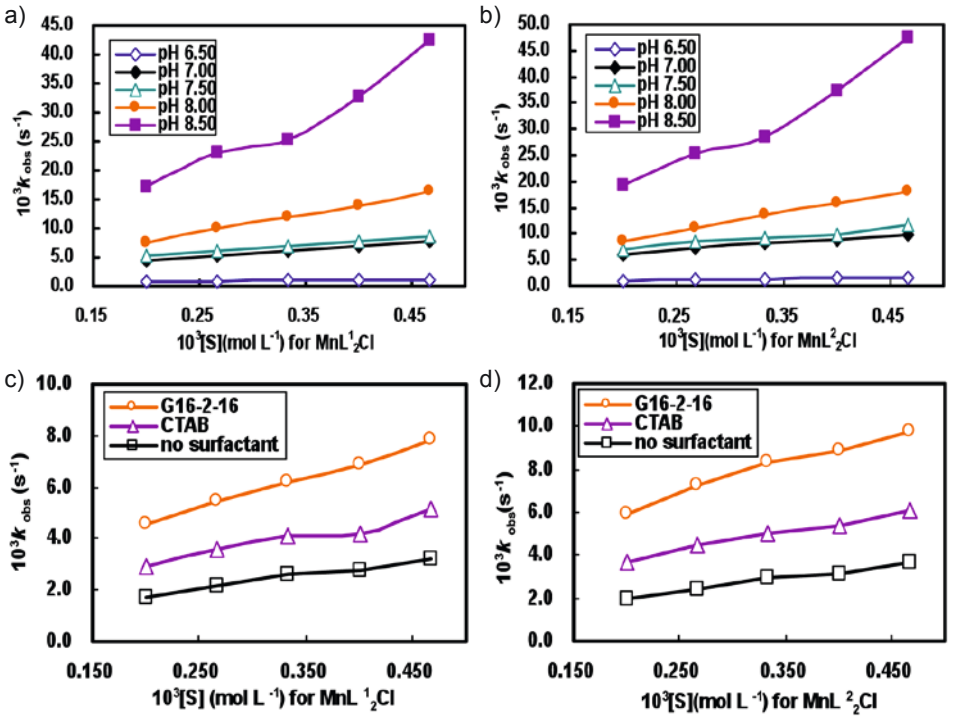


Figure 2. The k_{obs}-[S] profiles for PNPP hydrolysis promoted by MnL_2Cl in various solutions at 25°C. Profiles (a) and (b) show the rate constants for PNPP hydrolysis in Gemini 16-2-16 micellar solution covering a pH zone of 6.50 to 8.50. Profiles (c) and (d) display the variation of rate constants for PNPP hydrolysis catalyzed by MnL_2Cl in various solutions at pH 7.00. Conditions: I = 0.1M(KCl), [16-2-16] = 1.0×10^{-4} mol L^{-1}, [CTAB]=1.0×10^{-3} mol L^{-1}

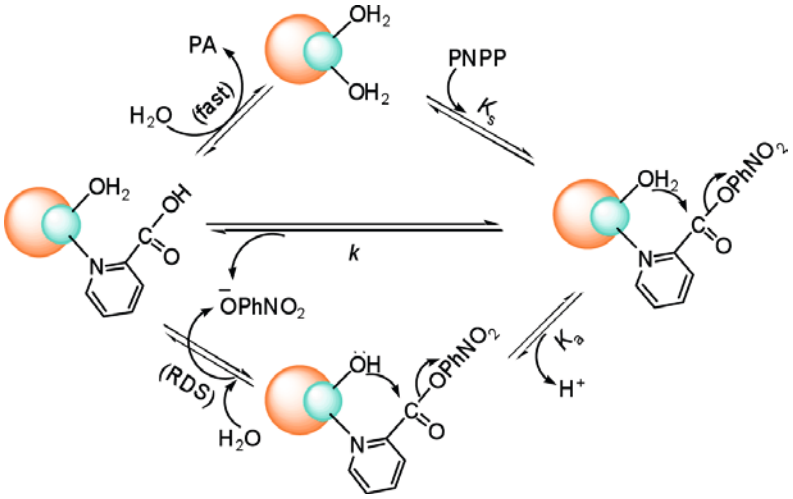
reaction is a pseudo-first-order kinetic. As compared to the background rate constant k_0 [36] (25ºC), the k_{obs} for PNPP hydrolysis catalyzed by the two synthesized Mn(III) complexes increased by a factor of ca. 586 for MnL^1_2Cl/16-2-16 and 758 for MnL^2_2Cl/16-2-16, respectively, under the conditions of pH 7.00, 25±0.1ºC, [PNPP]=2.0×10^{-4} mol L^{-1}.

With the goal of evaluating the advantage of Gemini 16-2-16 micellar system, we further investigated the Mn(III)-catalyzed hydrolysis of PNPP with and without any surfactants and in another single-chain surfactant CTAB micelles (Figs. 2c and d). The observations indicate that hydrolytic process of PNPP was faster in Gemini 16-2-16 micellar solution than in other two conventional solutions, possibly resulting from the unique structure of Gemini 16-2-16 compared with CTAB surfactants [38]. Additionally, the rate constants of PNPP catalytic hydrolysis in different micellar media decreased in the order of Gemini 16-2-16 > CTAB. The hydrolytic rates of PNPP are higher in two cationic micellar solutions than that in aqueous solution without surfactant. This implies that the addition of two cationic surfactants played a positive role in the Mn(III)-induced PNPP hydrolysis. Correlative causes will be elucidated in Section 3.4.

3.1 Proposed Mechanism of MnL_2Cl-promoted PNPP Hydrolysis

In general, the metal-catalyzed hydrolysis of the majority of common carboxylic esters occurs through a pseudo-intramolecular nucleophilic attack of the metal-coordinated hydroxide ion at the carbon center of the carbonyl [39]. Scheme 1 gives a schematic representation of the possible mechanism of PNPP hydrolysis, in this case, catalyzed by Schiff base Mn(III) complex. First, the metal-promoted hydrolysis of PNPP undergoes the formation of the catalyst-substrate complex [39,40] with an association constant (K_s) of substrate (PNPP) to the $MnL_2(H_2O)_2$ species *via* a substitution of a Mn-bound water into the substrate molecule. Next, the metal-bound hydroxyl that originated from the acidic ionization (K_a) of the Mn-bound water attacks the carbonyl group of substrate with the release of *p*-nitrophenolate anion. This process is generally regarded as the rate-determining step [41]. Finally, a substitution of one water molecule by the picolinic acid is followed by the release of Mn(II) catalyst.

On the basis of a typical double reciprocal equation [12], $1/k_{obs} = 1/(K_s k)\ 1/[S] + 1/k$, all thermodynamic (association constant, K_s) and kinetic parameters (first-order rate constant for the formation of products, k)



Scheme 1. Proposed mechanism of PNPP hydrolysis. In this Scheme, orange and glaucous moieties respectively denote the Schiff base ligands and Mn(III) cationic ion, "PA" represents picolinic acid, and the abbreviation "RDS" displays the "rate-determining step".

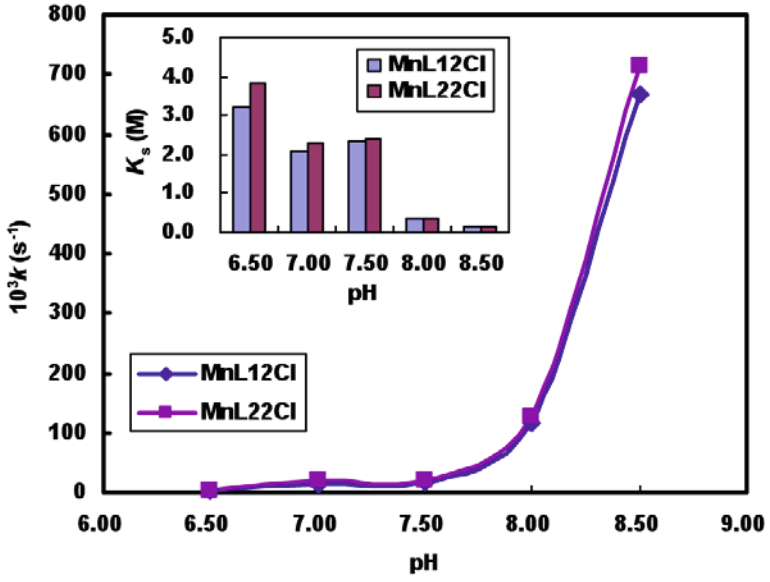


Figure 3. Plots of *k* versus pH for the hydrolysis of PNPP catalyzed by Schiff base Mn(III) complexes in Gemini 16-2-16 micellar solution at 25.0 °C. The insert shows the relationship between K_s and pH for MnL_2Cl/16-2-16.

were obtained from the linear k_{obs}^{-1}-$[S]^{-1}$ plots (see Supplementary Fig. 1), and all K_s and *k* values are given in Fig. 3. As can be seen from these constants obtained, the linkage strength between PNPP and MnL^2_2Cl is stronger than that between PNPP and MnL^1_2Cl under all the conditions applied in the present paper. This further testifies that the open environment around the centre Mn(III) of MnL^2_2Cl is in favor of the formation of the PNPP-MnL^2_2Cl intermediate.

3.2 Effect of acidity on PNPP hydrolysis

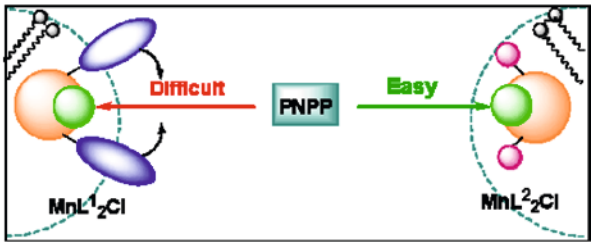
As shown in Figs. 2a and b, the hydrolysis rates of PNPP increased with increasing pH, which means that an acid-base equilibrium process was involved in the hydrolysis pathway of PNPP (Scheme 1). Additionally, we did not observe the deactivation of the two catalysts over the pH range operated that meant, both Schiff base Mn(III) catalysts possessed a high acid-base stability. Fig. 3 portrays the change in trend of first-order rate constant with an increase in the pH. It is seen that values of *k* showed a slower increase below pH 7.50 but a sharper increase in *k* value was observed above a pH of 8.00.

We deduced that pK_a value for each catalyst fell in the pH region from 7.60 to 8.00, thereby, corresponding pK_a values of the two complexes were estimated using the inflexions of the two *k* – pH curves to be at 7.95 for MnL^1_2Cl and 7.97 for MnL^2_2Cl. Li *et al*. [13] earlier reported that unsymmetrical Salen-type Schiff base Mn(III) or Co(II) complexes with benzoaza-15-crown-5 pendants had smaller pK_a values due to synergic effect of the Lewis acid activation of the cationic metal ion and the hydrogen bond activation between the oxygen atom of benzoaza-15-crown-5 and Mn(or Co)-linked H_2O. In our case, however, a similar synergic effect possibly did not exist because of the longer distance between the Mn-linked H_2O and the oxygen atom of aza-15-crown-5 in MnL^1_2Cl. Therefore, the 0.02 p*K* unit difference in pK_a of both Mn(III) catalysts used in this case can be neglected.

According to the proposed mechanism, the deprotonation of the aqueous substrate-catalyst complex $MnL_2(H_2O)$(PNPP) gave an active species MnL_2(OH)(PNPP) followed by a nucleophilic attack of the Mn-bound hydroxyl on the carboxyl group of PNPP. Normally, MnL^1_2Cl with a slightly smaller pK_a would possess higher activity in comparison with MnL^2_2Cl. On the contrary, the experimental results obtained showed that MnL^2_2Cl with a larger pK_a had a good catalytic activity relative to MnL^1_2Cl in catalyzing the hydrolysis of PNPP. Thus, a 0.02 p*K* unit difference though not enough to give a broad difference in catalytic activities of the two Mn(III) catalysts but the steric hindrance due to aza-15-crown-5 may be an important influencing factor, resulting in the above-mentioned anomalous behaviour (Section 4.3).

3.3 Relationship between hydrolysis rate and the structure of complex

It is very important that an efficient association of guest molecule to the active site of enzyme take place in enzyme catalyzed reactions [42]. In our case, catalytic activities of the two Schiff base Mn(III) complexes increased in the order $MnL^1_2Cl < MnL^2_2Cl$. As mentioned above, MnL^1_2Cl displayed lower activity even though it had a smaller pK_a (= 7.95) in comparison to MnL^2_2Cl, which hinted to the fact that the steric hindrance of aza-15-crown-5 played a crucial role in tuning their catalytic activities. We have previously [8,10] reported on the activities of varied mono-Schiff base Mn(III) complexes containing benzoaza-15-crown-5 or morpholine pendants in catalyzing the hydrolysis of esters. The results showed that the complexes containing morpholine pendants exhibited better activities compared to the complexes containing benzoaza-15-crown-5 pendants, since the benzoaza-15-crown-5 with huge geometrical structure highly blocked the linkage between substrate and catalyst.



Scheme 2. The level of difficulty for the association between Schiff base Mn(III) complexes (MnL_2Cl) to PNPP In the schemetic, two catalysts are respectively shown in color solids. Ligand moiety containing benzo-15-crown-5, light brown; aza-15-crown-5 pendant, blue ellipsoid; hydrogen atom, purple; manganese ion, light green.

An open coordinated microenvironment of artificial enzyme is required in the PNPP hydrolysis reaction, which facilitates the formation of the productive catalyst-substrate intermediates. In this case, two aza-15-crown-5 substituents in MnL^1_2Cl gave a huge block for the proximity of PNPP molecule to the central Mn(III) ion, while an open central Mn(III) ion in MnL^2_2Cl without aza-15-crown-5 groups highly benefited the linkage of substrate molecule to catalyst. Scheme 2 schematically portrays the association level of PNPP with MnL^1_2Cl or MnL^2_2Cl, in which the association between PNPP and MnL^1_2Cl is much difficult than MnL^2_2Cl. This can be confirmed by relational K_s values for MnL_2Cl/16-2-16 system shown in the inset of Fig. 3. In the pH range under consideration, the bigger values of K_s reveal that the linkage of PNPP to MnL^2_2Cl was stronger than that of PNPP to MnL^1_2Cl. Hence, the productive PNPP-MnL^2_2Cl binary complex was produced in higher concentration and resulted in a larger rate enhancement as compared to the other catalytic system containing MnL^1_2Cl. Similarly, bigger association constant (see Supplementary Fig. 2) for the linkage between PNPP and MnL^2_2Cl were obtained compared to MnL^1_2Cl in a CTAB micellar solution. It further demonstrates that an open active site favors the efficient association between substrate and catalyst, leading to the convenient generation of an active substrate-catalyst complex. On the other hand, Choi *et al*. [43] have once mentioned that smaller molecule easily solubilizes in micellar solutions. As a result, MnL^2_2Cl with smaller geometrics can expediently penetrate into Gemini 16-2-16 micelles relative to MnL^1_2Cl, which benefits the PNPP hydrolysis. In brief, the difference in catalytic behavior of the two complexes indicates that the presence of aza-15-crown-5 moiety

inside MnL^1_2Cl is an essential structural element, decreasing the hydrolysis rate of PNPP. Hence, bulky substituents closer to the active site of catalyst may play a negative role in the metal-catalyzed hydrolysis of PNPP. Thus, apart from the factors such as mimic of a hydrophobic microenvironment and catalytic site, an appropriate exposure of catalytic centre is necessary in the consideration of design of artificial enzymes.

3.4 Impact of various surfactant micelles on the catalytic hydrolysis of PNPP

Surfactants in aqueous solutions can affect the kinetic behavior of enzymatic reactions either below or above their critical micelle concentration [44,45]. Among the surfactants, Gemini surfactants especially attract scientists' attention [37,38,46-52] for its surface properties such as CMC, surface tension, aggregate number, micelle number although there were seldom reports involving the application of Gemini surfactants in the field of ester hydrolysis. Hence, we have further investigated the comparable effects of two type of surfactants, Gemini 16-2-16 and CTAB, on the PNPP hydrolysis (Figs. 2c and d). It is seen that hydrolysis rates of PNPP catalyzed by MnL_2Cl in Gemini 16-2-16 micellar solution were approximately 1.5 ~ 1.7 times (Table 1) faster than those in CTAB micellar solution over the entire range of substrate concentration studied.

It is also known that one of the most important processes leading to micellar effects on reactions is the solubilization of solutes in micellar phase [53]. In this study, both Mn(III) catalysts and substrate PNPP are less water-soluble, so the introduction of cationic surfactants benefit an increase in local concentration of catalyst and PNPP molecules in a small volume inside micelle aggregates. This may enable accelerate the hydrolysis of PNPP, which is testified by the corresponding ratios of $k_{obs}^{(G)}/k_{obs}^{(OM)}$ (Table 1) in this survey. Owing to the excellent surface activity of Gemini 16-2-16, it displayed stronger capacity of concentrating hydrophobic PNPP molecules and catalyst molecules in the Stern layer of 16-2-16 micelle aggregates. So, the collision chances between PNPP and catalyst increased and thereby larger rate acceleration was observed in Gemini 16-2-16 micellar solution. Also, a high positive charge density of head groups of Gemini 16-2-16 micelles can efficiently stabilize the negative tetrahedron transition state [54] compared with CTAB micelle aggregates. In addition, a higher local concentration of hydroxide anion in the interfacial region of cationic Gemini micelles also contributed to the increase in hydrolytic rate of PNPP hydrolysis which is correlated by the experimental k value (see Supplementary Fig. 2). Keeping with the trend, the largest rates were detected in MnL_2Cl/16-2-16 system in comparison to MnL_2Cl/CTAB system.

4. Conclusion

In conclusion, the catalytic hydrolysis of PNPP by two Schiff base Mn(III) complexes with Schiff base ligands in different micellar solutions was evaluated. The experimental results reveal that Gemini 16-2-16 micellar system is the best among all of reaction mediums applied in the present paper. Moreover, MnL^2_2Cl without aza-15-crown-5 as ligand exhibited better catalytic activity than MnL^1_2Cl containing the said ligand. The result implies that an opening in the coordination site for access is essential to the association between substrate PNPP and the Mn(III) catalyst. On the basis of our studies, we believe that there will be increasing research focusing on the introduction of modified Gemini surfactants in the field of ester hydrolysis.

Table 1. Varied ratios of k_{obs} values for PNPP hydrolysis in Gemini 16-2-16 surfactant micellar solutions and other medium [a]

Catalysts	$k_{obs}^{(G)}/k_{obs}^{(OM)}$	10^3 [PNPP] (mol L^{-1})				
		0.200	0.267	0.333	0.400	0.467
MnL^1_2Cl	n_1	1.56	1.52	1.51	1.64	1.52
	n_2	2.70	2.49	2.35	2.50	2.46
	n_3	1.73	1.64	1.56	1.52	1.62
MnL^2_2Cl	n_1	1.59	1.60	1.66	1.66	1.65
	n_2	3.00	3.01	2.82	2.82	2.63
	n_3	1.89	1.88	1.70	1.70	1.64

[a] *Conditions are the same in Fig. 2.* $k_{obs}^{(G)}$ *represents the pseudo-first-order rate constant for PNPP hydrolysis in Gemini 16-2-16 micellar solution at pH 7.00.* $k_{obs}^{(OM)}$ *denotes the pseudo-first-order rate constant for PNPP hydrolysis in other comparable systems. All "*n_i*" listed in Table 1 were respectively defined as below:* n_1, $k_{obs}^{(G)}/k_{obs}^{(CTAB)}$; n_2, $k_{obs}^{(G)}/k_{obs}^{(no\ surfactant)}$; n_3, $k_{obs}^{(CTAB)}/k_{obs}^{(no\ surfactant)}$

Acknowledgements

This work was supported by the Scientific Research Foundation for PhD (Sichuan University of Science & Engineering, No: 07ZR14) and Key Scientific and Technological Project (No: 208118) issued by Ministry of Education.

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