Hydrolytic cleavage of *bis*(*p*-nitrophenyl) phosphate by Schiff base Mn[III] complexes containing morpholine pendants in Gemini 16–6–16 micelles

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Abstract.   Catalytic efficiency of two Schiff base manganese(III) complexes toward the hydrolysis of *bis*(*p*-nitrophenyl) phosphate (BNPP) was evaluated in a micellar media formed by *bis*(hexadecyl-dimethylammonium)hexane bromide (abbr.16–6–16, 2Br⁻) at 25°C. Effects of various reaction conditions on the hydrolysis of BNPP were systematically investigated. The observations obtained indicate that the two Mn(III) catalysts can efficiently promote hydrolysis of BNPP with a six order of magnitude rate enhancement relative to the background rate constant (k_0). Different structures of the two complexes lend to their distinguishing activities each other. Furthermore, rates of BNPP hydrolysis in Gemini 16–6–16 micellar medium are much higher than that in hexadecyltrimethylammonium bromide (CTAB) and *n*-lauroylsarcosine sodium (LSS) micelles.

Keywords.   BNPP; hydrolysis; structural difference; Schiff base manganese(III) complexes; Gemini surfactant 16–6–16.

1. Introduction

It is well-known that phosphate diester backbone is usually highly resistant toward hydrolytic cleavage, and thereby it is still a bigger challenge to make catalysts reactive enough to hydrolyse the target bonds rapidly under physiological conditions.[1] In addition, the extraction of natural phosphoesterases is so difficult that their application in industry and scientific research has not been expanded. Based on these facts, there is much interest in developing artificial hydrolases that catalyse the hydrolytic cleavage of phosphodiester bonds.[2] The hydrolysis of phosphodiesters using small organic molecules is expected to have a fundamental impact on the development of artificial, possibly sequence-specific nucleases for use in biotechnology as well as for the detoxification of insecticides.[3]

Metal catalysts with Schiff base ligands were mostly used in the field of catalytic hydrogenation, addition polymerization, epoxidation reaction, bionic catalytic oxidation, etc.[4] Interestingly, some groups found that some synthesized Mn(III)(salen)-type and *mono*-

Schiff base complexes have been shown to be highly reactive for hydrolysing phosphate esters or diesters in non-micellar solutions.[5] Some available information has also been obtained, involving in the effects of temperature, pH, structural difference, etc.

To mimic the active center and the hydrophobic environment of nature hydrolase, metallomicelle consisted of metal complex and micelle has gained extensive attention.[6] However, it is noteworthy that many conventional micelles have mostly been used as reaction medium in these studies. Gemini surfactant, a type of novel surfactant, usually exhibits much better surface activity compared to those conventional surfactants.[7] Even though most researchers have already focused on the related physico-chemical properties (e.g. critical micellization concentration (CMC), viscosity, aggregation number and micelle number) of Gemini surfactants,[8] there are few researches involving in the application of Gemini surfactants in the hydrolysis of phosphate diesters or carboxylic acid esters[9] by now.

To that end, we here synthesized two kinds of *mono*-Schiff base Mn(III) complexes (figure 1) with morpholine pendants (the ratio of metal/ligand is 0·5), and further investigated their reactivity toward the

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hydrolysis of *bis*(*p*-nitrophenyl) phosphate (abbre. BNPP, a DNA or RNA model substrate) in Gemini surfactant micelles formed by *bis*(hexadecyldimethyl-ammonium)hexane bromide (represented as 16–6–16) monomers at 25°C. For comparison, the effects of two traditional surfactants, hexadecyltrimethylam-monium bromide (CTAB) and *n*-lauroylsarcosine sodium (LSS), on BNPP hydrolysis were also evaluated under a comparable condition.

2. Experimental

2.1 *Materials and instruments*

The pH values of these buffer solutions were measured at 25°C using a Radiometer PHM 26 pH meter (Made in China). Kinetic runs of BNPP hydrolysis were carried out at 25 ± 0.1°C, employing a GBC 916 UV-vis spectrophotometer (Made in Austrilia) equipped with a thermostatic cell holder. The ionic strength of catalytic system was maintained at 0·1 M KCl.

All reagents were of analytical grade and used without further purification unless otherwise indicated. Redistilled and deionized water was used in the present experiment. *Bis*(4-nitrophenyl) phosphate (BNPP), the buffer reagent *Tris* [tris(hydroxy-methyl) aminomethane] and KCl were products from Sigma Chemical Co. Acetonitrile (MeCN) was obtained from Chengdu Kelong Chemical Co. (China). Acetonitrile as solvent for the preparation of BNPP stock solution was redistilled. Schiff base Mn(III) complexes as hydrolases were prepared according to the literature method.[4e] *Bis*(hexadecyldimethyl-

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

ammonium)hexane bromide was synthesized with the method described earlier.[8e]
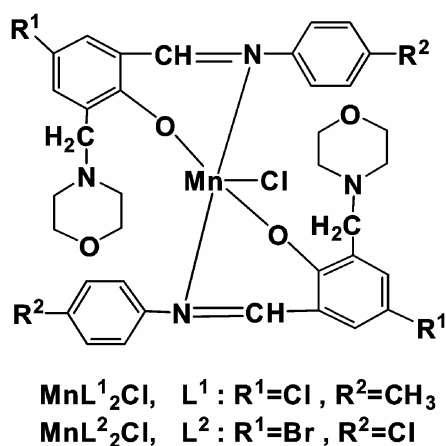
2.2 *Kinetic measurements*

In a typical kinetic experiment, the hydrolysis reaction was started by rapid injection of the stock solution of BNPP into a 1cm cuvette containing 3 ml mixed solution, to which the Schiff base Mn(III) complexes and Gemini surfactant 16–6–16 of desired concentration was previously added. To ensure the formation of micelle aggregates composed of surfactant monomers, the concentration of buffered surfactant solution is respectively higher than their corresponding critical micellization concentration (abbre. CMC). The hydrolysis of BNPP catalysed by the two Mn(III) complexes was determined spectro-scopically from the formation of the *p*-nitrophenolate anion at 400 nm under a condition of excessive substrate over catalyst (ca. 20–47 folds). All rate constants were obtained in triplicate and were reproducible to within 3% error.

3. Results and discussions

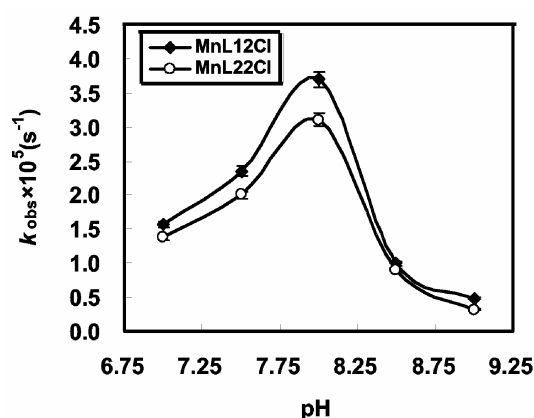### 3.1 *Observed first-order- rate constants of BNPP hydrolysis at 25°C*

Usually, the catalytic activities of nature hydrolases reach their corresponding maximums at the varied optimum acidities.[10] For investigating dependence of catalytic efficiency of two complexes for the acidity of catalytic system, the hydrolysis rate of BNPP as a function of pH was primarily studied over a pH zone of 7·00–9·00 under the selected conditions ([BNPP] = 2.0×10^{-4} mol L^{-1}, [catalyst] = 1.0×10^{-5} mol L^{-1}, [16–6–16] = 1.0×10^{-4} mol L^{-1}). Figure 2 portrays two bell-shaped profiles of k_{obs} vs pH for the Mn(III)-catalysed hydrolysis of BNPP in Gemini 16–6–16 micellar solution. As shown in figure 2, both maximums in two curves were almost reached at pH ~ 8·00. Further, we have investigated effects of varied conditions on hydrolytic property of BNPP promoted by the title complexes at the optimum pH (8·00).

Under a fixed pH (= 8·00), figure 3 shows an increasing trend in rate (solid square and solid triangle) of BNPP catalysed by the two Schiff base Mn(III) complexes (MnL$^1_2$Cl and MnL$^2_2$Cl) as a function of BNPP concentration which covers a range of 1.33×10^{-4}–4.00×10^{-4} mol L^{-1}. Additionally, other two curves (pH 7·50, open square and open triangle) as

the references (marked as complexes Ref-1 and Ref-2) (correlative data have already been reported in our earlier paper[9a]) were also depicted in figure 3. Observations obtained in the present work reveal that hydrolysis rates of BNPP increase linearly with the increasing concentration of BNPP (correlative coefficient > 0.99) in two catalytic systems containing Schiff base Mn(III) complexes with morpholine pendants. Moreover, the rates of BNPP hydrolysis in this work at pH 8.00 are slightly higher than reference values (refer to figure 3) at optimum pH 7.50. It appears that a major factor in influencing corresponding reactivity of four Mn(III) catalysts is their distinguishing structural difference (refer to the description in §3.4).
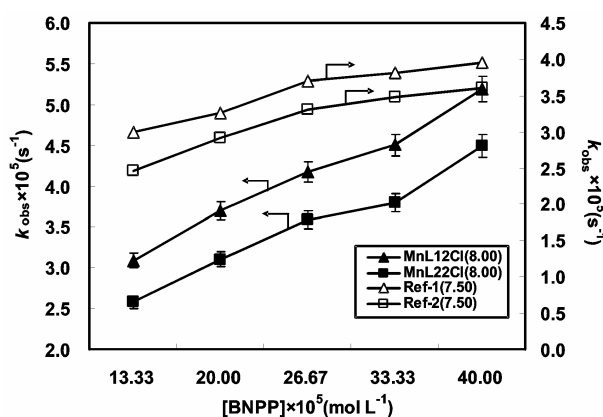
In the Gemini 16–6–16 micellar solution, the hydrolysis of BNPP catalysed by the two manganese(III) catalysts with Schiff base ligands containing morpholine pendants gave a six orders of magnitude rate enhancement in comparison with the background value $(k_0 = 1.12 \times 10^{-11}\ s^{-1})^{11}$ at pH 7.00. It shows that both Schiff base Mn(III) complexes are efficient catalysts for catalysing the hydrolysis of BNPP, and MnL^1_2Cl possesses a higher activity relative to MnL^2_2Cl. Furthermore, we had studied the catalytic activity of MnL^2_2Cl as catalyst in promoting BNPP hydrolysis in various micellar medium, i.e. Gemini 16–6–16, CTAB and LSS micelles. All of k_{obs} values are listed in table 1. As shown in table 1, $MnL^2_2Cl/$ 16–6–16 system achieves ca. $4.4 \sim 6.9$ times and $6.4 \sim 8.6$ times kinetic advantage in comparison with $MnL^2_2Cl/CTAB$ and MnL^2_2Cl/LSS systems over the total range of [BNPP] $(1.33 \times 10^{-4} \sim 4.00 \times 10^{-4}$ mol L^{-1}), respectively.

3.2 *Proposed mechanism for BNPP hydrolysis*

Previous studies have lead to a proposed mechanism for the metal-catalysed hydrolysis of phosphate diesters that requires at least one adjacent metal hydroxide nucleophile attacking a bound phosphorus center.[2d] By analogy, scheme 1 represents the supposed mechanism of BNPP hydrolysis catalysed by the title complexes. In the hydrolysis process, *bis*-aquo Mn(III) complex (represented as $MnL_2(H_2O)_2$) undergoes a two-step ionization (K_{a1} and K_{a2}), in which a real active form $MnL_2(H_2O)(OH)$ (represented as 'AS') generates. The most active form of the catalyst has a metal-aquo site that exchanges with substrate BNPP, which results in a reactive catalyst-substrate complex (TC) with a binding constant (K_s). This is usually regarded as a key step in enzymatic reaction.[12] Next, Mn(III)-bound hydroxide attacks

Figure 2. pH dependence of observed first-order rate constants at 25°C. Conditions: $I = 0.1$ mol L^{-1} KCl, [16–6–16] = 1.0×10^{-4} mol L^{-1}, [MnL$_2$Cl] = 1.0×10^{-5} mol L^{-1}, [BNPP] = 2.0×10^{-4} mol L^{-1}. Legends: ■, MnL$^1_2$Cl; ○, MnL$^2_2$Cl.
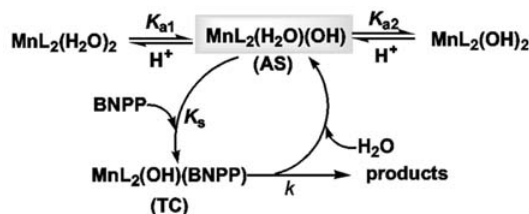

Figure 3. Rate-[BNPP] profiles for BNPP catalytic hydrolysis in Gemini 16–6–16 micellar solution at 25°C. Conditions: pH 8.00, $I = 0.1$ mol L^{-1} KCl, [16–6–16] = 1.0×10^{-4} mol L^{-1}, [MnL$_2$Cl] = 1.0×10^{-5} mol L^{-1}. Other two plots (open square and open triangle) are assigned to the observations reported in our previous paper [9a].

Scheme 1. Hydrolysis mechanism of BNPP induced by Schiff base Mn(III) complexes containing morpholine pendants.

Table 1. Observed first-order rate constants ($k_{obs} \times 10^5$, s^{-1}) of BNPP hydrolysis in various catalytic systems at pH 8.00[a].

10^5 [BNPP](mol L^{-1})	13·33	20·00	26·67	33·33	40·00
MnL$^1_2$Cl/16–6–16	3·091	3·700	4·176	4·503	5·191
MnL$^2_2$Cl/16–6–16	2·581	3·106	3·589	3·795	4·496
MnL$^2_2$Cl/CTAB	0·375	0·579	0·728	0·853	0·919
MnL$^2_2$Cl/LSS	0·301	0·463	0·520	0.594	0·707

[a]25 ± 0.1°C, $I = 0.1$ mol L^{-1}(KCl), [MnL$_2$Cl] = 1.0×10^{-5} mol L^{-1}, [16–6–16] = 1.0×10^{-4} mol L^{-1}, [CTAB] = 1.0×10^{-2} mol L^{-1}, [LSS] = 5.0×10^{-3} mol L^{-1}

the positive phosphorus atom of BNPP to promote release of the *p*-nitrophenolate anion with the first-order-rate constant (*k*) (determining-rate step). Lastly, the real catalyst MnL$_2$(H$_2$O)(OH) is regenerated through a quick substitute of phosphoric acid by another water molecule.

According to previous report,[5a] we can have:

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{1}{K_s k[\text{BNPP}]}. \tag{1}$$

In eq. (1), [BNPP] is the free substrate BNNP concentration and can be replaced by the substrate initial concentration based on the initial rate method. The correlative *k* and K_s values (listed in table 2) can be obtained from figure 4, in which two linear plots of k_{obs}^{-1} vs [BNPP]$^{-1}$ for MnL$^1_2$Cl/16–6–16 (solid square) and MnL$^2_2$Cl/16–6–16 (solid triangle) are respectively portrayed. Good linear relationship ($R > 0.98$) reveals that the proposed mechanism for BNPP catalytic hydrolysis is reasonable. For hydrolysis of BNPP in MnL$^2_2$Cl/CTAB and MnL$^2_2$Cl/LSS, corresponding values of *k* and K_s can be obtained by other two plots (not shown in figure 4) of k_{obs}^{-1} vs [BNPP]$^{-1}$ using the same method mentioned above.

As shown in table 2, MnL$^1_2$Cl/16–6–16 shows ca. 1·12-folds kinetic advantages over MnL$^2_2$Cl/16–6–16. In addition, it can be seen that hydrolysis rates of BNPP catalysed by MnL$^2_2$Cl in Gemini 16–6–16 micellar solution are respectively 1·34-fold and 3·21-fold higher than in CTAB and LSS micellar solutions. These results represent that catalytic activities of the two Mn(III) complexes as artificial enzyme are correlative to their intrinsic structures, and that higher hydrolytic rate of BNPP in Gemini 16–6–16 micellar solution may be due to the better surface activity of Gemini 16–6–16. Correlative reasons will be elucidated in §3.5.
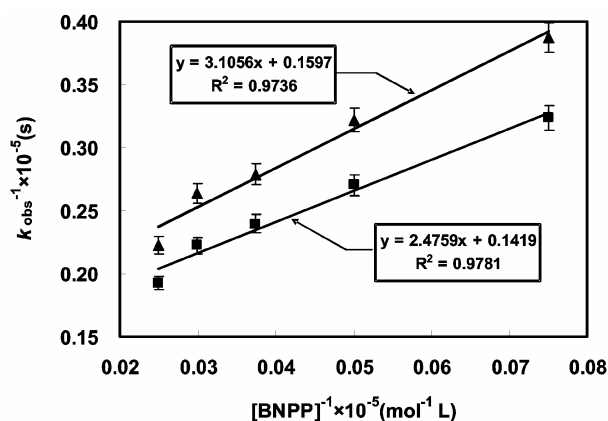
Figure 4. Plots of $k_{obs^{-1}}$ vs [BNPP]$^{-1}$ for BNPP catalytic hydrolysis by Schiff base manganese (III) complexes in Gemini 16–6–16 micellar solution at 25°C. Conditions: pH 8·00, $I = 0.1$ mol L^{-1} KCl, [16–6–16] = 1.0×10^{-4} mol L^{-1}, [MnL$_2$Cl] = 1.0×10^{-5} mol L^{-1}.

3.3 *Rate-pH profiles for Mn(III)-catalysed hydrolysis of BNPP*

The enzymatic activity is highly sensitive to the acidity of the reaction system, namely, a bell-shaped profile of rate-pH is generally observed in enzyme reaction.[10] All of natural enzymes have their optimum pH's, at which the highest catalytic activities for enzymes are reached in some special enzyme reactions. In our study, dependence of rate for pH values also gives two classic bell-shaped curves (figure 2), which is in line with the catalytic properties of natural enzymes.

Bell-shaped rate-pH profiles in figure 2 suggest the reaction process may undergo a two-step acid dissociation of *bis*-aquo Mn(III) complex over a pH range of 7·00–9·00. We are able to obtain the pK_{a1} and pK_{a2} values of the hydrated complexes by estimating from the inflexions, i.e. 7·75 and 8·16 for MnL$^1_2$Cl, 7·79 and 8·12 for MnL$^2_2$Cl. Combined

Table 2. First-order-rate constants (k, s^{-1}), binding constants (K_s, M^{-1}) and relative k values at pH 8·00.

Entry	System	$k \times 10^5$ (s^{-1})	K_s (M^{-1})	Relative k
1	MnL$^1_2$Cl/16–6–16	7·05	5731·25	3·6
2	MnL$^2_2$Cl/16–6–16	6·26	5142·32	3·2
3	MnL$^2_2$Cl/CTAB	4·67	1404·04	2·4
4	MnL$^2_2$Cl/LSS	1·95	669·92	1·0

Conditions are the same as in table 1

figure 2 with scheme 1, it is accepted that the metal–aqua–hydroxyl form MnL$_2$(H$_2$O)(OH) is the real active species in the hydrolysis process of BNPP. When pH > 7·75 (for MnL$^1_2$Cl) or 7·79 (for MnL$^2_2$Cl), the concentration of the active form MnL$_2$(OH$_2$)(OH) gradually increased, and a substitution of a Mn-bound water molecule by the substrate leads to the formation of a reactive ternary complex MnL$_2$(OH)(BNPP) with a higher concentration. As a result, hydrolytic rates of BNPP sharply increased, and rate maximums reached around pH 8·00 in MnL$_2$Cl/16–6–16 system. Since the *bis*-aquo form [MnL$_2$(OH$_2$)$_2$] is not able to provide a nucleophile to attack the substrate, slower hydrolysis rates for BNPP in both catalytic systems may be a result of the smaller concentration of the active MnL$_2$(OH$_2$)(OH) below corresponding pK_{a1}. As pH values are above pK_{a2} (8·16 for MnL$^1_2$Cl, or 8·12 for MnL$^2_2$Cl), the sharp decrease in rate shall be ascribed to the formation of inactive dihydroxide [MnL$_2$(OH)$_2$] and hydroxo-bridged dimer [L$_2$Mn(OH)$_2$MnL$_2$]. To avoid the generation of these inactive species, the acidity of catalytic system shall be strictly adjusted to the optimum pH (= 8·00) so that two Mn(III) complexes as catalysts can exhibit the best activities towards the hydrolysis of BNPP.

3.4 *Effects of complex structures on the hydrolysis of BNPP*

As can be seen from tables 1 and 2, MnL$^1_2$Cl displays higher catalytic activity than MnL$^2_2$Cl. In general, metal ions inside metalloenzymes play an important role in the enzyme reactions.[13] Especially, the charge density of central metal directly influences the catalytic activity of hydrolase. Because charge density of the central Mn(III) ion inside MnL$_2$Cl is primarily controlled by R^1 group closer to Mn(III) ion not by R^2 away from Mn(III) centre, MnL$^1_2$Cl has a much stronger electron-withdrawing R^1 (=Cl) group in contrast with MnL$^2_2$Cl containing a bromium substi-

tute, and hereby MnL$^1_2$Cl exhibits better activation for promoting the acidic disassociation of H$_2$O linked with the Mn(III) ion, and this was demonstrated by the slightly smaller pK_{a1} (7·75) for MnL$^1_2$Cl relative to MnL$^2_2$Cl (pK_{a1} = 7·79). Alternatively, the active MnL$^1_2$ (H$_2$O)(OH) reaches a slightly higher concentration at lower pH than MnL$^2_2$ (H$_2$O)(OH), which leads to larger rate accelerations of BNPP hydrolysis by MnL$^1_2$Cl/16–6–16 than MnL$^2_2$Cl/16–6–16. Additionally, the positive Mn(III) ion of MnL$^1_2$Cl has stronger power of activating the substrate (BNPP) coordinated to itself and stabilizing the tetrahedral transition state.[14] Thus, MnL$^1_2$Cl gave ca. 1·12-fold kinetic predominance than MnL$^2_2$Cl. Further, values of K_s in entry 1 and 2 (table 2) can be used to evaluate the linkage strength between the negative BNPP and the positive Mn(III) ion. So, larger K_s for MnL$^1_2$Cl indirectly confirms that MnL$^1_2$Cl holds a higher charge density of Mn(III) ion over MnL$^2_2$Cl.

Obtained results in this work are compared with reference values reported in literature,[9a] it can be found that the activities of the two Schiff base Mn(III) complexes containing morpholine groups are respectively higher than those two complexes containing benzoaza-15-crown-5 pendants at corresponding optimum pH's (8·00 and 7·50), i.e. MnL$^1_2$Cl > Ref-1, MnL$^2_2$Cl > Ref-2. In spite of the stronger hydrophobic property of the benzoaza-15-crown-5 which can contribute to the concentration of hydrophobic substrate (BNPP), Schiff base Mn(III) complexes containing benzoaza-15-crown-5 pendants (i.e. Ref-1 and Ref-2 in figure 3) still have lower catalytic activities than the two Mn(III) catalysts applied in this case. As mentioned above, the formation of catalyst–substrate complex is important for enzyme reaction.[12] In other words, an open catalytic site is required to benefit the linkage between substrate molecule and central metal. Besides the effects of hydrophobic interaction, we think the steric hindrance of two kinds of pendant groups (benzoaza-15-crown-5 and morpholine) may be the major factor for tun-

ing the activities of these Mn(III) catalysts. The steric hindrance of benzoaza-15-crown-5 is bigger than morpholine group, the association of the substrate (BNPP) and Mn(III) catalyst containing benzoaza-15-crown-5 is more difficult than that of BNPP and Mn(III) catalyst containing morpholine pendants. Then, the concentration of productive MnL_2Cl-BNPP complex is slightly higher than that of BNPP-Ref-1(or -Ref-2) complex, which ultimately results in the much higher rates of BNPP induced by MnL^1_2Cl (or MnL^2_2Cl) containing morpholine rings in this case.

3.5 *Dependence of various micelles on the catalytic hydrolysis of BNPP*

The data in table 1 indicate that hydrolytic rates of BNPP catalysed by $MnL^2_2Cl/16–6–16$ are ca. $4·4 \sim 6·9$ times and $6·4 \sim 8·6$ times than that by $MnL^2_2Cl/CTAB$ and MnL^2_2Cl/LSS over the total range of [BNPP] $(1·33 \times 10^{-4} \sim 4·00 \times 10^{-4}\ mol\ l^{-1})$, respectively. The larger difference in rate shall be a result of the excellent surface activity of Gemini surfactant 16–6–16 in comparison with CTAB and LSS, two kinds of traditional single-chain surfactants.

Gemini surfactants manifest lower CMC, higher viscoelasticity, and enhanced propensity for lowering the oil–water interfacial tension in comparison to their monovalent single headgroup/single chain counterparts.[7,8(g),8(h)] In metallomicelle-catalysed hydrolysis of BNPP, micellar aggregates are generally regarded as hosts for concentrating hydrophobic BNPP and metal catalyst by a hydrophobic interaction. At the same time, electrostatic interaction between reaction reagents partly influences hydrolysis rate of BNPP. Since BNPP and Schiff base Mn(III) complexes (MnL_2Cl) are less water-soluble, the introducing of surfactant is in favour of an increase in local concentration of BNPP and Schiff base Mn(III) complexes. Among the three kinds of micelles applied in this case, Gemini 16–6–16 micelles bear preferable solubilization for hydrophobic reactants (BNPP and MnL_2Cl). Accordingly, higher hydrolysis rates were observed in Gemini 16–6–16 micellar solution in contrast with CTAB and LSS micelles.

On the other hand, the rates of BNPP hydrolysis promoted by MnL^2_2Cl in varied medium decrease in the order of Gemini 16–6–16 > CTAB > LSS (table 2). As described in last paragraph, it is easier to understand that Gemini 16–6–16 micelles provide the best reaction microenvironment for BNPP hydrolysis.

Why reactivity of BNPP hydrolysis is slightly higher in CTAB than in LSS? Over the working pH range of 6·50–9·00, LSS micelles show anionic characteristics.[15] The electrostatic repulsion between the negative BNPP molecules and head groups of LSS lends to a lower local concentration of BNPP in LSS micelle phase, whereas higher concentration of BNPP is given in CTAB micelles. Hence, the concentration of reactive ternary complex $MnL_2(OH)(BNPP)$ in LSS micellar solution is smaller than that in CTAB micellar solution. Consequently, the hydrolysis of BNPP is faster in CTAB micelles than in LSS micelles.

4. Conclusion

In summary, the reactivity of BNPP hydrolysis catalysed by $MnC^1_2Cl/16$-16 has been investigated in this paper. Observations reveal that the two Mn(III) catalysts exhibit remarkable catalytic activities (excess a six-orders of magnitude rate enhancement) for the catalytic hydrolysis of BNPP in Gemini 16–6–16 micellar solution. Moreover, the activities of the two complexes are mainly dependence on the R^1 substituent closer to central metal. In addition, bell-shaped profiles of rate-pH demonstrate that $MnL_2(OH_2)(OH)$ is a real active species for catalysing the hydrolysis of BNPP. Two control experiments in CTAB and LSS micellar mediums show that hydrolysis of BNPP promoted by the title complexes are much slower in CTAB and LSS micelles than in Gemini 16–6–16 micelles. It is anticipated that Gemini surfactant micelles with various structures will be the best candidate for use as hosts in the hydrolytic cleavage of organophosphate esters, such as DNA, RNA or pesticides.

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