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Review

Metallomicellar supramolecular systems and their applications in catalytic reactions

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ABSTRACT

This review presents advances in metallomicelles-catalyzed reactions, including hydrolysis of carboxylic esters and phosphates, oxidation-reductions, C–C bond forming reactions, etc. These novel supramolecular vehicles can not only mimic the active center, but also the hydrophobic microenvironments of metalloenzymes. As emphasis, the kinetic models and mechanism studies of metallomicelles-catalyzed hydrolysis, which were intensively studied in our group, were particularly reviewed.

1. Introduction

Micelle is an aggregate formed by surfactants when the concentration of amphiphilic molecules reaches a certain level named as critical micelle concentration (CMC) [1,2]. According to Hartley's spherical model [3], the micellar structure contains, from outer sphere to inner, named as Gouy-Chapman layer, Stern layer and a hydrocarbon center with 50–100 molecules and a diameter of 10–28 Å. In general, chemical reactions in micellar structures can take place in the Stern layer with enhanced reaction rates or selectivities. This effect is referred to as micellar catalysis, which goes back to the late 1960s. This enhancement can be the result of (i) an increased local concentration of the reactants at the surface or in the interior of the micelle; (ii) stabilization of the transition state of the reaction due to a favorable interaction with the surfactant molecules; and (iii) a combined polarity, microviscosity, and charge effect inside the micelle. In other words, by the enrichment of substrate in Stern layer of micelle, the substrate, intermediate or product could be stabilized and oriented. As a result, the reaction rate and mechanism could also be changed, and the regio- and

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stereoselectivity could even be achieved. Therefore, micelles have often been used to mimic the microenvironments of enzyme active centers in the past decades. Besides the simple micellar systems, in-depth studies focused on functional micelles, co-micelles and polymer micelles, etc. are included [4].

In recent metalloenzyme-mimic research, more attention has been paid to the simulation of structures and functions of the enzyme active centers, while the contributions from microenvironments were usually not considered. On the other hand, micelles alone as enzyme model often display low efficiency and limited specificity for substrates. For these reasons, a type of new artificial metalloenzyme model, metallomicelle, has been developed, in recent decades, by the combination between the systems of metalloenzyme simulation and micelles. Metallomicelles were formed from metal complexes of surfactant ligands or by blending metal-lipid complexes with non-functional surfactants. This kind of aggregate synchronously has the properties and functions of micelles and metalloenzyme models. So these novel supramolecular vehicles can not only mimic the enzyme active center, but also simulate the hydrophobic microenvironments. Moreover, chiral metallomicelles, with great importance for the clarification of the enzymic mechanisms, were also developed to enhance chiral molecular recognition and stereoselectivity.

Herein, the hydrolysis of carboxylates and phosphates aided by metallomicelles, including kinetic studies, are extensively reviewed, as are some other reactions catalyzed by metallomicelles.

2. Metallomicelles-catalyzed hydrolysis

Micelle-catalyzed hydrolysis of carboxyl acid esters has been extensively [5]. As far as the mimetic model of catalytic function is concerned, the investigation of Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} complexes as hydrolytic metalloenzyme models have been extensively reported [6]. They show good catalytic properties in the hydrolysis of *p*-nitrophenyl picolinate (PNPP). In these hydrolytic processes, the transition metal ions play a very important role [7]; several research groups developed some binuclear metal complexes that show significantly higher catalytic activity as an artificial hydrolytic enzyme model.

As an effective biomimetic system for hydrolytic metalloenzymes, metallomicelle made up of functionalized surfactant or co-surfactant capable of effective chelation of metal ions has been extensively investigated [7]. In metallomicellar catalysis, ligands containing one or more hydroxyl groups are very significant for the catalytic hydrolysis of carboxylate or phosphate esters. The hydroxyl group of the ligand can be activated by the transition metal ion, and acts as a more effective nucleophile than the chelating water molecule. The use of macrocyclic metal complexes as biomimetic models of hydrolytic metalloenzymes has attracted considerable attention due to their similarities to the macrocyclic metal complexes found in biological systems, such as metalloporphyrin complexes. Some macrocyclic metal complexes illustrated significant catalytic activity in the hydrolysis of some esters.

2.1. Metalloenzyme models for the hydrolysis of carboxylates

The synergistic effect between multifunctional groups is an important feature of enzyme catalysis. The active center of serine proteinase is made up of the hydroxyl on serine, imdazole on histidine and carboxyl on aspartic acid. Metalloenzyme-mimic studies by using metallomicelles began in middle 1980s. Typical models are Tagaki's imidazole derivatives, Tonellato's α-substituted pyridines, and Engbersen's 1,10-phenanthroline derivatives.

p-Nitrophenyl picolinate was a commonly used substrate for the studies of protease mimics. Tagaki et al. reported the catalytic hydrolysis efficiencies of metal complexes of **1**–**7** (Fig. 1) or some co-micelles formed from metal complexes **1**–**7** and other non-functional surfactants. For the anionic surfactant ligands **1**–**3**, the pseudo-first-rate constants (k_{obsd}) of the hydrolysis of PNPP in the presence of **1** and **2** are much higher than that in the presence of **3** [8]. The reason might be that the hydroxyl group can be activated by transition metal ions such as Cu^{2+} and Zn^{2+}, therefore it may serve as a nucleophilic reagent in the process of transacylation. On the other hand, the catalytic activity of ligand **4** is far greater than that of **5**, indicating that the active site is 2-hydroxymethyl, but not 5-hydroxymethyl. This result was confirmed by NMR. The hydrolysis rate reached a maximum when the 1:1 Cu-complex of **1** was formed.

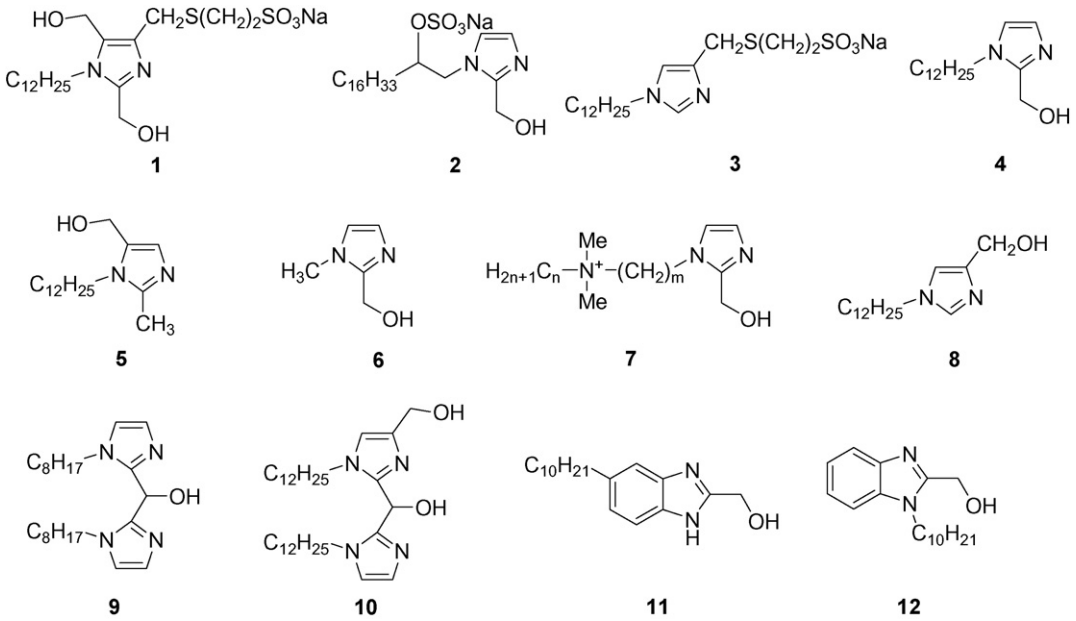


Fig. 1. Tagaki's imidazole-derived surfactant ligands.

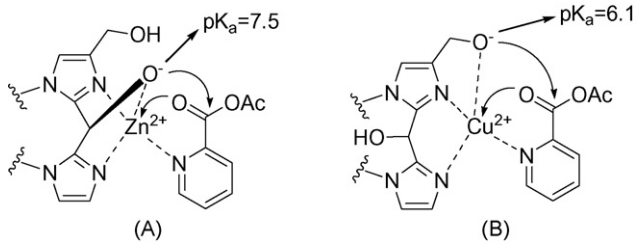


Fig. 2. Selective activation of primary and secondary hydroxyls of bis-imidazole ligand **12** by Zn^{2+} (A) and Cu^{2+} (B).

Compared to water-soluble ligand **6**, the lipophilic ligand **4** can only dissolve in micelles formed by non-functional surfactants, such as cetyltrimethyl ammonium bromide (CTAB) and polyoxyethylene lauryl ether (Brij 35). The copper complex of **4** can form co-micelles with CTAB, TritonX-100 or sodium dodecylsulfate (SDS) and catalyze the hydrolysis of PNPP. The rate constant of nucleophilic hydrolysis initiated by the attack of alkoxy anion of Cu-**4** was 100 times greater than that of Cu-**6** [9]. Furthermore, the cationic surfactant ligand **7** can form co-micelles with non-functional surfactants such as CTAB [10]. Cu^{2+} can largely increase the reaction rate, and the catalytic activity was increased in parallel with the increase of the m value.

The rate constants of hydrolysis of PNPP in the presence of non-ionic surfactant ligand (**4**, **8**–**10**, Fig. 1) were significantly affected by metal ions [11]. As shown in Fig. 2, ligand **10** uses secondary and primary hydroxyl to coordinate with Zn^{2+} and Cu^{2+}, respectively. The intermediates of PNPP hydrolysis catalyzed by Cu-**10** and Zn-**10** could be detected by HPLC.

In the presence of Zn^{2+}, the benzimidazole ligands **11** and **12** form co-micelles with CTAB and catalyze the hydrolysis of PNPP. The ratio of metal/ligand in the metal complex (1:1 or 2:1) was determined by the position of long-chain substituent group and the concentration of surfactants [12].

For the ionic substrates, very different metallomicellar catalytic activities were observed [13]. Anionic surfactant ligand **2** greatly promotes the hydrolysis of cationic substrate **13**. On the other hand, little effect was found on the hydrolysis of anionic substrate **14** in the presence of **2**. It was supposed that the metal complex-substrate intermediate is greatly stabilized by the electrostatic interaction between the surfactant and substrate (Fig. 3). For the same reason, in the presence of Cu^{2+}, the hydrolysis of **14** is promoted by cationic surfactant ligand **7**.

A series of cationic 2-hydroxymethyl pyridine surfactant ligands **15** (Fig. 4) were prepared by Tonellato et al. [6b,14a]. In the hydrolysis of PNPP catalyzed by Cu-**15a**, the reaction rate was enhanced 10^6 times. **15c** has much lower catalytic efficiency than **15a** or **15b**. The reason might be that the distance between ammonium cation in **15c** and coordinative metal ion is too close, and as a result, the stability of metal-ligand-substrate tertiary complex is lowered due to electrostatic repulsion. The catalytic efficiency of **15d** is also much lower than that of **15a** for the lack of lipophilic long chain. The lipophilic ligand **16d** can coordinate with Cu^{2+} to form metallomicelles to catalyze the hydrolysis of PNPP or other amino acid esters. The absence of hydroxyl group (**17**) led to lower catalytic abilities comparing to **16**. Suitable length of hydrophobic chains is needed for satisfying catalytic results: the tertiary complex formed from **16c**, which has a longer chain than **16d**, showed lower stability than that from **16d** [14].

The co-micelles formed from Cu-**18a** or Zn-**18a** and CTAB displayed excellent catalytic hydrolysis activities towards PNPP. The catalytic ability of methylated ligand **18b** is far lower than **18a**, even lower than the ligand without a hydrophobic long chain, such as **18c**. This phenomenon also proved the distinctive features of hydroxyl group in the ligand structures [15]. Tonellato divided the hydrolysis mechanism into 3 steps: (i) the formation of a tertiary complex between metal ion, lipophilic ligand, and the substrate; (ii) a pseudo-intramolecular nucleophilic attack of the ligand hydroxyl leading to the release of p-nitrophenol and the formation of the transacylation intermediate; (iii) metal ion-promoted hydrolysis of the intermediate and regeneration of the catalytic species [16].

Tonellato addressed that in the catalytic hydrolysis by metallomicelles, the effect of the leaving group is significant [17]. Cu-**16d** only catalyzes the hydrolysis of relatively active α-picolinates. In the catalytic process, competitive nucleophilic attack to the carbonyl existed between the hydroxyl of ligand and water that coordinate to Cu^{2+} ion. For the esters with strong leaving groups, the hydroxyl group of ligand serves as nucleophilic reagent; for the esters with weak leaving groups, the coordinated water takes up the role (Fig. 5).

Another type of ligands featuring a *N*-alkylaminomethyl-2-pyridinealdoxime moiety (**19**) have been synthesized, and the reactivity of their Ni(II) and Zn(II) complexes in the cleavage of *p*-nitrophenyl acetate (PNPA) and hexanoate (PNPH) has been investigated in the absence (**19a**) or in the presence (**19b**) of CTAB micelles [7c]. The micellar complexes are effective in promoting the cleavage of the substrate with acceleration strongly dependent on the pH. This acceleration is larger in moderately acidic environment than that in neutral solutions. Analysis of the second-order rate constants allows the conclusions that the increased reactivity of the micellar system is due to concentration and local-pH effects and not to the activation of the nucleophile.

Engbersen and co-workers prepared some lipophilic and water-soluble ligands derived from 9-hydroxymethyl-1,10-phenanthroline (Fig. 6). In co-micelles, 1:1 type complex was formed between **20a** and M^{2+}, and the catalytic activity order of different metal complexes was $Zn^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+}$. On the contrary, 1:1 or 2:1 type complexes were formed between water-soluble ligand and metal ions, and the catalytic activity order of these metal complexes was $Co^{2+} > Ni^{2+} \approx Zn^{2+} > Cd^{2+}$. The Zn complex of **21** which has no hydroxyl group showed catalytic activity 25 times lower than that of Zn-**20a** [18]. Although the lipophilic ligands **22**–**24** have no hydroxyl group in their structures, the metal complexes of imidazole-contained ligands **22** and **24** form co-micelles, which were efficient catalysts for the hydrolysis of PNPP, with non-functional surfactants such as CTAB and Brij 35 [19].

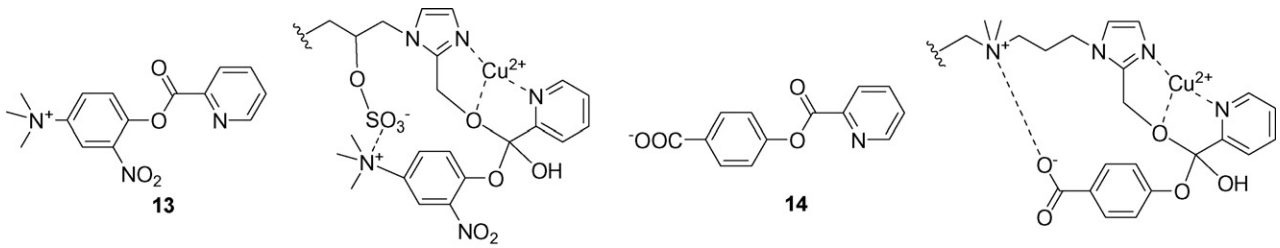


Fig. 3. Hydrolysis promoted by electrostatic interactions.

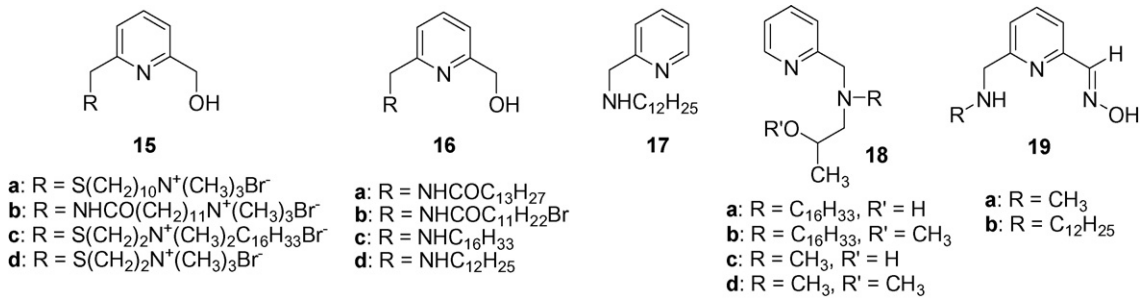


Fig. 4. Tonellato's α-substituted pyridine ligands.

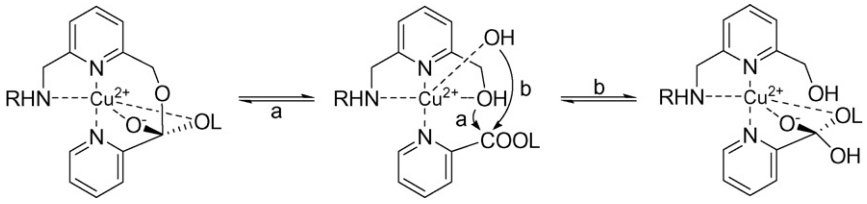


Fig. 5. Competitive nucleophilic attack to the carbonyl between the hydroxyls coordinated to Cu^{2+} ion.

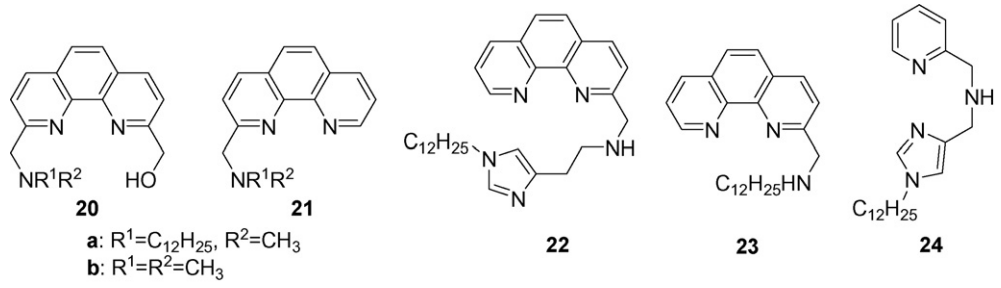


Fig. 6. Engbersen's 1,10-phenanthroline derivative surfactants.

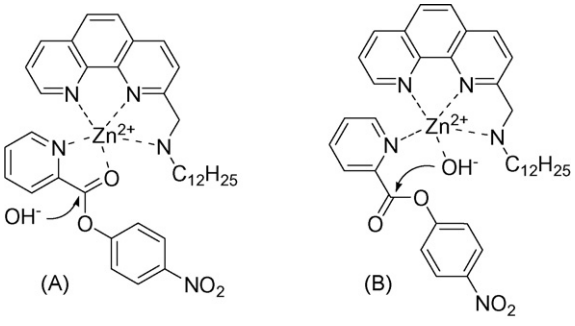


Fig. 7. Mechanisms of PNPP hydrolysis catalyzed by Zn-**23**.

Kimura et al. studied the long chain-containing macrocyclic complex **25** and its catalytic activity towards the hydrolysis of PNPA [20]. **25a** forms co-micelles with TritonX-100 and displayed 50 times greater activity than that of the water-soluble complex **25b**. They deduced the active species to be the structure of **25a** with hydroxide anion coordinated to Zn^{2+} ion. Görgl and co-workers prepared two copper complexes (**26**, **27**) of lipophilic macrocyclic polyamines [21]. The morphology of micelles formed by these two metallosurfactants was studied by small-angle neutron scattering (SANS) and small-angle-X-ray scattering (SAXS). More recently, Hughes et al. prepared metallosurfactant Cu(II)-1-tetradecyldiethylenetriamine (Cu(II)TDET, **28**) [22], and examined its catalytic activity towards the hydrolysis of several esters in the presence of metallosurfactant ligand **28**.

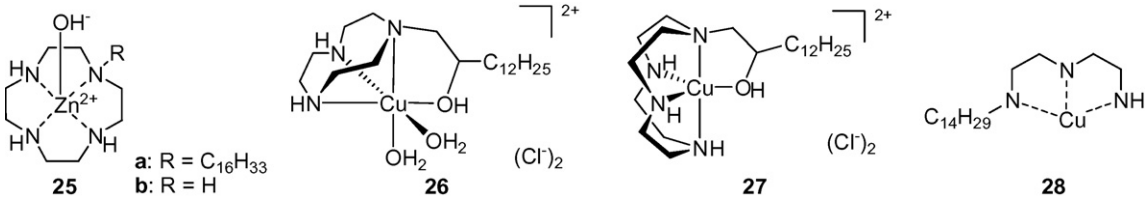


Fig. 7 shows the hydrolysis mechanism of PNPP catalyzed by **23**. The metal ion is coordinated by carbonyl oxygen, and the electrophilic activation towards carbonyl facilitated the nucleophilic attack of free hydroxide anion (**A**). In model **B**, Zn^{2+} ion is coordinated by the free hydroxide anion to induce an intramolecular nucleophilic attack.

Recently, a new generation of surfactants, Gemini surfactants, have attracted great interest [23]. These surfactants possess many unique properties, such as lower CMC, greater efficiency in lowering the surface tension of water, lower Krafft temperature and better solubilization in comparison with conventional surfactants. Qiu et al. reported the hydrolysis of PNPP catalyzed by Cu(II)-**29** complexes in the presence of Gemini surfactant 12-s-12 (**30**)

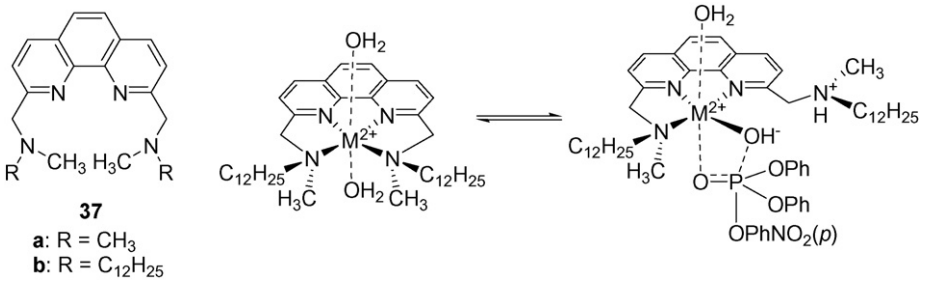
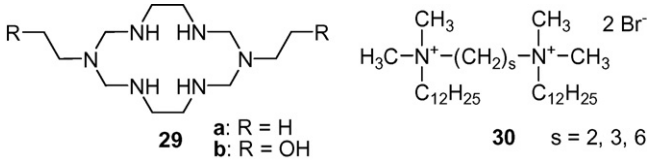


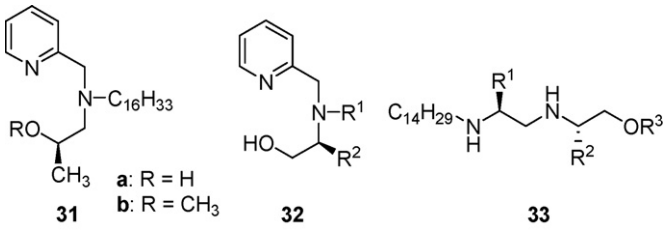
Fig. 8. Supposed mechanism of DPPNPP hydrolysis catalyzed by M^{2+}-**36**.

[24]. Metallomicellar systems containing Gemini surfactants exhibited more efficient activities for hydrolysis than those containing the corresponding single-chained conventional surfactant such as dodecyltrimethylammonium bromide (DTAB). Similarly, ligand bearing pendant hydroxyl groups (**29b**) showed higher catalytic activities.

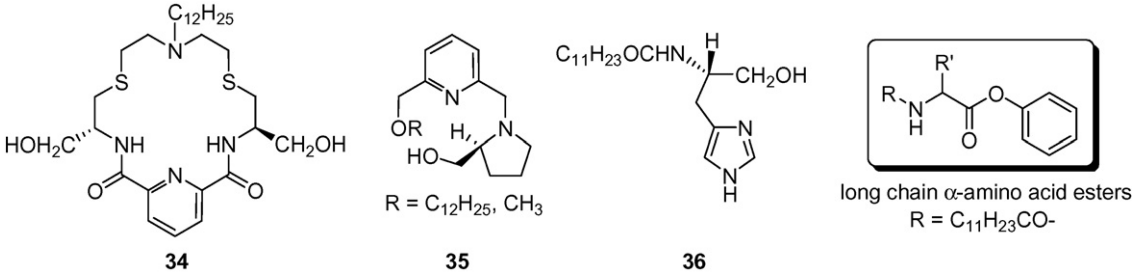


2.2. Enantioselective hydrolysis of esters catalyzed by chiral metallomicelles

The selectivity of a chemical reaction can also be affected by the microenvironment provided by the aggregates: remarkable enantioselectivities have been reported by several groups [25] in the hydrolytic cleavage of chiral esters by histidine containing chiral oligopeptides in the presence of micelles. In order to clarify the catalytic mechanism of proteolytic enzyme, much attention was paid to the studies of enantioselective hydrolysis of esters. Tonellato and co-workers prepared chiral lipophilic 2-substituted pyridines **31** and **32** [16,26]. Their Cu(II), Zn(II) or Co(II) complexes catalyzed the enantioselective cleavage of *p*-nitrophenyl esters of α-amino acids with remarkable stereoeffects. They found that (i) faster hydrolysis was observed in the reactions using chiral ligands and substrates with opposite absolute configurations; (ii) hydroxyl group (**31a**) was necessary for the reaction; (iii) poor enantioselectivities were obtained by using water-soluble ligands without long chains in the structure of **32** ($R^1 = R^2 = CH_3$), indicating that the chiral metallomicellar microenvironments facilitated the induction of enantioselectivity. Furthermore, in the cleavage of *p*-nitrophenyl esters of phenylalanine (PhePNP) and phenylglycine (PhgPNP) catalyzed by Cu(II)-**33** complexes, large rate accelerations (up to two order of magnitude) and quite remarkable enantioselectivities (up to 35, as the ratios of the rate constants measured for the faster and slower reacting enantiomers) were observed [27].



Several types of chiral lipophilic ligands **34**–**36** [28–30] were designed and synthesized by You et al. Their metal complexes as catalysts in the hydrolysis of long chain α-amino acid esters were studied. The results indicated that the hydrophobic interactions between substrate and metallocatalyst, the rigidity of the ligand, the hydroxyl group of the ligand acting as a nucleophile for the transacylation process, and the micellar microenvironment are important factors for the activity and enantioselectivity. Among these complexes, Cu(II)-**35** (R = $C_{12}H_{25}$) displayed the best enantioselective catalytic ability [29]. The reaction in the presence of this metallocatalyst gave large rate accelerations (up to three orders of magnitude) and moderate enantioselectivities (up to 7.81 k_R/k_S).



2.3. Metalloenzyme models for hydrolysis of phosphates

The biological importance of phosphate esters and anhydrides is well-known. The significance of these classes of compounds extends beyond the wide variety of naturally occurring examples to man-made derivatives that are employed for pest control, chemical warfare, and numerous industrial tasks. The chemistry of substituent exchange, such as hydrolysis, at phosphorus(V) centers has received considerable attention because such processes occur in many crucial enzymatic reactions and are relevant to the detoxification of some pesticides and chemical weapons [31].

Engbersen and co-workers synthesized lipophilic 1,10-phenanthroline-derived ligands **37**. The co-micellar system formed by the metal complex of **37b** and Brij 35 acts as an efficient catalyst for the hydrolysis of phosphate esters. In the **37b**-promoted hydrolysis of diphenyl p-nitrophenyl phosphate (DPPNPP), 8700 times of rate acceleration was observed [32]. Fig. 8 shows the supposed mechanism for the reaction.

Lipophilic ligand **16d** forms 2: 1 type complexes with Cu^{2+} in the catalytic hydrolysis of DPPNPP (Fig. 9, A), while a 1:1 type complex

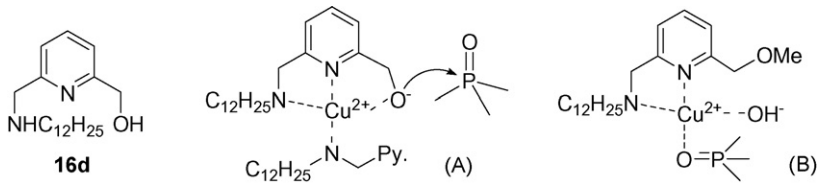


Fig. 9. Schematic representation of ternary complexes in Cu-**16d**-catalyzed-hydrolysis of phosphate ester.

was formed between Cu^{2+} and O-methylated **16d** (Fig. 9, B). Unlike the catalytic hydrolysis of carboxylate esters, the free hydroxyl in **16d** did not play an important role in the cleavage of the phosphate triester [14b].

A derivative of the zinc tetraaza macrocycle complex carrying a long alkyl chain (**38**) was examined as the catalyst for hydrolysis of DPPNPP in a Brij micelle by Breslow and co-workers [31]. This lipophilic complex is even more effective, acting as a zinc hydroxide species **38b** with pK_a = 9.1. In this system, catalysis by aggregates was apparently also occurring. Besides these studies, some other lipophilic ligands (Fig. 10, **39**–**42**) were applied for the hydrolysis [33–36]. Their metal complexes form metallomicelles and act as good to excellent hydrolytic metallocatalysts.

3. Construction of kinetic models of metallomicelles-catalyzed hydrolysis

An important feature of the efficient enzyme-catalysis is the synergistic effect between the functional groups. Thus, in the studies of chemical simulation of the structures and functions of enzyme active center, the most commonly used method is to prepare small organic multi-functional molecules and to mimic the catalytic function of enzyme active center. Metallomicelle is one of the biomimetic systems. However, studies towards the catalytic kinetics and mechanisms of metallomicellar catalysis remain rare, and the approximate quantitative treatment of metallomicellar catalysis and the establishment of its mathematical model have rarely been reported. The kinetic model of the metallomicellar mimic system towards carboxypeptidase A was constructed in our group. This provides an important way to study the catalytic mechanisms and to understand the catalytic processes.

3.1. The kinetic model for metallomicellar catalysis

Tagaki and co-workers developed a "binary complex model" for the quantitative treatment of metallomicellar catalytic kinetic study. This model assumes that substrate moiety can weakly interact with the metal ion as a ligand base in aqueous buffer and the metallomicellar catalysis is an intermolecular reaction [9]. To consider that there is a strong interaction between the metal ion M, ligand L and substrate S, Zeng and co-workers established a "ternary complex kinetic model" for metallomicellar catalysis [37]. The following is a brief introduction to the "ternary complex kinetic model" for hydrolysis reaction.

The "phase separation" model of micellar system assumes that there is two phases (micellar pseudo-phase and the bulk phase) in micellar solution, and the reaction takes place simultaneously in both micellar pseudo-phase and the bulk phase [38–40]. So we can use the following equation to describe the reaction process.

$$\begin{array}{ccc} S + Mi & \overset{K_s}{\rightleftharpoons} & MiS \\ \downarrow k_W & & \downarrow k_m \\ P & & P \end{array} \qquad (1)$$

where S represents substrate, Mi is micelle, Ks is the association constant between micelle and substrate, k_m and k_w are the apparent rate constants for product formation in micellar phase and in bulk phase.

Generally, in the metallomicellar system, an equilibrium exists between ligand (L), metal ion (M), and substrate (S). On the basis of the phase-separation model of micelle, the metallomicelle-catalyzed reaction can be supposed to take place in the bulk phase and the metallomicellar phase simultaneously to afford the products (P).

$$xM + yL \overset{K_M}{\rightleftharpoons} M_xL_y + S \overset{K_T}{\rightleftharpoons} M_xL_yS \overset{k'_N}{\rightleftharpoons} P$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow k'_0$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad P \qquad (2)$$

$$K_M = \frac{[M_xL_y]}{[M]^x[L]^y} \qquad (3)$$

$$K_T = \frac{[M_xL_yS]}{[M_xL_y][S]} \qquad (4)$$

$$k'_o = k_o + k_M[M] + k_L[L] \qquad (5)$$

where K_M is the association constant between x metal ions and y ligands, K_T is the association constant between a binary complex (M_xL_y) and a substrate, k'_N and k'_o are the apparent first-order rate constants for product formation in the metallomicellar phase and in the bulk phase, respectively, k_o is the rate constant due to the buffer, k_L and k_M are the second-order rate constants due to the ligand and metal ion alone, [L], [M], and [S] are the concentrations of ligand, metal ion, and substrate in the bulk phase, respectively, $[M_xL_y]$ is the concentration of x metal ions or y ligands in the metallomicellar phase, and $[M_xL_yS]$ is the concentration of substrate in the metallomicellar phase.

$$[S] = [S]_T - [M_xL_yS] \qquad (6)$$

$$[M] = [M]_T - x[M_xL_y] \qquad (7)$$

$$[L] = [L]_T - y[M_xL_y] \qquad (8)$$

where $[L]_T$, $[M]_T$, and $[S]_T$ are the total concentrations of ligand, metal ion, and substrate, respectively.

According to the rate law, the rate equation of reaction (2) can be written as

$$r = k_{obsd}[S]_T = k'_N[M_xL_yS] + k'_o[S] \qquad (9)$$

Combination of Eqs. (3)–(9) and rearrangement give

$$\frac{1}{k_{obsd} - k'_o} = \frac{1}{K_T(k'_N - k'_o[M_xL_y]} + \frac{1}{k'_N - k'_o} \qquad (10)$$

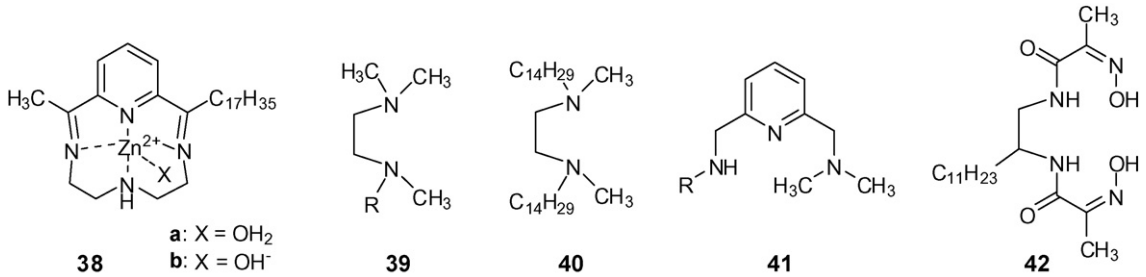


Fig. 10. Materials for catalyzed hydrolysis of phosphate esters.

by neglecting the high order terms of $[M_xL_y]$, Eq. (10) can be written

$$\frac{1}{k_{obsd}-k'_o} = \frac{1}{K_T(k'_N-k'_o)K_M[M]_T^x[L]_T^y} + \frac{y^2}{K_T(k'_N-k'_o)[L]_T} + \frac{x^2}{K_T(k'_N-k'_o)[M]_T} + \frac{1}{k'_N-k'_o} \quad (11)$$

For the particular case in which $y=1$ and $x=1$, Eq. (11) may be written as

$$\frac{1}{k_{obsd}-k'_o} = \frac{1}{K_T(k'_N-k'_o)}\left(\frac{1}{K_M[M]_T}+1\right)\frac{1}{[L]_T} + \frac{1}{K_T(k'_N-k'_o)[M]_T} + \frac{1}{k'_N-k'_o} \quad (12)$$

Equations (10)–(12) are the ternary complex kinetic equations for metallomicellar catalysis. To obtain the thermodynamic and kinetic parameters K_M, K_T and k'_N, the consecutive graphic method should be used. For example, for the case of $x=2$ and $y=1$ in a metallomicellar catalytic system, if the concentration of [M] is kept constant, the plot of $1/(k_{obsd}-k'_o)$ versus $1/[L]_T$ should give a straight line. The intercept, I, and slope, Q, of the straight line are, respectively, expressed as

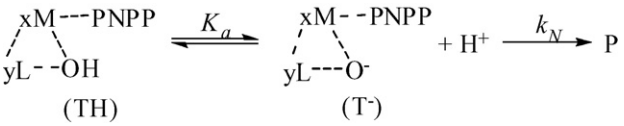
$$I = \frac{4}{K_T(k'_N-k'_o)[M]_T} + \frac{1}{k'_N-k'_o} \quad (13)$$

$$Q = \frac{1}{K_TK_M(k'_N-k'_o)[M]_T^2} + \frac{1}{K_T(k'_N-k'_o)} \quad (14)$$

According to Eqs. (13) and (14), the plot of I versus $1/[M]_T$ and Q versus $1/[M]_T^2$ would allow the estimations of k'_N, K_M and K_T.

3.2. The pH effect of hydrolysis reaction in metallomicellar solution

In general, the OH^- (or H^+) ion plays an important role in the metallomicelles-catalyzed hydrolysis reaction. k'_N and K_M display obvious pH dependence. The pH effect can be accounted by assuming that the dissociated complex anion (T^-) is much more active than the undissociated complex (TH).



(15)

where TH is the undissociated complex, T^- is the dissociated complex anion assumed to be the active species in metallomicellar phase, K_a is the acid dissociation constant of the ternary complex, and k_N is the first-order rate constant which is pH-independent. Then the reaction rate is determined by the amount of the dissociated complex anion, hence the real first-order rate constant for metallomicellar catalysis can be obtained

$$k_N = \frac{K_a}{K_a+[H^+]}k'_N \quad (16)$$

Rearrangement of Eq. (16) leads to

$$\frac{1}{k'_N} = \frac{1}{k_N} + \frac{1}{k_NK_a}[H^+] \quad (17)$$

According to Eq. (17), the values of k_N and K_a can be evaluated by a plot of $1/k'_N$ *vs.* $[H^+]$.

Based on the "phase separation" theory, the quantitative treatment of metallomicellar catalysis using "binary complex model" and "ternary complex model" for kinetic calculation has been successfully applied in the catalysis of ester hydrolysis [16,22,41,42].

4. Other metallomicelles-catalyzed reactions in water

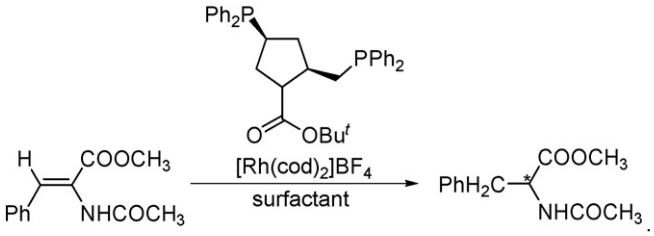
Although water is safe, benign, environmentally friendly and cheap compared with organic solvents, the latter are needed for most chemical reactions of organic substances as reaction media. The reasons may lie in: First, most organic substrates are insoluble in water, and as a result, water is not a suitable reaction medium. Second, many reactive substrates, reagents, and catalysts are decomposed or deactivated by water. The first drawback in the use of water may be overcome by using surfactants, which solubilize organic materials or form colloidal dispersions with them in water [43]. Most of metallomicelles-catalyzed reactions were performed in water.

4.1. Hydrogenations

The concept of micellar catalysis goes back to the late 1960s [44]. However, the discovery in 1992 by Oehme et al. [45] that rhodium(I)-catalyzed asymmetric hydrogenations of unsaturated α-amino acid derivatives in water proceeded with higher enantioselectivity when micelle-forming surfactants were present in the reaction mixture has led to a newfound interest in the use of aqueous micelles to promote organic reactions. Reductive reactions in water catalyzed by transition metal complexes are promoted by surfactants as well [46]. Micelle-forming amphiphiles significantly increase both the reaction rate and the enantioselectivity of Rh(I)-catalyzed hydrogenations of amino acid precursors [45,47].

This enhancement is only observed when the concentration of the surfactant is above its CMC [48]. Table 1 shows results in asymmetric hydrogenation of (*Z*)-methyl α-acetamidocinnamate with and without amphiphiles. The improvement upon addition of an amphiphile is significant with respect to activity and enantioselectivity. In these examples the product was isolated in high purity by extraction with chloroform. Asymmetric hydrogenation within aqueous micelles can also be adapted for unsaturated α-amino phosphonic acid and α-amino phosphinic acid derivatives [49]. Significantly the enantioselectivities are sometimes higher than in organic media. To facilitate the separation of catalyst and

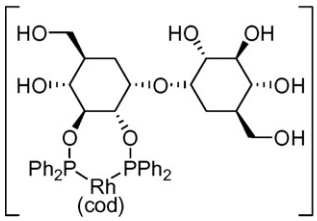
Table 1
Hydrogenation with different types of surfactants. Rh:surfactant:substrate = 1:20:100.



Surfactant	*t*/2 (min)	Optical yield (%ee *R*)
None in water (methanol)	90 (2)	78 (90)
Anionic		
Sodium dodecylsulfate (SDS)	6	94
Cationic		
Cetyltrimethyl ammonium hydrogen sulfate (CTA HSO_4)	5	95
Zwitterionic		
N-dodecyl-N,N-dimethyl-3-ammoniol-propanesulfonate	5	93
Nonionic		
Polyoxyethylene(10)hexadecylether (Brij 56)	7	95

product at the end of the reaction, Oehme and co-workers substituted the monomer amphiphiles by amphiphilized polymers or polysoaps [48].

Water-soluble rhodium complexes containing glucose-based phosphino ligands **43** proved to be effective catalysts in the asymmetric hydrogenation of various enamides and itaconic acid in water in the presence of SDS (7.5×10^{-3} to 1.0×10^{-1} M). The use of SDS significantly improved the enantioselectivity (up to 99.9% ee) and reduced the amount of catalyst, which was suggested to be a consequence of micelle formation [50]. The enantioselectivity of the asymmetric hydrogenation of some chelating olefinic substrates with hydroxy-DIOP rhodium(I) chelate **44** as catalyst is also influenced by amphiphiles in water to an unprecedented degree [51]. The differences in enantiomeric excesses compared with blanks (without amphiphile) were in excess of 70 Δ%ee. Long alkyl chains in the amphiphile are essential for high Δ%ee. Mechanistic studies on this enantioselective process have been conducted using pulsed field gradient spin-echo NMR experiments [52]. The association of the catalyst to the micelles is of key importance for obtaining the increase in enantioselectivity. The authors, however, point out that it is difficult to extrapolate these observations to transition metal catalysis in micellar systems in general.



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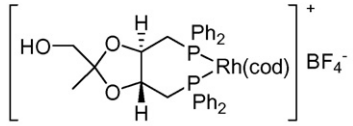

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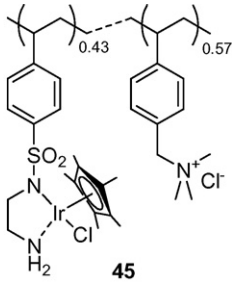

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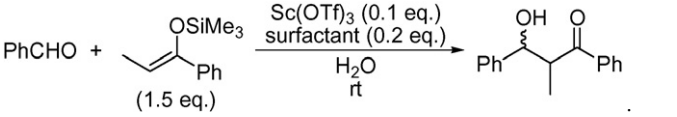
More recently, Li et al. reported that an amphiphilic polymer-based iridium catalyst **45** (Ir-PTsEN) assembled at the interface of emulsion droplets shows a remarkable rate acceleration for the transfer hydrogenation of aldehydes in water [53], the highest TOF is up to 3.0×10^5 h^{-1}. The excellent performance can be ascribed to the assembly of catalyst at the interface of emulsions, resulting in a large reaction area. Furthermore, the cooperative effects of both the hydrophobic and hydrophilic parts of the catalyst ensure the high concentrations of reactants, both organic substrates and $HCOO^-$, around active sites. This study demonstrates that emulsion catalysis provides a promising and general strategy to develop organic synthesis in water.

Table 2
Effect of surfactants on Aldol reaction in water.



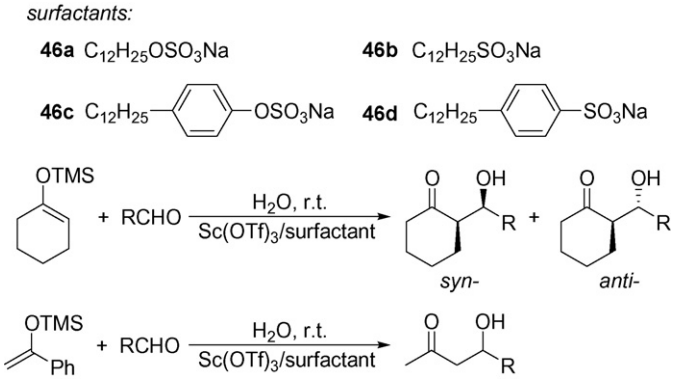
Surfactant	Time (h)	Yield (%)
–	4	3
SDS	4	88
Triton X-100	60	89
CTAB	4	Trace

4.2. Aldol-type reactions

Catalytic asymmetric aldol reactions have emerged as one of the most powerful types of carbon–carbon bond forming processes affording synthetically useful, optically active β-hydroxy carbonyl compounds [54]. Among these reactions, the chiral Lewis acid-catalyzed reactions of aldehydes with silyl enol ethers are one of the most promising methods. Although many successful examples have been developed since 1990, most of the reactions have to be conducted at low reaction temperatures (e.g., −78 °C) in aprotic anhydrous solvents such as dry dichloromethane, toluene, and propionitrile.

Although some water-tolerable metal salts as Lewis acid catalyze aldol reactions in water-containing solvents, a certain amount of organic solvents such as THF and ethanol still had to be combined with water to dissolve the organic substrates and promote the reactions efficiently. From the viewpoint of today's environmental consciousness, however, it is desirable to avoid the use of harmful organic solvents. The main drawback in the use of water (low solubility of most organic substances in water) could be overcome by using surfactants, which solubilize organic materials or form emulsions with them in water. However, large quantities of surfactant molecules compared with the reaction substrates are needed for many cases.

With the intention to develop more environmentally friendly reaction conditions, Kobayashi and co-workers studied a variety of acid-catalyzed reactions in water in the presence of surfactants [55]. In a model reaction, first the surfactant aided Lewis acid-catalyzed aldol reaction was tried, the results of this study are summarized in Table 2. An unexpected enhancement of the reactivity was found when SDS (20 mol%) was added to the $Sc(OTf)_3$ catalyst. A non-ionic surfactant (Triton X-100) was also effective in this aldol reaction, but only a trace amount of product was observed when a cationic surfactant was used. These results prompted the investigators to combine the surfactant with the catalyst. This so-called LASC (Lewis acid-surfactant combined catalyst, for a typical example: $Sc(DS)_3$,

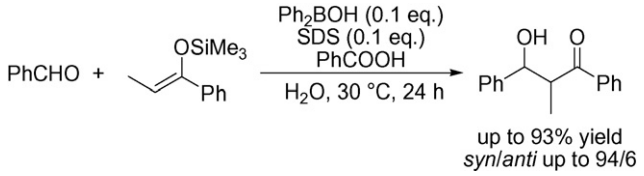


Scheme 1. Anionic surfactants-promoted Aldol reactions.

scandium tris(dodecyl sulfate)) was expected to act both as a Lewis acid to activate the reactants and as a surfactant to form stable colloidal dispersions [56]. These types of catalyst were subsequently successfully used in water to perform several other Lewis acid-catalyzed carbon–carbon bond forming reactions such as allylations [57], Mannich-type conversions [57a], Michael additions [58], and Friedel-Crafts-type conjugate additions [59]. Light scattering and microscopy studies on these systems revealed that the colloidal dispersion consisted of micrometer-sized spherical particles, for which it was suggested that the substrates and catalysts are concentrated in the hydrophobic interior, in this way enabling the organic conversions to take place rapidly. In some cases with special substrates, $Sc(DS)_3$ does not give any improvement comparing with $Sc(OTf)_3$ [60]. Recently, it was shown that in a similar system using Fe(III) as a Lewis acid catalyst, the aldol reaction in Table 2 proceeded in a diastereoselective fashion [61].

Li and co-workers also employed aromatic and aliphatic anionic surfactants in $Sc(OTf)_3$-catalyzed aldol reactions of some labile silyl enol ethers (Scheme 1) with aromatic aldehydes in water [62]. The results indicated that the aromatic surfactants **46c** had a better ability to inhibit the hydrolysis of labile silyl enol ethers and promoted the aldol reaction, leading to higher yields of aldol adducts.

Catalytic amounts of boron compounds can also be used as Lewis acid catalysts instead of metal salts. Kobayashi found that highly diastereoselective aldol reactions via boron enolates could successfully be performed in water using a catalytic amount of a boron source [63]. The reactions proceed smoothly in water at ambient temperature while traditional boron aldol reactions need lower temperature and strictly anhydrous conditions. Water is used as the sole solvent, and thus should lead to environmentally friendly systems (Scheme 2). Akiyama et al also used fluoroboric acid to catalyze Mannich-type reactions of ketene silyl acetals with aldimines



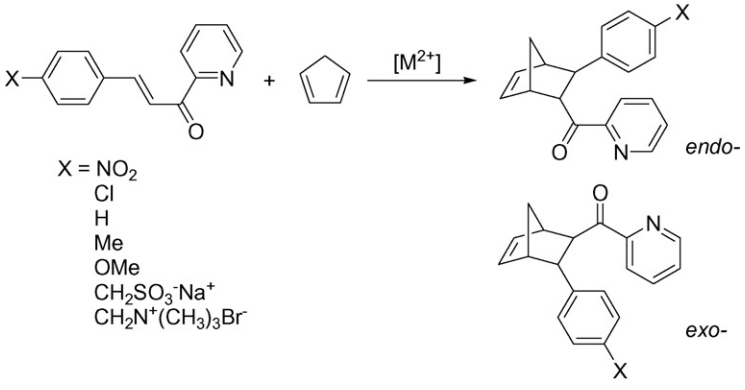
Scheme 2. Mukaiyama Aldol reaction using diphenyl boric acid in water.

in the presence of SDS [64]. The reaction proceeded smoothly in the presence of 1 mol% of SDS. Formation of small particles was observed by transmission electron microscopy.

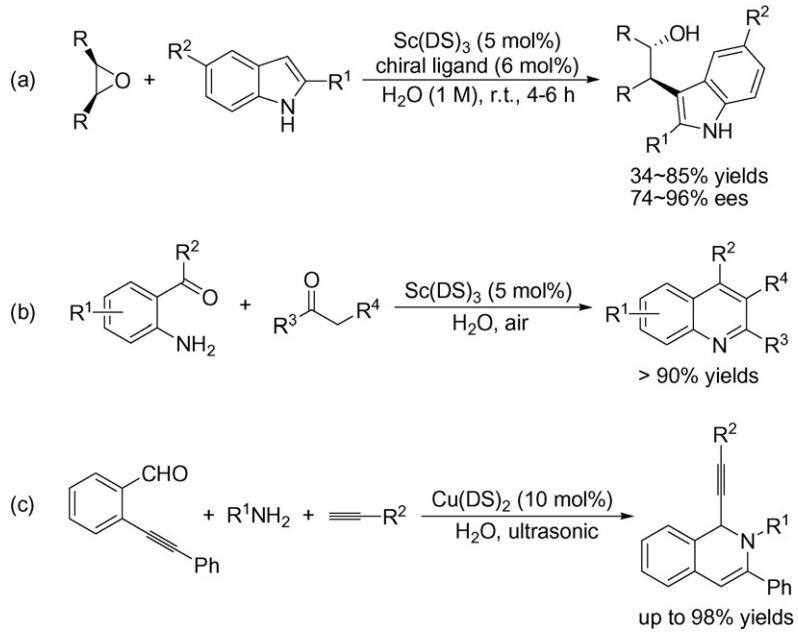
4.3. Diels-Alder reactions

The Diels-Alder (D-A) reaction is an important tool in synthetic organic chemistry, forming the key step in the preparation of many six-member rings. Many procedures have been developed to improve the yields and (stereo) selectivities of this type of cycloaddition. Important milestones in these areas are the discovery that Lewis acids can catalyze D-A reactions in organic solvents, and that in water remarkable acceleration of the reaction are possible [65]. The applicability of the D-A reaction was extended by Engberts et al. [66], by performing the Lewis acid-catalyzed reaction in micellar media. The reaction (Scheme 3) was initially performed in micelles formed from SDS, CTAB, and $C_{12}E_7$ (dodecyl heptaoxyethylene ether). In these cases, the conversions were slowed. The micelles were unable to catalyze this type of reactions [67], actually often retarding them [68]. The diene and the dienophile apparently reside in different location of the micelle. In contrast, this reaction turned out to become highly efficient when it was performed in $Cu(DS)_2$ micelles, and rate enhancements up to 1.8 million as compared to the uncatalyzed reaction in acetonitrile were measured. Complete complexation of the dienophile to the copper ions at the micellar surface accounts for this effect. In this way, both reactants are brought in close proximity to each other at the micellar surface, possibly in an even more favorable orientation to give a distinctly more efficient D-A reaction. The micelle here indeed brings the reactants together and provides a confined reaction environment [69]. In the reaction between cyclopentadiene and acrylate esters, increasing the chain length of acrylates resulted in a decrease of *endo*/*exo* ratio of D-A products. Surfactants clearly have a significant effect on product selectivity and isolated yields especially if used around their CMC [70].

Engberts also found that vesicles formed from a cyclic phosphate ester (5,5-di-*n*-dodecyl-2-hydroxy-1,3,2-dioxaphosphorinan-2-one) with copper(II) counterions ($Cu(dDP)_2$, **47**) are able to catalyze D-A reaction shown in Scheme 3 efficiently at low (0.1 mM) concentrations [71], making vesicular catalysis more attractive than

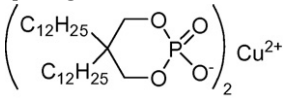


Scheme 3. D-A reaction in micellar media.



Scheme 4. Some LASC-catalyzed reactions.

micellar catalysis from the viewpoint of "green chemistry". The rate depends on the exact reaction conditions, as well as on the exact method of preparing the vesicular solutions.



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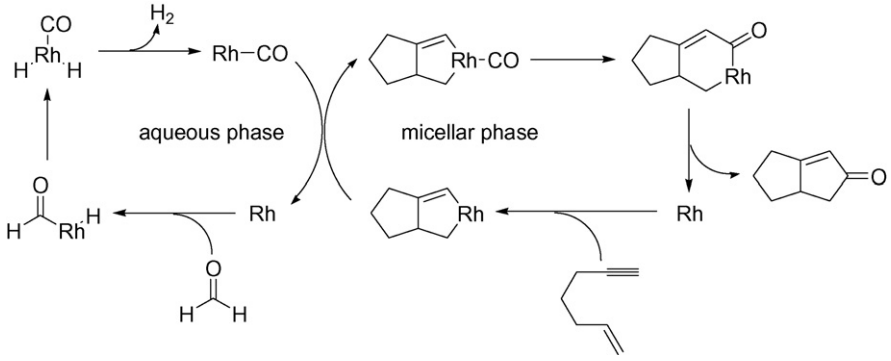
4.4. Other reactions

Actually, metallomicelles have been applied to a number of chemical reactions. Besides the reactions mentioned in Section 4.2, LASC were suitable for many other reactions. Kobayashi et al. found that in the presence of catalytic amounts of $Sc(OSO_3C_{12}H_{25})_3$ [$Sc(DS)_3$] and a chiral bipyridine ligand, asymmetric ring-opening of meso-epoxides with aromatic N-heterocycles [72], an alcohol and thiols proceeded smoothly to afford the corresponding products in moderate to good yields with high to excellent enantioselectivities (Scheme 4, a). Water was used as the sole and essential solvent in these important enantioselective transformations. Moreover, $Sc(DS)_3$ catalyzes the Friedländer annulation in water [73]. Friedländer annulation using Lewis acid-surfactant-combined catalyst provided a mild and efficient route for the synthesis of quinolines (Scheme 4, b). Employing a catalytic amount of $Sc(DS)_3$, various polysubstituted and polycyclic quinolines were obtained in exellent yields. LASC also showed efficiency in the three-component reactions of 2-alkynylbenzaldehydes, amines, and nucleophiles in water [74]. This method offers a mild and efficient route for the synthesis of 1,2-dihydroisoquinoline derivatives (Scheme 4, c). The advantages of this method include good yields, environmentally benign, and experimentally operational ease.

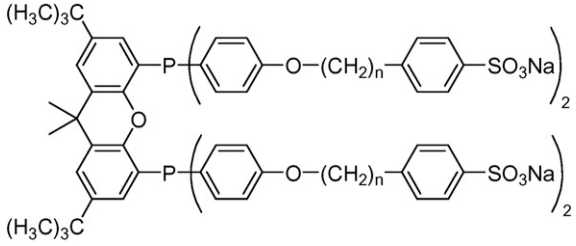
An elegant rhodium-based example of micellar catalysis was reported by Morimoto et al. [75]. An aqueous catalytic Pauson–Khand-type reaction of enynes in the presence of formaldehyde as a water-soluble source of carbon monoxide was developed. The decarbonylation and the carbonylation processes took place independently in different phases of the reaction system, namely in the aqueous and SDS micellar phases, respectively, which results in a more efficient catalytic carbonylation reaction (Scheme 5). This strategy had the potential to become a general protocol that could be used in a wide variety of carbonylation reactions.

Van Leeuwen and co-workers [76] described some rhodium complexes of a series of xantphos derivatives with surface-active pendant groups (**48**). Electron microscopy experiments show that these ligands and their complexes form vesicles in water if the hydrophobic part of the ligand is large enough ($n = 3$ or 6). The presence of aggregates formed from these rhodium complexes led to



Scheme 5. Working hypothesis for aqueous transfer carbonylation.

a significant enhancement of the solubility of organic substrates in aqueous solution. This enhanced solubility results directly in a higher reaction rate in the rhodium-catalyzed hydroformylation of 1-octene. The aggregates stay intact during the recycling and the active rhodium complex is retained in the water-phase quantitatively.



48 n = 0, 3, 6

5. Outlook and conclusions

Comparing with micelles as reaction media that can alter the rate, mechanism, product distribution, regio- and stereoselectivity of reactions [1a,77], the applications of metallomicelles have less commonly been reported. The unique characteristic of metallomicelles is that they can not only mimic the active center, but also the hydrophobic microenvironments of metalloenzymes, which serve as important natural catalysts in living beings. More attention will be paid on the chemistry and biological applications of metallomicelles. Besides the applications mentioned in this review, metallomicelles or metallosurfactants are widely applied in composite superfine powder, nanoparticles [78], magnetic resonance imaging (MIU) [79], photochemical and analysis chemistry studies [80], drug delivery [81], nerve agent destruction [82], transphosphorylation catalysts [83], and RNA cleavage [84].

Acknowledgments

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