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Effective Cleavage of β-1,4-Glycosidic Bond by Functional Micelle with L-Histidine Residue

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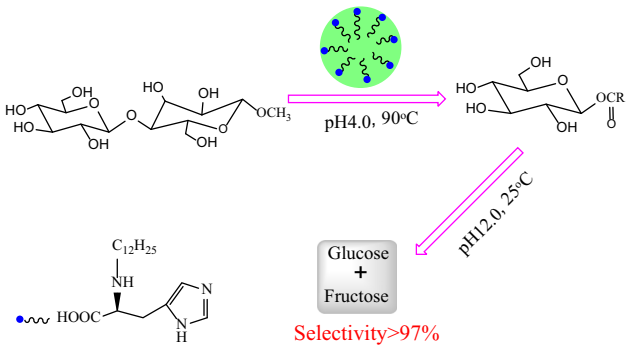
Abstract A novel functional surfactant N^{α}-dodecyl-L-histidine (NDH) was synthesized and its micelle was used as mimic of β-1,4-endoglucanase to catalyzed the hydrolysis of methyl-β-D-cellobioside (MCB) under relatively low temperatures (80–110 °C). The results showed that the micelle of NDH displayed excellent catalytic activity for the cleavage of β-1,4-glycosidic bond and the formation of L-histidine-5-D-glucopyranosyl. The micelle-catalyzed first-order reaction rate constant k_m of degradation of MCB was calculated. The conversion of MCB and selectivity of reducing sugars (glucose and fructose) could reach 58.9 and 87.1 %, respectively, for a reaction time of 10 h at pH 4.0 and 110 °C. In NDH micelle-catalyzed reaction sugar ester was deduced as the chief product. The reaction pathways of MCB hydrolysis were proposed and the activation energy *E*a for the hydrolysis was calculated.

Graphical Abstract



Keywords Kinetics · Cellulose · Biomass · Catalysis · Hydrolysis

1 Introduction

The efficient utilization of lignocellulosic biomass is of great practical significance to solve the problems of resource shortage, energy depletion and environmental pollution [1–3]. Cellulose is generally the main component of lignocellulosic biomass [4, 5]. Glucose is an important platform compound to produce biofuel, chemicals and polymer materials [6–8]. At present, hydrolysis of cellulose into glucose is still one of the bottlenecks and challenging problems in the field of utilization of biomass [9, 10]. In recent years, some researchers have reported the hydrolysis of cellulose into glucose through acid catalysts [11–13], subcritical and supercritical water [14–16] and ionic liquid [17–19]. However the problems of low activity and/or selectivity, severe reaction conditions and potential

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environmental pollution have not been resolved [20, 21]. Cellulase-catalyzed way shows fast reaction rate and high selectivity of glucose for the hydrolysis of cellulose under mild conditions. However, the high cost and instability of the enzyme restrict its further application [22]. There are three kinds of cellulase for hydrolysis of cellulose by synergistic action: endo-β-1,4-glucanase; exo-β-1,4-glucanase; β-glucosidases [23].

Endo-β-1,4-glucanase hydrolyzes internal glycosidic bonds in cellulose with a random, on–off fashion [24, 25]. And the catalytic mechanism of endo-β-1,4-glucanase was believed to consist of two reaction steps involving glycosylation and deglycosylation steps [26, 27].

Functional micelle, a new kind of self-assembly supramolecular system, which possesses hydrophilic and hydrophobic chemical functional groups and could simulate the active center and the hydrophobic microenvironment of enzyme, attracts many attentions of chemists and biologists [28–30]. In this work, a novel functional surfactant with L-histidine (His) residue was synthesized and its micelle was used as mimic of endo-β-1,4-glucanase to catalyzed the hydrolysis of methyl-β-D-cellobioside, which is regarded as a good structural unit model of cellulose, in weakly acidic aqueous solution at relatively low temperatures (80–110 °C). This micelle displayed excellent catalytic activity and selectivity of reducing sugar for MCB hydrolysis.

2 Experimental Section

2.1 Materials and Instruments

β-D-(+)-Cellobiose purchased from J&K Corp company. methanol, ethanol, sodium chloride, concentrated sulfuric acid, sodium hydroxide, potassium sodium tartrate, sodium borohydride, ethyl acetate, sodium sulfate, acetone, L-histidine, dodecyl sulfate, hexadecyl trimethyl ammonium bromide, Polyoxyethylene (23) lauryl ether, all of the reagents were analytical grade and purchased from Kelong reagent company and used after certain purification. MCB was prepared according to previously reported procedures [31], the characterization data was provided in Supporting Information (SI).

NMR (AM-400, Bruker, Switzerland). Pulsed amperometric detection and mass spectrometry (PAD-MS) (LCMS-IT-TOF, Shimadzu, Japan). Elemental analyses were implemented with an elemental analyzer (MOD 1106, Carlo Erba company, Italy). Conductivity meter (Bante950-DH, Shanghai HeChen Company, China). High Performance Liquid Chromatography (HPLC) (LC-10T, Shodex, Japan) with a RI detector (RI-201R, Shodex, Japan) and a sugar-D chromatographic column.

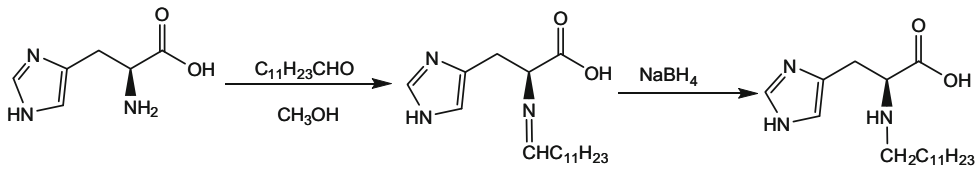
2.2 Synthesis of N^{α}-dodecyl-L-Histidine (NDH)

NDH surfactant was synthesized by a modification of published procedures as described in Scheme 1 [32]: lauraldehyde (3.11 ml, 14 mmol) was dissolved in hot absolute ethanol (30 ml), then it was added into 30 ml absolute methanol solution of L-histidine (1.5516 g, 10 mmol) with NaOH powder (0.52 g, 13 mmol). The mixture was heated to 45 °C and stirred for 10 h, then the solution was cooled with an ice bath and $NaBH_4$ (0.49 g, 13.0 mmol) was added in small portions. The mixture was stirred about 12 h at 0 °C. The solvent was evaporated, the resulting solid was dissolved in ethyl acetate and washed by the saturated sodium chloride solution to remove the remainder histidine. The organic solvent was evaporated and the write solid was dissolved in acetone. Then it was acidified with 37 % HCl up to the isoelectric point of histidine to obtain the desired product as white powder (1.45 g, 45 %). IR (KBr, cm^{-1}) 3670–2000, 1578, 1457, 1398, 1138, 1111, 984, 940, 841, 811, 752, 667, 628, 553. MS (ESI, H_2O/CH_3OH): m/z: calc.: 323.47 $[M+H]^+$; Found: 324.26. Elemental analysis calc. for $C_{18}H_{33}N_3O_2$: C, 66.83; H, 10.28; N, 12.99 %. Found: C, 66.80; H, 10.26; N, 13.02 %. ^{1}HNMR (300 MHz, D_2O–NaOH, δppm): 0.64 (t, J = 7.5, 3H, CH_3), 1.10–1.50 (m, 20H, $10CH_2$), 2.11–2.36 (m, 2H, NCH_2), 2.63 (d, J = 6.6, 2H, *$CHCH_2$), 3.11 (t, J = 6.6, 1H, *CH), 6.65 (s, 1H, Im-5H), 7.40 (s, 1H, Im-2H).

2.3 Methods

The hydrolysis of MCB was carried out for two reaction steps. Typically, the first step, the reaction solution of pH 4.0, containing 2.0×10^{-3} mol L^{-1} MCB and 2.0×10^{-4} mol L^{-1} catalyst, was heated and kept at desired temperature; the second step, the reaction solution was adjusted to pH 12 and kept at 25 °C for 10 h. Before heating, N_2 gas was passed into the solution for 30 min for the cases of reaction at temperature below 100 °C. For the cases of reaction above 100 °C the N_2 was passed into reaction solution until the reaction was completed. The sample was extracted from the reactor periodically, the concentrations of MCB and products were determined by HPLC with external standard method. The pH of solution was adjusted by H_2SO_4 or NaOH. On a carbon basis, the conversion of MCB X was calculated as $X = (C_0 - C_t)/C_0$), yield of reducing sugar Y was calculated as $Y = C_t'/C_0$ and the selectivity of reducing sugar S was calculated as S = Y/X. Where C_0, C_t are the concentrations of MCB at reaction time $t = 0$ and $t = t$, respectively. C_t' is the total concentration of reducing sugars (glucose, fructose) at time t.

Scheme 1 Synthesis of N^{α}-dodecyl-L-histidine



3 Results and Discussion

3.1 Critical Micelle Concentration of Surfactant

Surfactant molecules can aggregate to form micelles above the critical micelle concentration (*cmc*). The characteristics and the self-assembly supramolecular structure of micelle are far different from its monomer [33, 34]. In this work, the *cmc* of surfactant NDH was measured with the electrical conductivity method. From the plots of electric conductivity versus concentrations of NDH (Fig. 1), it can be seen that although the electric conductivity increased with increasing temperature at the same concentration, the shape of plots of κ versus c were similar at three temperatures. The values of cmc_1 were evaluated as 8.6×10^{-6}, 9.4×10^{-6} and 1.0×10^{-5} mol L^{-1}, respectively. And the values of cmc_2 were evaluated as 9.8×10^{-5}, 9.9×10^{-5} and 1.1×10^{-4} mol L^{-1}, respectively. It was possible that the aggregate state of NDH micelle changed with increasing concentration, and this resulted in two *cmc*. The phenomenon of several aggregate states appeared in aqueous solution were also reported by many researchers [35]. The increased effect of temperature on *cmc* may contribute to the destruction of the water structure surrounding the hydrophobic groups [36].

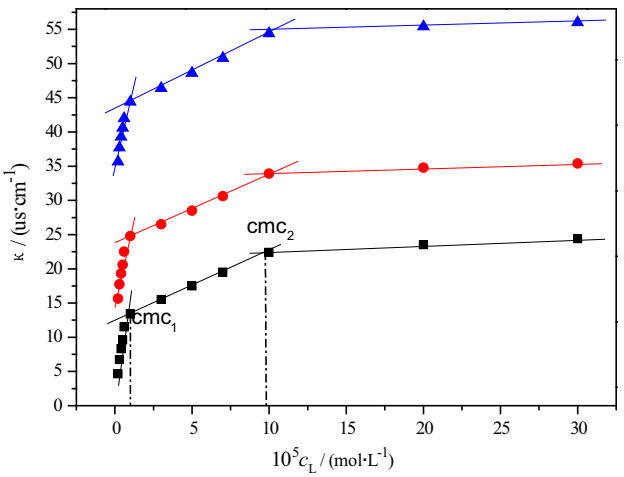


Fig. 1 Plots of electrical conductivity versus concentration of N^{α}-Dodecyl-L-histidine (NDH) at pH 4.0 and temperature 25 °C (*square*), 50 °C (*circle*), 90 °C (*triangle*)

3.2 Comparison of Catalytic Activity

MCB is stable and difficult to hydrolyze at pH 3–11 and 90 °C in aqueous solution. It was observed that MCB could be efficiently degraded only under strong acidic conditions in aqueous solution (Fig. S1 in the SI). However histidine and NDH micelle systems can catalyze the hydrolysis of MCB. The conversion of MCB and yield of reducing sugar for the MCB hydrolysis catalyzed by different systems at pH 4.0, 90 °C and reaction for 10 h were listed in Table 1. From Table 1 we can see that in the absence of catalyst MCB could degrade only 0.37 % and the yield of reducing sugar was just 0.36 % under this work' conditions, the NDH micelle showed excellent catalytic activity even at relatively low concentration. In previous reports it was found that the hydrophobic microenvironment of micelle played an important role in activating substrates, as well as changing the catalytic activity of catalysts [37, 38]. From Table 1 we found that the conventional micelles SDS, CTAB and Brij35 indeed promoted the catalytic activity of histidine. However the activity was obviously less than that of NDH micelle. In latest study, we found metallomicelle $La(DMBO)_2$ with N–OH functional group displayed excellent catalytic activity for conversion of cellobiose and the selectivity of monosaccharides (glucose, fructose and 1,6-anhydroglucose) reached 71 % in weakly alkaline aqueous solutions [39]. From Table 1 we can see that for NDH micelle catalyzed system, through two step processes the final hydrolysis products were glucose and fructose and the selectivity of monosaccharide reached 96.8 %. This is an ideal selectivity, which is even better than those caused by natural enzymes [40, 41].

3.3 Micelle-Catalyzed Kinetics for the Hydrolysis of MCB

In aqueous solution, micelle forms a pseudophase. Reaction can occur simultaneously in the micellar pseudophase and aqueous solution phase. The reaction kinetics of micelle catalysis was generally dealt with phase separation model [42], as described in Scheme 2. In micellar pseudophase, micelle M associates firstly substrate S to form an micelle-substrate complex MS with association constant K_s, then MS reacts to product P with rate constant k_m and releases simultaneously M. In aqueous solution phase, substrate S spontaneously reacts with rate constant k_w. The

Table 1 Comparison of catalytic activity for various systems

Systems	Conversion of MCB/ %	Yield of reducing sugar		Selectivity of reducing sugar/%
		Glucose/%	Fructose/%	
Bulk solution	0.37	0.36	–	97.3
His	4.60	3.40	1.10	97.8
NDH	15.4	11.2	3.70	96.8
SDS-His	9.4	6.59	2.45	96.2
CTAB-His	7.80	5.44	2.10	96.7
Brij35-His	6.60	4.53	1.84	96.5

$[MCB]_0 = 2.0 \times 10^{-3}$ mol L^{-1}, $[NDH] = 2.0 \times 10^{-4}$ mol L^{-1}, $[His] = 2.0 \times 10^{-4}$ mol L^{-1}, $[SDS] = 1.0 \times 10^{-2}$ mol L^{-1}, $[CTAB] = 5.0 \times 10^{-3}$ mol L^{-1}, $[Brij35] = 1.0 \times 10^{-3}$ mol L^{-1}, pH 4.0, 90 °C, 10 h

SDS-His, CTAB-His and Brij35-His are mixture systems of histidine with micelles SDS, CTAB and Brij35, respectively

$$M + S \underset{}{\overset{k_s}{\rightleftharpoons}} MS \xrightarrow{k_m} P + M$$

$$S \xrightarrow{k_w} P$$

Scheme 2 Kinetic model of micelle catalysis

first-order rate constant k_m in micellar phase can be calculated from Menger–Portnoy Eq. (1) [43, 44].

$$\frac{1}{k_{obsd} - k_w} = \frac{1}{k_m - k_w} + \frac{1}{k_m - k_w}\frac{N}{K_s}\frac{1}{c_D - cmc} \quad (1)$$

Equation (1) is the kinetic treatment model of micelle catalysis, where the k_{obsd} is the apparent first-order rate constants, c_D is the total surfactant concentration, N is the micelle aggregation number, cmc is the critical micelle concentration. In this work the value of cmc is 8.79×10^{-6} mol L^{-1}. From the Fig. 2 we can seen that the apparent first-order rate constants k_{obsd} increased with increasing concentration of surfactant. According to Eq. (1) the values of k_m and N/k_s can be calculated from slope and intercept of the plot of $1/(k_{obsd}-k_w)$ versus $1/(c_D-cmc)$, as shown in Fig. 3. The k_m and N/k_s was evaluated as 6.13×10^{-6} s^{-1} and 2.21×10^{-5} mol L^{-1}, respectively. The linear correlation coefficient was above 0.98. The values of $k_m/k_w = 4.23 \times 10^5$ was very large, which indicated that NDH micelle displayed excellent catalytic activity for the MCB degradation.

3.4 Effect of pH

From Fig. 4 it can be seen that for the micelle catalyzed system, pH has great influence on the yield of reducing sugar. Initially the yield of monosaccharide increased with increasing pH and reached a maximum at pH 4.0. The reduced sugar was detected as monosaccharides glucose and fructose. The effect of pH is related to the pKa of two

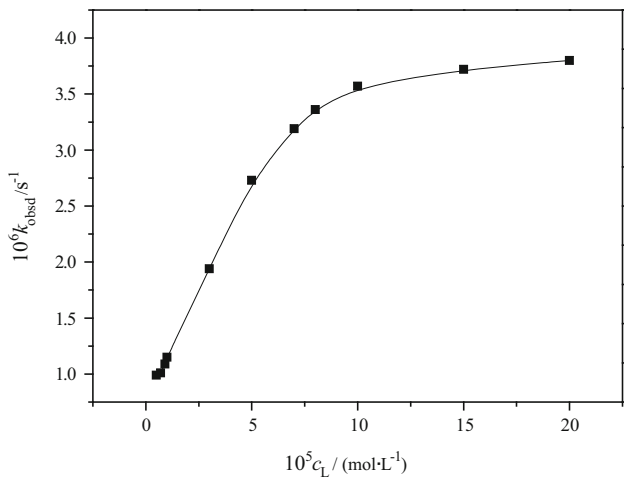


Fig. 2 Plot of the apparent first-order rate constants (k_{obsd}) versus concentration of surfactant NDH. $[MCB]_0 = 2.0 \times 10^{-3}$ mol·L^{-1}, pH 4.0, 90 °C

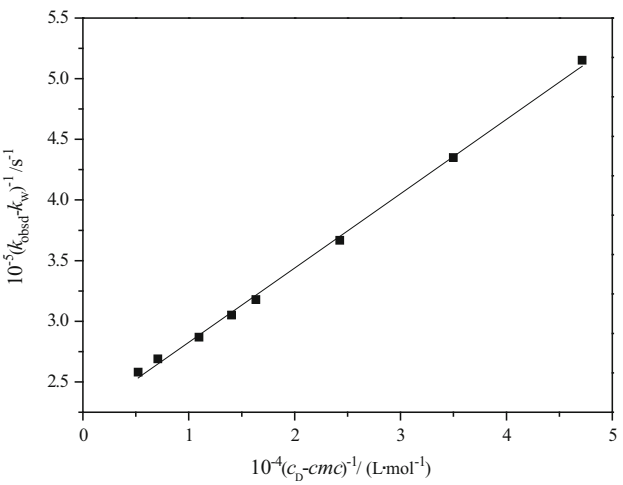


Fig. 3 Plot of $1/(k_{obsd}-k_w)$ versus $1/(c_D-cmc)$

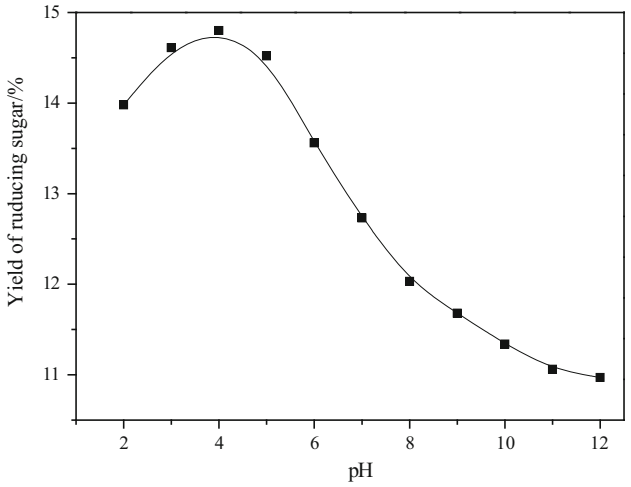


Fig. 4 Effects of pH on yield of reducing sugar catalyzed by NDH micelle. $[MCB]_0 = 2.0 \times 10^{-3}$ mol L^{-1}, $[NDH] = 2.0 \times 10^{-4}$ mol L^{-1}, 90 °C, 10 h

functional groups of NDH. The values of pKa_1(–COOH) and pKa_2(–Imidazole) of histidine are 1.82 and 6.86, respectively. Under the condition of pH 4.0, the imidazole group of histidine exists in its protonated form, the carboxylic acid group of histidine in its anionic form. It is considered that the imidazole served as an acid to protonate glycosidic oxygen and the carboxylic anion acts as a nucleophile to attack the C_1 atom. Thus this catalytic mechanism is very similar to that of endo-β-1,4-glucanase [45].

3.5 The Reaction Intermediate and Reaction Pathway

In this work, the hydrolysis of MCB underwent two processes: the first step was the reaction of MCB with NDH molecule in micellar solution at pH 4.0 and 80–110 °C; then the reaction intermediate was hydrolyzed at pH 12.0 and 25 °C. In order to understand the reaction pathway, we investigated the reaction product for the first step. Owing to the difficulty of detecting large molecule NDH and its derivative, a small molecule histidine was used as a substitute to react with MCB. After reacting 10 h at pH 4.0 and 90 °C, the reaction solution was checked by PAD-MS analysis. From the PAD-MS (E+) spectrum, it can be seen that a sugar ester intermediate L-histidine-5-D-glucopyranosyl ester (HDGE) which mass spectrometry peaks at 217.0 obviously appeared, as shown in Fig. 5. Therefore, it can be deduced that in the NDH micelle catalyzed process a substitution reaction occurred through the attack of COO^- to C_1 atom and resulted in the generation of sugar ester.

The sugar ester HDGE can be easily hydrolyzed in alkalic solution at room temperature. The catalytic mechanism, which first form sugar ester intermediate and then the ester is hydrolyzed, is similar to that of natural β-1,4-endoglucanase [46]. It is noted that although NDH micelle showed excellent catalytic activity for the cleavage of glucosidic bond and the formation of sugar ester, it showed very low activity for the hydrolysis of sugar ester under the condition of pH 4.0. This conclusion can be further reached by the quantitative analysis of concentration changes of MCB, sugar ester and glucose during reaction process. Figure 6 showed the HPLC profiles of reaction solution after the first and second step reaction, respectively. From Fig. 6 it can be seen that after hydrolysis at pH 12 and 25 °C for 10 h, the concentrations of MCB and methyl-glucoside were almost unchanged, however the total concentration of monosaccharides (glucose and fructose) obviously increased from 2.6 $\times 10^{-5}$ to 9.0×10^{-5} mol L^{-1}, which was attributed to the hydrolysis of sugar ester. The generation of fructose was owing to the isomerization of glucose under alkaline condition.

3.6 Reaction Kinetics and Activation Energy

Cellulose is difficult to hydrolyze because of the high reaction activation energy of β-1,4-linkages, it was reported that the rate constant k values was on the order of 10^{-15} s^{-1} at room temperature [47]. In order to accelerate the reaction, many researches were carried out at relative high temperature (>200 °C) [12, 13, 18]. However the defects of low selectivity and generation of lots of side-products obviously appeared under the elevated temperature condition. In this work we found that the reaction rate might be accelerated by increasing reaction temperature. And the selectivity of monosaccharide was good enough (>87 %) at the relative low temperature of less than 110 °C. The effects of temperature on conversion of MCB and yield of reducing sugar were described in Figs. S2 and 7, respectively. From Fig. S2 it can be observed that the conversion of MCB increased with increasing reaction temperature as well as reaction time. However the variation of yield of reducing sugar with reaction time was complex. Below 100 °C, the yield of reducing sugar increased with reaction time. Above 100 °C, initially the yield of monosaccharide increased with reaction time and reached a maximum for reaction about 10 h. At higher temperature products glucose and fructose would continue to degrade and thus led to the decrease of selectivity of monosaccharide. In kinetics, the consecutive reaction of monosaccharide would result in the appear of maximal point of yield of monosaccharide with time. The yield of reducing sugar were 9.7, 14.9, 27.7, 42.1, 51.3 % for a reaction time of 10 h at pH 4.0 at temperature of 80, 90, 100, 105 and 110 °C, respectively.

Kinetic reaction of hydrolysis of cellulose was generally described as pseudo-first-order reactions [48, 49]. From the

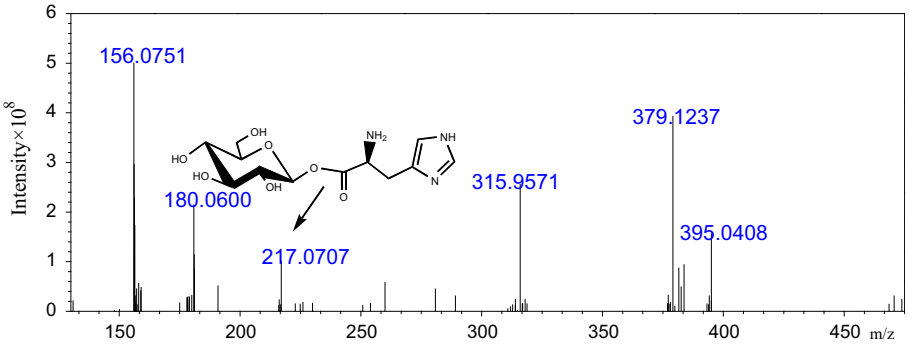


Fig. 5 PAD-MS (E+) spectrum of reaction solution of MCB degradation catalyzed by histidine. $[MCB]_0 = 2.0 \times 10^{-3}$ mol L^{-1}, [His] = 2.0×10^{-3} mol L^{-1}, pH 4.0, 90 °C, 10 h

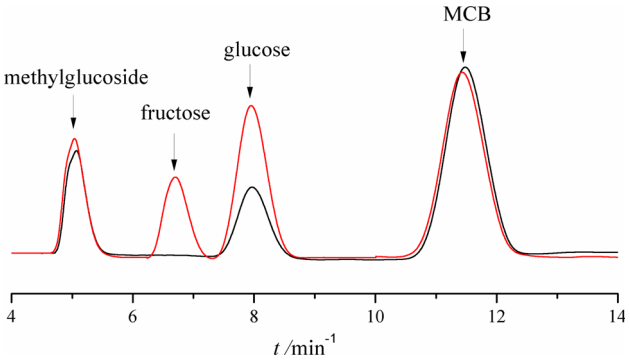


Fig. 6 HPLC profiles of reaction solution. $[MCB]_0 = 2.0 \times 10^{-3}$ mol L^{-1}, [His] = 2.0×10^{-3} mol L^{-1}. The first step reaction catalyzed by NDH micelle at pH 4.0, 90 °C, 10 h (*black line*); the second step reaction under alkalic condition at 25 °C, 10 h (*red line*)

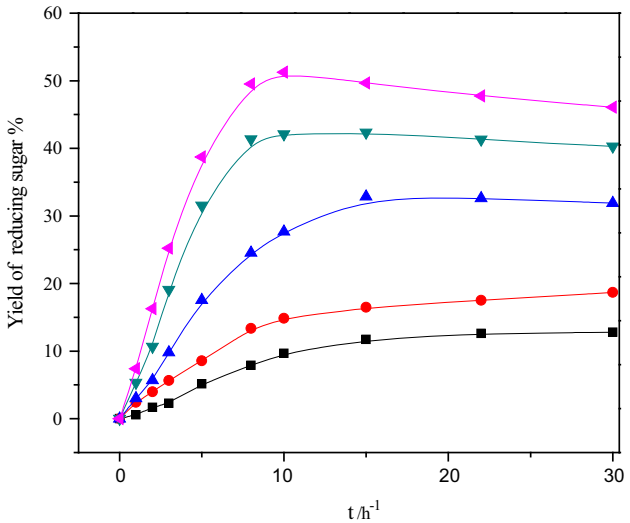


Fig. 7 Plots of yield of reducing sugar versus reaction time *t* for NDH micelle catalyzed system at pH 4.0 and temperatures 80 °C (*square*), 90 °C (*circle*), 100 °C (*up-pointing triangle*), 105 °C (*down-pointing triangle*), 110 °C (*left-pointing triangle*)

Figs. S3 and S4, we can seen that the plots of $-\ln(1-c_t/c_0)$ versus reaction time for the MCB conversion and generation of reducing sugar catalyzed by NDH micelle system at different temperature were all good linear lines. The activation energy E_a and pre-exponential factor A for MCB conversion and generation of reducing sugar were evaluated from the Arrhenius plots of $\ln k_{obsd}$ versus $1/T$, which were obtained easily through slope and intercept of liner respectively. As shown in Fig. 8, the correlation coefficient of linear were above 0.99. The activation energy Ea_1 and pre-exponential factors A_1 of MCB conversion were evaluated as 102.6 kJ mol^{-1} and 2.4×10^9 s^{-1}, respectively. The activation energy Ea_2 and pre-exponential factors A_2 of generation of reducing sugar catalyzed by NDH micelle system were evaluated as 93.8 kJ mol^{-1} and 1.5×10^8 s^{-1} respectively. The activation energy Ea_1 is somewhat larger than Ea_2 implied that there might be an undetectable parallel reaction occurred during the process of degradation of MCB. It has been reported that the activation energies of cellulose hydrolysis was in the range of 110–260 kJ mol^{-1} [50–52], and the activation energy of generation of reducing sugar was in the range of 130–180 kJ mol^{-1} [53, 54]. In this work, the activation energy of MCB conversion is relatively small, which indicated that the NDH micelle system displayed excellent catalytic activity for the breakage of β-1,4-glycosidic bond under mild conditions.

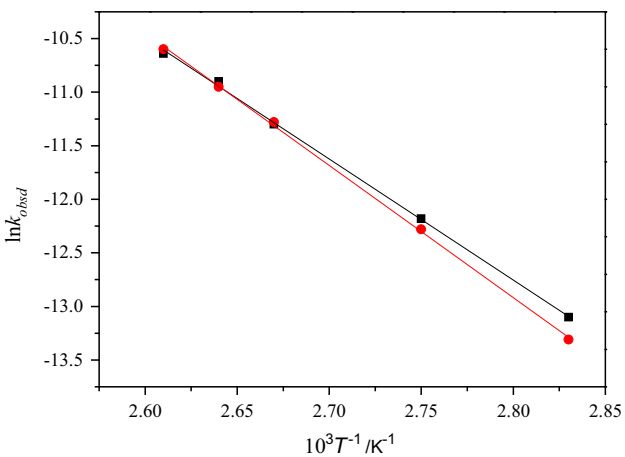


Fig. 8 Plots of $\ln k_{obsd}$ versus $1/T$ for MCB conversion (*circle*) and generation of reducing sugar (*square*) catalyzed by NDH micelle

4 Conclusions

A novel functional surfactant NDH was synthesized and its micelle was used to catalyzed the cleavage of β-1,4-glycosidic bonds of MCB under mild conditions. The results indicated that the micelle displayed excellent catalytic activity for the conversion of MCB in weakly acidic aqueous solution at relative low temperature (80–110 °C). Interestingly, this catalysis system display outstanding selectivity of monosaccharide below 100 °C ($S > 97$ %). The catalytic reaction first generated intermediate sugar ester and the ester readily hydrolyzed into reducing sugar in alkalic solution at ambient temperature. The reaction pathway and catalytic mechanism were similar to that of endo-β-1,4-glucanase. The activation energies for conversion of MCB and generation of monosaccharide in NDH micellar medium were evaluated as 102.6 and 93.87 kJ mol^{-1}, respectively.

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