

# Studies on 1-dodecene hydroformylation in biphasic catalytic system containing mixed micelle

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## Abstract

Hydroformylation of 1-dodecene catalyzed by water-soluble rhodium-phosphine complex,  $\text{RhCl}(\text{CO})(\text{TPPTS})_2$  (TPPTS:  $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})$ ), in the presence of various mixed micelles was investigated. When either an anionic surfactant sodium dodecyl sulfate (SDS) or dodecylbenzenesulphonate (DBS), a nonionic surfactant Triton X-100 or Brij 35, or alcohol was added into cationic surfactant cetyl pyridinium bromide (CPB) solution, a mixed micelle formed. The decrease in critical micelle concentration (CMC) and the increase in solubilization of 1-dodecene in the mixed micelle were observed. Hydroformylation of 1-dodecene exhibited higher conversion and higher regioselectivity in the mixed micellar solution than in the single micelle of CPB. The synergistic mechanism of two different surfactants was discussed.

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## 1. Introduction

Long-chain olefin hydroformylation catalyzed by water-soluble rhodium-phosphine complexes is a potential method for production of alcohols that are used as intermediates for surfactants, detergents, plasticizers and perfumery chemicals [1,2]. However, owing to the extremely low solubility of long-chain olefins in the aqueous phase, the reaction rate in biphasic catalytic system is very low. Extensive efforts have been devoted to finding an effective way to increase the reaction rate [3–6]. We previously

reported that 1-dodecene hydroformylation catalyzed by water-soluble rhodium complex was greatly accelerated when a cationic surfactant was added into the organic/aqueous biphasic system [7]. If the reaction is carried out in a mixed micellar solution containing two kinds of surfactants, the activity of rhodium-phosphine complex would be improved; it was observed that the mixture of dissimilar surfactants exhibited some superior properties to those of single surfactant component. In this paper, we studied the hydroformylation of 1-dodecene in different mixed micellar systems. The results indicated that there was a synergism of two surfactants forming a mixed micelle, which would construct a favorable microenvironment for the reaction acceleration.

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## 2. Experimental

### 2.1. Materials

Rhodium catalyst  $[\text{RhCl}(\text{CO})(\text{TPPTS})_2]$  and water-soluble phosphine (TPPTS) were synthesized in our laboratory according to the report [8]. All surfactants, alcohols and solvents were AR reagents. Cetyl pyridinium bromide (CPB) was recrystallized in acetone. Sodium dodecyl sulfate (SDS) was recrystallized in 95% alcohol. Nonionic surfactants: Brij 35 (Sigma) and Triton X-100 (Farco), anionic surfactants: dodecylbenzenesulphonate (DBS), 1-pentanol, 1-heptanol and substrate 1-dodecene (Fluka) were used without further purification. Distilled and deionized water was used in these experiments. Hydrogen (99.99%) and carbon monoxide (99%) were mixed directly with the ratio of 1:1 and treated with deoxidizer and desulfurizer prior to use.

### 2.2. Hydroformylation experiment

The hydroformylation reactions were carried out in a 60 ml stainless autoclave with magnetic stirrer. A typical reaction procedure was conducted as follows: rhodium catalyst, TPPTS, surfactant, alcohol, water and 1-dodecene were added into the autoclave, then the autoclave was evacuated and purged with syngas three times. When the temperature reached the desired value, syngas was introduced; its pressure was kept constant during the entire run. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water until ambient temperature, and the gas was vented slowly. The products were analyzed by GC HP 1890II with a FID and a capillary column of SE-30, 0.25 mm  $\times$  30 m.

### 2.3. Determination of critical micelle concentration

The critical micelle concentration (CMC) was determined by the conductivity method with a DDSJ-308 conductometer. The break point which indicated CMC was obtained by plotting the coefficient of conductivity  $\kappa$  against the surfactant concentration.

### 2.4. Measurements of 1-dodecene solubilization

The solubilization of 1-dodecene in various mixed micelles was measured after equilibrium using a TU-1901 ultraviolet-visible spectrometer. When 1-dodecene was solubilized fully in the micelle, the solution became cloudy. The break points were obtained by plotting absorbance against 1-dodecene volume.

## 3. Results and discussions

### 3.1. Critical micelle concentration of mixed micelle

We proved in our previous work [7] that only cationic micelle had an acceleration effect for 1-dodecene hydroformylation in the biphasic catalytic system. In this paper, CPB was used as a cationic surfactant and its concentration was kept constant. Another kind of surfactant or alcohol was added into the reaction system to form a mixed micellar solution. Papers [9,10] reported that in the system containing two kinds of surfactant there was a synergistic effect between the components, which could promote the mixed micelle formation under low surfactant concentration than in the single surfactant system. However, the thermodynamics of the mixed micelle was not investigated in detail. Therefore, it is necessary to determine CMC of the mixed micelles.

The changes of CMC with the addition of another surfactant or alcohol are shown in Figs. 1–3. At the

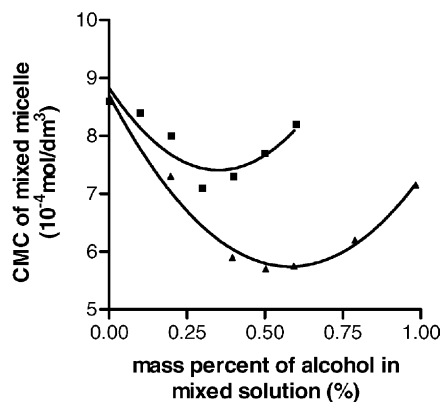


Fig. 1. Change of CMC with addition of alcohol. (▲) CPB and 1-pentanol, (■) CPB and 1-heptanol.

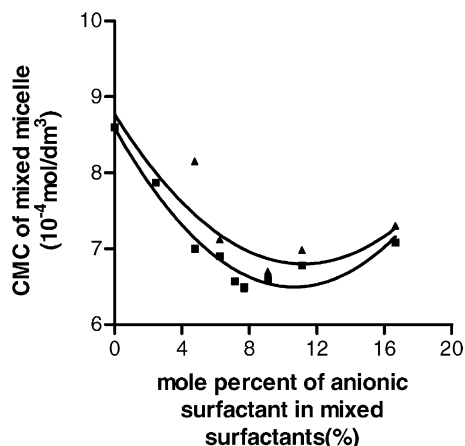


Fig. 2. Change of CMC with addition of anionic surfactant. ( $\blacktriangle$ ) CPB and DBS, ( $\blacksquare$ ) CPB and SDS.

beginning, CMC decreased obviously and there was a lowest point in the curve. The decrease in CMC was connected with the synergistic effect of the two components in the mixed micelle, which was named “nonideality” or “negative deviation from ideality” [11].

When another kind of surfactant or an alcohol was inserted into the micelle consisting of cationic surfactants like CPB, the hydrophilic group partly counterbalanced the charge of cationic hydrophilic groups. This would cause the increase of micelle size and the reduction of the electrical repulsion in the Stern layer of the micelle [12,13]. In other words, the charge den-

sity at the micelle surface decreased, and thereby the absolute value of the electrical potential was also reduced [13]. This charge separation effect would be more favorable for the formation of the mixed micelle at lower concentration of cationic surfactant. In addition to electrostatic forces, another contribution to nonideality was due to the interaction between hydrophobic groups of CPB and additive surfactant or alcohol. The “hydrophobic interaction” [14] could be a second effect on the mixed micelle formation in our research system.

### 3.2. Solubilization of 1-dodecene in mixed micelle

As seen in Fig. 4, the solubilizations of 1-dodecene were higher in all mixed micelles than in the single CPB micelle. The mixed micelle formed by CPB and either SDS or DBS had also higher solubilization ability than the mixed micelle formed by CPB and either Brij 35 or 1-heptanol. The results were connected with the strong electrostatic interaction between the cationic and anionic surfactants which would lead to larger negative deviation from ideality [11]. The decrease in CMC in the mixed surfactant solution would result in the formation of more micelle under the same cationic surfactant concentration and thus the total amount of olefin solubilization in micelle would increase.

It was well known that the micelles always were in dynamic equilibrium with individual surfactant

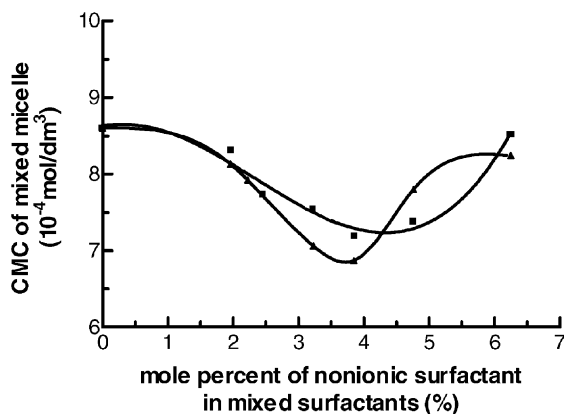


Fig. 3. Change of CMC with addition of nonionic surfactant. ( $\blacktriangle$ ) CPB and Triton X-100, ( $\blacksquare$ ) CPB and Brij 35.

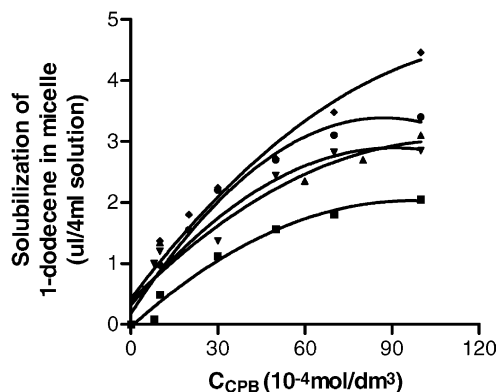


Fig. 4. Solubilization of 1-dodecene in various micelles. ( $\blacktriangle$ ) CPB, ( $\blacksquare$ ) CPB/Brij 35 = 22, ( $\blacktriangledown$ ) CPB with 0.5% 1-pentanol, ( $\bullet$ ) CPB/SDS = 12, ( $\blacklozenge$ ) CPB/DBS = 13.

molecules being constantly exchanged into and out of micelle. The micelle itself was continuously disintegrating and reforming. The micellar stability would influence many processes such as foaming, wetting, and solubilization [15]. In our research system, the hydrophobic groups of DBS and SDS had similar chain length to CPB but different from Brij 35 or alcohol, which could enhance the chain length compatibility effect [16] and increase the stability of the mixed micelles. This would also make the solubilizations of 1-dodecene in the mixed micelle of CPB/DBS and CPB/SDS larger than in mixed micelle of CPB/Brij 35 and CPB/1-heptanol.

### 3.3. Effect of temperature and mixed micelle composition on reaction rate

The effect of temperature on the reaction is listed in Table 1. The results suggested that the conversion of 1-dodecene increased with increasing temperature. When the temperature was over 100 °C, the conversion decreased, which could be attributed to the reduction of syngas solubility in the solution.

The data in Figs. 5–7 showed that when another surfactant or alcohol was added in a suitable amount into the solution containing CPB, the conversion of 1-dodecene was significantly increased from about 8–11 to 30–50% except for the system of CPB/Triton X-100. The regioselectivities of 1-dodecene hydroformylation also increased slightly. When anionic surfactant SDS or DBS was introduced, the content of normal aldehyde increased from 77.8 to 81.5%, but it decreased to 76.7% with the further addition of anionic surfactant over 9%. The addition of nonionic surfactant or alcohol also caused the content of normal aldehyde to increase from 77.8 to 81.8%. If the concentrations of anionic surfactant were too high, the reaction rate decreased to a certain extent. In hydro-

Table 1  
Effect of temperature on the reaction (CPB/DBS = 8)

Temperature (°C)	Conversion (%)
80	24.9
90	40.3
100	68.9
110	60.0

Reaction conditions are same as in Fig. 5.

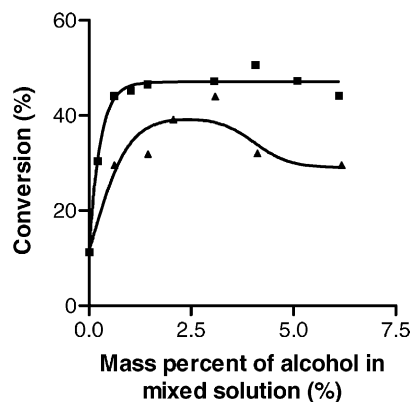


Fig. 5. Relationship between conversion and concentration of alcohol. (■) CPB and 1-pentanol, (▲) CPB and 1-heptanol. Reaction conditions: 1 MPa (constant), 90 °C, 1-dodecene/[Rh] = 2343, [RhCl(CO)(TPPTS)<sub>2</sub>] = 9.6 × 10<sup>-4</sup> mol/dm<sup>3</sup>, P/Rh = 18 (mole ratio), 1-dodecene = 2 ml, V<sub>aq</sub>/V<sub>oil</sub> = 2 (volume ratio), [CPB] = 3 × 10<sup>-3</sup> mol/dm<sup>3</sup>, 3 h.

formylation of 1-dodecene the hydrogenation product dodecane was less than 2% and no isomeric dodecene was detected. The acceleration of 1-dodecene hydroformylation in the mixed micellar solution was attributed to the following factors: Firstly, the rhodium catalyst was enriched in the micellar interfacial layer by the electrostatic attraction of CPB cationic end for the anionic species of rhodium complexes as we had reported in the literature [7]. If the concentration of anionic surfactant in the solution was too high, it was

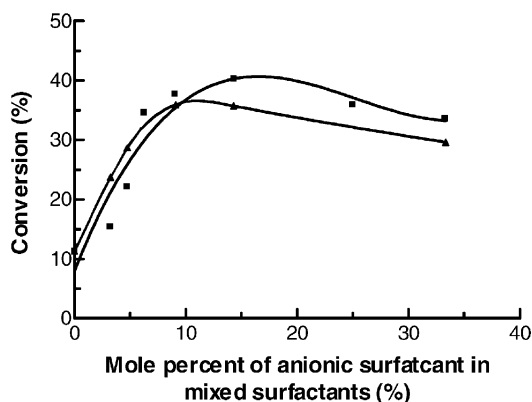


Fig. 6. Relationship between conversion and concentration of anionic surfactant. (■) CPB and DBS, (▲) CPB and SDS. Reaction conditions are same as in Fig. 5.

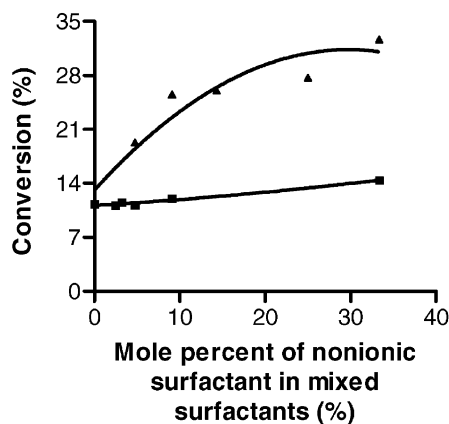
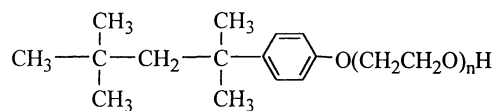
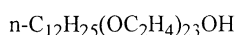


Fig. 7. Relationship between conversion and concentration of non-ionic surfactant. (▲) CPB and Brij 35, (■) CPB and Triton X-100. Reaction conditions are same as in Fig. 5.



$n \approx 10$

Triton x-100



Brij-35

Scheme 1.

unfavorable for the enrichment of rhodium catalyst in interfacial layer because the positive charge density of the micellar surface was reduced. Therefore, the conversion rate of 1-dodecene decreased at high concentration of SDS or DBS. Secondly, the olefin solubilization amount was much higher in the mixed micelle than in the single CPB micelle as shown in Fig. 4. This was more favorable for the transfer of olefin from micellar core to its interfacial layer where olefin coordinated with rhodium complex. Thirdly, the addition of alcohol could cause the change of the solution properties, which would enhance the solubility of olefin in the aqueous phase, thereby promoting the reaction.

The obvious difference in the conversions with the mixed micelle formed by CPB and nonionic surfactant Brij 35 or Triton X-100 could result from their different structures. As shown in Scheme 1, the hydrophobic

group in Brij 35 was a longer linear alkyl chain. This was favorable for the formation of the mixed micelle because of the stronger hydrophobic interaction between CPB and Brij 35. However, the hydrophobic interaction between CPB and Triton X-100 was weaker and the mixed micellar structure of CPB/Triton X-100 was looser than CPB/Brij 35 system because the hydrophobic group in Triton X-100 contained a branched alkyl chain and a phenyl group. Therefore, the addition of Triton X-100 did not obviously increase the reaction rate.

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