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Long chain olefin hydroformylation in biphasic catalytic system—how the reaction is accelerated

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Abstract

The effect of TPPTS [$p(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$], $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ and olefin on CMC (critical micelle concentration) of the aqueous solution containing cationic surfactant cetyltrimethylammonium bromide (CTAB) was studied by the maximum bubble pressure method. The apparent molar mass of micelle was determined by a light scattering method. The results showed that the addition of TPPTS and $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ into aqueous solutions of CTAB caused the decrease of CMC and the increase of the apparent molar mass of micelle. The data supported the suggestions about enrichment of rhodium catalyst in micelle interface layer and about the solubilization of olefin in micelle. This explanation was confirmed by the measurements of rhodium concentration in the interface layer using ICP method. The acceleration mechanism of long chain olefin hydroformylation in a biphasic catalytic system containing a cationic surfactant was provided.

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Keywords: Olefin hydroformylation; Biphasic catalysis; Rhodium complex; Micelle concentration

1. Introduction

The interfacial chemistry in biphasic catalysis is an attractive and infant field for many chemists. Cornils and co-workers [1] had investigated the hydroformylation of propylene in aqueous biphasic catalysis. They demonstrated that the reaction took place in the liquid boundary layer at the gas/liquid interface and did not take place in the bulk of the liquid. Fell and Papadogianakis [2] and Hanson and co-workers [3] inferred that the hydroformylation of long chain olefins of aqueous/organic biphasic catalytic system occurred in the interfacial layer. Russel [4] assumed that there

was an organized array in a reaction solution containing catalyst, surfactant and substrate molecules. Li and co-workers had reported that [5–8] the addition of a cationic surfactant such as CTAB greatly accelerated the hydroformylation of long chain olefins. They suggested that the solubilization of olefin in cationic surfactant micelle and the anionic catalytic species binding to the interface of cationic micelle were the important factors for the reaction acceleration.

In order to obtain more information about the function of CTAB and the interfacial reaction mechanism in biphasic catalytic systems, we studied the changes of the critical micelle concentration (CMC) of CTAB and the apparent molar mass of micelle in different constituent solutions. The concentrations of rhodium catalyst in aqueous, organic and interfacial layers were determined. Such results can help us to understand

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how the long olefin hydroformylation was accelerated in aqueous/organic biphasic systems.

2. Experimental

2.1. Materials

1-Dodecene (>96%, Fluka), CTAB (Denmark), Pyrene (Sigma) and organic solvents (AR) were commercial products and were not treated prior to use. The trisodium salt of [tri(*m*-sulfonphenyl)-phosphine] (TPPTS) was prepared by the method described in the literature [9]. The content of TPPTS oxide was less than 5%. The catalyst precursor, $\text{RhCl}(\text{CO})(\text{TPPTS})_2$, was synthesized according to our report [10]. Water was doubly distilled. Hydrogen (99.9%) and carbon monoxide (99%) were purchased and treated with deoxidizer and desulfurizer.

2.2. Measurement methods

The surface tensions (γ) were measured by the maximum bubble pressure method. The γ values were calculated according to the Laplace equation [11]:

$$\Delta P = \frac{2\gamma}{r}$$

where ΔP is maximum pressure difference between the inside and outside of the bubble and r is the radius of capillary of the instrument. Light scattering measurements of the micelle solutions were conducted on a laser light scattering analyzer as reported in the literature [12]. The experimental device was designed based on the Raleigh scattering formula. A CCD camera system was used to collect the scattering light caused by the micellar solution. The signals were sent to a computer and the molar mass of micelle was found from a Debye Plot as described later. The hydroformylation of 1-dodecene was carried out in an autoclave of 100 ml with a magnetic stirrer. The typical procedure had been described in the literature [6]. At the end of the reaction, the solution was cooled and then transferred to a separatory funnel. Organic layer and aqueous layer were taken out from the top and bottom of the funnel, respectively. The middle layer (about 1 ml) containing a part of organic solvent and water was kept in the funnel. The rhodium complexes in the

organic layer and the middle layer were converted to water-soluble rhodium species using aqua regia treatment after organic compounds were removed. The concentration of rhodium in the three solutions was determined by ICP [Jarrel-Ash Division IACP 9000 (N + M)]. The products of 1-dodecene hydroformylation were analyzed by GC HP1890II, equipped with (FID) and a column (30 m \times 0.25 mm) SE-30.

3. Results and discussions

3.1. Change of surface tension

In order to understand the properties of micelle in the catalytic reaction system, the change of surface tension of CTAB solutions in water and in a mimic reaction mixture of different constituents was measured at 60 °C. The results are plotted in Fig. 1. From the profiles, we found that the CMC of CTAB decreased gradually with the addition of $\text{RhCl}(\text{CO})(\text{TPPTS})_2$, TPPTS or 1-dodecene. CMC of CTAB in water was about 1.0×10^{-3} mol/l. When rhodium complex was added into aqueous solution of CTAB, CMC decreased to about 0.7×10^{-3} mol/l. The value of CMC decreased further to about 0.4×10^{-3} mol/l with the addition

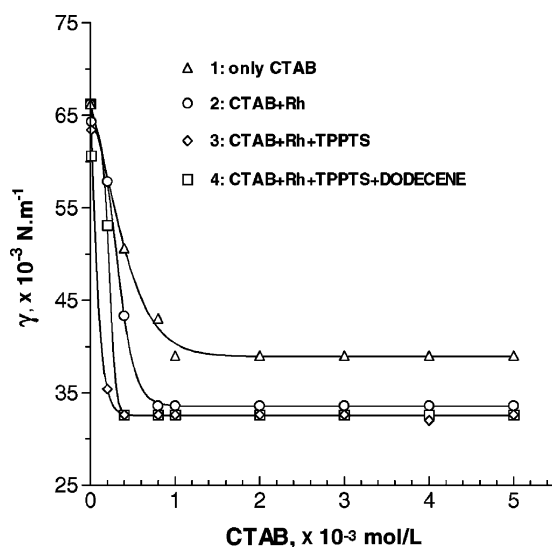


Fig. 1. Profiles of surface tension γ vs. CTAB concentration, $[\text{RhCl}(\text{CO})(\text{TPPTS})_2] = 9.6 \times 10^{-4}$ mol/l, $[\text{TPPTS}]/[\text{Rh}] = 16$ (mole ratio), 1-dodecene: 2.5 ml, 60 °C.

of TPPTS and 1-dodecene into the solution containing the rhodium complex. These results suggested that the acceleration of 1-dodecene hydroformylation in biphasic catalytic system was correlated with micelle formation and CMC decrease.

3.2. Apparent molar mass of micelle

The change of apparent molar mass M of micelle was determined by a laser light scattering method [13]. M values were calculated from the intercept $1/M$ in Debye plots of CTAB solution. Light scattering for the dilute solutions of micelle, when the scattering angle θ is 90° , can be described as follows [14–16]:

$$\frac{K(C-\text{CMC})}{(R_{90}^C - R_{90}^{\text{CMC}})} = \frac{1}{M} + 2A_2(C-\text{CMC}) \quad (1)$$

where M is the apparent molar mass of micelle, A_2 the second virial coefficient, R_{90}^C the Rayleigh ratio at the scattering angle of 90° for the solution at the surfactant concentration C , R_{90}^{CMC} the Rayleigh ratio at the scattering angle of 90° for the solution at the critical micelle concentration CMC and K is the optical constant and is written as:

$$K = \frac{2\pi^2 n_1^2 (dn/dc)^2}{N_A \lambda^4}$$

here dn/dc is the specific refractive index increment of the solution, n_1 the refractive index of the solvent, N_A the Avogadro number and λ is the wavelength of incident light (633 nm). Based on the experimental data, $K = 3.64 \times 10^{-9} \text{ dm}^2 \text{ mol/g}^2$.

If C , CMC and R_{90}^C are determined, according to Eq. (1) a Debye plot describing the linear relation between $(C-\text{CMC})/(R_{90}^C - R_{90}^{\text{CMC}})$ and $(C-\text{CMC})$ can be drawn. The M value can be calculated from the intercept $1/M$ in the plot. The plots for different solutions are shown in Fig. 2. The M of CTAB micelle in water was 32.3 kg/mol. When rhodium catalyst and TPPTS were added into the CTAB solution, the M increased to 45.5 kg/mol. This could be attributed to the binding of anionic species produced by dissociation of $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ and TPPTS on the micelle surface of cationic end of CTAB. If 1-dodecene was introduced into the above-mentioned solution, the M value rose further to 50.0 kg/mol. This was owing to the solubilization of 1-dodecene in hydrophobic core of micelle, as reported in the literature [14].

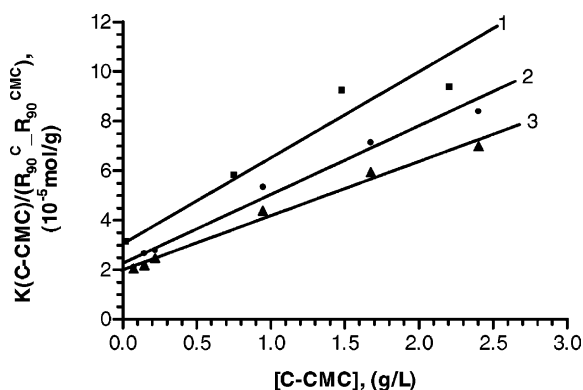


Fig. 2. Debye plot of CTAB solutions (1) CTAB aqueous solution; (2) CTAB aqueous solution containing rhodium catalyst and TPPTS; (3) CTAB aqueous solution containing rhodium catalyst, TPPTS and 1-dodecene.

3.3. Distribution of rhodium in a biphasic system

Rhodium concentration values in aqueous phase, in organic phase and in the middle interface layer between water and organic phase were determined by ICP method after the end of the reaction. The results listed in Table 1 suggest that rhodium concentrations in the three layers exhibited very large differences. According to the rhodium distribution, 69.0% of rhodium still remained in the aqueous layer; this value was higher than 30.1% in the interfacial layer and 0.9% in the organic layer. However, the rhodium concentrations were different from the rhodium contents in the three layers. Rhodium concentration in the interfacial layer was 29.1 ppm, which was about 91 and 727 times higher than in the aqueous layer (0.32 ppm) and in the organic layer (0.04 ppm), respectively. Although, rhodium catalyst was not soluble in organic solvent, the organic layer was saturated by water owing to the violent stirring during the reaction thus a little amount of rhodium catalyst was brought by water into the organic phase. After the organic layer was

Table 1
Rhodium distribution in three layers after the end of hydroformylation

	Aqueous layer	Interfacial layer	Organic layer
Volume (ml)	29.0	2.0	9.0
Rh content (%)	69.0	30.1	0.9
Rh concentration (ppm)	0.32	29.1	0.04

extracted by water, the content of rhodium in it was similar to the blank value. The above-mentioned determinations demonstrated the enrichment of rhodium catalyst in the micellar interfacial layer. These results were in agreement with the data of light scattering measurements.

3.4. Discussion

Our investigations further confirmed that the micelle of cationic surfactant created a very suitable microenvironment for the olefin hydroformylation in aqueous/organic biphasic systems. Two factors played important roles in the reaction. One was the enrichment of rhodium catalyst in the micellar interfacial layer. A positively charged electrostatic field formed on the cationic micelle interface. This field would attract anionic active species, $[\text{HRh}(\text{CO})[p(m\text{-(C}_6\text{H}_4\text{SO}_3)_3)_n]^{3n-}]$, from aqueous solution. The other factor was the solubilization of olefin in the hydrophobic core of micelle. This provided a transport passage and reduced the energy barrier in the transport process of olefin molecule from the core of micelle to its interface. Therefore, in the micelle microenvironment, an olefin molecule easily coordinated with the active species of rhodium catalyst in the interfacial layer; thereby the hydroformylation would be greatly accelerated.

The experimental data of 1-dodecene hydroformylation in biphasic system as listed in Table 2 and reported in the previous literature [17] also supported the explanation. If CTAB was not added into the solution, the reaction did not occur at 100 °C and 1.0 MPa for 2 h. However, when CTAB was introduced into the solution and its concentration was higher than the CMC, the conversion of 1-dodecene was 79.4% under

the same reaction conditions. If the anionic surfactant SDS (sodium dodecyl sulfate) was added into the solution, the hydroformylation of 1-dodecene was inhibited completely, because the negative charge on the anionic micelle interface repulsed the anionic active species of rhodium catalyst and thus the olefin did not easily coordinate with the rhodium complex. Therefore, we suggested that the acceleration of 1-dodecene hydroformylation in biphasic catalytic system in the presence of CTAB was a synergistic effect of the above-mentioned two factors, but the enrichment of rhodium catalyst in the micelle interface was the most key factor.

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Table 2
Effect of surfactant on 1-dodecene hydroformylation

Surfactant	Conversion (%)
Nil.	0
CTAB ^a	79.4
SDS ^b	0

Reaction conditions: $[\text{Rh}] = 3.54 \times 10^{-4}$ mol/l, $[\text{TPPTS}]/[\text{Rh}] = 16$ (mole ratio), 1-dodecene = 0.04 mol, 100 °C, total pressure = 1.0 MPa, $\text{H}_2/\text{CO} = 1 : 1$, 2 h.

^a $[\text{CTAB}] = 9 \times 10^{-3}$ mol/l.

^b $[\text{SDS}] = 5.5 \times 10^{-3}$ mol/l.