

# Micellar effect of cationic gemini surfactants on organic/aqueous biphasic catalytic hydroformylation of 1-dodecene

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## Abstract

The promotional effect of cationic gemini surfactants for the hydroformylation of 1-dodecene in the organic/aqueous biphasic catalytic system is reported. Cationic gemini surfactants with a flexible spacer (G(Eth), G(But) and G(Hex)) and rigid spacer (G(Xyl)) group were used in the reaction. The critical micelle concentration (CMC) and solubilization of laurylbenzene in gemini surfactant solutions were determined. The influence of the concentration of gemini surfactants and the stirring rate on 1-dodecene hydroformylation were investigated. The reaction results showed that in the biphasic catalytic system the hydroformylation of 1-dodecene catalyzed by  $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ -TPPTS [TPPTS = tris(sodium-*m*-sulfonatophenyl) phosphine] in the presence of gemini surfactants occurred with higher turn over frequency (TOF) and higher regioselectivity toward linear aldehyde (L/B) than those obtained with the conventional monomeric surfactant CTAB. The phenomena could be attributed to the fact that the gemini surfactant has lower CMC and better surface tension reduction ability; moreover it could form more compact and spherocylindrical micelle in the solution. These properties would be favorable for the decrease in the phase transfer energy barrier, thereby greatly accelerating the reaction rate. Meanwhile, the more compact structure of the spherocylindrical micelle formed from gemini surfactant could construct a favorable microenvironment for the formation of linear aldehyde. The comparison of the acceleration effect of the three type surfactants (monomeric surfactant CTAB (cetyltrimethylammonium bromide), gemini surfactant G(Eth), G(But), G(Hex)), G(Xyl) as well as double chain surfactant DCMAB (di(cetylmethyl)ammonium bromide) indicated that the surfactant structure had an important effect on the reaction rate. Their promotion order is  $\text{DCMAB} > \text{G(Eth)} \approx \text{G(But)} \approx \text{G(Hex)} \approx \text{G(Xyl)} > \text{CTAB}$ . © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Hydroformylation; 1-Dodecene; Gemini surfactant; Biphasic catalysis; Rhodium catalyst

## 1. Introduction

Aqueous/organic two-phase catalysis has recently become a very active field of research [1,2]. The processes using water as the solvent are environmentally and economically attractive. The water-soluble transition metal complexes have been used as catalysts in several important commercial processes. For example, the water-soluble catalyst  $\text{HRh}(\text{CO})(\text{TPPTS})_3$  has been used for the hydroformylation of propene [3]. However, in the case of higher olefins, this process is limited owing

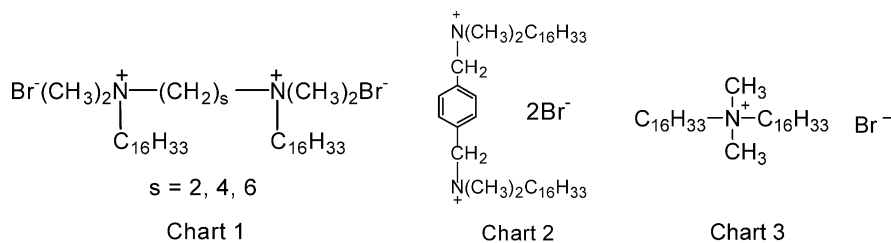
to the very slow reaction rate resulting from the extreme low solubility of the substrate in the aqueous phase [4]. To solve this problem, we added surfactants into the system to increase the solubility of the substrate in water [5]. The amphiphilic nature of the surfactants drastically lowers the surface tension of water because the aggregates such as micelles or vesicles form above the critical micelle concentration (CMC). The hydrophobic substances could be solubilized in the aggregates, thus resulting in the improvement in the mass transfer process [6]. This strategy has been used in the rhodium-TPPTS system [7,8].

In recent years, extensive attentions in research have been given to the solution behavior of a new kind of bis (quaternary ammonium bromide) surfactants named as gemini [9–13] with general formula (charts 1 and 2)

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in which two alkyldimethylammonium bromide moieties are connected by a polymethylene or *p*-xylyl, referred to as a spacer. The spacer may be flexible (chart 1) or rigid (chart 2). This type of gemini surfactant has already been comprehensively characterized and shows interesting properties in aqueous solution [11]. For example, they can be more easily adsorbed in the interface between water and air and more easily concentrate in the bulk water phase and form micelle than the corresponding single tail surfactants [9].

Up to now, extensive micellar catalytic reactions carried out in conventional monomeric surfactant solutions have been reported [14,15]. However, only few papers deal with micellar effect on the catalysis in gemini surfactant solutions [16–18]. To the best of our knowledge, it still remains unknown as to the micellar effect of gemini surfactants in the organic/aqueous biphasic system catalyzed by water-soluble transition metal complex.

In our previous work [19–21], we studied the biphasic hydroformylation of 1-dodecene catalyzed by Rh–TPPTS complexes in monomeric surfactant solutions. The results showed that cationic surfactant such as CTAB could form cationic micelle, thereby greatly accelerating the reaction rates. In this paper, we went further into the biphasic catalytic hydroformylation of 1-dodecene in the gemini surfactant solutions. For comparison, surfactant DCMAB [di(cetylmethyl)ammonium bromide] (chart 3) with one ionic head and two long alkyl tails was also studied. The results indicated that gemini surfactants were superior to monomeric surfactant of CTAB in micelle formation and surface tension reduction; the higher conversion of 1-dodecene and higher regioselectivity toward the linear aldehyde could be obtained in the gemini surfactant solutions.

## 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 [22]. Cetyltrimethylammonium bromide [CTAB] (Sigma), *N,N,N',N'*-tetramethyl-1,2-ethylene(1,4-butane, or 1,6-hexane)diamine (Acros), *N,N*-dimethylhexadecylamine (Acros), 1-bromohexadecane (Fluka),  $\alpha,\alpha'$ -dibromo-*p*-xylene (Aldrich) and 1-dodecene (Fluka) were commercially obtained and used without further purification. Deionized and distilled water was used in all these experiments. Hydrogen (99.99%) and carbon

monoxide (99%) were mixed directly with the ratio of 1:1 and treated with deoxidizer prior to use.

### 2.2. Synthesis and characterization

The gemini surfactants (chart 1) were synthesized according to the literature [9]. The gemini surfactants ( $s = 2, 4$  and 6) were named as G(Eth), G(But) and G(Hex), respectively. The gemini surfactant containing a *p*-xylyl spacer (chart 2) named as G(Xyl) was synthesized as the literature reported [13]. Surfactant DCMAB was obtained by refluxing 1-bromohexadecane with *N,N*-dimethylhexadecylamine in absolute ethanol (at 80 °C) for 48 h. The solvent was removed in vacuum from the reaction mixture and the solids thus obtained were recrystallized from ethanol/petroleum ether mixture for at least three times. The identity was confirmed by  $^1\text{H}$  NMR with a Bruker AVANCE-300 (300 MHz) NMR spectrometer.  $\text{CDCl}_3$  was used as solvent.

For G(Eth),  $\delta$ : 0.87–0.89 (6H, alkyl chain,  $2 \times 1\text{CH}_3$ ), 1.27 (44H, alkyl chain,  $2 \times 11\text{CH}_2$ ), 1.39 (8H, alkyl chain,  $2 \times 2\text{CH}_2$ ), 1.84 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{N}^+$ ), 3.42–3.53 (12H,  $2 \times 2\text{CH}_3\text{N}^+$ ), 3.72 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{N}^+$ ), 4.76 (4H, spacer chain,  $2 \times 1\text{CH}_2\text{N}^+$ ).

For G(But),  $\delta$ : 0.87–0.89 (6H, alkyl chain,  $2 \times 1\text{CH}_3$ ), 1.26–1.36 (52H, alkyl chain,  $2 \times 13\text{CH}_2$ ), 1.61 (4H, alkyl chain,  $2 \times 1\text{CH}_2$ ), 1.73 (4H, spacer chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{N}^+$ ), 2.06 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{N}^+$ ), 3.40 (12H,  $2 \times 2\text{CH}_3\text{N}^+$ ), 3.75 (4H, spacer chain,  $2 \times 1\text{CH}_2\text{N}^+$ ).

For G(Hex),  $\delta$ : 0.89 (6H, alkyl chain,  $2 \times 1\text{CH}_3$ ), 1.26–1.36 (52H, alkyl chain,  $2 \times 13\text{CH}_2$ ), 1.78 (4H, spacer chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+$ ), 2.16 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{N}^+$ ), 2.68–2.72 (4H, spacer chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{N}^+$ ), 3.29 (12H,  $2 \times 2\text{CH}_3\text{N}^+$ ), 3.43 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{N}^+$ ), 3.97 (4H, spacer chain,  $2 \times 1\text{CH}_2\text{N}^+$ ).

For G(Xyl),  $\delta$ : 0.85–0.88 (6H, alkyl chain,  $2 \times 1\text{CH}_3$ ), 1.26–1.36 (48H, alkyl chain,  $2 \times 12\text{CH}_2$ ), 1.83 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+$ ), 2.30–2.37 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{CH}_2\text{N}^+$ ), 3.22 (12H,  $2 \times 2\text{CH}_3\text{N}^+$ ), 3.56 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{N}^+$ ), 5.26 (4H, benzyl,  $2 \times 1\text{CH}_2\text{N}^+$ ), 7.79 (4H, phenyl,  $4 \times 1\text{CH}$ ).

For DCMAB,  $\delta$ : 0.87 (6H, alkyl chain,  $2 \times 1\text{CH}_3$ ), 1.26–1.82 (56H, alkyl chain,  $2 \times 14\text{CH}_2$ ), 3.43 (6H,  $2 \times 1\text{CH}_3\text{N}^+$ ), 3.49–3.55 (4H, alkyl chain,  $2 \times 1\text{CH}_2\text{N}^+$ ).

### 2.3. Solubilization measurements

The solubilization of laurylbenzene in gemini surfactant micelles was examined as follows. Aqueous solutions of

G(Eth) covering a suitable range of concentration below and above its critical micelle concentration (CMC) were prepared. Different small volumes of laurylbenzene were added to the series of G(Eth) solutions by a microinjector. After they were shaken for 24 h at  $37 \pm 1^\circ\text{C}$  in a water bath incubator, the solutions were kept thermostatically for 16 h. The ultraviolet absorption of the transparent solution was determined using a TU-1901 ultraviolet–visible spectrometer. The solubility of laurylbenzene in G(Eth) solutions at a certain concentration was obtained by plotting adsorption against the volume of added laurylbenzene.

#### 2.4. Hydroformylation experimental

The hydroformylation was carried out in a 60 mL stainless autoclave with a magnetic stirrer. A typical reaction procedure was conducted as follows: rhodium catalysts, TPPTS, surfactant, water and 1-dodecene were added into the autoclave, then the autoclave was evacuated and purged with syngas for three times. When temperature reached the desired value, syngas was introduced and kept at a constant pressure during the entire reaction run. After a given reaction time, the stirring was stopped and the autoclave was cooled quickly with cold water to 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,  $0.25\text{ mm} \times 30\text{ m}$ .

### 3. Results and discussion

#### 3.1. CMC and solubilization ability of gemini surfactants

The CMC of G(Eth) and G(Hex) in water was determined using the drop volume method. The results were  $3.8 \times 10^{-5}$  and  $6.1 \times 10^{-5}\text{ mol/dm}^3$ , respectively. These CMC values are lower than that of CTAB, which is  $9.6 \times 10^{-4}\text{ mol/dm}^3$ . Gemini surfactants contain two identical amphiphilic moieties covalently connected at the level of head groups by a spacer. In this way, the separation gap between the polar head groups within the gemini surfactants is smaller than that in monomeric surfactants when they aggregate, therefore, the surface activities enhance significantly and CMC values decrease substantially [23].

Since 1-dodecene has no absorption in UV–vis region, the laurylbenzene which has a similar normal dodecyl chain, was used as the solubilizing agent in G(Eth) solution. As seen in Fig. 1 the solubility of laurylbenzene increased gradually as the concentration of G(Eth) increased. This trend is in agreement with the report [24] and demonstrates that the non-polar substances can be significantly solubilized in gemini micelle.

#### 3.2. Influence of surfactant concentration

As shown in Fig. 2, the influences of gemini surfactants G(Eth), G(But), G(Hex) and monomeric surfactant CTAB

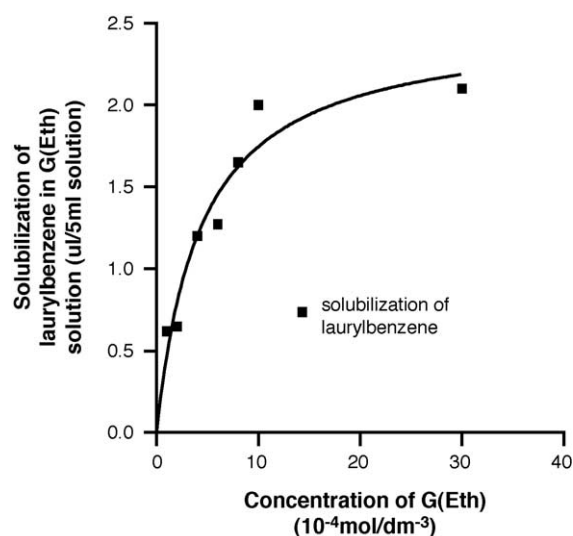


Fig. 1. Solubilization of laurylbenzene in G(Eth) solutions.

concentration on the reaction rate exhibited a similar trend; i.e. all TOFs of 1-dodecene hydroformylation increased with the increase in surfactant concentration. When the concentration was low, the conversion was very low. Actually, almost no aldehyde was detected if no surfactants were added to the reaction solution, because of the super low solubility of 1-dodecene in the aqueous phase. However, with the increase in surfactant concentration, the TOF increased quickly and in a high concentration the TOF reached a very high value. But there was a difference between the TOF values in gemini surfactant solutions and those in monomeric surfactant CTAB solutions. The high TOF values were obtained in a lower concentration in gemini surfactant solutions, while the high TOF values in CTAB solutions emerged at a higher concentration.

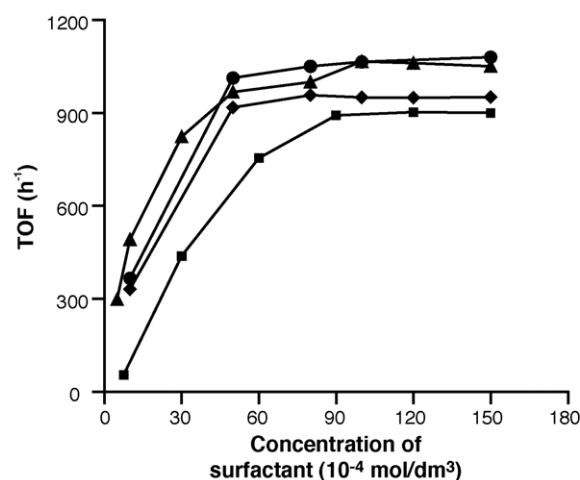


Fig. 2. Influences of spacer chain length on TOF in gemini surfactant and CTAB solutions. (■) CTAB; (□) G(Hex); (▲) G(Eth); (●) G(But). Reaction conditions: syngas 2 MPa (constant),  $100^\circ\text{C}$ , 1-dodecen/[Rh] = 2343,  $[\text{RhCl}(\text{CO})(\text{TPPTS})_2] = 9.6 \times 10^{-4}\text{ mol/dm}^3$ , P/Rh = 18 (mole ratio), 1-dodecene = 2 mL,  $V_{\text{aq}}/V_{\text{oil}} = 2$  (volume ratio), 2 h, 600 rpm.

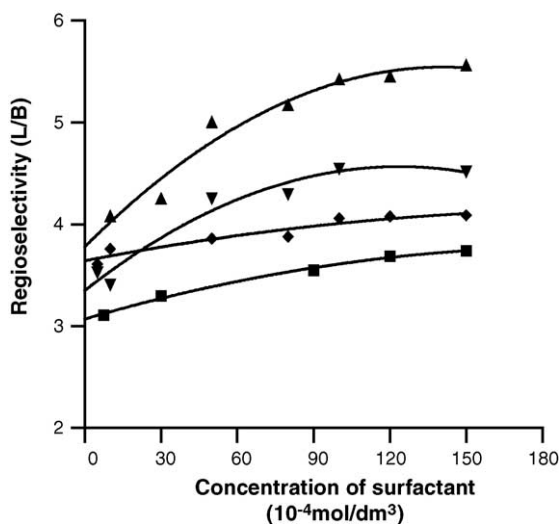


Fig. 3. Influences of spacer chain length on regioselectivity in gemini surfactant and CTAB solutions. (■) CTAB, (□) G(Hex), (▼) G(But), (▲) G(Eth). Reaction conditions are the same as in Fig. 2.

In the hydroformylation of 1-dodecene the hydrogenation product dodecane and isomeric dodecene were less than 3 and 2%, respectively.

The regioselectivity toward linear aldehyde, L/B (mole ratio between linear aldehyde and branched aldehyde) showed obviously different dependence on the concentration for the four surfactants. As shown in Fig. 3, L/B values increased a little from 3.1 to 3.7 with the increase in CTAB concentration. For the three dimeric surfactants G(Eth), G(But) and G(Hex), L/B values of aldehyde were marked different as shown in Fig. 3. For G(Hex) with six methylene groups as the spacer the L/B increased a little from 3.6 to 4.1. But for G(But) with four methylene groups as the spacer the L/B increased from 3.6 to 4.6. Very interestingly, in G(Eth) with only two methylene groups as the spacer, L/B increased substantially from 3.6 to 5.5. The results suggested that the shorter the carbon chain length of the spacer, the higher was the regioselectivity of 1-dodecene hydroformylation. This confirms again that the compact micelle structure is favorable for the formation of normal aldehyde [19].

Since the polymethylene chain spacer introduces a chemical “constraint” between the surfactants by connecting them two by two at the level of the ionic head [9], the gemini surfactant, unlike CTAB, could not form the conventional spherical micelle, especially when the spacer is short. When the surfactant concentration reaches its CMC, the formation of micelle can promote the substrate transfer from the core of micelle to interface of organic/aqueous phases and thus the TOF values increased quickly. With further increase in the surfactant concentration, more and larger micelle formed and the TOF increased to a high value near  $1100 \text{ h}^{-1}$ . At high surfactant concentrations the O/W microemulsion may form in the presence of organic compounds, especially in the presence of polar aldehydes formed in the reaction [19]. This could also cause the increase in interfacial area, but its increase

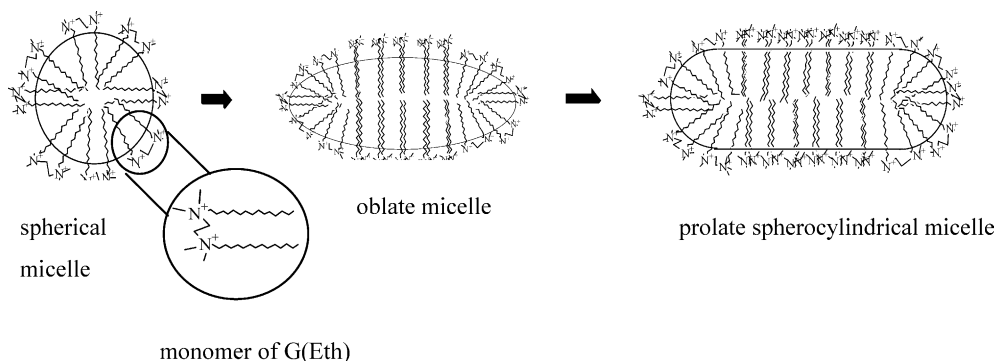
was limited. Therefore, the increase in the conversion became gradually slow and leveled off at high concentrations. The decrease in the conversion was also observed with the formation of emulsion when the surfactant concentration was too high.

However, the regioselectivity of the reaction, L/B of aldehyde exhibited very different trends among the three gemini surfactants as shown in Fig. 3. When the surfactant concentration was low, the L/B ratio was almost at the same value of 3.6 for the three gemini surfactants. But with the increase in the G(Eth) concentration the L/B ratio increased substantially while in the other two G(But) and G(Hex) solutions, L/B increased only a little. This reaction result could be attributed to the fact that the three gemini surfactants have different chain length of spacers. As Soma De and co-workers [25] reported that the SANS (small angle neutron scattering) analysis clearly indicated that the extent of aggregate growth and the variations of shapes of the dimeric micelles depend primarily on the spacer chain length. Zana and co-workers [26] reported that the dimeric surfactants with short spacers have a very strong propensity for micellar growth and formation of micelles with very low curvature. Talmon and co-workers [27] also reported a sphere-to-cylinder transition in aqueous micellar solutions of a gemini surfactant. The low curvature prolate micelle has a more compact and orderly structure than the spherical micelle. It is well known that in this reaction system the micelle works as a microreactor and its structure plays an important role in the regioselectivity of the reaction. So L/B of aldehyde has a higher value in micelle than in alcoholic solvents [19]. The reaction results that L/B decreased gradually from G(Eth) to G(Hex) with the increase in spacer chain length at a higher surfactant concentration could be attributed to the fact that G(Eth) forms large, compact and prolate micelle while G(But) and G(Hex) form spherical micelle. The spherocylindrical part of the prolate micelle also has a more orderly and compact structure than the spherical micelle as shown in Scheme 1. Therefore, this orderly and compact microcircumstance is favorable for the formation of a linear aldehyde.

### 3.3. Influence of the stirring rate

The influences of stirring rates on the hydroformylation of 1-dodecene in the four surfactant solutions are shown in Table 1. The conversions increased gradually with the increase in the stirring rate. Stirring could increase the contact interface area between organic and aqueous phases [28]. The conversions were low without stirring owing to the low solubility of 1-dodecene in the aqueous phase. Interestingly, the conversions were high in the gemini surfactant solutions, although the reaction mixtures were not stirred. Especially in the G(Eth) solution, the conversion achieved 56%, which was much higher than that in CATB solution (5%). The large increase in the conversion may be due to the high surface tension reduction ability [9] and solubilization [24] of olefin in micellar solution of gemini surfactants. Actually, C<sub>20</sub> of the gemini surfactant, which stands for the surface tension





Scheme 1. Schematic structure of three kinds of micelle with different curvatures.

Table 1  
Influence of stirring rates on the reaction

Stirring rates (rpm)	G(Eth)		G(But)		G(Hex)		CATB	
	Conversion (%)	L/B	Conversion (%)	L/B	Conversion (%)	L/B	Conversion (%)	L/B
0	56.05	7.0	52.24	5.8	36.56	4.6	4.29	3.7
300	80.17	5.3	78.27	4.3	63.55	3.8	62.45	3.5
500	83.96	4.7	79.30	4.2	69.92	3.6	64.61	3.4
600	84.88	4.4	85.59	4.3	78.4	3.9	73.47	3.4
800	81.49	4.2	78.13	4.1	78.67	3.6	71.59	3.4

Reaction conditions are the same as in Fig. 2 except the variation of stirring rates. Surfactant concentrations are kept at  $5 \times 10^{-3}$  mol/dm<sup>3</sup> constantly.

lowering efficiency of surfactant, is about two to three orders of magnitude lower than that of single chain surfactant [29]. It is this high surface tension lowering ability of gemini surfactant that leads to the greatly higher conversion.

The L/B values decreased gradually with the increase in stirring rates. The high stirring rate would disturb the regular structure of micelle and thereby decrease the selectivity toward linear aldehyde as shown in the literature [30].

### 3.4. Influences of surfactant structure

The comparative investigation on the promotion of catalytic performance of three types of surfactant, monomeric surfactant CTAB, gemini surfactant G(Eth) and G(Xyl), as well as double chain surfactant in 1-dodecene hydroformylation was carried out in the organic/aqueous biphasic system. The data listed in Fig. 4 shows that the activity promoting order of the surfactants was DCMAB > G(Eth) ≈ G(Xyl) > CTAB. In CTAB solution TOF value was about 800 h<sup>-1</sup> at a high surfactant concentration (10<sup>-2</sup> mol/L). In G(Eth) and G(Xyl) solutions higher TOF values (1000 h<sup>-1</sup>) were observed at a low concentration (5 × 10<sup>-3</sup> mol/L). DCMAB exhibited the best promoting catalytic performance, TOF values could achieve about 1200 h<sup>-1</sup> at the same low concentration (5 × 10<sup>-3</sup> mol/L). The difference may be attributed to the different structures of these surfactants. The lower CMCs of surfactants G(Eth) (about 3.8 × 10<sup>-5</sup> mol/L), G(Xyl) (about 6.7 × 10<sup>-5</sup> mol/L) and DCMAB, as well as their stronger ability for surface tension reduction, were responsible for the better acceleration in 1-dodecene hydroformylation. The difference in regioselectivities is shown in Fig. 5. The L/B values in G(Xyl)

solutions were lower than that in G(Eth) solutions. Menger and co-workers reported [10] that the gemini surfactant G(Xyl) with a rigid *p*-xylyl unit as the spacer tended to assemble into small, rapidly tumbling micelle. When the surfactant G(Xyl) concentration increases, the <sup>1</sup>H NMR signals indicate little or no sphere-to-rod transitions of micellar shape. This phenomenon is in contrast to the G(Eth) with flexible methylene spacer as reported by Zana and co-workers [26]. In addition, a benzene ring can be approximated, generally, as being equivalent to 3–3.5 methylene units in length, and then the *p*-xylyl spacer is equivalent to 5–5.5 methylene units just as the spacer length of G(Hex). Therefore, the small spherical micellar structure,

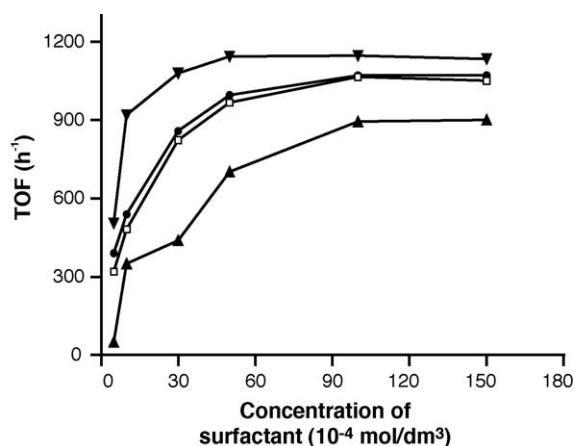


Fig. 4. Influences of spacer structure on TOF in various surfactant solutions. (▲) CTAB, (□) G(Eth), (●) G(Xyl), (▼) DCMAB. Reaction conditions are the same as in Fig. 2.

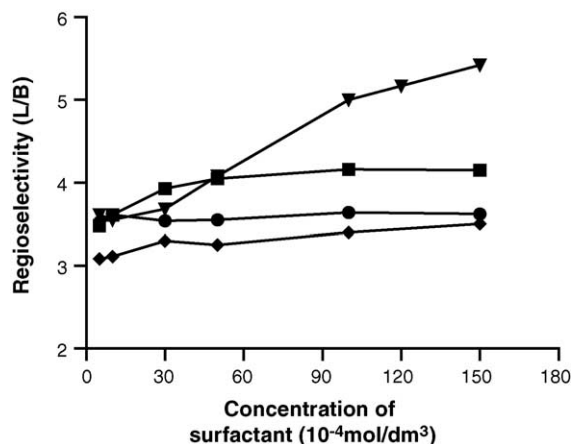


Fig. 5. Influences of spacer structure on regioselectivity (L/B) in various surfactant solutions. (□) CTAB, (●) DCMAB, (■) G(Xyl), (▼) G(Eth). Reaction conditions are the same as in Fig. 2.

long spacer chain length and larger head group of G(Xyl) would lead to low selectivity toward linear aldehyde.

The second long alkyl chain of the double-chained surfactant DCMAB is long enough to penetrate into the micelle core and the hydrophobic interaction is enhanced in the DCMAB solution as Bai and co-workers reported [31]. So the CMC of surfactant DCMAB is much lower than that of CTAB, which is able to lead to higher TOF value at lower surfactant concentrations but its influence on L/B value is very small.

### 3.5. Recycling experiments

The major merit in using water-soluble catalyst would be a facile recycling of the costly rhodium complex. The recyclability of this RhCl(CO)(TPPTS)<sub>2</sub>-TPPTS-gemini surfactant system in the hydroformylation of 1-dodecene was studied by performing a series of consecutive runs for five times. After each run and cooling the reaction mixture to room temperature the separation of the organic phase from aqueous phase was carried out. The results listed in Table 2 suggest

Table 2  
Catalyst recycling results for the hydroformylation of 1-dodecene<sup>a</sup>

Entry	Conversion (%)	L/B
1	76.42	5.6
2	74.22	5.0
3 <sup>b</sup>	72.48	5.4
4 <sup>c</sup>	68.56	5.1
5	65.47	4.9

<sup>a</sup> Reaction conditions are the same as in Fig. 2. The catalyst recycling experiments were performed as follows: after completion of the reaction the autoclave was cooled for 30 min to ambient temperature and the syngas was vented slowly. The reaction solution system was transferred into a separatory funnel and let it stand for 10 min until the two phases were separated. The aqueous phase containing rhodium catalyst was transferred into the autoclave and reused directly. The organic product phase was separated and analyzed.

<sup>b</sup> Five milligrams of gemini surfactant G(Eth) was added into the aqueous phase.

<sup>c</sup> Five milligrams of TPPTS was added into the aqueous phase.

that when a little quantity of gemini surfactant or TPPTS was supplemented this catalytic system could be recycled pretty well with a little decrease in activity and selectivity. However, the rhodium loss and leaching into organic phase could not be avoided completely using this Rh-TPPTS-surfactant system especially when the surfactant concentration was higher. Furthermore, since the amphiphilic nature of gemini surfactants and its aggregation in the interface layer between the aqueous and organic phases, the catalytically active species were attracted and concentrated at the micelle interface, leading to a part of rhodium loss in the operation of phase separation. To solve this problem, we could use two methods. One method was the increase in the amount of TPPTS (P/Rh ratio) added, which could coordinate and immobilize the rhodium catalyst in aqueous phase. The rhodium leaching into organic phase was 9.8 ppm (0.18% in total rhodium) as detected by the ICP method after the reaction when P/Rh ratio was 18. But the rhodium loss was not detected when the P/Rh ratio is increased to 54 with the increase in the L/B ratio of aldehyde production from 5.2 to 7.2 and a little decrease in the conversion. The other method was the extraction of organic phase by concentrated TPPTS aqueous solutions after the reaction. After the extraction for five times 25–50% of the total lost rhodium in organic phase could be extracted back to the TPPTS solutions.

## 4. Conclusions

The application of gemini surfactant micellar system in hydroformylation of higher olefin is an efficient alternative approach to the acceleration of biphasic catalytic processes. Higher conversions and better selectivity toward the linear aldehydes can be obtained in gemini surfactant solutions with short spacer chain length than those obtained with conventional monomeric surfactants.

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