Biphasic Catalytic Hydroformylation of 1-Dodecene in Micellar System with Cationic Gemini Surfactants

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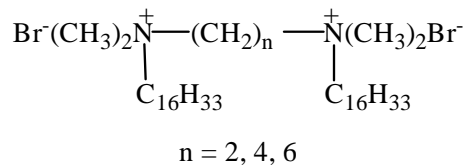Xue Yuan HUANG, Yao Zhong LI, Xian Jun LI*

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Abstract: The promotion effect of cationic gemini surfactants for the hydroformylation of 1-dodecene in the organic/aqueous biphasic catalytic system is reported. The hydroformylation reaction in the presence of gemini surfactant occurred with higher turnover frequency and higher selectivity for linear aldehyde than using conventional monomeric surfactant CTAB.

Keywords: Hydroformylation, gemini surfactant, 1-dodecene, rhodium catalyst.

The water-soluble transition metal complexes have been used as catalysts in several important industrial processes. For example, the water-soluble catalyst $HRh(CO)(TPPTS)_3$ is used in the hydroformylation of propene[1]. However, hydroformylation of long chain olefin is limited due to the very low solubility of the substrate in the aqueous phase. The results of our research[2-4] showed that the micelle formation of cationic surfactant could greatly accelerate the hydroformylation of long chain olefins in biphasic catalytic system.

In the recent years, the extensive attentions have been paid to a new kind of bis(quaternary ammonium bromide) surfactants named as gemini surfactant[5] in which two alkyldimethylammonium bromide moieties are connected by polymethylene referred as a spacer. This type of gemini surfactant had been already characterized and showed interesting properties in aqueous solution[6]; but its catalytic performance in olefin hydroformylation has not been reported. The three gemini surfactants, containing two, four and six methylene groups as spacer, were synthesized according to the literature[7]. They are named as G(Eth), G(But) and G(Hex), respectively.

$$Br^-(CH_3)_2\overset{+}{N}\text{———}(CH_2)_n\text{———}\overset{+}{N}(CH_3)_2Br^-$$

$$\underset{C_{16}H_{33}}{|}\qquad\qquad\underset{C_{16}H_{33}}{|}$$

$$n = 2, 4, 6$$

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The hydroformylation of 1-dodecene was carried out in the biphasic catalytic system containing water soluble phosphine ligand TPPTS [TPPTS=tris(sodium-*m*-sulfonatophenyl) phosphine], catalyst $RhCl(CO)(TPPTS)_2$ and the cationic surfactants. The results indicated that gemini surfactants are superior to monomeric surfactant of CTAB in micelle formation and surface tension reduction, therefore the higher turn over frequency (TOF) of 1-dodecene and higher regioselectivity for the linear aldehyde can be obtained in the gemini surfactant solution.

As shown in **Figure 1**, the relation between TOF and the concentration of surfactant exhibited a similar trend whether in gemini surfactants G(Eth), G(But), G(Hex) or monomeric surfactant CTAB solutions.   All values of TOF increased with the increase of surfactant concentration. TOF increased quickly in the range of low surfactant concentration.   The values of TOF almost did not change when the surfactant concentration were higher than 5×10^{-3} mol/L [G(Eth), G(But) and G(Hex)] or 8×10^{-3} mol/L (CTAB).   However the values of TOF for gemini surfactant solution were always higher than that of CTAB solution.   Especially there was a large difference with TOF in the range of low surfactant concentration.   For example, when the surfactant concentration was 3×10^{-3} mol/L, the values of TOF were about 850 h^{-1} and 450 h^{-1} for gemini surfactant and CTAB solution, respectively.   These phenomena were attribute to that gemini surfactant could form micelle under lower concentration in aqueous solution than that of CTAB and the solubility of olefin in gemini surfactant solution was higher than that in CTAB solution.

The regioselectivities of the hydroformylation of 1-dodecene showed different trends for the four surfactants.   As shown in **Figure 2**, the L/B ratio of aldehyde increased from 3.1 to 3.7 with the increase of monomeric surfactant CTAB concentration.   For the three gemini surfactants G(Eth), G(But) and G(Hex) the L/B ratio of aldehyde rose from 3.6 to 4.1, 4.6 and 5.7, respectively with the increase of gemini surfactant concentration.   These phenomena suggested that the gemini surfactant with short spacer could form more compact structure of the spherocylindrical micelle[6] and construct a favorable microenvironments for the formation of linear aldehyde.

The influences of stirring rate on the hydroformylation of 1-dodecene in the four surfactants solutions were shown in **Table 1**.   The conversions exhibited a similar trend, *i.e.* they increased gradually with the increase of stirring rate.   Without stirring the conversions were low due to the low solubility of 1–dodecene in aqueous phase.   In this condition the conversion was lower than 5% in monomeric surfactant CTAB solution. Interestingly, the conversions were rather high (36-56%) in the gemini surfactant solutions even the reaction mixtures were not stirrd, especially in the G(Eth) solution.   The high surface tension reduction ability and solubility of olefin in micellarsolution of gemini surfactants may be the reason.

The high stirring rats would disturb the regular structure of micelle of surfactant and thereby the selectivity for linear aldehyde decreased as reported in the literature[2].

Summarily, the above-mentioned results indicated clearly that the gemini surfactants were more superior catalyst promoter than monomeric surfactants.   They were more favorable for acceleration and regioselectivity of the reaction for linear aldehyde in the biphasic catalytic hydroformylation of 1-dodecene.

Figure 1   TOF of 1-dodecene hydroformylation in surfactant solutions
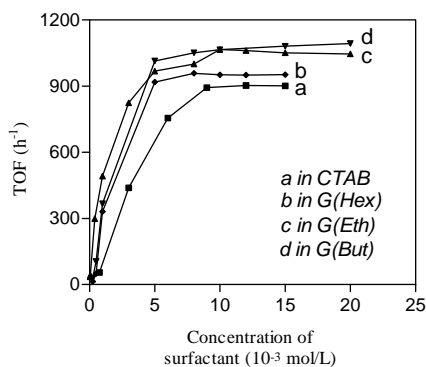
Figure 2   Regioselectivity of 1-dodecene hydroformylation in surfactant solutions
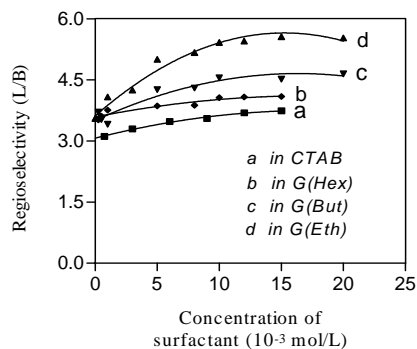
Table 1   Influences of stirring rates on the reaction

Stirring rates (rpm)	G(Eth)		G(But)		G(Hex)		CATB	
	Conv.(%)	L/B	Conv.(%)	L/B	Conv.(%)	L/B	Conv.(%)	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

The other reaction conditions are the same as in **Figure 1**, except the variation of stirring rates and surfactant concentration=5×10^{-3} mol/L

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