ELSEVIER

Catalysis Today 42 (1998) 459–470

CATALYSIS TODAY

Catalytic asymmetric hydrogenation in micellar media with amphiphilic and non-amphiphilic ligands

Günther Oehme*, Ingrid Grassert, Silke Ziegler, Roland Meisel, Hans Fuhrmann

Institut für Organische Katalyseforschung an der Universität Rostock e.V., Buchbinderstraße 5-6, 18055 Rostock, Germany

Abstract

The transfer of a homogeneous catalytic hydrogenation catalyst into an aqueous micellar system was investigated. In case of the asymmetric hydrogenation activity and enantioselectivity were enhanced in water due to the addition of surfactants. A variation of the microheterogenization in water was realized with new amphiphilic ligands derived from Brij (polyoxyethylene ethers) and PPM (4-diphenylphosphino-2-diphenylphosphinomethyl-pyrrolidine). The substrate could be solubilized in the micellar assemblies. Best results were observed in mixed micelles: the enantioselectivity achieved 96% ee. New practical aspects are given by use of polymerized surfactants which we prepared by polymerization of assemblies.

1. Introduction

Homogeneous catalysis in a technical scale has been established since 1950. In comparison to heterogeneous catalytic systems homogeneous catalysts have the advantages of high activity and selectivity, good reproducibility and mild conditions but often have the disadvantage of product and catalyst separation and recycling of the catalyst. Therefore, much research has been done to convert homogeneous systems into multiphase systems. Scheme 1 exhibits different possibilities of heterogenization.

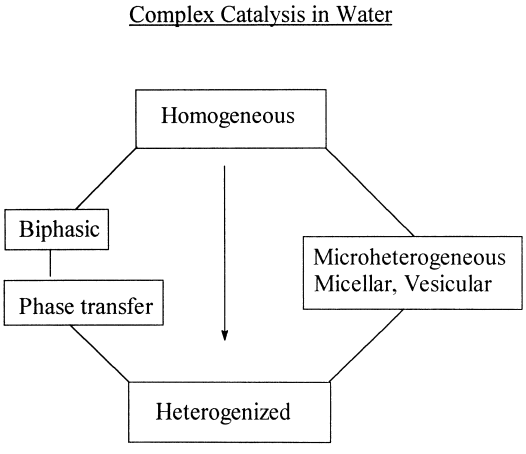
The central method is the immobilization of a homogeneous catalyst on the surface of an organic or inorganic support. In many examples the activity is lower than in the homogeneous system and the stability of the supported catalyst is not satisfying. More successful in technical application seems to be the transformation into a biphasic or phase transfer liquid–liquid system, which is realized in the Shell Higher Olefin Process (SHOP) [1] and also in the hydroformylation process of Ruhrchemie-Rhone Poulenc [2]. Precondition of a biphasic system are two immiscible solvents of extremely different polarity, usually water and an organic solvent. This is an important argument for the use of water as solvent in complex catalysis (water is also the solvent for natural processes and useful for enzyme mimetic reactions).

A third method of heterogenization is given in Scheme 1 on the right. It is a microheterogenization in the colloidal range with self-organized amphiphilic molecules as the catalyst support. A simplified interrelation between surfactant structure and the morphology of spherical aggregates is given in Fig. 1.

The real order of surfactants in micelles and vesicles is less regular than depicted in Fig. 1[3]. Significantly, micelles are kinetically labile assemblies

*Corresponding author. Tel.: int. 381 4669330, fax: int. 381 4669324; e-mail: goehme@chemie1.uni-rostock.de

0920-5861/98/$32.00
PII S0920-5861(98)00128-X



Scheme 1.

with an association–dissociation rate within milliseconds [4]. Nevertheless, micelles can solubilize organic and inorganic compounds and influence their reactivity in a positive and sometimes in a negative manner [5]. A consequence of the extreme polarity gradient between surface and core of the micelle is that a substrate can be enclosed in an appropriate environment. Activation of encapsulated reactants is called micellar catalysis [6].

Different types of micellar catalysis are discussed by Morawetz in an early review [6]:

The functionalized surfactant forms the micelle and reacts as an educt.
The interaction between the reacting species and the micelle influences the rate of reaction.
The micelle carries catalytically active groups and acts as a catalyst.

The influence of the second point seems to be most common, but surfactants with catalytically active groups are gaining more importance as models for enzymes, particulary in the case of metal complexes as active groups for metalloenzymes [7]. There are certain similarities between enzymatic and micellar catalysis with respect to hydrophobic and hydrophilic zones but usually the effects in micellar catalysis are much smaller [8].

According to Brown et al. [9] the rate enhancement consists in a combination of the following effects:

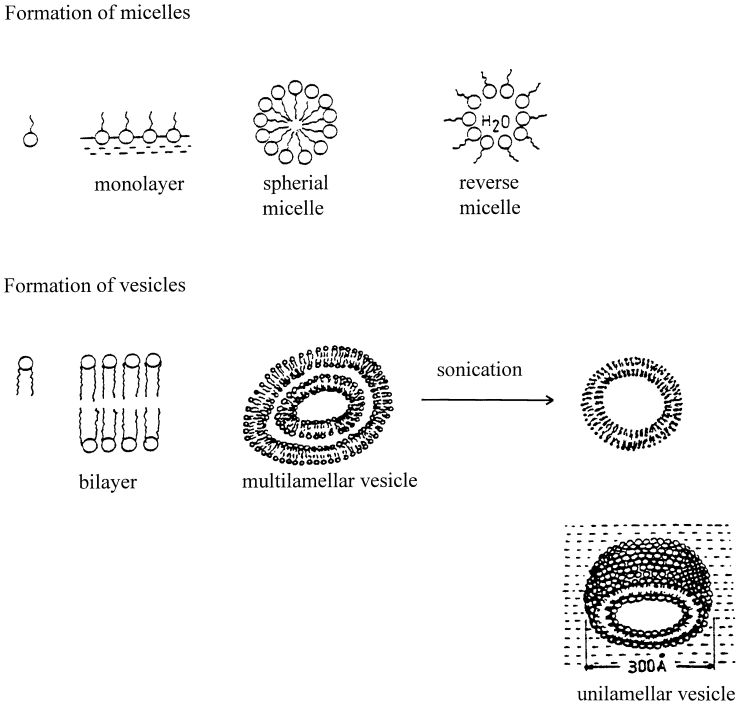


Fig. 1. Principle of self-organization of different types of amphiphiles (all pictures are idealized).

A medium effect due to the lower dielectric constant within the micelle compared to water.
The transition state of the reaction is stabilized by the polar head group.
The reactants are concentrated within the micelle. Thus the rate of bimolecular reactions should be increased. Surfaces of ionic surfactant micelles are more acid or more basic than the surrounding water phase.

The early literature of micellar catalysis and their critical discussion is summarized in a series of books and reviews [10].

A micellar influence is observed in the following types of complex catalyzed reactions:

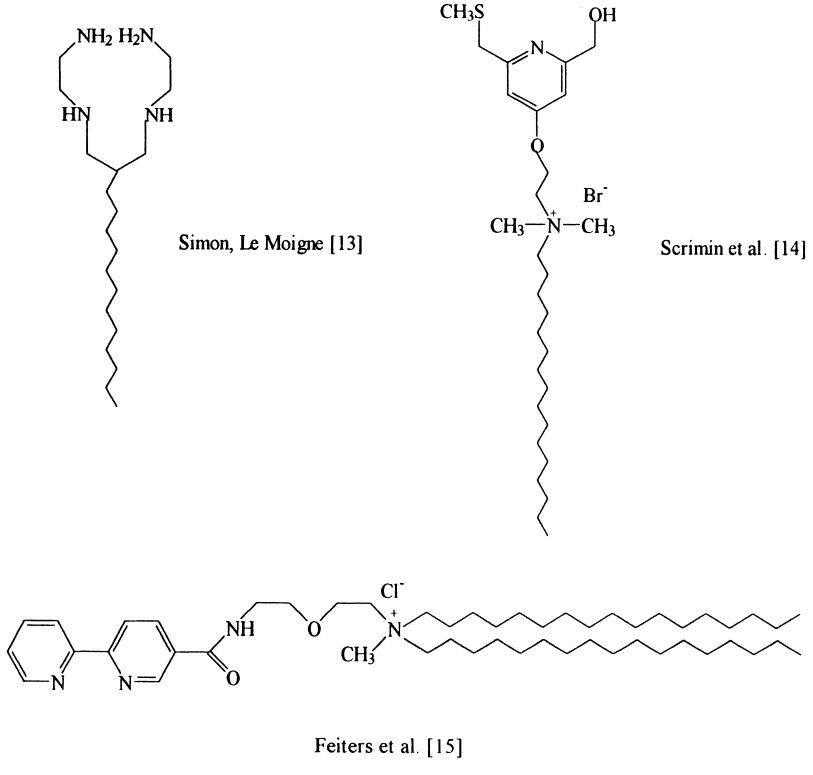
Hydrolytic reactions
Oxidation reactions
Hydrogenation and other reductive reactions
Carbon–carbon coupling reactions.

Sometimes only low concentrations of surfactants are necessary to generate a micellar effect. Although the real morphology of the assemblies in presence of an excess of substrate is unknown, it is very helpful to create micelles and vesicles. As a rule kinetic effects are observable only above the critical micelle concentration (cmc). It is also interesting to use reverse micelles and microemulsions as novel reaction media [11]. In the case of the hydrogenation of prochiral imines with different transition metal complexes, Buriak and Osborn [12] showed that the enantioselectivity is improved mainly by a simple anion effect.

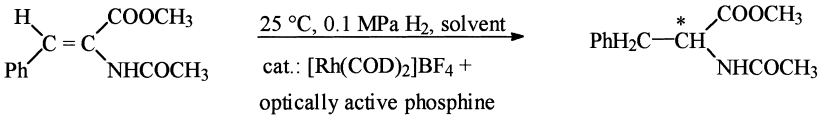
Scheme 2 exhibits a selection of surfactants functionalized with anchor groups for catalytically active transition metal complexes synthesized with the aim to create metalloenzyme models [13–15].

2. Asymmetric hydrogenation in presence of surfactants

In this paper we compare the suitability of complex catalysts solubilized in different types of micelles with



Scheme 2. Amphiphilic ligands for transition metals.



Scheme 3. Asymmetric hydrogenation reaction.

amphiphilized complexes in pure and mixed micelles. The asymmetric hydrogenation of unsaturated amino acid derivatives catalyzed by rhodium(I) complexes was chosen as a standard reaction. Scheme 3.

This reaction is well investigated in organic solvents, but usually the presence of water causes loss of activity and loss of enantioselectivity [16]. This effect often disappeared upon addition of micelle forming surfactants [17]: the mixture disperses and hydrogen is consumed. Activity and enantioselectivity increases and in some cases exceeds results obtained in methanol as solvent.

Table 1 exhibits selected experiments with different amphiphiles [18].

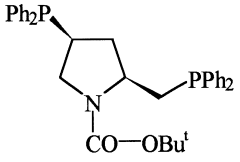
All examples of anionic, zwitterionic and nonionic surfactants were active as promoters, but in the case of cationic amphiphiles only the hydrogen sulfate exhibited an effect whereas tetrafluoroborate and triflate were without any influence. The most favorable ligand was BPPM described by Achiwa [19] but even DIOP [20], Phenyl-ß-glup-OH [21] and other ligands show the effect.

In highly diluted solutions, a dependence of activity and enantioselectivity on the concentration is found. There is a sudden increase near the cmc of the surfactant which might be an indication for the existence of micelles. In an aromatic substitution reaction Broxton et al. [22] used this phenomenon to estimate the cmc. The enhancement of the enantioselectivity cannot be a result of solubilization because water soluble substrates are more active in hydrogenation but the enantioselectivity is only scarcely enhanced in the aqueous system [23].

The work up of the experiments with amphiphiles is relatively simple: extraction with chloroform. Unfortunately, recycling of the catalyst was unsuccessful. The challenge of the catalyst recycling still remains. One possibility for successful recycling should be the

Table 1
Selected examples of hydrogenation experiments with the optically active catalytic system $[(COD)_2Rh]BF_4$+BPPM (according to Scheme 3)

Surfactant	*t*/2 in min	Optical yield in % ee R
None in water (methanol)	90 (2)	78 (90)
Anionic		
Sodium dodecylsulfate (SDS)	6	94
Cationic		
Cetyl-trimethylammonium		
Hydrogen sulfate (CTA HSO_4)	5	95
Zwitterionic		
N-dodecyl-*N*,*N*-dimethyl-3-ammonio		
-1-propanesulfonate	5	93
Nonionic		
Decaoxyethylene-hexadecylether (Brij 56)	7	95

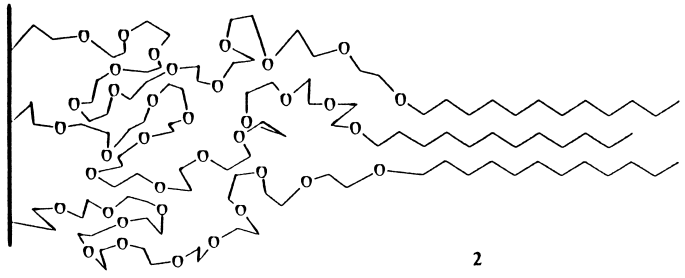
BPPM = 

COD = cis,cis-1,5-cyclooctadiene

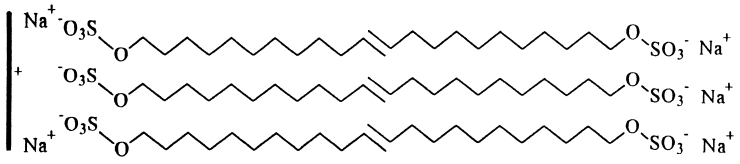
cat.: surfactant: substrate=1:20:100

1

organic or inorganic support



2



3

Scheme 4. Examples of immobilized amphiphiles.

immobilization of amphiphiles on the surface of organic and inorganic supports leading to polysoaps [24].

Scheme 4 contains some structures which we have used with success [25].

Best results were observed with highly cross-linked organic ion exchange resins and with inorganic ion exchangers 1. Polyether-surfactants bound to silica 2 and admicelles 3 were also suitable as micellar medium. The handling is very simple and the separation after each cycle is done by filtration and recovery of the catalyst within the solid phase. No rhodium was found in the aqueous phase and the reaction was recycled up to ten times with decreasing activity and nearly constant enantioselectivity.

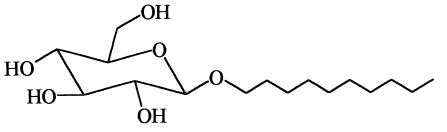
The experiments with polysoaps show that the complex is located within the amphiphile assemblies. More information about the site of this incorporation were obtained by the study of the chiral induction in optically active micelles. In the model system achiral rhodium(I) complexes were used like [(BDPP)(COD)Rh]BF_4 and [(BDPB)(COD)Rh]BF_4 (BDPP=1.3-bis(diphenyl-phosphino)propane and BDPB=1.4-bis(diphenylphosphino)butane).

Scheme 5 displays two types of optically active surfactants and the chiral induction measured in the hydrogenation reaction according to Scheme 3.

The effect was less than 10% ee in all cases but could be measured unambiguously.

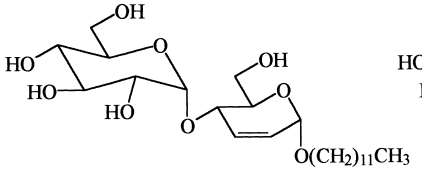
Only surfactants with a chiral center near the borderline between hydrophilic headgroup and hydrophobic tail gave induction, see the examples of dipeptides 7 and 8 and carbohydrate derivatives 5 and 6. That means, the reactants should be located in the palisade layer which is defined as ''the layer of the micelle between the hydrophilic groups and the first few carbon atoms of the hydrophobic groups'' [26].

Unfortunately, no insight about the mechanism of the educt and product transfer during the reaction, which is sometimes very fast, is possible at this time.

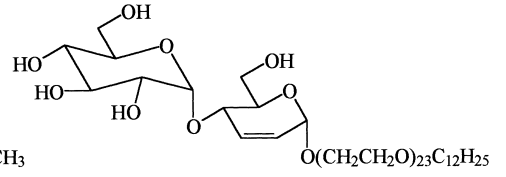


7 % ee (R)

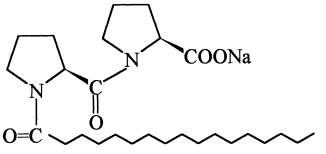
4



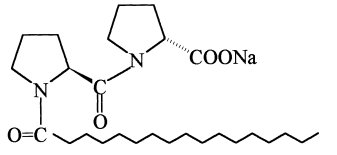
7 % ee (R) 5



Racemat 6



8 % (S) 7



3 % (S) 8

Scheme 5. Selected optically active amphiphiles.

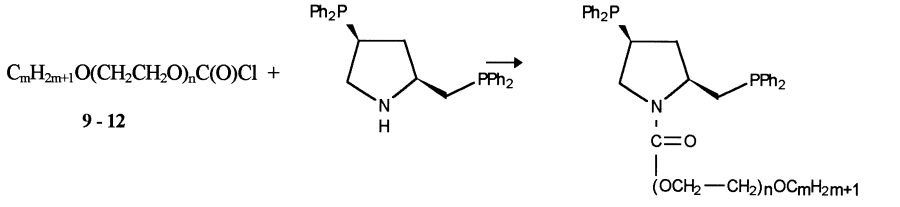
2.1. *Use of metallosurfactants*

As a new aim we were interested in the synthesis of amphiphilic ligands and their rhodium(I) complexes suitable to form micelles. Two questions should be answered: first, does this combination give an optimum medium for the reaction between complex, hydrogen and substrate and second, can we simulate interactions in mixed micelles? Recently, Ding et al. [27] gave examples of using chiral amphiphilic ligands in biphasic systems. The rhodium is bound in the hydrophobic part of the molecule and the formation of micelles as aggregates is rather unlikely.

Scheme 6 shows the synthesis of amphiphilic PPM derivatives.

Commercially available polyoxyethylene ethers (Brij-type) were converted with phosgene to chlorocarbonic esters and these used for the *N*-acylation of PPM Scheme 6. The chiral phosphine is bound to the hydrophilic polyether group via a carbamate linker and the hydrophobic tail is represented by the dodecyl group. Compound 13 contains only a methyl group instead of a long-chain alkyl group, thus water solubility and perhaps association is expected but no ability to form micelles. Micelle formation should also be a problem for compounds 14 and 15 because of the lack of hydrophilicity. That means, that the hydrophile–lipophile balance (HLB) is too small for a good dispersion in water. Sufficiently balanced in hydrophilicity and hydrophobicity is compound 16 which contains twenty three polyoxyethylene groups and one dodecyl group.

We were not able to measure the cmc of the highly sensitive phosphines or phosphine complexes but



13-16

9 and **13** n = 16; m = 1

10 and **14** n = 4; m = 12

11 and **15** n = 10; m = 12

12 and **16** n = 23; m = 12

Scheme 6. Synthesis of water soluble and amphiphilic ligands.

Table 2
Physical data of amphiphilic pyrrolidine derivatives

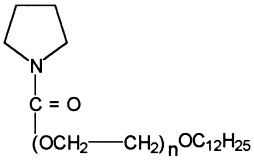
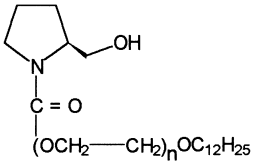
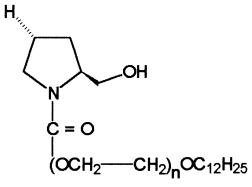
Amphiphile	Compound	cmc in mol/l	Hydrodynamic radii r_H in nm	HLB
	17 n=10	$<3\times10^{-5}$	4.0 nm	5.30
	18 n=23	5×10^{-5}	4.4 nm	9.5
	20 n=10	4×10^{-5}	3.6 nm	6.70
	21 n=23	6×10^{-5}	4.3 nm	11.27
	22 n=10	5×10^{-5}	4.0 nm	8.60
	23 n=23	7×10^{-5}	4.4 nm	13.17

Table 2 summarizes some cmc's of pyrrolidine, (*S*)-2-hydroxymethyl-pyrrolidine, and (2*S*, 4*R*)-4-hydroxy-2-hydroxymethyl-pyrrolidine derived surfactants.

Table 2 contains cmc's measured by titration calorimetry [28] and also hydrodynamic radii investigated by dynamic light scattering [29]. The HLB-values were estimated by an increment method [30] and are not compatible with the related rhodium complexes. The difference between compounds with ten and twenty three polyoxyethylene groups is obvious.

Table 3
Use of amphiphilic ligands in asymmetric hydrogenation of (Z)-methyl α-acetamidocinnamate. Conditions: 1 mmol substrate, 0.01 mmol catalyst in situ formed, 15 ml solvent, 25°C, 0.1 MPa H_2O

	Ligand L*	Solvent/Amphiphile	$t/2$ [a] in min	% ee (*R*)
1	BPPM [b]	MeOH	2	93
2	13 n=16, m=1	MeOH	3	94
3	14 n=4, m=12	MeOH	1	95
4	15 n=10, m=12	MeOH	1	94
5	16 n=23, m=12	MeOH	4	94
6	BPPM	H_2O	90	78
7	13 n=16, m=1	H_2O	22	85
8	14 n=4, m=12	H_2O [c]	-	-
9	15 n=10, m=12	H_2O	10	83
10	16 n=23, m=12	H_2O	13	91
11	BPPM	H_2O+SDS, 0.2 mmol	6	94
12	13 n=16, m=1	H_2O+SDS, 0.2 mmol	4	93
13	14 n=4, m=12	H_2O+SDS, 0.2 mmol	14	95
14	15 n=10, m=12	H_2O+SDS, 0.2 mmol	7	95
15	16 n=23, m=12	H_2O+SDS, 0.2 mmol	7	96
16	BPPM	H_2O+18, 0.1 mmol	12	96
17	13 n=16, m=1	H_2O+18, 0.1 mmol	10	89
18	14 n=4, m=12	H_2O+18, 0.1 mmol	21	89
19	15 n=10, m=12	H_2O+18, 0.1 mmol	9	95
20	16 n=23, m=12	H_2O+18, 0.1 mmol	8	94
21	13 n=16, m=1	H_2O [d]	11	84
22	16 n=23, m=12	H_2O [d]	6	89
23	16 n=23, m=12	H_2O [e]	17	88
24	16 n=23, m=12	H_2O+SDS, 0.2 mmol [e]	7	96

[a] $t/2$=halftime. Half of theoretical amount of H_2 is consumed.
[b] (2*S*, 4*S*)-(-)-*N*-*tert*.-butoxycarbonyl-4-diphenylphosphino-2-diphenyl phosphinomethyl-pyrrolidine.
[c] Not dispersed.
[d] With the double amount of catalyst (0.02 mmol).
[e] With 0.0025 mmol catalyst.

The HLB is suitable for an estimation of the dispersion of surfactants in water.

Table 3 summarizes a selection of results obtained in the hydrogenation of (Z)-methyl α-acetamidocinnamate to methyl α-acetamidophenylalaninate with in situ formed rhodium complexes of the novel ligands in comparison to the analogously formed BPPM complex. In methanol as solvent all five ligands are comparable with respect to activity and enantioselectivity.

In water as medium complexes of the ligands 13 and 15 show a significant increase in activity but only a small increase in enantioselectivity compared to the BPPM complex. The water soluble ligand 13 and the poorly dispersible ligand 15 is rather similar to BPPM and only ligand 16 gave the expected increase in enantioselectivity. An increase of the ligand concentration in relation to the rhodium concentration led to inhibition because of the lack of free coordination sites. An enhancement of the complex concentration in relation to the substrate concentration for the ligands 13 and 16 only, gave an increase in the reaction rate and a small decrease of enantioselectivity. The solubility of the ligands 14 and 15 in water is so small that the increase of the concentration is without any effect.

A micellar system formed by amphiphilic complexes leads to an extreme concentration of active centers near the surface of the micelle and limits probably the accessibility. This should be overcome by mixing with nonfunctionalized surfactants. Experiments with the new synthesized amphiphile 18 or with SDS display this ‘embedding effect’ as evident in an enhancement of activity and enantioselectivity for all ligands including BPPM.

The causes for this effect seem to be different. In case of the nonamphiphilic ligands (13 and BPPM) it is a solubilization by encapsulation, in case of the amphiphilic ligands (15, 16 and probably 14) it should be due to the formation of a mixed micelle. An argument for this assumption is given due to the following observation:

The dependence of the activity and enantioselectivity on the SDS concentration for the BPPM complex shows an increase near the cmc of SDS whereas for the amphiphilic ligand 16 the activation begins much earlier because of the lower cmc of the polyether ligand. A comparable effect is observed with polymerized micelles [23]. As a consequence we found the amphiphilic ligand 16 to be very versatile in its use. It is efficient as the rhodium complex in both methanol and in water; its activity and enantioselectivity in water can be improved by addition of neutral or anionic surfactants.

The miscibility obtained with differently functionalized and non-functionalized amphiphiles should lead to interesting synergisms in multifunctional systems. An idea about the interaction between rhodium complex and substrate within the micelle is represented in Fig. 2(a) and (b).

The polyether headgroup can give a spherical agglomerate and the linked complex should dip into the micelle and attack the substrate near the palisade layer. The efficiency and simplicity of our system could be a way to a practical use of complex catalysis in aqueous micelles.

3. Experiments with polymerized micelles

The application of micelles in a reactor is limited due to their kinetic instability.

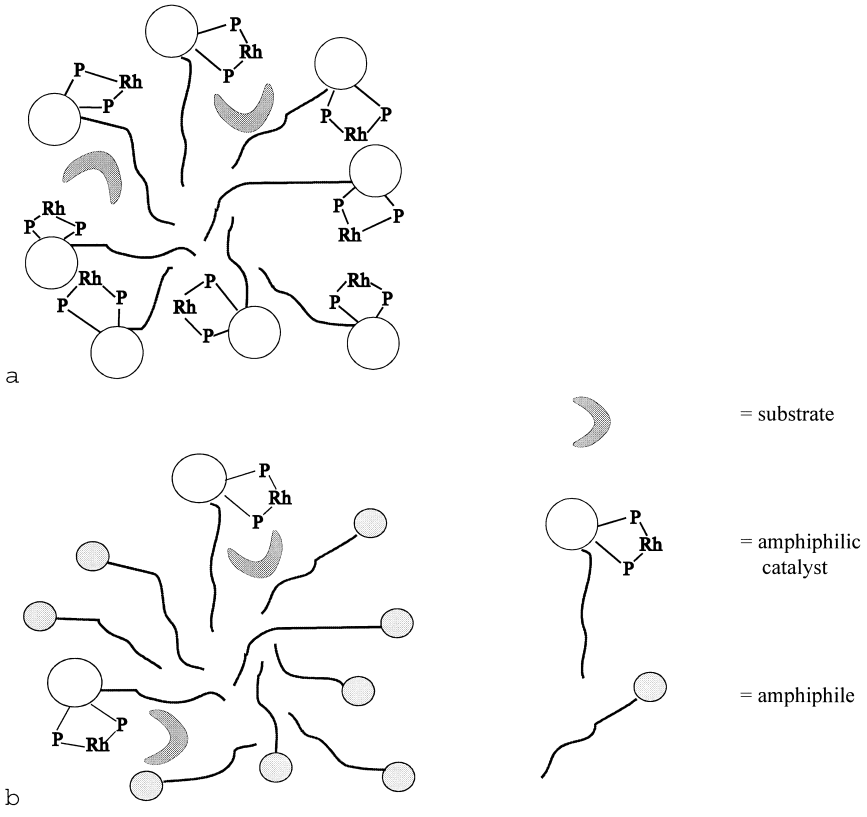
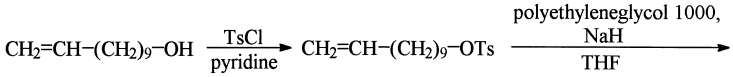


Fig. 2. Schematic proposal of the catalyst–substrate interaction in a micelle of the amphiphilic catalyst (2a) and in a mixed micelle with an added non-functionalized amphiphile (2b).



24

$CH_2=CH-(CH_2)_9-O-(CH_2CH_2O)_{23}-H$

25

Scheme 7. Synthesis of unsaturated polyether amphiphiles.

Therefore, we synthesized unsaturated polyether surfactants according to Scheme 7.

The monomer surfactant 25 was used in asymmetric hydrogenation and exhibits similar effects (7 min halftime; 96% ee) as polyethyleneglycol dodecylether and analogous compounds.

The unsaturated surfactant 25 is polymerized in a UV-apparatus at 254 nm and in presence of azoisobutyronitrile (AIBN) as radical initiator. After 8 h irradiation the ^{1}H-NMR signal of the double bond is no longer observed. The polymer has a waxy consistency and gives a clear dispersion in water.

The complete mixture of complex, ligand, surfactant and substrate was stirred overnight in an argon atmosphere and the hydrogenation started at the next morning. With BPPM as ligand we obtained satisfying results (7–8 min halftime and 94% ee). To be sure that there are no monomers in the surfactant a dialysis was carried out for 17 h using a membrane with a molecular weight limit of about 3500. After this purification the hydrogenation results were reproducible. No satisfying results could be observed with the amphiphilic ligand 16 and polymerized micelles. It is planned to study copolymerized functionalized micelles.

4. Experimental

4.1. Materials and methods

4.1.1. Methods

All synthesized compounds were characterized by elemental analysis (Leco C, H, N, S automatic analyzer), FTIR spectroscopy (Nicolet Magna 550) and ^{1}H-,^{13}C-,^{31}P-NMR spectroscopy (Bruker AC 250; ^{1}H : 250 MHz; ^{13}C : 62.896 MHz; ^{31}P : 101.237 MHz).

The determination of cmc's has been done with a titration calorimeter 2277 Thermal Activity Monitor (Fa. Thermometric) starting with a 5×10^{-3} M solution of the amphiphile in water.

Hydrodynamic radii were measured at 25°C, a 0.02 M solution of the amphiphile with the apparatus DLS 5000 (Fa. ALV Langen) equipped with a 532 nm Laser (1000 mW).

Optical rotation was measured with a Perkin Elmer 241 polarimeter.

4.1.2. Chemicals

All chemicals were purchased by Aldrich, Germany, except the phosgene (Fluka, Switzerland).

4.1.3. Syntheses

Compounds 9–16 (see Scheme 6). All operations were done in argon atmosphere. A solution of 1.1 mmol of the pyrrolidine and 1.32 mmol of triethylamine were cooled to 0°C and under stirring 1.1 mmol alkylpolyoxyethylene oxycarbonyl chloride in 3 ml CH_2Cl_2 was added dropwise. The mixture was stirred for 3 h at room temperature, solvents removed in vacuum and the residue dissolved in 10 ml ether. After storing overnight the crystallized triethylamine hydrochloride were filtered over celite 545 and glass wool, the filtrate concentrated in vacuum and the residue dried in vacuum.

Ligand 13: yield: 85%; IR (capillary): $\tilde{\nu}$ =1696 cm^{-1} (C=O); elemental analysis: calcd. for $C_{63}H_{95}NO_{18}P_2$: C 62.20, H 7.87, N 1.15, P 5.09; found: C 61.14, H 7.86, N 1.07, P 4.81; ^{1}H-NMR (250 MHz, $CDCl_3$, 25°C): δ=1.8–2.2 (*m*, 4 H; CCH_2C, CH_2P), 2.6–3.0 and 3.8–4.4 (*m*, 4 H; $CHCH_2NCH$), 3.2 (s, 3 H; OCH_3), 4.2 (*m*, 64 H; CH_2O), 7.1–7.8 (*m*, 20 H; ArH); ^{31}P-NMR ($CDCl_3$, 25°C): δ −8.2; −22.4 (^5J(P–P)=28 Hz).

Ligand 14: yield: 87%; IR (capillary): $\tilde{\nu}$=1698 cm^{-1} (C=O); elemental analysis: calcd. for $C_{50}H_{69}NO_6P_2$: C 71.32, H 8.27, N 1.66, P 7.36; found: C 71.11, H 8.23, N 1.61, P 7.40; $[\alpha]_D^{27.0}=-1.9$ (c=0.52 in benzene); ^{1}H-NMR (250 MHz, $CDCl_3$, 25°C): δ 0.8–0.9 (t, J(CH3–CH_2)=6.5 Hz, 3 H; CH_3), 1.2–1.4 (m, 20 H; CCH_2C), 1.5 (m, 2 H; CH_2Me), 1.8–2.4 (m, 4 H; CCH_2C, CH_2P), 2.6–3.2 and 3.8–4.4 (m, 4 H; $CHCH_2NCH$), 3.2–4.2 (m, 16 H; CH_2O), 7.1–7.8 (m, 20 H; ArH). ^{31}P-NMR ($CDCl_3$, 25°C): δ −7.9; −22.4 (^5J(P–P)=21 Hz).

Ligand 15: yield: 85%; IR (capillary): $\tilde{\nu}$=1698 cm^{-1} (C=O); elemental analysis: calcd. for $C_{62}H_{93}NO_{12}P_2$: C 67.30, H 8.47, N 1.27, P 5.60; found: C 66.84, H 8.53, N 1.28, P 5.85; $[\alpha]_D^{22.4}=-10.2$ (c=0.67 in MeOH); ^{1}H-NMR (250 MHz, $CDCl_3$, 25°C): δ 0.8–0.9 (t, J(CH_3–CH_2)=6.5 Hz, 3 H; CH_3), 1.2–1.4 (m, 20 H; CCH_2C), 1.5 (m, 2 H; CH_2Me), 1.8–2.4 (m, 4 H; CCH_2C, CH_2P), 2.6–3.2 and 3.8–4.4 (m, 4 H; $CHCH_2NCH$), 3.2–4.2 (m, 40 H; CH_2O), 7.1–7.8 (m, 20 H; ArH). ^{31}P-NMR ($CDCl_3$, 25°C): δ −8.3; −22.5 (^5J(P–P)= 29 Hz).

Ligand 16: yield: 65%; IR (capillary): $\tilde{\nu}$=1698 cm^{-1} (C=O); elemental analysis: calcd. for $C_{88}H_{145}NO_{25}P_2$: C 62.95, H 8.70, N 0.83, P 3.69; found: C 62.42, H 8.75, N 1.21, P 3.90; $[\alpha]_D^{22.9}=-6.3$ (c=0.56 in MeOH); ^{1}H-NMR (250 MHz, $CDCl_3$, 25°C): δ 0.8–0.9 (t, J(CH_3–CH_2)=6.5 Hz, 3 H; CH_3), 1.2–1.4 (m, 20 H; CCH_2C), 1.5 (m, 2 H; CH_2Me), 1.8–2.4 (m, 4 H; CCH_2C, CH_2P), 2.6–3.2 and 3.8–4.4 (m, 4 H; $CHCH_2NCH$), 3.2–4.2 (m, 92 H; CH_2O), 7.1–7.8 (m, 20 H; ArH). ^{31}P-NMR ($CDCl_3$, 25°C): δ −8.3; −22.5 (^5J(P–P)=29 Hz).

10-Undecen-1-yl tosylate, 24: 10-Undecen-1-ol (20.45 ml, 0.1 mol) was dissolved in 100 ml dry pyridine and cooled below 0°C. While stirring p-toluene sulfonic acid chloride (20.97 g, 0.11 mol) was added and the mixture kept below 0°C. After 1 h it was stored at 0–4°C in a refrigerator for two days. Work up was done by adding 400 ml of ether, washing the organic layer with 100 ml of concentrated hydrochloric acid, diluted with 400 ml of water and once with 20 g of $NaHSO_4$ dissolved in 200 ml of water, drying and evaporating the organic layer giving 30.4 g (94%) of 24 as pale yellow oil. The residue was taken for the next step without further purification.

IR (capillary): $\tilde{\nu}$ =1177.6, 1188.9, 1362.9 cm^{-1}; Elemental analysis calcd. for $C_{18}H_{28}O_3S$: C 66.63, H 8.70, S 9.88; found: C 66.65, H 8.79, S 9.43.

Polyethyleneglycol-1000-mono-10-undecen-1-yl ether, 25: Polyethyleneglycol 1000 (80 g, 80 mmol) 100 ml dry THF was added to a suspension of NaH (1.056 g, 44 mmol) in 30 ml of dry THF while stirring. After foaming had ceased 24 (12.98 g, 40 mmol) dissolved in 70 ml of dry THF was added and the mixture stirred for further 48 h. The precipitate was filtered off, THF removed by evaporation and the residue dissolved in chloroform for column chromatography giving 29 g (61.2%) of 25 (R_f=0.61) as a waxy solid separated from the diether (R_f=0.68) and starting material (polyethyleneglycol 1000; R_f=0.57).

Fp.: 30–33°C; ^{13}C-NMR ($CDCl_3$) δ =28.7–29.4, 33.6 (C–CH_2–C); 69.8–72.4 (O–CH_2–CH_2–O); 113.9 (CH_2=CH–); 138.9 (CH_2=CH–); Elemental analysis calcd. for $C_{57}H_{114}O_{24}$: C 57.84, H 9.71; found: C 58.01, H 9.63.

The cmc of 25 was determined by solubilization experiments of 1-(2-pyridylazo)-2-naphthol [31] as to 3×10^{-4} mol/l.

4.1.4. Polymerization of 25

The polymerization was carried out in a water-cooled 170 ml quartz UV-reactor in the presence of 10 mg of AIBN. The solution of monomeric micelles at a concentration of 7.5×10^{-3} mol/l (25 fold of cmc) was irradiated with a mercury high pressure lamp at 254 nm over a period of 8 h at 60°C with stirring. Under these conditions the polymerization went to completion as was judged by the disappearance of the ^{1}H-NMR signals of vinylic (5.8 and 5.05 ppm) and allylic (2.1 ppm) protons. To control the molecular weight and to remove possible traces of unpolymerized surfactant the polymerization product was treated by a 17 h dialysis with a molecular porous dialysis membrane (Spectra/Por, molecular weight cut off, MWCO 3500).

4.1.5. Hydrogenation

The hydrogenation was performed by an isobaric method at 25°C under air-free conditions in a thermostated apparatus. 0.01 mmol of $[(COD)_2Rh]BF_4$ and 0.01 mmol of the ligand together with 0.2 mmol of the monomer or polymer surfactant and 1 mmol of (Z)-methyl α-acetamidocinnamate were stirred in 15 ml

water under argon. After 15 min (or in the case of polymerized micelles stirring overnight) the argon was replaced by hydrogen at ambient pressure and the reaction was started and followed volumetrically.

The time necessary to consume half of the theoretical amount of hydrogen ($t/2$) was taken as a measure for the activity. After finishing the experiment, the mixture was extracted with 5 ml of chloroform. The enantiomeric excess of the product was determined by GLC (10 m fused silica capillary column, ID 0.2 mm, coated with XE-60-L-*N*-*tert*.-butyl-valinamide; FID, split 1:60; 150°C isothermal).

Acknowledgements

The authors thank Mrs. A. Lehmann, Mrs. B. Strübing, Mrs. K. Kortus, Mrs. D. Meißner, and Mrs. M. Jäkel for technical assistance. We are grateful to Dr. M. Michalik and Dr. M. Helmstedt for the measuring of NMR spectra and the determination of the hydrodynamic radii. Thanks are given also to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft, DFG, for financial support.

References

[1] E. Wiebus, B. Cornils, Chem. Ing. Technol. 66 (1994) 916.
[2] D. Vogt, Applied Homogeneous Catalysis with Organometallic Compounds, in: B. Cornils, W.A. Herrmann (Eds.), VCH, Weinheim, 1996, vol. 1, p. 251f.
[3] F.M. Menger, J.F. Chow, J. Am. Chem. Soc. 105 (1983) 5501.
[4] J.H. Fendler, Membrane Mimetic Chemistry, Wiley, New York, 1982, p. 25f.
[5] Solubilization in Surfactant Aggregates in: S.D. Christian, J.F. Scamehorn (Eds.), Marcel Dekker, New York, 1995.
[6] H. Morawetz, Adv. Catal. 20 (1969) 341.
[7] Y. Murakami, J. Kikuchi, Y. Hiseada, O. Hayashida, Chem. Rev. 96 (1996) 721.
[8] M.L. Carreto, S. Rubio, D. Perez-Bendito, Analyst 121 (1996) 33.
[9] J.M. Brown, S.K. Baker, A. Colens, J.R. Darwent, Enzymic and Non-enzymic Catalysis, in: P. Dunnill, A. Wiseman, N. Blakebrough (Eds.), Horwood, Chichester, 1980, p. 111.
[10] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975; T. Kunitake, S. Shinkai, Adv. Phys. Org. Chem. 17 (1980) 435; C.A. Bunton, G. Savelli, Adv. Phys. Org. Chem. 22 (1986) 213.
[11] H.J. Schwuger, K. Stickdorn, R. Schomäcker, Chem. Rev. 95 (1995) 849.
[12] J.M. Buriak, J.A. Osborn, Organometallics 15 (1996) 3161.
[13] J. Simon, J. Le Moigne, J. Mol. Catal. 7 (1980) 137.
[14] P. Scrimin, P. Tecilla, U. Tonellato, J. Am. Chem. Soc. 114 (1992) 5086.
[15] M.C. Feiters, R.J.M. Klein Gebbink, A.P.H.J. Schenning, G.P.F. van Strijdouck, C.F. Martens, R.J.M. Nolte, Pure and Appl. Chem. 68 (1996) 2163.
[16] L. Lecomte, D. Sinou, J. Bakos, I. Toth, B. Heil, J. Organomet. Chem. 370 (1989) 277.
[17] G. Oehme, E. Paetzold, R. Selke, J. Mol. Catal. 71 (1992) L1.
[18] I. Grassert, E. Paetzold, G. Oehme, Tetrahedron 49 (1993) 6605.
[19] K. Achiwa, J. Am. Chem. Soc. 98 (1976) 8265.
[20] H.B. Kagan, T.B. Dang, J. Am. Chem. Soc. 94 (1972) 6429.
[21] R. Selke, J. Organomet. Chem. 370 (1989) 241.
[22] T.J. Broxton, J.R. Christie, A.J. Dole, J. Phys. Org. Chem. 7 (1994) 437.
[23] A. Kumar, G. Oehme, J.P. Roque, M. Schwarze, R. Selke, Angew. Chem. 1994, 106, 2271; Angew, Chem., Int. Ed. Engl. 33 (1994) 2197.
[24] A. Laschewsky, Adv. Polym. Sci. 124 (1995) 1; J.M. Brown, J.A. Jenkins, J. Chem. Soc., Chem. Commun. (1976) 458.
[25] H.N. Flach, I. Grassert, G. Oehme, Macromol. Chem. Phys. 1994, 195, 3289; H.N. Flach, I. Grassert, G. Oehme, M. Capka, Colloid Polym. Sci. 274 (1996) 261.
[26] M.J. Rosen, Surfactants and Interfacial Phenomena, 2nd ed., Wiley, New York, 1989, p. 172f.
[27] H. Ding, B.E. Hanson, J. Bakos, Angew. Chem. 1995, 107, 1728; Angew, Chem., Int. Ed. Engl. 34 (1995) 1645.
[28] S. Paula, W. Sus, J. Tuchtenhaben, A. Blume, J. Phys. Chem. 99 (1995) 11742.
[29] M. Corti, Physics of Amphiphiles, Micelles, Vesicles and Microemulsions, in: V. Degiorgio, M. Corti (Eds.), North Holland Physics Publishing, Amsterdam, 1985, p. 122f.
[30] Y. Moroi, Micelles: Theoretical and Applied Aspects, Plenum Press, New York, 1992, p. 8f.
[31] K.G. Furton, A. Norelus, J. Chem. Educ. 70 (1993) 254.