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Complex catalyzed hydrogenation and carbon–carbon bond formation in aqueous micelles

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Abstract

Two reactions have been investigated in an aqueous micellar system: the asymmetric hydrogenation of α-amino acid precursors by means of optically active rhodium(I) phosphine complexes and the Suzuki reaction of aryl-, benzyl- and allylhalogenides, respectively, with arylboronic acids by means of water soluble palladium–phosphine complexes. Surfactants of different types significantly enhance both activity and enantioselectivity in the hydrogenation reaction, provided that the concentration of the surfactant is above the critical micelle concentration (cmc). We also show the application of amphiphilized polymers and polymerized micelles as surfactants in order to facilitate the phase separation after the reaction. Assemblies of surfactants also accelerate the Suzuki reaction but there is a limitation due to the low water solubility of the reaction products, and a high concentration of surfactant is necessary. As an effective alternative method a phase transfer system with water and toluene as the immiscible phases and long chain amphiphiles as phase transfer reagents has been investigated. The best results are observed with cationic and zwitterionic surfactants.

Keywords: Asymmetric hydrogenation; Micelles; Phase transfer catalysis; Suzuki reaction; Transition metal complexes

1. Introduction

For about 3 decades [1] homogeneous and heterogeneous catalytic processes have competed on an industrial scale. The advantages of a homogeneous system are its high activity, selectivity and reproducibility under relatively mild conditions, but the disadvantages of such a system include separation and recycling problems after the reaction cycle is finished [2]. Several methods have been developed to combine the benefits of homogeneous and heterogeneous catalysis. The basic concept is to transfer a homogeneous catalyst into a multiphase system as drawn in Fig. 1.

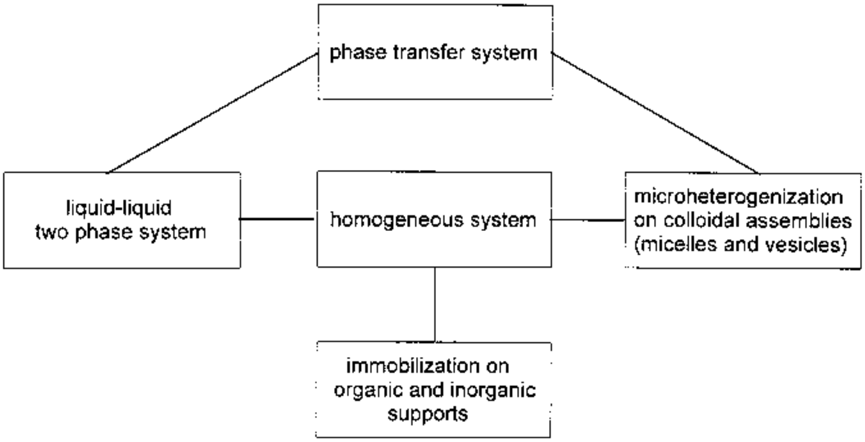


Fig. 1. Connections between homogeneous catalytic systems and multiphase systems.

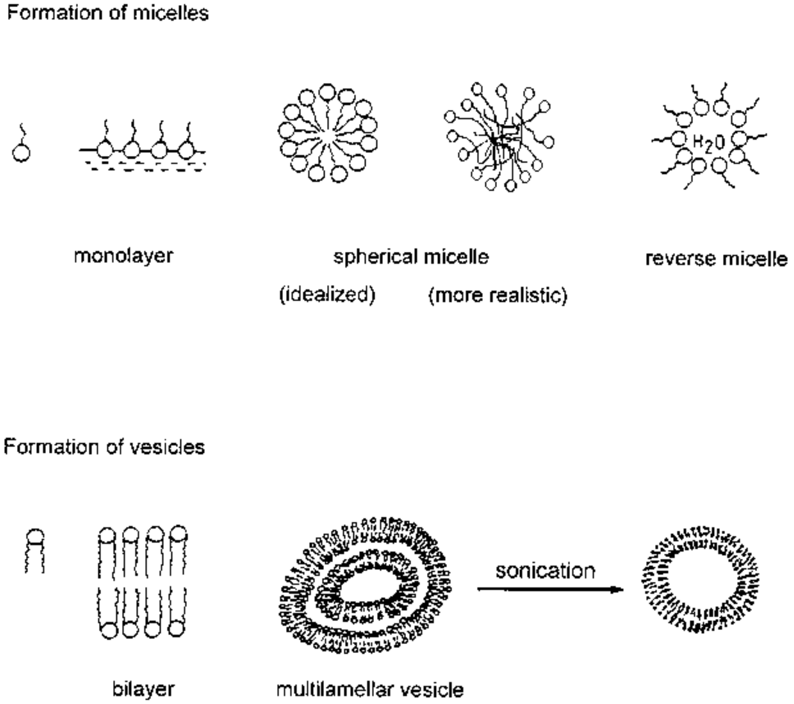


Fig. 2. Schematic presentation of the formation of surfactant assemblies.

One way is to bind the homogeneous system to an organic or inorganic support to give a liquid–solid system. A second method leads to a liquid–liquid two phase or phase transfer system. A third method of immobilization is microheterogenization of the catalytic system on organized amphiphiles in the colloidal or nanoscale dimension. To date only liquid–liquid two phase systems [3] and recently immobilized systems [4] are used on an industrial scale. The principle of a two-phase system with phase transfer reagents can be compared with a pseudophase micellar system [5].

The aggregation of surfactants (amphiphiles) in water is a thermodynamically spontaneous process. Different assemblies are formed which are dependent on the structure and the concentration of the surfactants [6]. Fig. 2 shows examples of such assemblies. Micelles are derived from amphiphiles with one polar headgroup and one hydrophobic chain, vesicles often are derived from amphiphiles with two chains per headgroup.

The second type of amphiphiles forms natural membranes and therefore chemistry within layers of amphiphiles is sometimes called *membrane mimetic chemistry* [7] and the enhancement of reaction rates within micelles is called *micellar catalysis* [8]. The highly ordered medium of the micelle can even influence the stereochemistry of a chemical reaction [9]. The formation of micelles is characterized by a special concentration, the critical micelle concentration (cmc). All amphiphiles shown in Table 1 form micelles. It should be noted that the cmc can be influenced in the presence of organic or inorganic compounds [10].

2. Experimental 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- and ^{31}P-NMR spectroscopy (Bruker AC 250; ^{1}H: 250 MHz, ^{13}C: 62.896 MHz, ^{31}P: 101.237 MHz).

The enantiomeric excess of methyl *N*-acetylphenylalaninate was determined by GLC on a Hewlett Packard chromatograph 5880 A fitted with a 10 m capillary column coated with XE-60-l-*N*-*tert*-butyl-valinamide (FID, split 1:60, 150°C). The standard deviation in enantiomeric excess (ee) was found to be $\pm 1\%$. Molecular weights of the polymerized micelles and the triblock copolymers, respectively, were measured with a membrane osmometer (Fa. Knauer, Germany), and by gel permeation chromatography (GPC) (HPLC Hewlett Packard HP 1090, column SDV 5 μ, PSS, Mainz).

The size of assemblies was determined by dynamic light scattering (Coulter N4 Plus) and electron microscopy (Zeiss, transmission electron microscope 912 OMEGA).

2.1. Materials

All chemicals were purchased from Aldrich, Germany. The triblock copolymers were a gift of the Fa. C.H. Erbslöh, Krefeld, Germany. The rhodium and palladium complexes were prepared by known methods: $[Rh(cod)_2]BF_4$ [11], $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$ [12]. (*Z*)-methyl α-acetamidocinnamate was prepared according to Cook et al. [13].

2.2. Syntheses

The polyoxyethylene undecenylethers PEGMU 400 und PEGMU 1000 were synthesized as described in [14].

2.2.1. Polyoxyethylene(23)dodecylether methacrylic ester M21

Polyoxyethylene(23)dodecylether (9.6 g, 8 mmol) in 150 ml of dry toluene was stirred with pyridine (0.8 ml, 10 mmol) and methacryloyl chloride (1 ml, 10 mmol)

Table 1
Critical micelle concentration values for different types of amphiphiles

Surfactant	Critical micelle concentration (mol l^{-1})
Sodium dodecylsulfate (SDS)	8.1×10^{-3}
Cetyltrimethylammonium bromide (CTAB)	9.2×10^{-4}
Dodecyldimethylammonio propanesulfonate	1.2×10^{-3}
Polyoxyethylene(20)hexadecylether (Brij 58)	7.7×10^{-5}
$HO–(EO)_{132}–(PO)_{56}–(EO)_{132}–H$ (Synperonics F108)[a]	3.1×10^{-3}

[a] EO: $–CH_2CH_2–O–$; PO: $–CH(CH_3)CH_2–O–$.

at 0°C for 5 h. The mixture was then allowed to warm up to room temperature and stirred overnight. The precipitate of pyridinium hydrochloride was filtered off and the solvent was removed by rotary evaporation. The yield was nearly quantitative (10.0 g). The product was purified by column chromatography on silica gel with chloroform/methanol 2:1 (v/v). The oily product was dried in a vacuum. Elemental Anal. for $C_{62}H_{122}O_{25}$ (1267.64). Anal. Calc (%): C 58.76, H 9.63. Found: C 58.35, H 9.33.

M21 (2.6 g, 2.05 mmol) with 2 mol% of AIBN were dissolved in 170 ml water and irradiated for 6 h at 60°C with UV light (254 nm). The resulting clear solution was concentrated in a vacuum and yielded an oily clear liquid (2.6 g, 100%). The product shows no methacrylic signals at 6.1, 5.5 and 2.2 ppm in ^{1}H-NMR. MW: 28500 (membrane osmometer, in water)

2.2.2. N-(carbonylpolyoxyethylene(23)undecenylether)-(S2,S4)-2-diphenylphosphinomethyl-4-diphenylphosphino-pyrrolidine (M57)

Polyoxyethylene(23)undecenylether (0.495 g, 0.42 mmol) was dissolved in purified chloroform (30 ml), cooled to -10°C and a solution of phosgene in chloroform (containing 0.6 g ml^{-1}, 6 mmol) was added. The mixture was stirred for 5 h at -10°C, the excess of phosgene was removed in an argon stream and the solvent evaporated in a vacuum. The residue was dissolved in abs. dichloromethane (10 ml) at 10°C and this solution was added to a mixture of PPM (Fig. 5) (0.189 g, 0.42 mmol) and triethylamine (0.06 ml, 0.43 mmol) in abs. dichloromethane (10 ml) at 0°C. The mixture was stirred at 0–5°C and the solvent was dispersed in abs. diethylether and the precipitate of triethylamine hydrochloride was filtered off. The product was obtained as a waxy residue by evaporating the sample to dryness and was used in asymmetric hydrogenation without further purification. Elemental Anal. for $C_{87}H_{141}O_{25}P_2$ (1663.04). Anal. Calc. (%): C 62.84, H 8.55, N 0.84, P 3.73. Found: C 62.04, H 8.32, N 0.88, P 3.62. ^{31}P-NMR ($CDCl_3$, 25°C) $\delta \pm -8.5, -22.9$ ppm

2.2.3. General procedure for Suzuki reactions

All preparations were performed in an argon atmosphere. In two separate Schlenk tubes *p*-iodoanisole (3.20 g, 13.5 mmol) was dissolved in 15 ml toluene and phenylboronic acid (1.83 g, 15 mmol) was dissolved in 15 ml ethanol. Sodium carbonate decahydrate (11.6 g, 45 mmol) and cetyltrimethylammonium bromide (1.27 g, 3.38 mmol) were placed in a 100 ml water jacketted flask and dispersed in 15 ml water. The solutions of *p*-iodoanisole and phenylboronic acid were added and the first sample was taken. Then the reaction mixture was heated at 78°C and the catalyst $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$ (9 mg; 0.01 mmol) was added under vigorous stirring (> 1000 rpm). Samples (0.20 ml) were taken after 10, 20, 30, 45, 60, 90, 120, and 180 min, diluted with 0.8 ml toluene, dried with sodium sulfate and analyzed by GLC (column HP1, program: 2 min at 50°C then 10°C min^{-1} up to 260°C).

After the end of the reaction the mixture was extracted with toluene, the organic phase was dried with sodium sulfate, the solvent evaporated and the residue dissolved in hexane. The product was purified by column chromatography (silica gel, e.g. n-heptane/ethylacetate = 7/1) and analytically characterized.

Asymmetric hydrogenation [14] [16] and a general procedure for polymerization [14] were described in previous papers.

3. Results

3.1. Asymmetric hydrogenation

In 1992 we found that the asymmetric hydrogenation of unsaturated α-amino acid derivatives catalyzed by optically active rhodium(I) phosphine complexes in an aqueous medium strongly can be promoted by the addition of surfactants [15].

Table 2 shows experiments in asymmetric hydrogenation with and without amphiphiles [16].

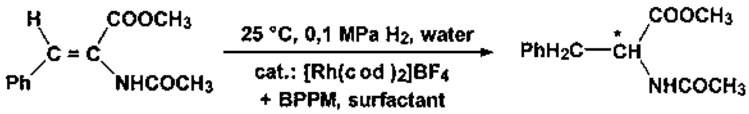
The improvement upon addition of an amphiphile is significant with respect to activity (here given as time of the consumption of half the stoichiometric volume of hydrogen) and enantioselectivity. In these examples the product was isolated in high purity by extraction with chloroform. Asymmetric hydrogenation within aqueous micelles can also be adapted for unsaturated α-amino phosphonic acid and α-amino phosphinic acid derivatives [17]. Significantly the enantioselectivities are sometimes higher than in organic media. To facilitate the separation of catalyst and product at the end of the reaction some variations in the system are possible. One variation is the substitution of the monomer amphiphiles by amphiphilized polymers or polysoaps [18].

Fig. 3 summarizes three examples of polymer bound amphiphiles based on inorganic supports [19]. In our experience all three types of polymers are useful as microreactors for micelle promoted asymmetric hydrogenations. Extremely simple are admicelles (type 3), these are irreversibly adsorbed micelle-forming amphiphiles on alumina or silica [20].

Table 3 displays some hydrogenation results with amphiphilized polymers. The catalytically active complex seems to be fixed near the hydrophilic surface and is not leached in recycling processes. Experiments with ten recycling steps show a practically constant enantioselectivity but with decreasing activity.

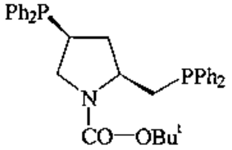
Another model for a phase separable system is the use of polymeric amphiphiles which are dispersible in water and their retention with semipermeable membranes. Good results are observed with commercially available block copolymers that contain poly(ethylene oxide) $(EO)_n$ as the hydrophilic block and poly(propylene oxide) $(PO)_m$ as the hydrophobic block in the scheme $(EO)_n$–$(PO)_m$–$(EO)_n$ (trade names Poloxamers, Synperonics, Pluronics).

Table 2
Hydrogenation with different types of surfactants. Rh:surfactant:substrate = 1:20:100



Surfactant	$t/2$ (min)	Optical yield (%ee *R*)
None in water (methanol)	90 (2)	78 (90)
Anionic		
Sodium dodecylsulfate (SDS)	6	94
Cationic		
Cetyltrimethylammonium hydrogen sulfate (CTA HSO_4)	5	95
Zwitterionic		
N-dodecyl-N,*N*-dimethyl-3-ammonio-1-propanesulfonate	5	93
Nonionic		
Polyoxyethylene(10)hexadecylether (Brij 56)	7	95

BPPM =



c o d = cis,cis-1,5-cyclooctadiene

Selected results are summarized in Table 4. The micellar properties of synperonics are well known [21]. The examples chosen here led to good enhancement of the activity and a satisfactory enantioselectivity.

An other way to generate amphiphilic assemblies of high molecular weight is the direct polymerization of micelles formed from unsaturated amphiphiles [22]. Two types may be differentiated: one with the unsaturation near the headgroup and another with the unsaturation at the end of the hydrophobic chain (Fig. 4). The conservation of the micelle topology during the polymerization is not yet clear but the size of the polymer is closely related to the size of the corresponding micelle [14].

We synthesized a series of different amphiphiles and tried a polymerization with and without radical initiators in an UV-reactor.

In all polymerizations we used the amphiphile in water at a concentration at least two times above the cmc to be sure that micelles are formed. Fig. 5 contains three examples of nonionic amphiphiles derived from polyoxyethylene monoalkylether.

M21 is an ester of methacrylic acid which is bound to the headgroup. This type of unsaturation is very sensitive toward UV light and is polymerized in a reactor with a radiation maximum at 254 nm. In the case of a spherical polymer the micelle should be enclosed in a net. The determination of size and shape by different methods like GPC, membrane osmometry, dynamic light scattering, cryo transmission electron microscopy, and electrospray MS gave MW's between 6000 and 28500 D and diameters between 4 and 180 nm dependent on the chemical structure of the amphiphile and the polymerization conditions.

Table 5 shows selected results with nonpolymerized and polymerized micelles in the asymmetric hydrogenation of methyl α-acetamidocinnamate.

The methacrylic ester M21 under our standard conditions gives moderate activity and excellent enantioselectivity. Activity and enantioselectivity are improved in the presence of the polymerized micelle of M21. Surprisingly, there is no hindrance in

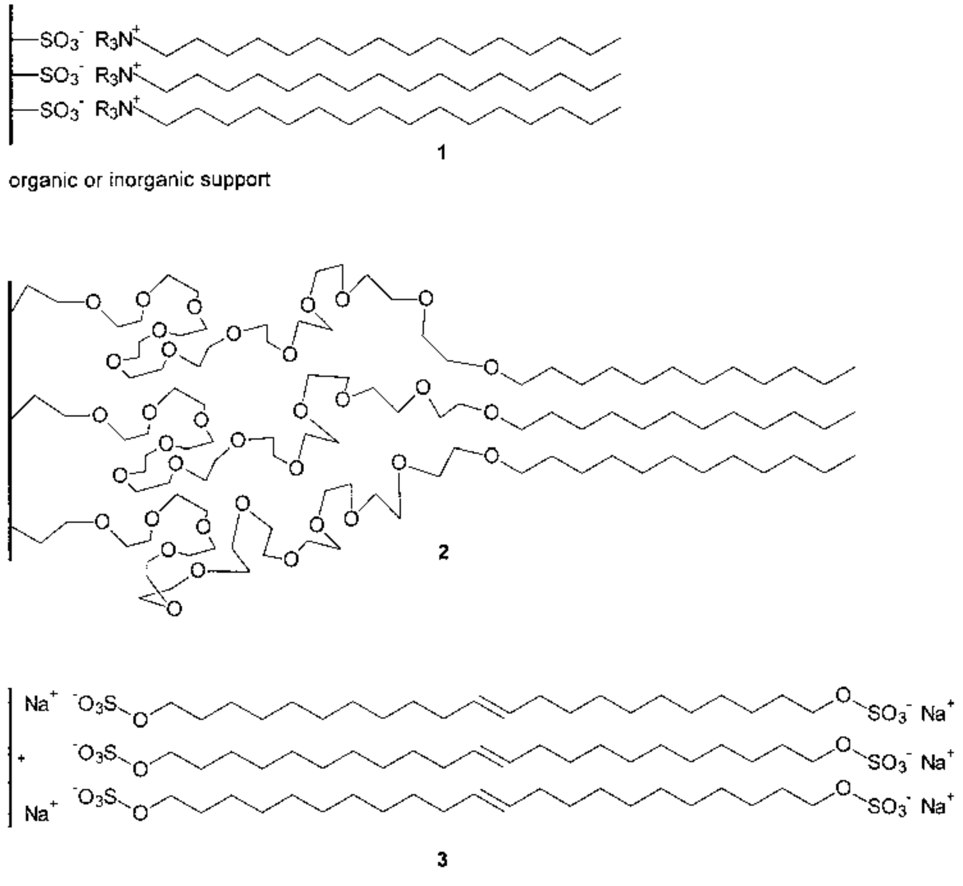


Fig. 3. Amphiphilized inorganic supports: **1** Ionic exchanger; **2** Silica bound polyether amphiphiles; **3** SDS adsorbed on silica or alumina, respectively (admicelles).

Table 3
Hydrogenation of (*Z*)-methyl α-acetamidocinnamate with the catalytic system [Rh(bppm)(cod)]BF_4 + amphiphiles bound to inorganic supports (see Fig. 3)[a]

Amphiphile	Rh:amphiphile	*t*/2 (min)	Optical yield (%ee *R*)
Pure water		90	78
Silica ion exchanger			
Without		40	70
1 0.63 mmol g^{-1}	1:20	11	92
Silica bound amphiphile			
2 0.31 mmol g^{-1}	1:20	24	93
Alumina adsorbed SDS			
3 0.25 mmol g^{-1}	1:20	7.5	90

[a] Reaction conditions: 0.1 MPa H_2; 20 ml water; 25°C; substrate:catalyst = 1:0.01 mmol.

the exchange of educts and products, but we don't know exactly the topology and the shape of the polymerized micelle. Both polyoxyethylene undecenylether M10 and M13 give comparable results in the nonpolymerized and polymerized state. In all examples the time of exposure of the catalytic system before the start of hydrogenation is different. The loading of the micelle with complex and substrate requires more time in the polymerized state.

The last example is the polymerizable ligand M57. The monomer is used in an equimolar ratio to rhodium and leads in water to satisfying activities and enantioselectivities. As observed in other cases [23], enhancement of activity and enantioselectivity is observed in the presence of nonfunctionalized amphiphiles, in our case PEGMU 1000. Both amphiphiles should give mixed micelles with an improved accessibility to the coordinating groups and a higher capacity. Polymerization should give complete microreactors for the catalytic asymmetric hydrogenation. This work is currently on the way in our laboratory.

Table 4
Hydrogenation of (*Z*)-methyl α-acetamidocinnamate (1 mmol) in 25 ml water with the catalytic system [Rh(bppm)(cod)]BF_4 (0,01 mmol) at 25°C and 0.1 MPa H_2, molar ratio amphiphile:Rh = 20:1[a]

Amphiphile	*m*	*n*	Enantiomeric excess (%)	*t*/2 of hydrogenation (min)
L101	56	5	93	7
F108	56	132	92	6
L121	69	4	92	11
P123	69	20	92	5

[a] Structure of polymeric amphiphiles: $HO\text{–}(EO)_n\text{–}(PO)_m\text{–}(EO)_n\text{–}H$. EO = CH_2CH_2O; PO = $CH(CH_3)CH_2O$.

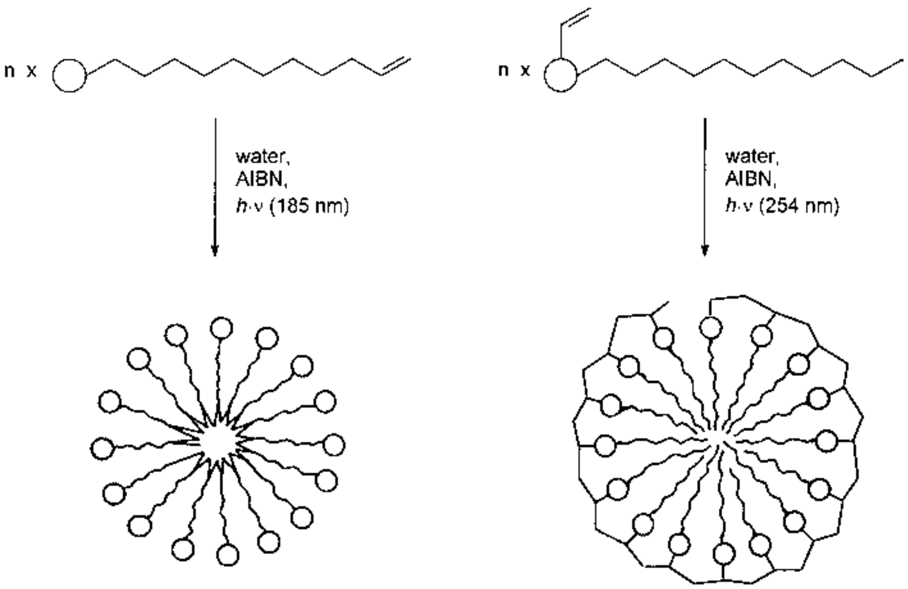


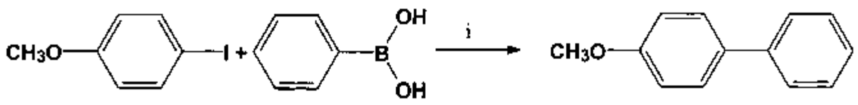
Fig. 4. Polymerized micelles (idealized pictures).

3.2. C–C bond coupling reactions

The formation of carbon–carbon bonds is of fundamental importance in organic chemistry. The area has received new interest due to the development of transition metal catalysis [24]. With the aim of a convenient separation of catalyst and product some new aqueous multiphase systems have been developed [25]. Most investigations have been done in the field of hydroformylation [26]. Montflier et al. [27] described the telomerization of 1,3-butadienes into octadienol in a micellar medium by means of palladium–phosphine complexes. The promoting effect of different amphiphiles was indicated above the cmc's of the surfactants.

Also Heck [28] and Suzuki [29] reactions, both catalyzed by palladium complexes were transferred into an aqueous medium. Beletskaya and coworkers used amphiphiles for a solubilization in organic and aqueous media [30].

We have chosen the Suzuki reaction with 4-iodoanisole and phenylboronic acid as starting materials for investigation in biphasic systems in the presence of amphiphiles.



i: Pd complex (cat.), base, (amphiphile, water/ethanol/toluene)

The water soluble complex of palladium with the potassium salt of 4-diphenylphosphinobutane sulfonic acid as ligand was used as catalyst. The ligand was synthesized in our laboratory [12]. Both educts of the Suzuki reaction are insoluble in water but can be solubilized by addition of surfactants.

The diagram of Fig. 6 shows the Suzuki reaction in the presence of one or fewer equivalents of cetyltrimethylammonium bromide (CTAB) as the micelle forming reagent. The coupling leads to high conversion but the product precipitates during the process. The procedure can be improved by use of different tetraalkylammonium hydroxides instead of sodium carbonate as the base (Fig. 7).

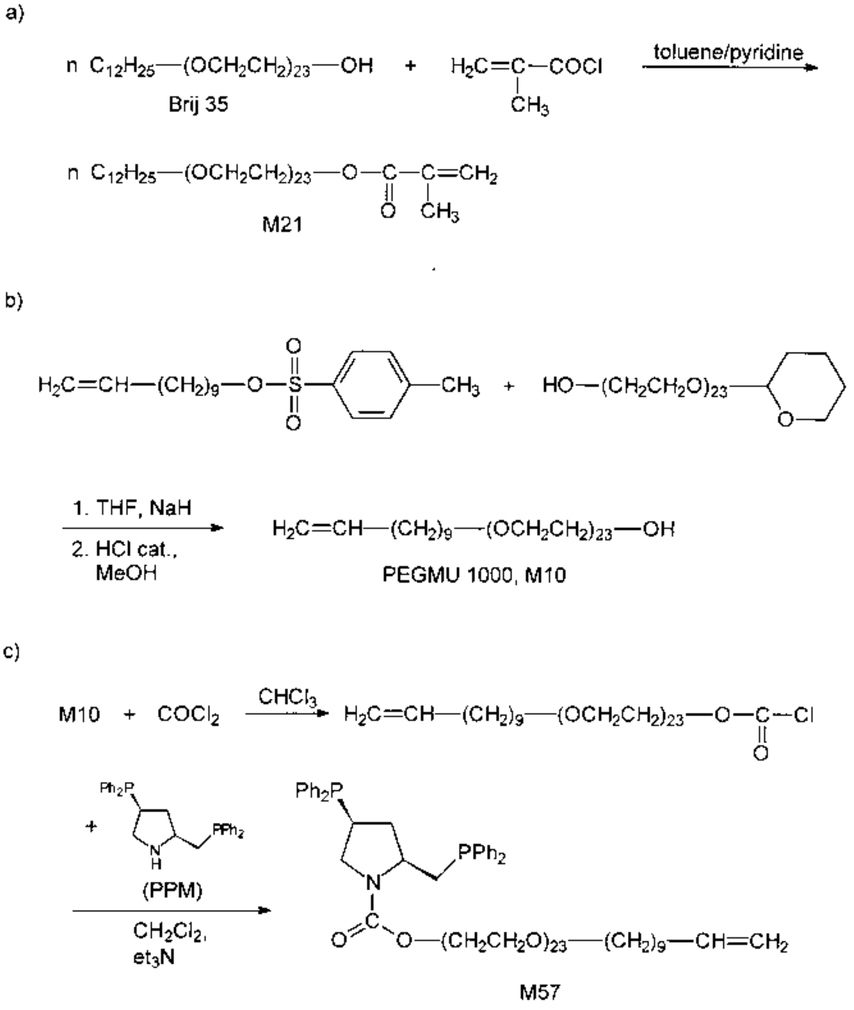
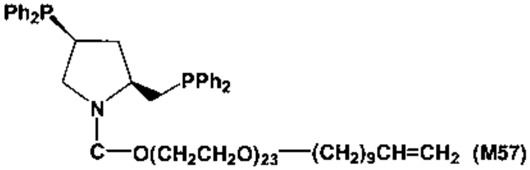


Fig. 5. Synthesis of polymerizable polyether-amphiphiles.

Table 5
Asymmetric hydrogenation in water with the catalytic system $[Rh(cod)_2]BF_4 = L_2^{*a}$ in the presence of nonpolymerized and polymerized micelles, cat.:amphiphile:substrate = 1:20:100[b]

Entry	Amphiphile	$t/2$ (min)	%ee R	Preparation
	Unsaturation in the headgroup			
1	$C_{12}H_{25}$–$(O$–$CH_2CH_2)_{23}$–OCO –$C(CH_3)$=CH_2 (M21)	23	94	15 min stirring
2	M21-polymerized	9	96	4 h stirring
	Unsaturation in the chain			
3	CH_2=CH–$(CH_2)_9$–$(OCH_2CH_2)_9$ –OH (PEGMU 400, M13)	6	96	15 min stirring
4	M13-polymerized	14	95	18 h stirring
5	CH_2=CH–$(CH_2)_9$–$(OCH_2CH_2)_{23}$ –OH (PEGMU 1000, M10)	6	95	15 min stirring
6	M10-polymerized	7	94	18 h stirring
	Unsaturated amphiphilic phosphine			
7		14	91	15 min stirring without amphiphile Rh precipitation
8	M57 + 2 eq. M10	7	91	
9	M57 + 5 eq. M10	6	92	
10	M57 + 10 eq. M10	4	94	

[a] L_2^* = entries 1–6 BPPM, entries 7–10 M57.
[b] Entries 1–6.

It should be noted that the ammonium hydroxides act only in the presence of CTAB thus indicating the central role of micelles.

Unfortunately, the selectivity of this micellar reaction is only moderate and we observed up to 20% biphenyl side product after 240 min.

As an alternative we tried a phase transfer system with toluene as the organic phase and ethanol as the phase mediator. As shown in Fig. 8 the reaction occurs with the palladium complex in the absence of any surfactant but with a low rate and low conversion (curve D = 0). Addition of a surfactant promotes the reaction rate and conversion significantly.

Fig. 9 gives an impression of the effect with different types of surfactants. It is clear from these results that CTAB and the zwitterionic 3-(cetyl-dimethyl-ammonio) propanesulfonate are favored as the phase transfer reagents. The polyether surfac-

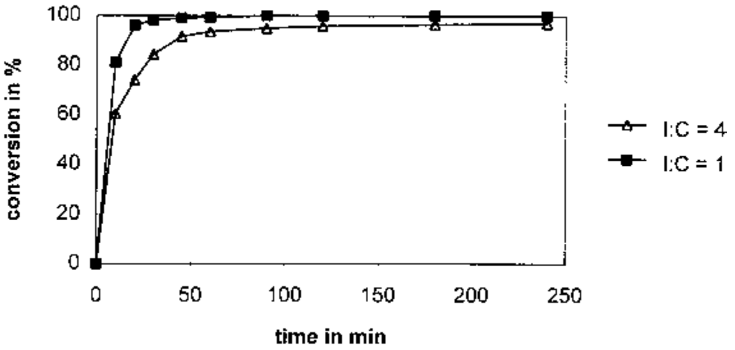


Fig. 6. Suzuki reaction of 15 mmol phenylboronic acid with 13.5 mmol *p*-iodoanisole in 45 ml water; catalyst: 0.01 mmol $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$. CTAB as micelle forming reagent and 45 mmol Na_2CO_3 as base. Ratio iodoanisole: CTAB (I:C) = 1 or 4, at 78°C.

tants Tween 20, hexaoxyethylene dodecylether (E_6C_{12}) and decaoxyethylene dodecylether ($E_{10}C_{12}$) gave the smallest effect. The block copolymers (Synperonics, Poloxamers, Pluronics, mentioned in Table 4) are also suitable as amphiphiles in the Suzuki reaction.

The results obtained with some of this polymers are comparable to those with zwitterionic surfactants.

In the following experiments CTAB was used as the standard phase transfer reagent.

Fig. 10 displays the temperature dependence of the standard reaction between 30 and 78°C. In our experience the temperature should not be lower than 50°C.

The reaction rate depends also on the reactivity of the educts: 3-fluorophenyl-, 2,4-dichlorophenyl- and α-naphthylboronic acid have about the same reactivity as phenylboronic acid at 78°C, whereas the activity of 2-methyl-phenylboronic acid is moderate and *n*-butyl-boronic acid is inactive.

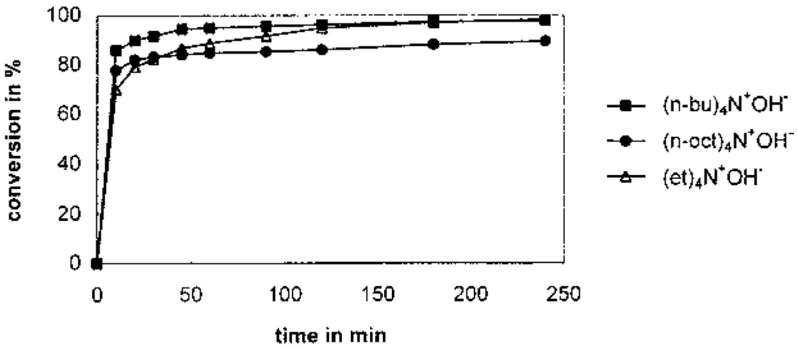


Fig. 7. Suzuki reaction. Conditions see Fig. 6 with I:C = 4 different tetraalkylammonium hydroxides (15 mmol) instead of Na_2CO_3 (45 mmol).

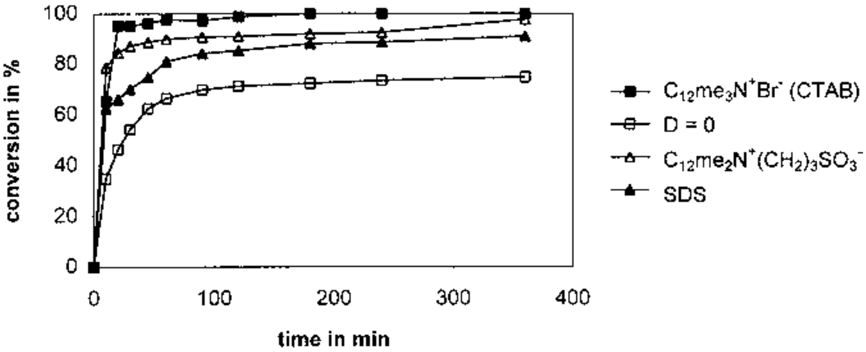


Fig. 8. Suzuki reaction under phase transfer conditions: 15 mmol phenylboronic acid, 13.5 mmol *p*-iodoanisole, 0.01 mmol $PdCl_2[Ph_2P(CH_2)_4SO_3K]_2$, 45 mmol Na_2CO_3 in toluene/ethanol/water = 15:15:15 ml at 78°C. D = 0 without, all other curves with 3.4 mmol amphiphile.

Most iodine containing compounds are active in the Suzuki reaction. We had good success with 4-iodoanisole, iodobenzene, 2-, 3- and 4-iodotoluene and 4-iodoaniline but the reactivity of 2,6-dimethyl-iodobenzene and allyliodide was clearly reduced. However, with the latter complexes, a conversion of nearly 100% could be attained after about 3 h whereas the other compounds already yielded this result within 30 min.

It is well known, that reactivity decreases for aryl–X, X = halogen, in the series I > Br > Cl [31]. We found a differentiation also in the following series: 3-bromo- > 4-bromo- > 2-bromo-toluene > 2-bromopyridine. Allylbromide gave 100% conversion after 3 h but the reaction course is not regular.

The analogous chloro compounds are most interesting from a practical point of view but these are much less active than iodo- and bromo compounds. Only benzylchloride gave excellent results whereas allylchloride, 4-trifluoromethyl-chlorobenzene and 2-chloropyridine yielded less than 50% conversion after 6 h.

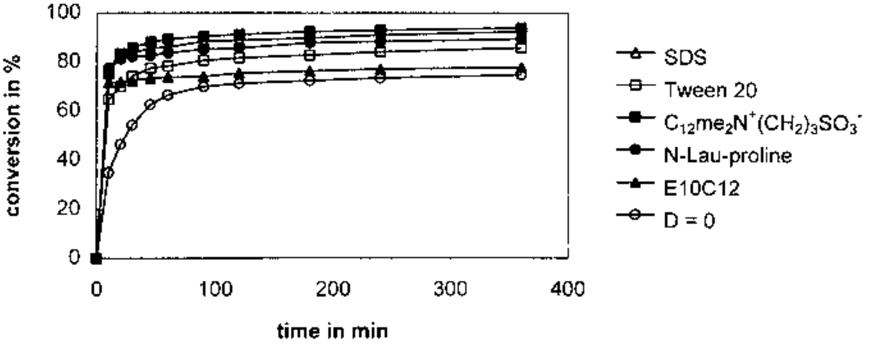


Fig. 9. Suzuki reaction like in Fig. 8 with different types of amphiphiles.

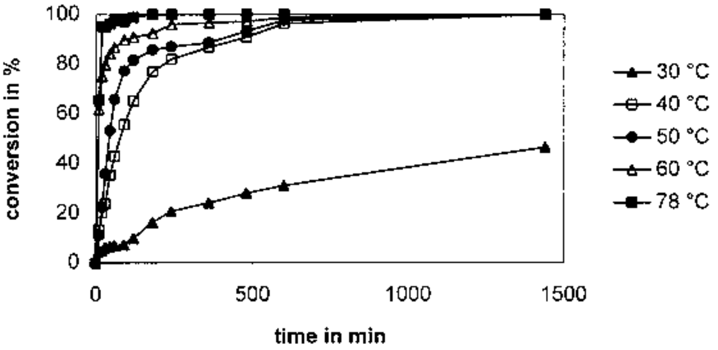


Fig. 10. Suzuki reaction under phase transfer conditions (like those of Fig. 8) with 3.4 mmol CTAB as amphiphile.

The amount of the palladium complex required is relatively low (< 0.1 mol%) in all standard experiments but systematic investigations indicated that lower concentrations (< 0.01 mol%) are still effective.

Comparing the course of the Suzuki reaction under different conditions presented here shows that the phase transfer systems are superior to micellar ones because of the latters solubility of educts and products in the organic phase. It seems also that the biphenyl formation side reaction is suppressed under phase transfer conditions.

4. Conclusion

The systems discussed here, the asymmetric hydrogenation of α-amino acid precursors and the Suzuki reaction, are quite different in their requirements. Two phase systems in asymmetric hydrogenation show, as a rule, low activity and moderate enantioselectivity [32], whereas the micellar systems have excellent properties with sometimes better enantioselectivities than in organic media. The observation of the enhanced enantioselectivity can be explained by the stereoregularity of the micelles. The exchange between educts and products with the micelle is very fast.

In contrast to this, the capacity of the micelles seems too small for a successful Suzuki reaction. In principle the micellar system works and perhaps there are facilitations to expect for stereoselective reactions. At this time the phase transfer systems developed here have advantages with respect to activity, capacity, and chemoselectivity, compared to their homogeneous analogs.

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