Phosphinoethyl-sulfonatoalkylthioethers and diphenyl-ω-sulfonatoalkyl-phosphines as ligands and polyoxyethylene–polyoxypropylene–polyoxyethylene triblock co-polymers as promoters in the rhodium-catalyzed hydroformylation of 1-dodecene in aqueous two-phase systems

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Abstract

The rhodium-catalyzed hydroformylation of 1-dodecene was investigated with a series of sulfonated water-soluble phosphine ligands at a pressure of 60 bar CO/H_2 and a temperature of 120 °C. Seven different groups of water-soluble phosphines were used for our investigations. We established an optimized ligand/rhodium ratio of 5 for the phosphines **1a**, $[Ph_2P(CH_2)_2S(CH_2)_2SO_3Na]$, and **1b**, $[Ph_2P(CH_2)_2S(CH_2)_3SO_3Na]$. The utilized arylphosphino-thioether-alkylsulfonates formed with Rh(I) compounds highly active catalysts which could be recycled. The addition of detergents speeds up the hydroformylation reaction, but disturbs the phase separation (recycling). The best promotion effect and the smallest negative influence on phase separation gave polyoxyethylene–polyoxypropylene–polyoxyethylene triblock co-polymers. The ratio of 1-dodecene/rhodium could be increased up to 10.000 and we achieved turnover numbers (TONs) > 50.000 without any surfactant and TONs of about 65.000 in presence of the co-polymers owing to the recycling on the catalytic system.
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1. Introduction

Recycling of the catalyst is one of the important problems in industrial homogeneous-catalytic processes. An essential method for recovery of the catalyst is the separation of the product from the catalyst system. The extension of the Ruhrchemie/Rhone Poulenc process as one of the first important industrial processes which work with aqueous multiphase systems allows to produce an annual quantity of 600.000 t of butyraldehyde [1]. In chemical industry and academic laboratories various catalytic reactions with water-soluble complexes are investigated (C–C coupling reactions, hydrogenations). They offer the advantage of separation of the aqueous catalyst phase. Recently, results of extensive investigations and discussions of hydroformylation reactions are published [2–10], even for higher olefines [11–22].

So far, the hydroformylation of higher olefines ($>C_6$) corresponding to the aqueous multiphase systems was performed only with non-satisfying olefin/catalyst ratios (<1.000). For these reactions solvents such as methanol or ethanol were applied and detergents are used as solubility mediators, e.g. cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyethylene glycol (PEG). In some cases, the instructions for the conditions are not clear in the literature.

Chen et al. [11] used as catalysts in the hydroformylation of higher olefines ($>C_8$) water-soluble rhodium–poly (enolate - co-vinylalcohol-co-vinylacetate) complexes. The authors observed a high reactivity (2.36×10^{-4} kmol/kg(Rh) s) for 1-dodecene at a temperature of $60\,°C$ and a pressure of about 40 bar. Fell et al. [12] found, that the application of surfactants leads to a successful hydroformylation of alkenes $>C_6$ in an aqueous/organic two-phase system. These authors used also catalysts with *p*-(poly-oxyethylene)phenylphosphines as ligands [13,14]. Similar ethoxylated phosphines are known from a Russian group [15], but there are no details available for using these ligands in catalysis. In a recent publication of the same group, the hydroformylation of 1-dodecene with rhodium complexes is also described with water-soluble phosphine and phosphinite ligands (ratio 1-dodecene/rhodium is about 150) [16]. Kalck and coworkers [17,18] reacted terpenes with water-soluble thiolate-bridged rhodium complexes. Rhodium–TPPTS complexes (TPPTS: Tris-(*m*-sulfonylphenyl)phosphine) have been used in the hydroformylation and hydroxycarbonylation of acrylic esters and for hydrocarboxylations with an olefin/rhodium ratio of 500 [19,20]. By using rhodium–TPPTS complexes for the hydroformylation of 1-dodecene with a large excess of the ligand ($>80/1$) no reaction was observed [21a]. By adding of 35 mass percent of polyethylene glycol [21b] 13% conversion of 1-dodecene could be achieved.

To realize a successful hydroformylation of long-chain alkenes the development of new ligands with amphiphilic properties [22] or the use of surfactants as phase-transfer reagents seems to be necessary. Chinese groups hydroformylated 1-dodecene with rhodium catalysts in biphasic media [23–25]. They conclude, that the catalysis takes place in the interface between the aqueous and the organic phase. Borrmann

et al. [26] reported highly reactive water-soluble hydroformylation catalysts based on rhodium polyethylene glycolate for the hydroformylation of 1-alkene at $100\,°C$. After 3 h a turnover frequency (TOF) >600 was obtained for 1-dodecene. Haumann et al. [27] worked in the hydroformylation of 1-dodecene even with TPPTS/Rh = 4 and a greater amount of surfactants (13%) with an ratio of alkene/Rh = 3.000.

In most publications, the recycling of the aqueous catalyst phase was discussed but the phase separation was not mentioned.

Here, from a critical point of view, experiments are described with sulfonated phosphines in presence and absence of surfactants that normally increase the yield of the hydroformylation reaction and decrease the separability of the aqueous and organic phase. The phosphines were prepared in our laboratory [28,29] and have been previously used in catalytic reactions [30–32].

2. Experimental part

All reactions were carried out under exclusion of oxygen using an argon atmosphere and solvents distilled under argon. Olefins, CTAB and SDS were purchased from Aldrich and Fluka, rhodium(II) acetate was a product of ABCR. The Synperonics were kindly donated by Fa. C.H. Erbslöh (Spezialchemikalien und Industriematerialien, Krefeld).

Phosphines **1–7** used in this work (Scheme 1) were prepared as mentioned below or from procedures given in [28–30].

The diphosphine **7** was synthesized by *p*-phenyl cleavage of 1,2-bis(diphenylphosphino)ethane with lithium followed by reaction with 1,4-butane-sultone [28]. The new type of water-soluble thioether-alkyl-phosphines (**1**, **2** and **6**) were easily prepared by reaction of the corresponding vinylphosphine with the commercially available sodium 2-mercaptoethanesulfonate or sodium 3-mercaptopropanesulfonate in ethanol/water [29]. The phosphine **5** was obtained by addition of 2-mercaptoethanesulfonic acid to divinylphenylphosphine followed by treatment with tetra-*n*-butylammonium hydroxide.

The phosphines **3a** and **3b** were prepared by addition of the corresponding sodium mercaptoalkane-sulfonates to ethynyldiphenylphosphine under reflux.

$Ph_2P-(CH_2)_2-S-(CH_2)_n-SO_3Na$

1a: n = 2 (325)
1b: n = 3 (250)

$PhP-[(CH_2)_2-S-(CH_2)_n-SO_3Na]_2$

2a: n = 2 (540)
2b: n = 3 (440)

$Ph_2P-CH_2\cdot CH \begin{cases} S-(CH_2)_n-SO_3Na \\ S-(CH_2)_n-SO_3Na \end{cases}$

3a: n = 2 (820)
3b: n = 3 (740)

$Ph_2P-(CH_2)_n-SO_3M$

4a: n = 3   M = Li
4b: n = 4   M = Li
4c: n = 3   M = K (360)
4d: n = 4   M = K (330)

$PhP[-(CH_2)_2-S-(CH_2)_2-SO_3^- \ \overset{+}{N}(n\text{-Bu})_4]_2$

5

$P[-(CH_2)_2-S-(CH_2)_n-SO_3Na]_3$

6a: n = 2 (1860)
6b: n = 3 (2500)

$\begin{array}{l} CH_2P(Ph)CH_2CH_2CH_2CH_2SO_3Li \\ | \\ CH_2P(Ph)CH_2CH_2CH_2CH_2SO_3Li \end{array}$

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Scheme 1. Sulfonated phosphines used in this paper. In parenthesis, solubility in water (g/l).

The purity of the phosphines was established by ^{31}P NMR, IR-spectra and elemental analysis.

2.1. General procedure for catalysis experiments

To perform the hydroformylation reaction an autoclave (100 ml, Fa. Parr) with teflon coating and equipped with a hollow shaft gas inlet stirrer (1000 rpm) was used. The reaction mixture containing water, olefin, surfactant and the catalytic system (see tables) was transferred from a Schlenk tube into the autoclave under an argon atmosphere. After that, the argon was displaced by purging with synthesis gas (CO/H$_2$, 1/1) the pressure was increased to 60 bar at room temperature. The autoclave was heated up to 120 °C within 30 min with stirring and kept for 5 h under these conditions. After cooling, the reaction mixture was isolated, the phases were separated, and the aqueous phase with the catalyst was recycled. The organic phase was mixed with 20 ml hexane and dried with sodium sulfate. A part of the experiments was worked up by distillation in vacuum.

GC analysis: 30 m capillary HP 5 (95% dimethylpolysiloxane + 5% diphenylpolysiloxane), temperature program 8 °C/min from 50 to 260 °C.

3. Results and discussion

All phosphines presented in Scheme 1 are active ligands in a water-olefin two-phase hydroformylation system except the extremely water-soluble phosphines **6a** and **6b**. The necessity of at least a small solubility of the rhodium complex in the organic phase could be an indication that the hydroformylation occurs at the interphase between aqueous and organic phase. A coloring of the organic phase at the reaction temperature by the catalytic system was never observed.

Table 1 summarizes the results obtained in the presence of different phosphines as ligands. The ligands **6a** and **6b** are omitted because of very low conversion.

1-Dodecene was the substrate in all experiments and the ligand/rhodium ratio used was 5. Hence, the ligand/rhodium ratio is much smaller compared to the hydroformylation of lower olefins and even in earlier two-phase experiments with 1-octene and 1-dodecene.

Table 1

Hydroformylation of 1-dodecene catalyzed by rhodium complexes with different ligands (see Scheme 1)[a]

Entry	Ligand	1-Dodecene/Rh			
		450		10,000	
		Conversion (%)	n/b[b]	Aldehydes per conversion (%)	n/b[b]
	Without	5	2.8		
1	TPPTS[c]	>99	1.2	55/55	1.3
	TPPTS[d]			71/75	0.5
2	TPPMS[e]	>99	3.2	75/76	0.7
	TPPMS[d]			89/89	0.5
3	**1a**	>99	1.2	77/80	0.7
	1a[d]			82/84	0.5
4	**1b**	>99	1.4	62/66	1.1
	1b[d]			84/86	0.6
5	**2a**	87	1.8	44/48	1.6
	2a[d]			25/25	1.8
6	**2b**	86	1.2	51/53	1.1
	2b[d]			42/42	0.9
7	**3a**	94	1.9	78/78	1.0
	3a[d]			25/43	1.3
8	**3b**	94	0.7	81	0.7
	3b[d]			28/47	0.9
9	**4a**	95	2.3	22/44	1.2
10	**4b**			29/46	1.6
11	**4c**	97	2.1	43/56	1.9
	4c[d]			32/48	0.9
12	**4d**	>99	2.3	36/58	1.3
	4d[d]			38/50	0.9
13	**5**	81	1.3	30/67	1.5
14	**7**			71/78	0.7

[a] 45 mmol 1-dodecene; 5 ml water; 0.05 or 0.00225 mmol [Rh(OAc)$_2$]$_2$; 0.5 or 0.0225 mmol ligand (ligand/Rh = 5); 0.54 mmol CTAB; 60 bar CO/H$_2$ (1/1); 5 h at 120 °C.

[b] Ratio of normal (n) and branched (b) aldehydes.

[c] TPPTS: Tris-(*m*-(sulfonylphenyl)phosphine).

[d] Without CTAB.

[e] TPPMS: *m*-sulfonylphenyl-diphenylphosphine.

The following investigations were focussed on the use of sulfonated thioether phosphines as ligands. As shown in Table 1, the monosulfonated and the disulfonated phosphines **1a**, **1b**, **2a**, **2b**, **3a**, **3b** and **5** gave good conversions. Comparable in the structure are the sulfonated diphenylalkylphosphines of the type **4**. As

Table 2

Hydroformylation of 1-dodecene[a] (variation of the ratios of ligands **1a** and **1b** and rhodium)

Entry	Ratio (**1**/Rh)	Aldehydes (%)	n/b[b]
1	5 (**1a**/Rh)[c]	82	0.5
2	5 (**1a**/Rh)	**77**	0.7
3	10 (**1a**/Rh)	5	1.7
4	20 (**1a**/Rh)	1	–
5	40 (**1a**/Rh)	0	–
6	60 (**1a**/Rh)	0	–
7	5 (**1b**/Rh)[c]	84	0.6
8	5 (**1b**/Rh)	62	0.8
9	10 (**1b**/Rh)	3	1.5
10	20 (**1b**/Rh)	2	–
11	40 (**1b**/Rh)	0	–
12	60 (**1b**/Rh)	0	–

[a] 45 mmol 1-dodecene; 5 ml water; 0.00225 mmol [Rh(OAc)$_2$]$_2$; x mmol ligand (ligand/Rh = see table); 60 bar CO/H$_2$ (1/1); 5 h at 120 °C.

[b] Ratio of normal (n) and branched (b) aldehydes.

[c] Without CTAB.

an indication for a P–S Rh chelate the ^{31}P NMR of the Rh complex [Rh(cod)1b]BF$_4$ showed a P/Rh coupling of 160 Hz [33]. Early investigations have shown, that the sulfur in thioetherphosphines act as a coordination site forming a P–S chelate with rhodium [34], but we found no significant difference between sulfonated thioetherphosphines and sulfonated alkylphosphines (**4**) in the hydroformylation reaction. A sulfur containing catalytic hydroformylation system with bridging thiolate groups in a dimeric rhodium complex was reported by Kalck and coworkers [17,18].

Table 2 shows the conversion of 1-dodecene in dependence on the ligand **1**/rhodium ratio. The reaction is inhibited in the presence of more than 5 mol **1**/mol rhodium. This result is quite different in comparison with the hydroformylation of propene. We observed for the aldehyde fraction an increase of the normal/branched (n/b) ratio with an increasing ligand concentration.

The reason can be the chelation of rhodium owing to the bidentate thioetherphosphine. Another reason could be the low solubility of the olefin as educt and the aldehyde mixture as product in the water phase containing the catalyst. In contradiction, propene is relatively soluble in water and a high ligand concentration gave a high n/b ratio of the butanals. In case of higher olefins, the water-soluble phosphine ligand

could inhibit the reaction of the catalytic system at the interface. As mentioned above, a solubility of the catalyst in the organic phase is to exclude.

With the aim to apply the resulting aldehydes as basis for plasticizers the n/b ratio should be tolerable in a wide range, but a high fraction of *n*-aldehydes would be necessary as basis for detergents. On the other hand, industry seems to prefer indeed the terminal aldehydes but a low n/b ratio is a general problem in the hydroformylation of higher olefins [22].

Hydroformylation with $[Rh(OAc)_2]_2$ without any P ligand yielded a relatively high n/b ratio of 2.8 but only a very low conversion (5%).

The variation of the substrate/rhodium complex ratio from 450 to 10,000 influences conversion and even the ratio of normal/branched aldehydes: an extremely low catalyst concentration increased the formation of branched aldehydes. The highest conversion was observed with ligands of medium hydrophilicity (TPPMS, **3a**, **3b** and **7** as a more hydrophilic exception). An increase of hydrophilicity seems to be combined with a decrease of efficacy (**3a**, **3b** > **1a**, **1b** > **2a**, **2b** ≫ **6a**, **6b**). The suitability of the ligands can be adjusted by the degree of sulfonation or the balance of hydrophilicity and lipophilicity. The easy to synthesize phosphines **1a** and **1b** were used in the following experiments.

Table 3 shows a selection of experiments with three ligands at different catalyst concentrations. The

n-selectivity seems to decrease with the decrease of the catalyst concentration. This might be explained by a parallel isomerization reaction, which is less dependent on the substrate/rhodium ratio than the hydroformylation reaction. At extremely low catalyst concentrations the conversion was found to be higher without use of CTAB. With the three checked ligands the conversion was satisfying at a substrate/catalyst ratio of 4500. Most of the following experiments were carried out with a substrate/rhodium ratio of 10,000 to differentiate activities.

A study of the time dependence of the conversion shows, that in the starting period of the reaction the n/b ratio is highest (Fig. 1).

Fig. 2 displays the dependence of the hydroformylation on the temperature. Below 60 °C there is no conversion but above there is a very fast enhancement. The maximum of conversion was found at 80 °C but the maximum yield of aldehydes was found at 120 °C. Although the best n/b ratio was observed at 80 °C we decided to work at 120 °C because of the higher yields of aldehydes.

The difference between conversion of 1-dodecene and the yield of aldehydes is explained by the formation of isomeric dodecenes, which are analyzed in Fig. 3. Apparently, there is a significant isomerization reaction of 1-dodecene to 3-dodecene.

To improve the transition of the water-soluble catalyst to the interphase we added cetyltrimethylammonium bromide (CTAB) as a typical phase-transfer reagent (Table 1). A positive effect of such surfactants in multiphase hydroformylation reactions is well known [2,3,11,12,22]. Chinese authors proposed the existence of aqueous micelles [23,25].

A disadvantageous side effect is the more difficult phase separation under our conditions. We found no satisfying effect on the conversion (Table 1), and no influence of the surfactant concentration on the ratio could be observed. Alternatively, the use of sodium dodecyl sulfate gave no advantage.

To decrease the soap effect we checked as non-ionic amphiphiles the commercially available polyoxyethylene–polyoxypropylene block co-polymers of the type $H(OCH_2CH_2)_n$–$(OCH(CH_3)CH_2)_m$–$(OCH_2CH_2)_nOH$ (Synperonics, Pluronics). These surfactants are important technical products which can be regulated in the consistence by the synthesis (L: liquid, P: pasty, F: solid) [35]. Selected data with 0.20 g

Table 3
Hydroformylation of 1-dodecene at different 1-dodecene/Rh ratios[a]

Entry	Ligand	1-Dodecene/Rh	Water (ml)	Aldehydes (%)	n/b[b]
1	**1b**	450	20	>99	1.4
2		4500	5	64	2.2
3		10000	5	62	0.8
4	Without CTAB	10000	5	84	0.6
5	TPPMS	450	20	85	3.2
6		4500	5	95	2.8
7		10000	5	75	0.7
8	Without CTAB	10000	5	89	0.5
9	TPPTS	450	20	99	2.1
10		4500	20	99	1.9
11		10000	5	50	1.5
12	Without CTAB	10000	5	71	0.5

[a] 45 mmol of 1-dodecene; 0.05, 0.005 or 0.00225 mmol $[Rh(OAc)_2]_2$; 0.5, 0.05 or 0.0225 mmol ligand (ligand/Rh = 5); 0.54 mmol CTAB; 60 bar CO/H_2 (1/1); 5 h at 120 °C.
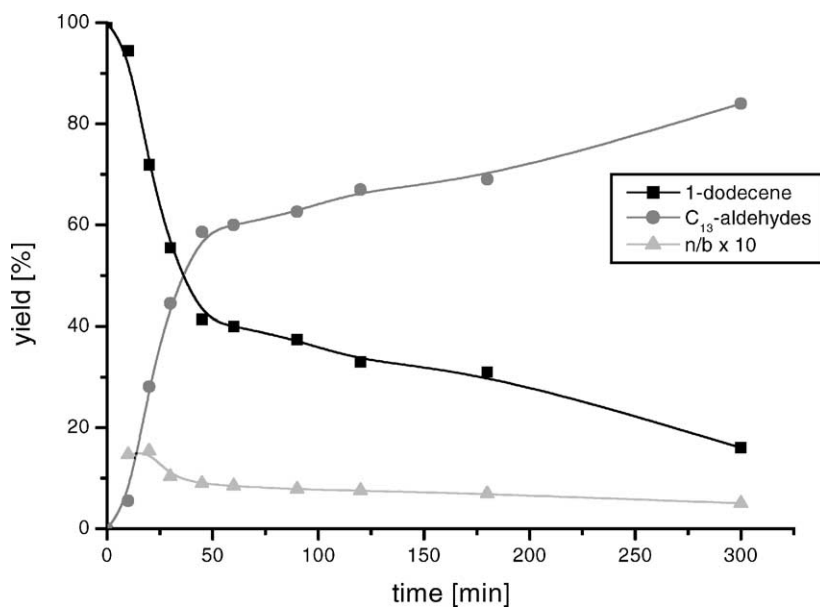[b] Ratio of normal (n) and branched (b) aldehydes.

Fig. 1. Hydroformylation of 1-dodecene at 120 °C (for conditions see Table 1; 1-dodecene/Rh = 10,000).
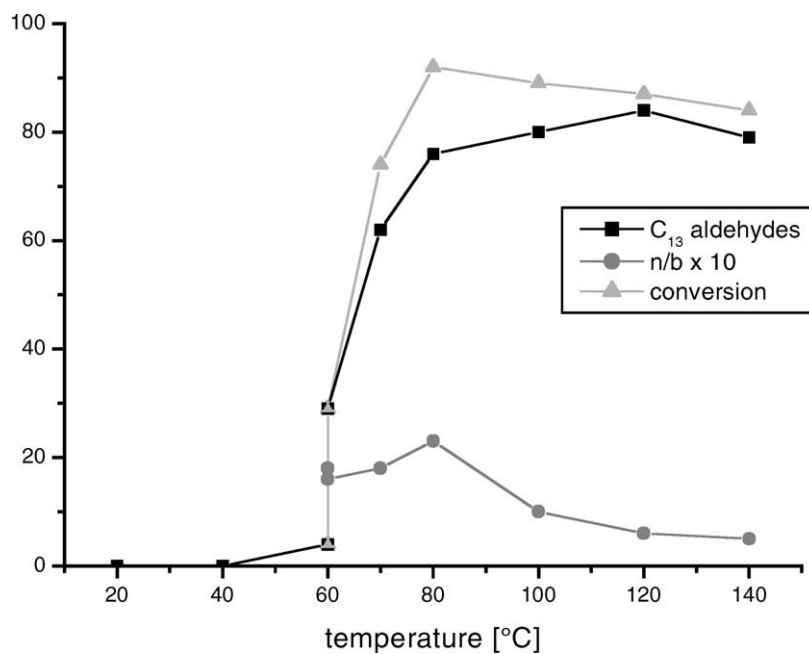

Fig. 2. Dependence of the hydroformylation of 1-dodecene on the temperature (for conditions see Table 1; 1-dodecene/Rh = 10,000).
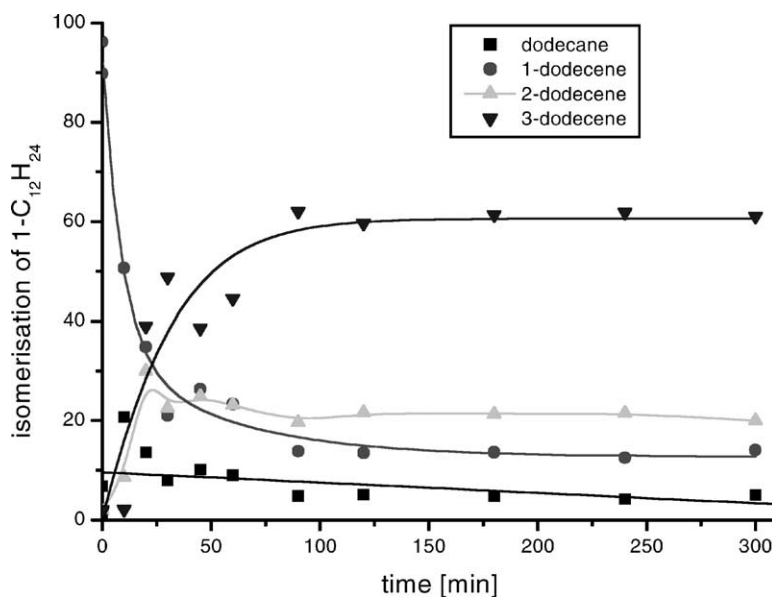
Fig. 3. Isomerization of 1-dodecene within the hydroformylation, 5 h at 120 °C (this fraction is the difference between conversion and yield of aldehydes).

of amphiphile as phase-transfer reagent are shown in Table 4.

In the bold marked examples the yield was more than 90% (F 68, L 101, P 103, P 105, L 121, P 123, F 127). In all cases, more branched aldehydes than normal aldehydes were formed. Obviously, some Synperonics showed a negative effect and led to lower yields than in the blank experiment. Not in all cases, there is a similarity to the influence of the amphiphiles on the asymmetric hydrogenation of methyl (Z)-α-acetamidocinnamate catalyzed by rhodium complexes [36].

The chosen concentration of Synperonics seems too high with respect to a convenient phase separation and Table 5 summarizes a selection of highly effective Synperonics used with a much lower concentration (0.05 g per experiment).

The conversion was almost quantitative in all experiments. The column "emulsion" gives an impression about phase separability. Only the entries 1, 2 and 8 with very low values of "emulsion" are suitable for a practical use. The dependence of separability on the amount of the Synperonic is demonstrated in Table 6 for F 68 ($m = 30$; $n = 76$).

Table 4
Hydroformylation of 45 mmol 1-dodecene catalyzed by 0.00225 mmol [Rh(OAc)$_2$]$_2$ and 0.0225 mmol **1b**

Entry	Synperonic[a,d]	m[a]	n[a]	m/n[a]	Yield[b] (%)	n/b[c]
1	Without				84	0.5
2	L 64	30	13	2.3	81 (−3)	0.8
3	**F 68**	30	76	0.4	99 (+15)	0.3
4	F 87	39	61	0.6	74 (−10)	0.6
5	F 88	39	103	0.4	77 (−7)	0.6
6	**L 101**	56	5	11.2	96 (+12)	0.6
7	**P 103**	56	17	3.3	97 (+13)	0.5
8	P 104	56	27	2.1	84 (±0)	0.6
9	**P 105**	56	37	1.5	96 (+12)	0.5
10	F 108	56	132	0.4	83 (−1)	0.6
11	**L 121**	69	4	17.3	99 (+15)	0.5
12	**P 123**	69	20	3.5	94 (+10)	0.5
13	**F 127**	69	99	0.7	95 (+11)	0.6

1-Dodecene/Rh = 10,000; **1b**/Rh = 5; 60 bar CO/H$_2$ (1/1); 5 ml water; 5 h at 120 °C; different Synperonics (0.20 g).

[a] 0.20 g Synperonic: HO(CH$_2$–CH$_2$–O)$_n$–(CH(CH$_3$)–CH$_2$–O)$_m$ –(CH$_2$–CH$_2$–O)$_n$H.

[b] Isolation of the water phase in presence of the amphiphile is difficult. In parenthesis, difference to the yield without Synperonic (see entry 1).

[c] Average ratio with 12 Synperonics n/b = 0.55.

[d] L 64, L 101, P 103, P 104, P105, F 108, P 123 co-catalyze the homogeneous hydrogenation [36].

Table 5

Hydroformylation of 45 mmol 1-dodecene catalyzed by 0.00225 mmol [Rh(OAc)$_2$]$_2$; 0.0225 mmol **1b** (different Synperonics (0.05 g))

Entry	Synperonic[a]	Normal/branched[b]	Emulsion[c] (ml)	m/n[b]
1	F 68	0.5	1	0.4
2	L 101	0.5	1	5
3	P 103	0.5	15	17
4	P 104	0.5	10	27
5	P 105	0.5	7.5	37
6	L 121	0.5	6	17.3
7	P 123	0.5	15	3.5
8	F 127	0.5	1	0.7

1-dodecene/Rh = 10,000; **1b**/Rh = 5; 60 bar CO/H$_2$ (1/1); 5 ml water; 5 h at 120 °C.

[a] Conversion was almost quantitative.

[b] See Table 4.

[c] Emulsion >5 ml shows no separated water phase.

The lowest amount of amphiphile with an acceptable effect and a satisfying separability seems to be 0.05 g Synperonic per experiment. It is an important conclusion to use Synperonics as phase-transfer reagents in the hydroformylation of 1-dodecene. The suitability of polymeric amphiphiles is better than those of monomeric such as CTAB or SDS.

The critical test of our system should be recycling experiments. Some experiments were carried out without surfactants (Table 7).

Without surfactant we achieved satisfying yields and the catalytic system was recycled eight times. The yields of aldehyde was decreased but the ratio of normal and branched aldehydes was increased after the recycle. As the sum of all successful reactions it gave a turnover number (TON) of 53.000 and a turnover frequency of 1.200 mol/h.

Table 8 summarizes a recycling experiment in presence of the Synperonic F 68 in a low concentration.

Table 6

Hydroformylation in dependence on small amounts of Synperonic F 68 (for conditions see Table 5)

Entry	Yield of aldehydes (%)	Normal/ branched	Emulsion (ml)	Synperonic F 68 (g)
1	96	0.7	15	0.20
2	94	0.6	10	0.10
3	96	0.6	1	0.05
4	87	0.5	1	0.02
5	73	0.5	0	0.01

Table 7

Hydroformylation of 1-dodecene catalyzed by 0.00225 mmol [Rh(OAc)$_2$]$_2$; 0.0225 mmol **1b**; 1-dodecene/Rh = 10,000; **1b**/Rh = 5; 60 bar CO/H$_2$ (1/1); 5 ml water; 5 h at 120 °C

	Yield of aldehydes (%)	Normal/branched
Use	84	0.6
Recycle	78	0.6
Recycle	75	0.7
Recycle	67	0.6
Recycle	65	0.7
Recycle	61	0.7
Recycle	51	1.4
Recycle	31	1.4
Recycle	20	2.0

The phase separation was convenient and the selectivity and activity were promoted in comparison to results in Table 7. Under the chosen conditions the use of amphiphilic block co-polymers gave the best results.

Finally, it should be mentioned some results with different buffer solutions. Buffers of pH 10 (carbonate or borate), pH 7 (carbonate) and pH 4 (citrate) were used, but the results in hydroformylation were not reproducible. We found that the pH of the carbonate and the borate buffers changed within the reaction. During 5 h at 120 °C and 60 bar CO/H$_2$ the pH 10 buffers decreased to values between pH 7.8 and 7.5 and the pH 7 buffer decreased to pH 6.4. Only the pH 4 buffer remains constant. The pH change was independent of the presence of the substrate. 1-Dodecene and an analysis of the residue indicated the formation of formate. A detailed investigation of this effect is in preparation.

Table 8

Hydroformylation of 1-dodecene in presence of 0.05 g of Synperonic F 68 (for conditions see Table 5)

	Yield of aldehydes (%)	Normal/branched
Use	99	0.5
Recycle	91	0.5
Recycle	90	0.5
Recycle	83	0.6
Recycle	66	0.7
Recycle	57	1.1
Recycle	51	1.4
Recycle	43	1.4
Recycle	31	1.5
Recycle	25	1.8
Recycle	18	2.0
Recycle	4	2.3

4. Conclusions

It was demonstrated that in situ complexes of a new type of sulfonated thioether-alkylphosphines (**1**, e.g. $Ph_2P(CH_2)_2S(CH_2)_{2.3}SO_3Na$) with $[Rh(OAc)_2]_2$ are active hydroformylation catalysts with the ratio 1-dodecene/Rh = 10.000 in aqueous two-phase systems at a pressure of 60 bar CO/H_2 and a temperature of 80 or 120 °C, respectively. For the catalytic aqueous systems, a thioetherphosphine/rhodium ratio of 5 is suitable. Turnover numbers of more than 50.000 were observed without surfactants within the successful recycling of the catalyst. The application of amphiphiles like CTAB or SDS increased not always the activity of the catalytic systems and complicated the separation of the water phase. In contrast to the above mentioned surfactants, the polymeric Synperonics increased the activity and allowed recycling at room temperature. The recycling experiment yielded about 30% higher TONs compared with a detergent-free system.

Acknowledgements

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