Catalytic conversions in aqueous media: Part 3. Biphasic hydrogenation of polybutadiene catalyzed by Rh/TPPTS complexes in micellar systems☆

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ABSTRACT

Water-soluble Rh/TPPTS complexes [TPPTS = $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$] are active catalysts (TOF > 1200 h^{-1}) for the biphasic hydrogenation of the completely water-insoluble heavy polybutadiene (PB) in single micelles formed by the cationic surfactant dodecyltrimethylammonium chloride (DTAC), or mixed micelles created by DTAC with either non-ionic or anionic surfactants. The reaction proceeds under mild conditions (T = 100 °C, P_{H_2} = 20 bar) at a molar ratio of P/Rh = 3 and C=C units/Rh = 1000 within 20 min and at a rhodium concentration of only 10 ppm in water. The pH of the aqueous catalyst solution markedly influenced the activity. High catalytic activities were achieved under neutral conditions whereas at acidic or basic conditions the catalytic activity dramatically decreased. The hydrogenation rate depends critically on the microstructure of PB and the nature of micellar catalysis. The 1,4-units content of PB plays a major role for performing the catalytic hydrogenation reaction in single or mixed micellar systems for obtaining maximum reactivity. When the PB possesses a high 1,4-units content (98.0 wt% of 1,4-units and 2.0 wt% of 1,2-units) higher reaction rates were achieved in mixed micellar systems created by DTAC/Brij-35 surfactants compared to the rates observed in single DTAC micelles. In contrast, with PB starting material consisting of 61.0 wt% of 1,2-units and 39.0 wt% of 1,4-units higher reaction rates were obtained in single DTAC micelles compared to those rates achieved in mixed micellar systems.

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1. Introduction

Trisulfonated triphenylphosphine (TPPTS) catalytic complexes of transition metals are highly soluble in water which provides for their facile recovery from organic reaction products by a simple phase separation in aqueous/organic biphasic processes [1]. Interest in this biphasic concept of heterogenization of homogeneous catalysis has been further stimulated by increasing environmental constrains because catalysis in aqueous media obviates the need for organic toxic solvents and water is a green solvent [1,2]. Rh/TPPTS catalysts have found important industrial applications *e.g.* in the biphasic Ruhrchemie/Rhône-Poulenc process for the hydroformylation of lower olefins [1].

The rates in the biphasic Rh/TPPTS-catalyzed hydroformylation decrease dramatically with increasing molecular weight of the olefins due to mass transfer limitations resulting from the lower solubility of higher olefins in water. For example, hexene-1 is hydroformylated with conversions up to 22% using Rh/TPPTS catalysts in a two-phase system, whereas under the same conditions the practically water-insoluble tetradecene-1 gives only traces of C_{15}

aldehydes [1,3]. An elegant approach to circumventing the solubility problem in biphasic catalytic reactions of higher olefins is to use tensides to create micelles and perform the catalytic conversion of heavier starting materials in micellar systems [1,3].

Hydrogenation of polydienes is an important catalytic process since it leads to polymers with unique properties and structures which are inaccessible or difficult to synthesize by conventional polymerization reactions [4]. Hydrogenation significantly changes and improves the chemical, physical and mechanical properties of polydiene elastomers. For example, hydrogenation of polybutadiene (PB) gives different products depending on the amount of C=C units with 1,4- or 1,2-structure in the PB starting material. In the case of 1,4-PB (~100%) the hydrogenation reaction transforms the elastomeric starting material to a tough crystalline product that is similar to high density polyethylene (HDPE). On the other hand, hydrogenation of PB with 1,2- and 1,4-microstructures lead to elastomers that could be regarded as poly(ethylene-*co*-butylene) [4].

There have been several reports on the hydrogenation of PB catalyzed by homogeneous $RhCl(PPh_3)_3$ catalysts in conventional organic media [4a–c,5]. However, only two reports are available on PB (M_n = 900; 60% of 1,4-PB; 40% of 1,2-PB) hydrogenation catalyzed by water-soluble rhodium catalysts modified with the tenside ligands $PPh_2(CH_2)_n$–COONa (n = 5,7) and $RhCl(TPPMS)_3$ catalysts [TPPMS = $PPh_2(C_6H_4\text{-}m\text{-}SO_3Na)$] in aqueous/organic two-phase systems [6]. Under these conditions massive leaching of

rhodium from the aqueous to the organic phase was observed with $Rh/PPh_2(CH_2)_n$–COONa ($n = 5,7$) catalysts and the activities of $RhCl(TPPMS)_3$ catalysts were low (TOF = 219 h^{-1}) [6]. Water-soluble $RhCl(TPPMS)_3$ catalysts exhibited very low catalytic activities (TOF = 4.0–9.3 h^{-1}) in the hydrogenation of nitrile butadiene rubber (NBR) latex in the presence of the non-ionic surfactant Triton-X-305 in order to stabilize latex in aqueous media [7]. TPPTS was used as a ligand to modify rhodium [8] and ruthenium [9] catalysts applied in the biphasic hydrogenation of PB, NBR, styrene butadiene rubber (SBR) and polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) in ionic liquids such as N,N′-butylmethylimidazolium tetrafluoroborate and polyether modified ammonium salts.

We reported [10] that water-soluble Rh/TPPTS complexes catalyze the aqueous phase hydrogenation of the amphiphilic block copolymer polybutadiene-1,4-*block*-poly(ethylene oxide) (PB-*b*-PEO) in mixed micellar nanoreactors formed by the cationic surfactant dodecyltrimethylammonium chloride (DTAC) with the tenside PB-*b*-PEO starting material. In this report we extend this study to the aqueous/organic biphasic hydrogenation of the completely water-insoluble heavy starting material PB catalyzed by water-soluble Rh/TPPTS complexes in both single micelles formed by the cationic surfactant DTAC which interacts with the anionic catalytic system $Rh/P(C_6H_4$-*m*-$SO_3^-)_3$ along with PB and mixed micelles created by DTAC with either various non-ionic Brij tensides or with the anionic sodium dodecylsulfate (SDS) surfactant.

2. Experimental

2.1. Materials

The PB starting materials (M_n = 3500 with 98% of 1,4-units and 2% of vinyl-units; M_n = 6000 with 80% of 1,4-units and 20% of vinyl-units; M_n = 2500 with 39% of 1,4-units and 61% of vinyl-units) used in this study were purchased from Aldrich. Hydrogen (quality 5.0) was purchased from Messer Hellas (Athens) and was used without further purification. Distilled demineralized water was deoxygenated in an ultrasound bath under vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times. $RhCl_3 \cdot 3H_2O$, DTAC, cetyltrimethylammonium chloride (CTAC), Brij-30, Brij-35, Brij-58, Brij-78 and sodium dodecylsulfate were purchased from Acros Organics and used without any further purification. TPPTS was prepared according to the procedure of Hoechst AG, Werk Ruhrchemie [11] and isolated with purity higher than 94%. $^{31}P\{^1H\}$NMR (121 MHz, 25 °C, D_2O): δ TPPTS = −5.4 ppm.

2.2. Synthesis of PB with M_n = 40,000 containing 84% of 1,4-units and 16% of 1,2-units

The PB homopolymer with M_n = 40,000 and a composition of 84% of 1,4-units and 16% of vinyl-units was synthesized by anionic polymerization high vacuum techniques in benzene using s-BuLi as initiator according to well established procedures [12]. All PB starting materials were analyzed by size exclusion chromatography (SEC) using a Waters SEC system composed by a Waters 510 Pump Controller, a set of four Styragel columns (continuous porosity range 10^3–10^6 Å) and a Waters 401 differential refractometer, operated at 40 °C. The instrument was calibrated with linear polystyrene and corrected for PB. THF was the carrier solvent at a flow rate of 1 ml/min. The PB homopolymers composition in 1,4- and 1,2-units was determined by ^1H NMR spectroscopy using a Varian 300 MHz instrument in $CDCl_3$ at 30 °C.

2.3. Typical hydrogenation procedure

$RhCl_3 \cdot 3H_2O$, TPPTS, surfactant(s), the remaining amount of distilled deoxygenated water (see Tables 1–5) and the PB solution in *n*-hexane were charged into a Hastelloy C Parr autoclave (2 l) which was previously filled with argon. After a number of pressurising–depressurising cycles with hydrogen to remove the last traces of oxygen, the autoclave was pressured and contents were heated with stirring. At the reaction temperature the pressure was 20 bar of hydrogen. After the reaction the autoclave was cooled to room temperature, vented of hydrogen and the reaction mixture removed. The organic phase was separated, concentrated in vacuum and hydrogenated polybutadiene (HPB) products were precipitated in acetone, dried over vacuum for a few days and analyzed by ^1H NMR or FTIR spectroscopy.

2.4. Product analysis

^1H NMR (300 MHz) and $^{31}P\{^1H\}$ NMR spectra (121 MHz, referenced to external 85% H_3PO_4) were recorered on a Varian Unity Plus 300/54 spectrometer. The Fourier transform infrared (FTIR) spectra were obtained with a Perkin Elmer Spectrum One FTIR spectrometer. The conversions in the hydrogenation of PB were determined by quantitative ^1H NMR analysis after addition of polystyrene (M_n = 37,000; M_w/M_n < 1.06) internal standard in $CDCl_3$; 5.41 ppm: olefinic protons from both *cis*- and *trans*-1,4-PB and olefinic protons of 1,2-PB; 4.95 ppm: vinylic protons (=CH_2) of 1,2-PB units; 6.32–7.16 ppm: aromatic protons

Table 1
Hydrogenation of PB homopolymers catalyzed by Rh/TPPTS complexes in various single and mixed micellar systems[a].

Run	Polymer	wt% 1,4 -units	M_n	Catalyst precursor	Cationic surfactant	Add. surfactant	DTAC/add. surfactant molar ratio	Conv. (mol%)	TOF[b] (h^{-1})
1/1	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	Brij-30	10/1	7	140
1/2	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	Brij-35	10/1	36	720
1/3	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	Brij-58	10/1	14	280
1/4	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	Brij-78	10/1	6	120
1/5	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	SDS	10/1	13	260
1/6	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	Brij-35	5/1	4	80
1/7	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	Brij-35	20/1	14	280
1/8	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	DTAC	–	–	23	460
1/9	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	CTAC	Brij-35	10/1	5	100
1/10	PB[c]	98.0	3500	$RhCl_3 \cdot 3H_2O$/TPPTS	CTAC	–	–	8	160

[a] Reaction conditions: $T = 100$ °C, $P_{H_2} = 20$ bar, $t = 30$ min, 7.89 mg (0.03 mmol) $RhCl_3 \cdot 3H_2O$, 56.0 mg (0.09 mmol) TPPTS (P/Rh molar ratio = 3), 0.27 mmol of cationic surfactant (cationic surfactant/TPPTS molar ratio = 3), additional non-ionic or anionic surfactant, addition of deaerated H_2O to give 237.1 g of aqueous reaction mixture, [Rh] = 10 ppm, pH 4.2 and a solution of PB [1.62 g (30 mmol of C=C units) in 52.0 g of *n*-hexane] (C=C units/Rh molar ratio = 1000). A two-phase system consisting of 236.9 g of aqueous solvent and of 52.0 g of *n*-hexane (H_2O/*n*-hexane = 82/18).

[b] Defined as mol of hydrogenated C=C units in the PB homopolymer per mol of rhodium per hour.

[c] M_w/M_n = 1.5.

Table 2
Hydrogenation of PB homopolymers catalyzed by Rh/TPPTS complexes in single DTAC micellar systems under various weight ratios of the aqueous/organic phase[a].

Run	Polymer	wt% 1,4 -units	M_n	Catalyst precursor	Ratio of H_2O/n-hexane (wt%)	Conv. (mol%)	TOF[b] (h^{-1})
2/1	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	90/10	10	200
2/2	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	82/18	23	460
2/3	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	70/30	16	320
2/4	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	60/40	4	80

[a] Reaction conditions: $T = 100\,°C$, $P_{H_2} = 20$ bar, $t = 30$ min, 7.89 mg (0.03 mmol) RhCl$_3$·3H$_2$O, 56.0 mg (0.09 mmol) TPPTS (P/Rh molar ratio = 3), 71.25 mg (0.27 mmol) cationic surfactant DTAC (DTAC/TPPTS molar ratio = 3), no addition of non-ionic surfactant, addition of 236.9 g of deaerated H_2O and n-hexane to adjust the various weight ratios, [Rh] = 10 ppm, pH 4.2 and a solution of PB [1.62 g (30 mmol of C=C units) in n-hexane] (C=C units/Rh molar ratio = 1000).

[b] Defined as mol of hydrogenated C=C units in the PB homopolymer per mol of rhodium per hour.

[c] $M_w/M_n = 1.5$.

Table 3
Hydrogenation of PB homopolymers catalyzed by Rh/TPPTS complexes in mixed micellar systems under various pH values[a].

Run	Polymer	wt% 1,4 -units	M_n	Catalyst precursor	pH	Conv. (mol%)	TOF[b] (h^{-1})
3/1	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	4.2	27	405
3/2	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	7.0[d]	83	1245
3/3	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	10.0[d]	17	255

[a] Reaction conditions: $T = 100\,°C$, $P_{H_2} = 20$ bar, $t = 20$ min, 7.89 mg (0.03 mmol) RhCl$_3$·3H$_2$O, 56.0 mg (0.09 mmol) TPPTS (P/Rh molar ratio = 3), 71.25 mg (0.27 mmol) cationic surfactant DTAC (DTAC/TPPTS molar ratio = 3), 32.38 mg (0.027 mmol) of non-ionic surfactant Brij-35 (DTAC/Brij-35 molar ratio = 10/1), addition of deaerated H_2O to give 236.9 g of aqueous reaction mixture, [Rh] = 10 ppm and a solution of PB [0.81 g (15 mmol of C=C units) in 52.0 g of n-hexane] (C=C units/Rh molar ratio = 500). A two-phase system consisting of 236.9 g of aqueous solvent and of 52.0 g of n-hexane (H_2O/n-hexane = 82/18).

[b] Defined as mol of hydrogenated C=C units in the PB homopolymer per mol of rhodium per hour.

[c] $M_w/M_n = 1.5$.

[d] 489.1 mg (3.6 mmol) KH$_2$PO$_4$, pH adjusted with 5% aqueous NaOH in the aqueous catalyst solution.

Table 4
Hydrogenation of PB homopolymers catalyzed by Rh/TPPTS complexes under various temperatures and TPPTS/Rh molar ratios in mixed micellar media[a].

Run	Polymer	wt% 1,4-units	M_n	Catalyst precursor	Temperature (°C)	TPPTS/Rh molar ratio	Conv. (mol%)	TOF[b] (h^{-1})
4/1	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	90	3	48	480
4/2	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	100	3	91	910
4/3	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	110	3	84	840
4/4	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	120	3	78	780
4/5	PB[c]	98.0	3500	RhCl$_3$·3H$_2$O/TPPTS	100	4	46	460

[a] Reaction conditions: $P_{H_2} = 20$ bar, $t = 30$ min, 7.89 mg (0.03 mmol) RhCl$_3$·3H$_2$O, addition of TPPTS, 71.25 mg (0.27 mmol) cationic surfactant DTAC (DTAC/TPPTS molar ratio = 3), 32.38 mg (0.027 mmol) of non-ionic surfactant Brij-35 (DTAC/Brij-35 molar ratio = 10/1), addition of deaerated H_2O to give 236.9 g of aqueous reaction mixture, [Rh] = 10 ppm, pH 7.0 and a solution of PB [0.81 g (15 mmol of C=C units) in 52.0 g of n-hexane] (C=C units/Rh molar ratio = 500). A two-phase system consisting of 236.9 g of aqueous solvent and of 52.0 g of n-hexane (H_2O/n-hexane = 82/18). Except run 4/5: 95.0 mg (0.36 mmol) cationic surfactant DTAC (DTAC/TPPTS molar ratio = 3) and 43.17 mg (0.036 mmol) of non-ionic surfactant Brij-35 (DTAC/Brij-35 molar ratio = 10/1).

[b] Defined as mol of hydrogenated C=C units in the PB homopolymer per mol of rhodium per hour.

[c] $M_w/M_n = 1.5$.

of the internal standard polystyrene. The conversions of 1,4-PB were also determined by quantitative FTIR analysis (KBr pellet). The most apparent changes in the FTIR spectra are the reduction in the absorption bands at 3008 cm^{-1} (ν olefinic=C–H), 1655 cm^{-1} (ν C=C), 967 cm^{-1} (δ olefinic=C–H of *trans*-1,4-PB), 912 cm^{-1} (δ vinylic=CH$_2$ of 1,2-PB) and 738 cm^{-1} (δ olefinic=C–H of *cis*-1,4-PB) as the extent of hydrogenation of C=C units increased.

Table 5
Hydrogenation of PB homopolymers with various microstructures catalyzed by Rh/TPPTS complexes in mixed and single micellar systems[a].

Run	Polymer	wt% 1,4 -units	wt% 1,2 -units	M_n	Catalyst precursor	Cationic surfactant	Non-ionic surfactant	Conv. (mol%)	TOF[b] (h^{-1})
5/1	PB[c]	98.0	2.0	3,500	RhCl$_3$·3H$_2$O/TPPTS	DTAC	Brij-35	91	910
5/2	PB[c]	98.0	2.0	3,500	RhCl$_3$·3H$_2$O/TPPTS	DTAC	–	72	720
5/3	PB[d]	39.0	61.0	2,500	RhCl$_3$·3H$_2$O/TPPTS	DTAC	Brij-35	57	570
5/4	PB[d]	39.0	61.0	2,500	RhCl$_3$·3H$_2$O/TPPTS	DTAC	–	61	610
5/5	PB[e]	80.0	20.0	6,000	RhCl$_3$·3H$_2$O/TPPTS	DTAC	Brij-35	80	800
5/6	PB[e]	80.0	20.0	6,000	RhCl$_3$·3H$_2$O/TPPTS	DTAC	–	75	750
5/7	PB[f]	84.0	16.0	40,000	RhCl$_3$·3H$_2$O/TPPTS	DTAC	–	25	250

[a] Reaction conditions: $T = 100\,°C$, $P_{H_2} = 20$ bar, $t = 30$ min, 7.89 mg (0.03 mmol) RhCl$_3$·3H$_2$O, 56.0 mg (0.09 mmol) TPPTS (P/Rh molar ratio = 3), 71.25 mg (0.27 mmol) cationic surfactant DTAC (DTAC/TPPTS molar ratio = 3), 32.38 mg (0.027 mmol) of non-ionic surfactant Brij-35 (DTAC/Brij-35 molar ratio = 10/1), addition of deaerated H_2O to give 236.9 g of aqueous reaction mixture, [Rh] = 10 ppm, pH 7.0 and a solution of PB [15 mmol of C=C units in 52.0 g of n-hexane] (C=C units/Rh molar ratio = 500). A two-phase system consisting of 236.9 g of aqueous solvent and of 52.0 g of n-hexane (H_2O/n-hexane = 82/18).
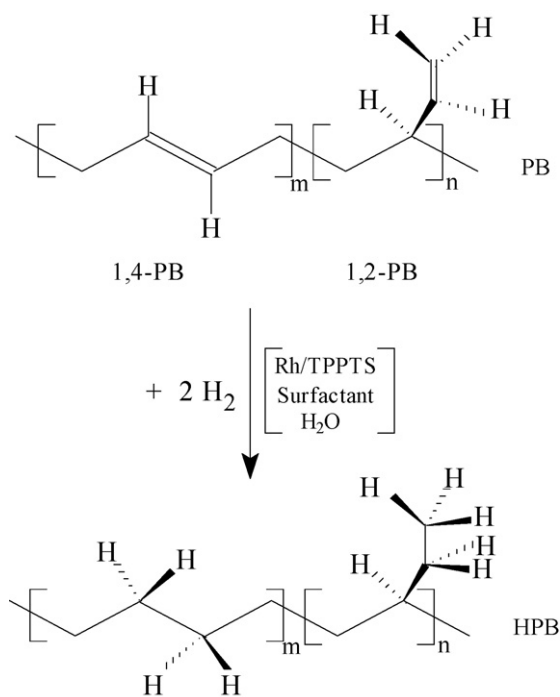
[b] Defined as mol of hydrogenated C=C units in the PB homopolymer per mol of rhodium per hour.

[c] $M_w/M_n = 1.5$.

[d] $M_w/M_n = 1.15$.

[e] $M_w/M_n = 1.01$.

[f] $M_w/M_n = 1.02$.

Scheme 1. Micellar Rh/TPPTS-catalyzed hydrogenation of PB homopolymers.

3. Results and discussion

3.1. Effect of the nature of single and mixed micelles on the Rh/TPPTS-catalyzed hydrogenation of PB in aqueous/organic two-phase systems

PB (M_n = 3500; 98.0% of 1,4-units and 2.0% of vinyl-units; M_w/M_n = 1.5) was hydrogenated in aqueous/organic two-phase systems to afford HPB (see Scheme 1) under mild reaction conditions at 100 °C and 20 bar H_2 partial pressure within 30 min in the presence of water-soluble Rh/TPPTS catalysts at low rhodium concentrations ([Rh] = 10 ppm) in the aqueous phase employing various single and mixed micellar systems (Table 1). Low catalytic activity (TOF = 460 h^{-1}) was observed in the Rh/TPPTS-catalyzed hydrogenation of PB in the presence of single micelles created by the

cationic surfactant DTAC (run 1/8). In contrast, when the non-ionic surfactant Brij-35 (Fig. 1) was added higher catalytic activity (TOF = 720 h^{-1}) was obtained in the Rh/TPPTS/DTAC-catalyzed hydrogenation of PB under the same conditions at a DTAC/Brij-35 molar ratio of 10/1 in aqueous/organic two-phase systems (run 1/2). When the molar ratios of DTAC/Brij-35 were lower (5/1) or higher (20/1) the catalytic activity was low with 80 and 280 TOF's, respectively (runs 1/6 and 1/7).

Using the non-ionic surfactant Brij-30 (Fig. 1) with a lower *hydrophilic–lipophilic balance* (HLB) value, namely a shorter hydrophilic [$(OCH_2CH_2)_nOH$, n = 4] -chain instead of Brij-35 (n = 23), the catalytic activity decreased dramatically from 720 to 140 TOF's (runs 1/2 and 1/1). Low catalytic activity (TOF = 280 h^{-1}) was also obtained in the same hydrogenation reaction using mixed micelles created with Rh/TPPTS/DTAC and the non-ionic surfactant Brij-58 possessing a longer hydrophobic cetyl-chain (Fig. 1) compared to the dodecyl-chain of Brij-35 (run 1/3). The catalytic activity further decreased (TOF = 120 h^{-1}) in the presence of Brij-78 (Fig. 1) with a much longer hydrophobic stearyl-moiety and a lower HLB value than Brij-58 to create mixed micellar Rh/TPPTS/DTAC catalytic systems for the hydrogenation of PB in biphasic media (run 1/4). Micellar Rh/TPPTS/DTAC-catalysts modified with the anionic surfactant sodium dodecylsulfate (Fig. 1) exhibited lower catalytic activity (TOF = 260 h^{-1}) in the PB biphasic hydrogenation reaction (run 1/5) than the same catalysts modified with non-ionic Brij-35 and Brij-58 surfactants (runs 1/2 and 1/3). This probably could be explained due to repulsions between the negative charge of the anionic $-OSO_3^-$ group of SDS tenside and the anionic $-SO_3^-$ groups of the catalytic system Rh/P(C_6H_4-m-SO_3^-)$_3$ in the polar Stern layer of the micelles (Fig. 2) which destabilizes the Rh/TPPTS/DTAC/SDS mixed micellar catalytic system. Replacement of DTAC by the more hydrophobic cationic surfactant cetyltrimethylammonium chloride (Fig. 1) in the Rh/TPPTS-catalyzed hydrogenation of 1,4-PB gives rise to a decrease in catalytic activity from 460 to 160 TOF's (runs 1/8 and 1/10). The catalytic activity drops further (TOF = 100 h^{-1}) with addition of Brij-35 to the micellar Rh/TPPTS/CTAC-catalyzed hydrogenation of 1,4-PB in aqueous/organic two-phase systems (run 1/9).

To rationalize the differences in catalytic activity dependent on the structure of tensides, especially the positive effect of the addition of non-ionic Brij-35 together with cationic DTAC surfactant observed in the Rh/TPPTS-catalyzed aqueous/organic two-phase hydrogenation of PB (98.0 wt% of 1,4-units) a simplified model of an ionic spherical mixed micelle [1b,3b,10,13,14] was proposed
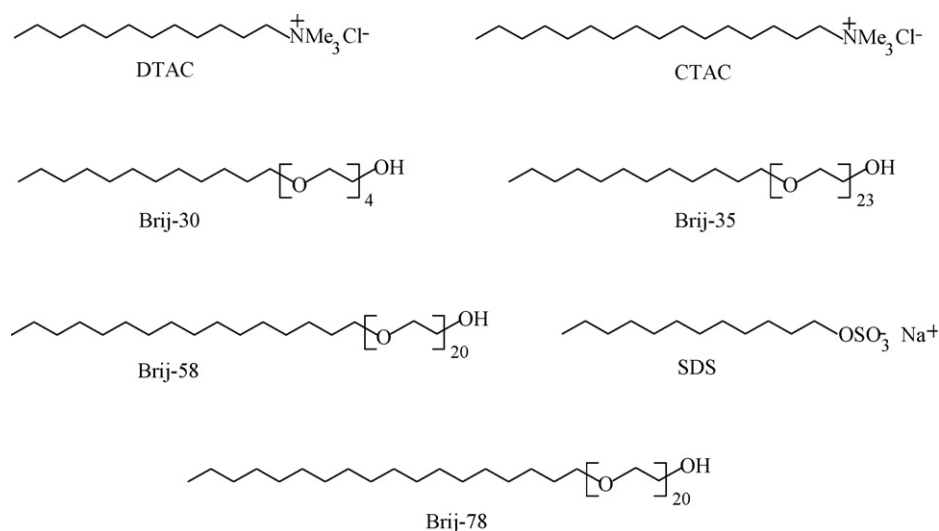
Fig. 1. Structures of the cationic, non-ionic and anionic surfactants dodecyltrimethylammonium chloride (DTAC), cetyltrimethylammonium chloride (CTAC), polyoxyethylene(4)lauryl ether (Brij-30), polyoxyethylene(23)lauryl ether (Brij-35), polyoxyethylene(20)cetyl ether (Brij-58), polyoxyethylene(20)stearyl ether (Brij-78) and sodium dodecylsulfate (SDS).
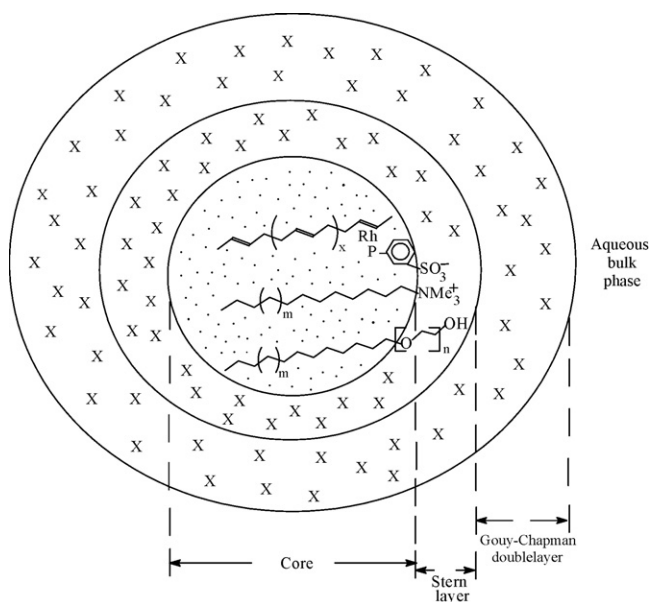
Fig. 2. Schematic two-dimensional simplified representation of a proposed spherical ionic mixed micelle containing the Rh/TPPTS catalyst, PB (98.0 wt% of 1,4-units), cationic alkyltrimethylammonium tensides and non-ionic Brij surfactants. The hydrocarbon chains of the alkyltrimethylammonium and Brij surfactants and the PB (98.0 wt% of 1,4-units) starting material in the core of mixed micelle (doted part), the hydrophilic head groups NMe_3^+ interacted with the SO_3^- groups of Rh/TPPTS catalyst and the hydrophilic $(OCH_2CH_2)_nOH$ groups of Brij in the Stern layer and Gouy–Chapman double layer, the counter ions (Na^+ and Cl^- depicted as X) are schematically indicated to denote their relative locations and not their configuration, number, distribution or relationship to their molecular sizes.

(Fig. 2). The core of micelle is composed of the hydrophobic tail of the cationic alkyltrimethylammonium tenside and the hydrophobic chain of non-ionic Brij surfactants where the PB (98.0 wt% of 1,4-units) starting material is solubilized. Surrounding the core is the Stern layer where the charged head groups (NMe_3^+ and SO_3^- of DTAC and TPPTS, respectively) are situated together with the hydrophilic groups $(OCH_2CH_2)_nOH$ of Brij along with the counter ions (Cl^- and Na^+) of the mixed micelle. The catalytically active rhodium atom of the Rh/TPPTS complex is probably located on the polarity gradient between the Stern layer and the micelle core in order to be able to coordinate the C=C unsaturation units of PB starting materials. Thus, the position of the rhodium in the mixed micelle should be dependent on the HLB value of both the cationic alkyltrimethylammonium surfactants and of the non-ionic Brij tensides.

3.2. Effect of the ratio of the aqueous/organic phase and of the pH value

Hydrogenation reactions of PB ($M_n = 3500$; 98.0% of 1,4-units and 2.0% of 1,2-units) were carried out with Rh/TPPTS/DTAC catalysts using different ratios of the aqueous to the organic phase. The results are summarized in Table 2. When the weight ratio of the aqueous/organic phase was 60/40 the catalytic activity was low with 80 TOF's (run 2/4) and the activity increased with increasing amount of added water up to a weight ratio of 82/18 exhibiting an activity of 460 TOF's (run 2/2). However, at a higher ratio of the aqueous/organic phase of 90/10 the catalytic activity decreased dramatically to give 200 TOF's (run 2/1).

The Rh/TPPTS-catalyzed hydrogenation of PB (98.0 wt% of 1,4-units) is strongly influenced by the pH of the aqueous catalyst solution (Table 3). The highest catalytic activity (TOF = 1245 h^{-1}) was obtained at neutral conditions with pH 7.0 which was adjusted by a KH_2PO_4/NaOH – buffer (run 3/2). At acidic conditions with a pH

value of 4.2 (run 3/1) the catalytic activity was low (TOF = 405 h^{-1}). Under basic conditions (pH 10.0) the catalytic activity was even lower exhibiting a TOF value of 255 h^{-1} (run 3/3). The lower activity of Rh/TPPTS catalysts at acidic conditions (pH 4.2) could probably not be explained by protonation of the hydride moiety of Rh/TPPTS intermediates involved in the catalytic cycles because at such acidic conditions (pH 4.3) very high catalytic activities (TOF = 117,000 h^{-1}) were achieved by Rh/TPPTS catalysts in aqueous/organic biphasic hydrogenation reactions of C=C units of renewable methyl esters of sunflower oil [1c] indicating that the hydride moiety of Rh/TPPTS catalytic intermediates remains stable at such acidic media.

The lower catalytic activity obtained in the biphasic hydrogenation of PB under acidic (pH 4.2) and basic (pH 10.0) conditions could probably be explained due to the destabilization of mixed micelles (Fig. 2) by lowering the interactions between the anionic catalytic system $Rh/P(C_6H_4$-m-$SO_3^-)_3$ and the cationic surfactant DTAC as well as the non-ionic surfactant Brij-35.

3.3. Effect of the temperature and the TPPTS/Rh molar ratio

Table 4 presents the activity of the Rh/TPPTS catalysts in the hydrogenation of PB ($M_n = 3500$ with 98.0% of 1,4-units and 2.0% of 1,2-units) in aqueous/organic two-phase systems as a function of temperature and the TPPTS/Rh molar ratio. The catalytic activity increases with increasing temperature up to 100 °C to give a TOF up to 910 h^{-1} (runs 4/1 and 4/2). Raising the temperature higher than 100 °C has a negative effect on the reaction rate to give 840 and 780 TOF's at 110 and 120 °C, respectively (runs 4/3 and 4/4). This biphasic hydrogenation reaction is strongly influenced by the amount of TPPTS added to the rhodium precursor. As expected, higher catalytic activity (TOF = 910 h^{-1}) was observed at a low TPPTS/Rh molar ratio of 3 (run 4/2) where as at the higher TPPTS/Rh molar ratio of 4 the activity dramatically decreased to give 460 TOF's (run 4/5). This reduced activity at a higher P/Rh molar ratio could probably be explained by a competition between the added free TPPTS ligand and the C=C units of PB for a coordination site on rhodium which may lead to a retardation in the activation of the hydrogenation reaction.

3.4. Effect of the microstructure of PB on the hydrogenation rate in single or mixed micellar systems

We next turned our attention to the dependence of reaction rate on the relationship between the microstructure of PB starting material and the presence of single or mixed micellar systems created by cationic DTAC or cationic/non-ionic DTAC/Brij-35 surfactants, respectively. The results are summarized in Table 5. The dependence of hydrogenation rate is in critical relationship between the microstructure of PB and the nature of micellar catalysis. The 1,4-content of the PB starting material plays a major role for performing the catalytic hydrogenation reaction in single or mixed micellar systems for obtaining maximum reactivity. Higher reaction rates were obtained in mixed micellar systems created by DTAC/Brij-35 surfactants in the biphasic hydrogenation when the PB starting material possesses a high 1,4-units content such as 98.0 or 80.0 wt% (run 5/1 with TOF = 910 h^{-1} and run 5/5 with TOF = 800 h^{-1}) compared to the reaction rates observed in the same reactions in single DTAC micelles (run 5/2 with TOF = 720 h^{-1} and run 5/6 with TOF = 750 h^{-1}). However, when the PB starting material possesses a 1,2-units content of 61.0 wt% higher rates were achieved in the hydrogenation reaction in single DTAC micelles (TOF = 610 h^{-1}, run 5/4) compared to the rates obtained in the same reaction in mixed DTAC/Brij-35 micellar systems (TOF = 570 h^{-1}, run 5/3).

These results were rationalized by assuming that micelles of a small size and therefore of a higher number probably with a low aggregation number were formed in mixed DTAC/Brij-35 micellar

systems which leads to a higher catalytic hydrogenation activity when the PB starting material possesses a high 1,4-units content whereas with PB starting materials consisting of a higher content of 1,2-units effects of sterical hindrance within the mixed micellar reactor are govern the whole micellar catalytic hydrogenation reaction.

The rates in the biphasic hydrogenation reaction of PB (80.0 and 84.0 wt% of 1,4-units) decrease dramatically with increasing M_n of PB in single DTAC micelles giving 750 TOFs with $M_n = 6000$ (run 5/6) and 250 TOFs with $M_n = 40,000$ (run 5/7).

4. Conclusions

For the first time an efficient hydrogenation reaction of a completely water-insoluble, heavy, starting material namely PB of $M_n = 2500$–40,000 using water-soluble Rh/TPPTS catalytic complexes has been achieved in aqueous media. High reaction rates (TOF > 1200 h^{-1}) were achieved in the PB biphasic hydrogenation reaction employing single and mixed micellar systems under mild reaction conditions. The dependence of hydrogenation rate is in critical relationship between the microstructure of PB and the nature of micellar catalysis. The 1,4-units content of PB starting material plays a major role for performing the catalytic hydrogenation reaction in single or mixed micellar systems for obtaining maximum reactivity. When the PB possesses a high 1,4-units content with a composition of 98.0 wt% of 1,4-units and 2.0 wt% of 1,2-units higher reaction rates were achieved in mixed micellar systems created by DTAC/Brij-35 surfactants compared to the rates observed in single DTAC micelles. In contrast, with PB starting material consisting of 61.0 wt% of 1,2-units and 39.0 wt% of 1,4-units higher reaction rates were obtained in single DTAC micelles compared to those achieved in mixed micellar systems.

This micellar catalytic reaction may yield a new route for the conversion of a broad spectrum of heavy, apolar, unsaturated starting materials in aqueous/organic two-phase systems employing water-soluble Rh/TPPTS catalysts which could be quantitatively recovered in active form by a simple phase separation.

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