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A Study of the Separation of 1-Dodecene and 1-Tetradecene Hydroformylation Products in Aqueous Medium

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Abstract: Experimental results of the solubilization of olefins in hydroformylation model systems, comprising 1-dodecene and 1-tridecanal or 1-tetradecene and 1-pentadecanal, water, butanol, sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), and/or tri(m-sulfofenyl)phosphine trisodium salt (TPPTS-Na) are presented. The selected systems were used for the hydroformylation of 1-dodecene and 1-tetradecene whereby high yields of aldehydes were obtained. After the reaction, the mixture spontaneously separated into an organic phase with the reaction products and an aqueous phase comprising the catalyst and excess phosphine ligand.

Keywords: Dodecene, hydroformylation, microemulsion, separation of aldehydes, tetradecene

INTRODUCTION

The process of *oxo* synthesis, consisting of hydroformylation of olefins to obtain aldehydes and hydrogenation of the latter to alcohols was developed in the 1930s (1,2). The products of hydroformylation of olefins are aldehydes having straight or branched hydrocarbon chains.

The global production capacity of aldehydes obtained by hydroformylation of olefins is roughly 7 mln t, of which approx. 25% relates to aldehydes comprising more than 5 atoms of carbon in a molecule (3).

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The principal processing direction of such aldehydes is their hydrogenation to alcohols, for use in the production of surface active agents.

Hydroformylation of olefins is usually carried out in a homogeneous system, in which both the reaction catalyst and the excess phosphine ligand are dissolved in the organic reaction medium (4). Such a solution is successfully used in the process of propylene hydroformylation to obtain butyl aldehydes. Low-boiling reaction products (aldehydes) are distilled in the process right from the hydroformylation reactor.

The problem of separation of reaction products is much more complex in the case of hydroformylation of olefins having longer hydrocarbon chains. Hydroformylation products have high boiling points, therefore, their separation from the reaction medium by distillation involves the risk of thermal deactivation of the catalyst. Consequently, alcohols containing roughly a dozen of carbon atoms in a molecule are obtained by the oxo method in complex processes. In the initial phase, hydroformylation of olefins having short hydrocarbon chains results in the obtaining of aldehydes which are subjected to aldol condensation later in the process, and the resulting aldol is then hydrogenated to obtain alcohols containing twice as many carbon atoms as the initial aldehydes. By this method, propylene is processed to obtain 2-ethylhexanol for use in the manufacturing of plastifiers for plastics.

Commercialization in the 1980s of a new class of water-soluble rhodium catalysts enabled the practice of hydroformylation of olefins in an aqueous/organic system (5–10). Owing to this solution, product separation from the reaction medium is much simplified. In this case, the catalytic system comprising a hydrophilic rhodium catalyst is dissolved in the aqueous phase, whereas the hydrophobic olefin material is dissolved in the organic phase. At high conversions of olefins to aldehydes, the reaction system is spontaneously separated into two phases. In the final phase of hydroformylation, the organic phase with the reaction products may be separated from the aqueous phase that contains the catalyst by settling.

A commercial implementation of the process was developed by Ruhrchemie with the use of laboratory results of Rhone Poulenc (the RCH/RP process). The RCH/RP process was first used commercially in 1984 in the process of propylene hydroformylation to obtain butyl aldehydes. High selectivity to straight-line products was then achieved and production costs were much reduced, compared with the conventional process to obtain butyl aldehydes with the use of a homogeneous rhodium catalyst.

The first approach to hydroformylation in micellar system was performed by Tinucci and Platone at 1994 (9). The authors described their trials of C12 type alkenes hydroformylation in the state of microemulsion stabilized with the mixture of SDS and *n*-butanol as a co-surfactant.

Yang et al. (11,12,13) led the 1-dodecene hydroformylation in the presence of rhodium-TPPTS-CTAB (cetyltrimethylammonium bromide) complex catalyst. The typical rhodium catalyst comprised of a complex compound of rhodium with TPPTS and CTAB ligands, with molar ratio appropriately 1:16:8. The conversion degree was increasing during the reaction time up to 75%, thereby greater values of conversion degree occurred if greater concentrations of CTAB were applied. The higher values of *n:iso* aldehydes ratio of 20 were observed for shorter reaction times and CTAB concentrations greater than 6 mole/m^3.

However, high difficulties with the mutual phase mixing are encountered in the reaction of aqueous-phase hydroformylation of olefins having 6 or more carbon atoms in a molecule. A two-phase water-hydrocarbon system is characterized by high interface tensions, e.g., about 50 mN/m for 1-hexene (14). Introduction into the reaction system of a surface active agent such as sodium dodecylsulfate will cause the interface tension to fall to about 4 mN/m, thus enabling emulsification of the system under the effect of a mechanical force, for instance, by mixing. Reduction of the interface tension to ultra low values was achieved on the introduction into the system of appropriate amounts of a co-surfactant (butanol). Adsorption equilibrium is then achieved rather quickly and the system shows high abilities to solubilize olefins. An O/W microemulsion produced in the hydroformylation process, will separate spontaneously at high conversions of olefins into aldehydes to an organic phase containing the reaction product, and an aqueous phase containing the catalyst (15–24). A microemulsion was formulated for a system of hydroformylation containing hydrocarbons of heptanal, water, sodium dodecylsulfate (SDS), and butanol in the presence or absence of sodium tri(m-sulfophenyl)phosphine (TPPTS-Na). In hydroformylation of hexene carried out in optimized microemulsion a high conversion of hexene (about 97%) and the yield of heptanals (above 94%) were obtained in a very short reaction time. The products were separated by dilution of microemulsion (14).

It was the objective of this author to find the conditions at which aqueous systems show high ability to solubilize the surfactant range of olefins, and to develop a method for product separation from a hydroformylation reaction mixture.

EXPERIMENTAL

Materials

The following materials were used in the tests: 1-dodecene, min. 98%, Fluka; 1-tetradecene, min. 98% Fluka; 1-tetradecanal, min. 95%, Fluka;

1-pentadecanal, min. 95% Fluka; synthesis gas (a mixture of $H_2 + CO$), made by the author from H_2 and CO; tri(m-sulfofenyl)phosphine trisodium salt (TPPTS-Na) (7); catalyst [HRh(CO)(TPPTS-Na)$_3$], made by the author (22); sodium dodecylsulfate (SDS), Fluka; sodium dodecylbenzenesulfonate (SDBS), Fluka; 1-butanol, 99%, Merck; buffer pH 7 ($KH_2PO_4 + Na_2PO_4$) 0.05 M solution, POCh S.A. Gliwice.

Methodology

The solubilization ability was measured in a glass cell with a magnetic stirrer. The glass cell was filled with 5 g of a butanol-water mixture at the butanol ratios by weight varying in the range 25–50% and SDS or SDBS was added by doses to obtain a homogeneous (transparent) system. This was followed by addition of the component to be solubilized (olefin or aldehyde), until turbidity was developed. The solubilization tests were performed at $20 \pm 1°C$.

Hydroformylation tests were carried out in a 100 cm^3 pressurized autoclave with an electric heating mantle, magnetic stirrer, and a system of inlet and outlet valves for raw materials and products.

The autoclave was fed with a reaction mixture containing 0.500 g [HRh(CO)(TPPTS-Na)$_3$] catalyst, 0.1 mole olefins, 50.0 g solvent, specified amounts of SDS or SDBS and TPPTS, and synthesis gas (a 1:1 mixture of H_2:CO), and the material was held at 100°C for 1 hr, while mixing continuously. After the reaction, the material in the autoclave was cooled down, pumped into the phase separator, and let to stand to achieve phase separation. The upper phase was separated. The aqueous phase was sent to the mixer and, after adding butanol, it was mixed and introduced into the separator. After separation, the upper phase was combined with the phase resulting from the first separation, and then weighed and distilled. The setup of the test apparatus for hydroformylation of olefins in the aqueous phase and separation of reaction products in shown in Fig. 1.

Analytical Methods

A gas chromatograph from Perkin-Elmer Model 8500 with flame-ionization detection was used for determining the composition of liquid hydroformylation products. The apparatus was equipped with a molten silica column (the series 530 μm HP-5) with the following dimensions: 5 m × 0.53 mm and with the phase containing 5% phenylmethylsilicone. Chromatographic separation conditions: column temperature 60–230°C, programming rate 12°C/min., detector temperature 250°C,

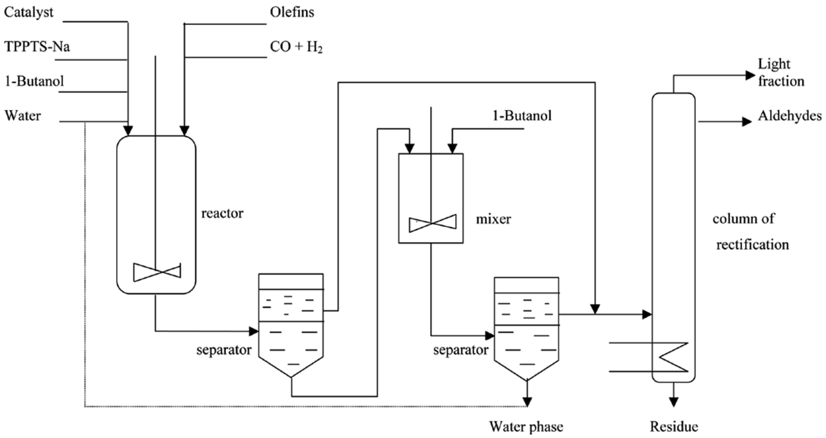

Figure 1. The setup of test apparatus for hydroformylation of olefins in the aqueous phase and separation of reaction products.

carrier gas: argon. The obtained results were quantifed according to the peak area percent.

The same GC method was used for determination of the water phase products content, except that the internal standard calibration was applied.

RESULTS AND DISCUSSION

From preliminary tests it follows that the SDS-butanol-aqueous system may be in a variety of forms, e.g., SDS suspension in butanol (10 g SDS and 45 cm^3 butanol), transparent solution (10 g SDS, 45 cm^3 butanol, and 10 cm^3 water) as well as a turbid solution (10 g SDS, 45 cm^3 butanol, and 25 cm^3 water). The SDS-butanol-aqueous system in question is sensitive to the addition of electrolytes, i.e., salt, e.g., NaCl, whose presence results in separation into two phases, one of which is rich in water while the other is rich in butanol.

Solubilization of 1-Dodecene in Aqueous Systems

Shown in Fig. 2 is the ability of aqueous solutions with various amounts of butanol and SDS to solubilize 1-dodecene.

It was found in the tests that, for a system containing butanol and water to achieve high abilities to solubilize 1-dodecene, SDS ought to

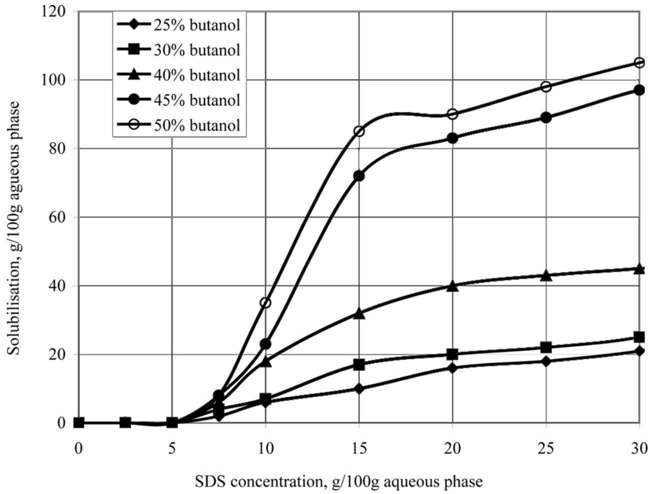

Figure 2. Solubilization of 1-dodecene by aqueous solutions comprising various amounts of butanol and SDS.

be at concentrations higher than 6 g/100 g of the water phase while the butanol co-surfactant ought to be at a concentration in the range from 25 to 50%. In the case of aqueous solutions containing from 25 to 40% butanol, the olefin solubilization ability was not higher than 45 g/100 g of the aqueous phase. In a system with 45% butanol it becomes possible to solubilize roughly 100 g 1-dodecene in 100 g of the aqueous phase, while SDS is at a concentration of 30 g/100 g of the aqueous phase. Still higher concentrations of butanol appear to have a minor effect on improving the ability to solubilize 1-dodecene.

Replacing SDS with sodium dodecylbenzenesulfonate (SDBS) results in shifting the ability to solubilize 1-dodecene towards higher concentrations of SDBS, Fig. 3. In order to achieve solubilization of olefins, the concentration of SDBS ought to be higher than 12 g/100 g of the aqueous phase, and that of butanol ought to be 25%. An increase in the concentration of SDBS in the range from 12 to 70 g/100 g of the aqueous phase results in a monotonous increase in the solubilization of 1-dodecene up to 65 g/100 g of the aqueous phase. High abilities to solubilize olefins (130 g/100 g of the aqueous phase) were achieved for an aqueous solution containing 45% butanol and 60 g SDBS /100 g of the aqueous phase. For higher butanol concentrations, i.e., 50%, much higher concentrations of SDBS, more than 95 g/100 g of the aqueous phase are required in order to achieve solubilization of olefins. However, at such higher concentrations of SDBS the viscosity of the mixture was observed to grow to high values.

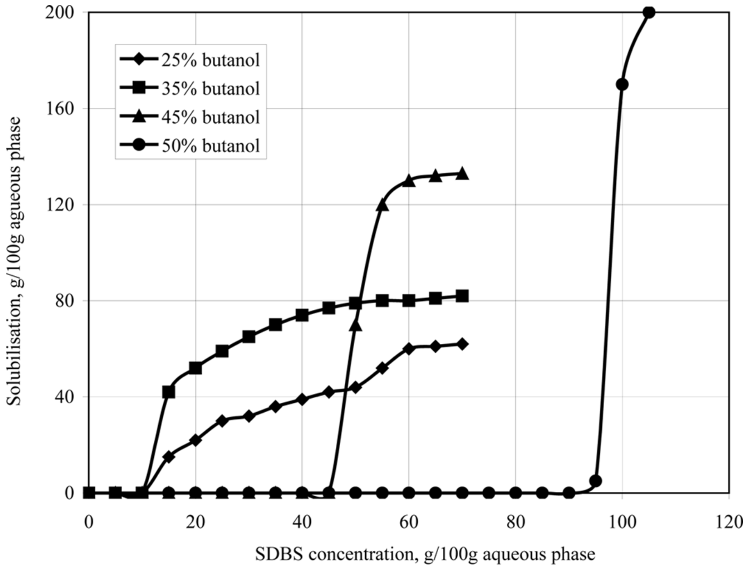

Figure 3. Solubilization of 1-dodecene by aqueous solutions comprising various amounts of butanol and SDBS.

Solubilization of 1-Tetradecene in Aqueous Systems

For 1-tetradecene, SDS concentrations in the range from 5 to 7 g/100 g of the aqueous phase are required, to achieve solubilization of 1-tetradecene by aqueous solutions containing from 25 to 45% butanol, Fig. 4. The solubilization ability of such a system grows rather fast, accompanying an increase in the concentration of butanol in the range of SDS concentrations of up to 10 g/100 g of the aqueous phase. When SDS concentrations were increased still higher, a monotonous increase in the solubilization of 1-tetradecene was observed, namely, up to approximately 55 g/100 g of the aqueous phase for an aqueous solution containing 45% butanol and 25 g SDS/100 g of the aqueous phase. On the other hand, a high ability to solubilize olefins is shown by an aqueous solution containing 50% butanol and from 20 to 25 g SDS/100 g of the aqueous phase. The ability of the system to solubilize 1-tetradecene is about 70 g/100 g of the aqueous phase and still growing slowly, accompanying an increase in the concentration of SDS.

The ability of 1-tetradecene solubilization by aqueous solutions containing 25 to 50% butanol and various amount of ABS is shown in Fig. 5.

For aqueous solutions containing 25 to 40% butanol, low SDBS concentrations in the range from 7 to 10 g/100 g of the aqueous phase

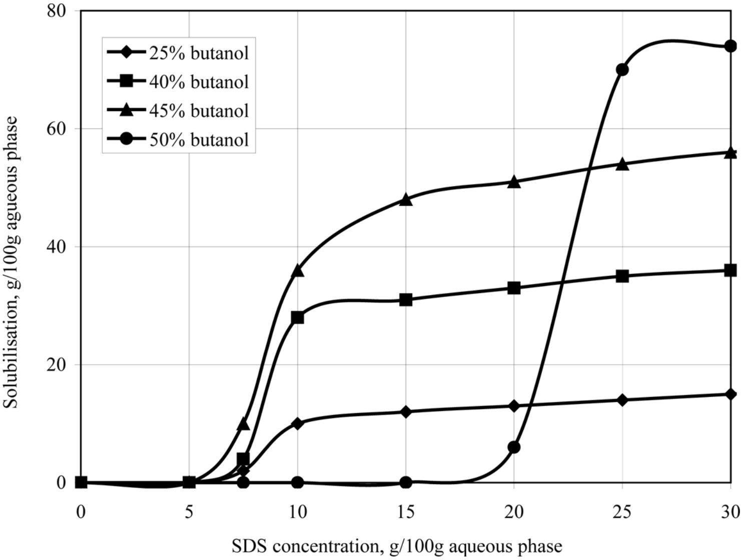

Figure 4. Solubilization of 1-tetradecene by aqueous solutions comprising various amounts of butanol and SDS.

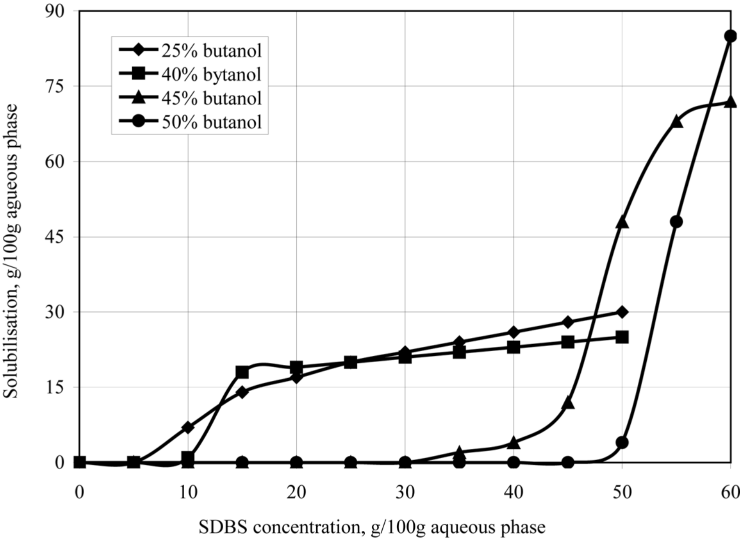

Figure 5. Solubilization of 1-tetradecene by aqueous solutions comprising various amounts of butanol and SDBS.

are required, to achieve solubilization of 1-tetradecene. In that case, the ability to solubilize olefins is rather insignificant, about 18 g/100 g of the aqueous phase. A prominent increase in the ability to solubilize 1-tetradecene was achieved only for higher concentrations of butanol, above 45%. A still higher increase in butanol concentration to 50% is made possible by about 85 g 1-tetradecene in 100 g of the aqueous phase, although high SDBS concentration, of 60 g/100 g of the aqueous phase, is then required.

The Effect of TPPTS-Na on Ability to Solubilize Olefins and Aldehydes

Real aqueous-phase hydroformylation systems are known to contain reaction products, aldehydes, and sodium salts of sulfonated phosphines, apart from olefins. A suitably selected hydroformylation reaction system is expected to show high ability to solubilize olefins. On the other hand, the ability to solubilize hydroformylation reaction products ought to be smaller so that the system may undergo spontaneous separation into an organic phase containing reaction products, and an aqueous phase containing the catalyst and a sodium salt of the sulfonated phosphine at high conversions of olefins to aldehydes.

Those water-butanol systems containing SDBS and SDS, which show high abilities to solubilize 1-dodecene and 1-tetradecene, were selected for the study of the effect of TPPTS-Na on solubilization ability.

Introduction of 3% TPPTS-Na into an aqueous system containing 45% butanol results in shifting the range of solubilization of 1-dodecene towards higher SDS concentrations, Fig. 6. Although, the above relationships determined experimentally are of significant practical value, their explanation needs more detailed studies.

In that case, to achieve solubilization of olefins an SDS concentration of 17 g/100 g of the aqueous phase is required. However, no significant differences in the ability to solubilize olefins and aldehyde were observed in the test system. The starting point of solubilization of 1-dodecene and 1-tridecanal is at SDS concentrations of about 17 g/100 g of the aqueous phase, while for SDS concentration of 23 g/100 g of the aqueous phase's ability to solubilize 1-dodecene is 25 g/100 g of the aqueous phase, which is about 2,5 times as high as that for 1-tridecanal. For higher concentrations of SDS, which is 30 g/100 g of the aqueous phase, the ability to solubilize 1-dodecene and 1-tridecanal is 120 and 160 g/100 g of the aqueous phase, respectively.

The ability to solubilize 1-dodecene and that of a hydroformylation product, i.e., 1-tridecanal in an aqueous system containing 25% butanol, 3% TPPTS-Na, and various amounts of ABS is compared in Fig. 7.

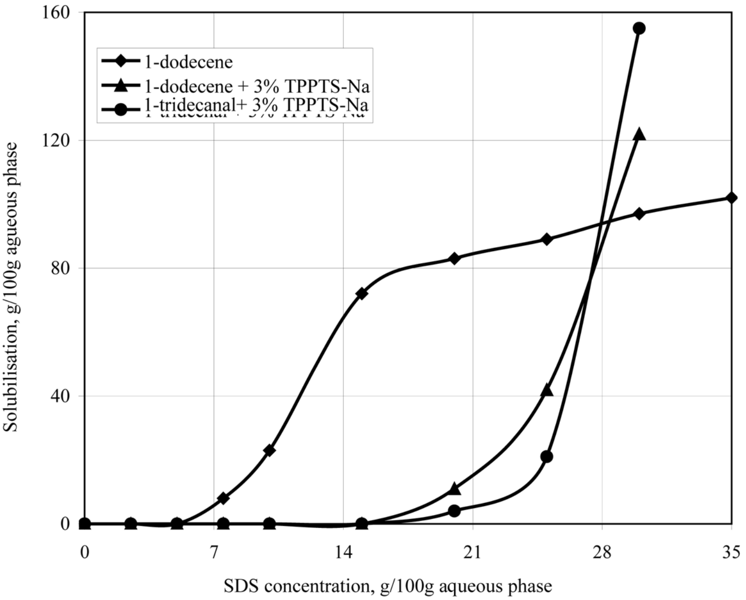

Figure 6. The effect of addition of TPPTS-Na on the ability of aqueous solutions containing 45% butanol and various amounts of SDS to solubilize 1-dodecene and 1-tridecanal.

Introduction of TPPTS-Na results in shifting the range of solubilization of 1-dodecene towards higher concentrations of SDBS, amounting to about 20 g/100 g of the aqueous phase. In the range of SDBS concentrations of up to 40 g/100 g of the aqueous phase, a higher ability to solubilize 1-dodecene is shown by an aqueous system without TPPTS-Na. In an aqueous system containing more than 40 g SDBS in 100 g of the aqueous phase, it is possible to solubilize more 1-dodecene than in a system without TPPTS-Na. For SDBS concentrations of more than 30 g/100 g of the aqueous phase, the aqueous system tested shows about 3 times as high an ability to solubilize 1-dodecene than does 1-tridecanal. It appears that it is possible to select such amounts of butanol and SDBS for which an aqueous system shows high ability to solubilize 1-dodecene, whereas solubilization of aldehydes is low. In such conditions, at high conversions of olefins to aldehydes, spontaneous separation of the reaction mixture into an aqueous phase with the catalyst and an organic phase with the reaction products may occur.

For an aqueous system containing 50% butanol and SDS, addition of 3% sodium salt of TPPTS-Na will not have any significant effect on the ability to solubilize 1-tetradecene over the entire range of SDS

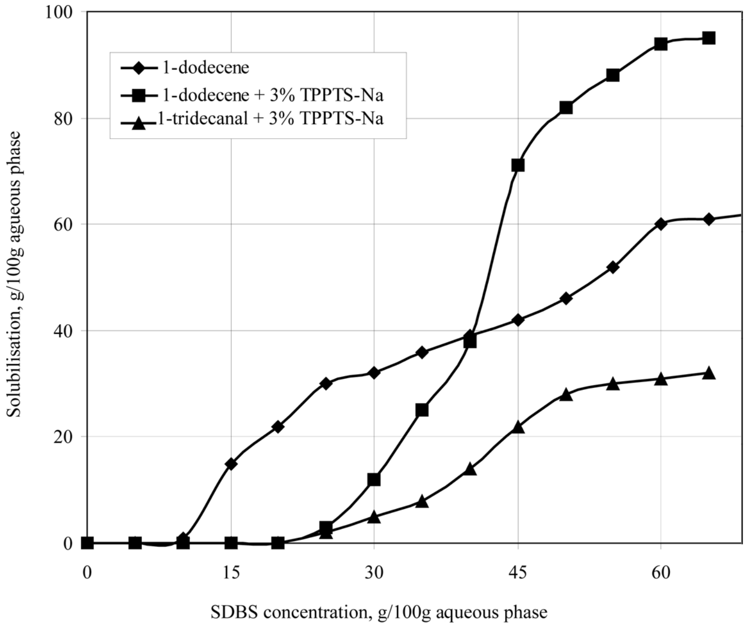

Figure 7. The effect of addition of TPPTS-Na on the ability of aqueous solutions containing 25% butanol and various amounts of SDBS to solubilize 1-dodecene and 1-tridecanal.

concentrations, Fig. 8. However, for solubilization of 1-pentadecanal, higher concentrations of SDS than in the case of a more hydrophilic 1-tetradecene are required. The starting point of solubilization of the aldehyde occurs at an SDS concentration of 20 g/100 g of the aqueous phase. For SDS concentration of 25 g/100 g of the aqueous phase in the test system it is possible to solubilize about 15 g/100 g of the aqueous phase of 1-pentadecanal. The ability to solubilize 1-tetradecene in this case is about 5 times as high and is 75 g/100 g of the aqueous phase.

The effect of addition of TPPTS-Na on the ability of aqueous solutions containing 25% butanol and various amounts of SDBS to solubilize 1-tetradecene and 1-pentadecanal is shown in Fig. 9.

To achieve solubilization of 1-tetradecene, SDBS concentrations higher by about 10 g/100 g of the aqueous phase are required, compared with the system without TPPTS-Na. For low concentrations of SDBS, up to 23 g/100 g of the aqueous phase, the aqueous system tested shows lower ability to solubilize 1-dodecene, compared with the system containing no salt. However, in the case of SDBS concentrations higher than 25 g/100 g of the aqueous phase, the ability of the test system to solubilize

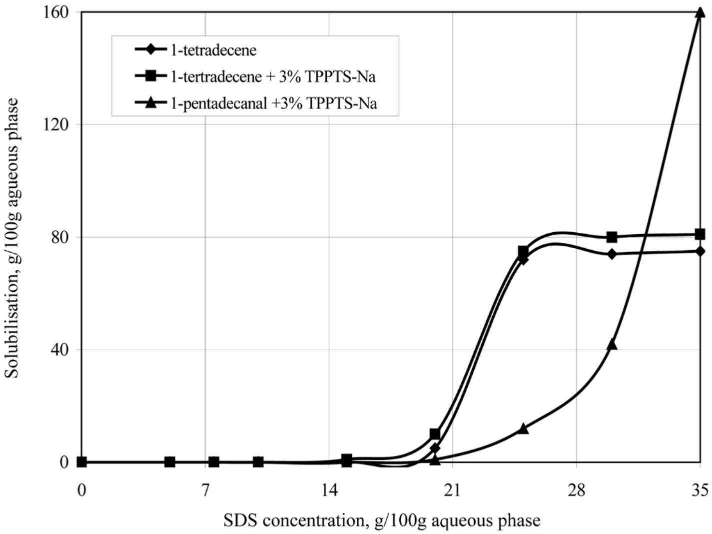

Figure 8. The effect of addition of TPPTS-Na on the ability of aqueous solutions containing 50% butanol and various amounts of SDS to solubilize 1-tetradecene and 1-pentadecanal.

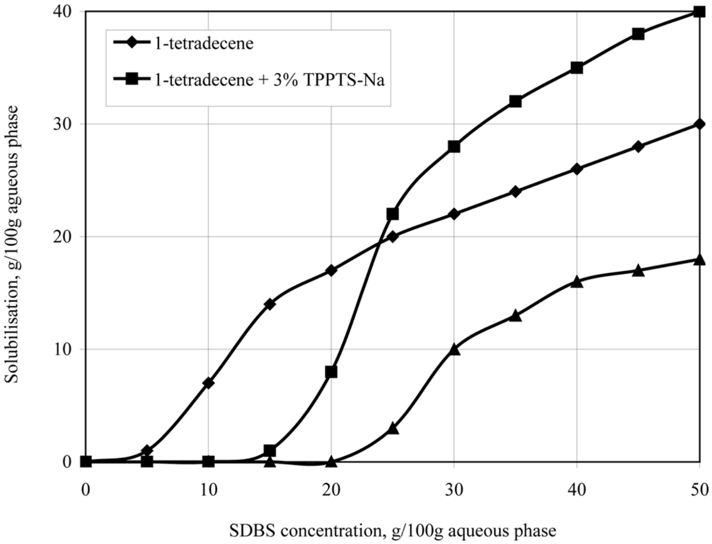

Figure 9. The effect of addition of TPPTS-Na on the ability of aqueous solutions containing 25% butanol and various amounts of SDBS to solubilize 1-tetradecene and 1-pentadecanal.

1-tetradecene is higher, and for SDBS concentrations of 50 g/100 g of the aqueous phase it is 40 g 1-tetradecene for 100 g of the aqueous phase. The starting point of solubilization of 1-pentadecanal is observed at an SDBS concentration of 20 g/100 g of the aqueous phase. The ability to solubilize an aldehyde grows higher together with the SDBS concentration, though it is much lower than that for solubilization of 1-tetradecene, and it is about 18 g/100 g of the aqueous phase for SDBS concentration of 50 g/100 g of the aqueous phase.

Hydroformylation of Olefins in the Aqueous Phase and Separation of Reaction Products

A study of the solubilization of olefins and their hydroformylation reaction products, i.e., aldehydes, was carried out using model systems. The results obtained show that a suitably selected model system containing water, butanol and 3% TPPTS-Na demonstrates high ability to solubilize 1-dodecene and 1-tetradecene. The ability to solubilize the products of hydroformylation of such olefins for the system in question is much less pronounced, therefore, at high conversions of olefins to aldehydes the system is expected to separate into an aqueous and an organic phase. To verify the validity of the theory of separation of reaction products the tests were carried out using real systems under hydroformylation reaction conditions.

Olefin hydroformylation tests in aqueous systems were carried out using a hydrophilic rhodium catalyst which is a complex rhodium system containing a CO ligand and three TPPTS-Na ligands. Since the catalyst is water soluble, the hydroformylation reaction may be carried out in a water-organic system. The reaction system contained also a free excess hydrophilic phosphine ligand (TPPTS-Na), suitable amounts of butanol, a surfactant, and an olefin.

The tests verifying the validity of the theory of phase separation of hydroformylation reaction products, i.e., 1-dodecene and 1-tetradecene, were carried out using selected systems with the following compositions (Figs. 10 and 11):

1. Hydroformylation of 1-dodecene –45% butanol, 3% TPPTS-Na trisodium salt, and 28 g SDS/100 g of aqueous phase.
2. Hydroformylation of 1-dodecene –25% butanol, 3% TPPTS-Na trisodium salt, and 35 g SDBS/100 g of aqueous phase.
3. Hydroformylation of 1-tetradecene –50% butanol, 3% TPPTS-Na trisodium salt, and 20 g SDS/100 g of aqueous phase.
4. Hydroformylation of 1-tetradecene –25% butanol, 3% TPPTS-Na trisodium salt, and 25 g SDBS/100 g of aqueous phase.

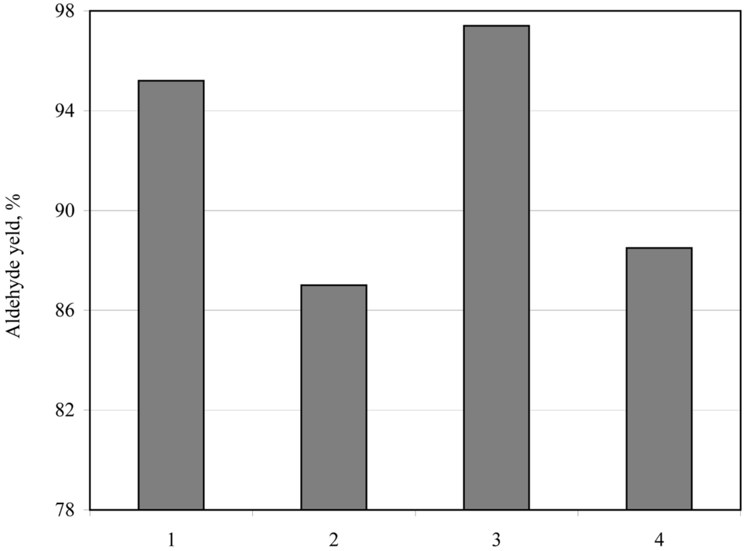

Figure 10. The output of aldehydes in test hydroformylations of 1-dodecene and 1-tetradecene in aqueous systems.

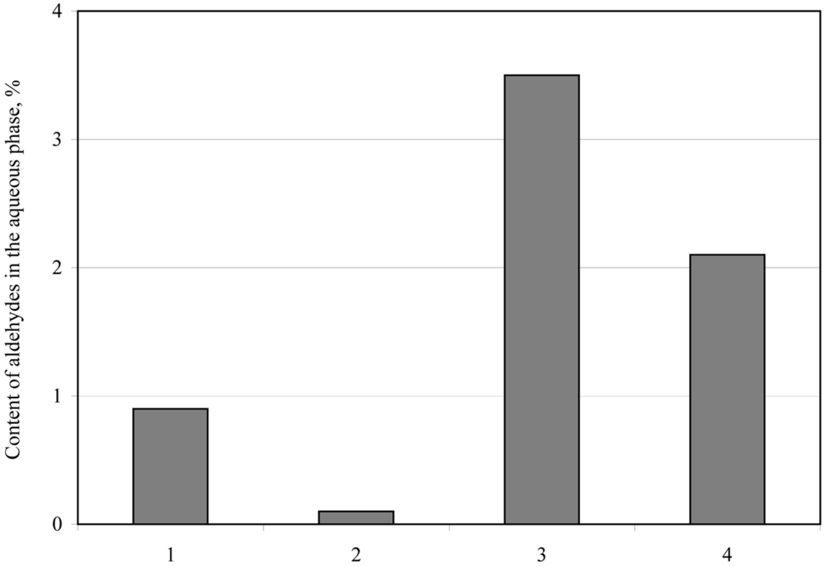

Figure 11. The content of aldehydes in the aqueous phase resulting from the separation of 1-dodecene and 1-tridecanal hydroformylation products in aqueous systems.

In each case the mixture obtained from the hydroformylation reaction is a light-brown solution without precipitated solids. Therefore, it may be assumed that the process catalyst was not decomposed. After the reaction, the solution separated spontaneously into two phases: an organic phase containing the reaction products and an aqueous phase containing the catalyst and excess phosphine ligand.

Higher outputs of aldehydes were achieved in test hydroformylations of 1-dodecene and 1-tetradecene using SDS as an interphase transfer catalyst, Fig. 10. In the tests where SDBS was used, roughly 10% lower outputs of aldehydes were obtained, which may be due to the use of lower concentrations of butanol, and some difficulties in the mutual phase mixing. In hydroformylations of 1-tetradecene both with the use of SDS and SDBS, the outputs of aldehydes were found to be about 2% higher.

The concentrations of aldehydes in the separated aqueous phase from the test hydroformylation were compared in Fig. 11. The lowest concentrations of aldehydes were found in the tests where SDBS was used. In that case, the aqueous phase from the test hydroformylation of 1-dodecene was found to contain about 0.1% tridecanals. In the aqueous phase from the test hydroformylation of 1-tetradecene, the concentration of aldehydes was approximately 0.25%. On the other hand, in the test hydroformylations of both 1-dodecene and 1-tetradecene with the use of SDS, clearly higher amounts of aldehydes were dissolved in the separated aqueous phase. The analyzed aqueous phases were found to contain 3.5% tridecanals in the test hydroformylation of 1-dodecene and about 4% pentadecanals in the test hydroformylation of 1-tetradecene. In those cases, high concentration of aldehydes in the aqueous phase is probably due to the doubled concentration of butanol in the reaction mixture with SDS compared to that with SDBS, which remains in the water phase and carries the organic phase of aldehyde into the water phase, as well. Higher solubilisation of butanol by SDBS may result from its higher HLB compared to that of SDS.

CONCLUSIONS

A suitably selected aqueous model system comprising butanol and SDS or SDBS shows high ability to solubilize olefins (1-dodecene or 1-tetradecene) and lower ability to solubilize the products of hydroformylation of such olefins. The selected aqueous systems were used for hydroformylation of 1-dodecene and 1-tetradecene whereby high outputs of aldehydes were obtained. The following compositions of the reaction medium were selected as optimal.

- For hydroformylation of 1-dodecene:
- −45% butanol, 3% TPPTS-Na trisodium salt, and 28 g SDS per 100 g of the aqueous phase, which yielded 95% selectivity towards aldehydes and 0,9% losts in water phase,
- while for hydroformylation of 1-tetradecene:
- −50% butanol, 3% TPPTS-Na trisodium salt, and 20 g SDS/100 g of aqueous phase, which yielded 97% selectivity towards aldehydes and 3,4% losts in water phase.

After the reaction, the mixture spontaneously separated into an organic phase containing most of reaction products, and an aqueous phase comprising the hydrophilic rhodium catalyst.

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