

BIPHASIC HYDROFORMYLATION OF 1-OCTENE USING [BMIM][PF₆]-DECANE BIPHASIC MEDIA AND RHODIUM/TPPTS COMPLEX CATALYST: THERMODYNAMIC PROPERTIES AND KINETIC STUDY

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Summary

A chemical reaction engineering approach is reported to investigate the biphasic hydroformylation of 1-octene using [Bmim][PF₆] ionic liquid. It is based on both a process parameter investigation (temperature, concentrations and pressures) and a thermodynamic study of the reaction medium, gas-liquid and liquid-liquid equilibria. Initial rate data show complex behaviour with respect to operating parameters and are best described by a rate equation based on a mechanistic model. Complete reaction scheme including isomerisation is then modelled accounting from the time dependent concentration of the organic substrates measured in organic phase and recalculated in ionic phase from liquid-liquid equilibria.

Keywords

Multiphase and particulate reactors. Green CRE.

1. Introduction

Homogeneous catalysts are used commercially for the synthesis of various bulk and fine chemicals, especially when a high selectivity to desired product is required. However the use of volatile solvents -often environmentally harmful- and the difficulties to separate the products from the reaction media are major drawbacks of homogeneous catalysis. Since the last decade, ionic liquids (ILs) have gained significant importance as alternative solvent systems for catalyst applications. ILs exhibit essential properties that could satisfy the requirements for the hydroformylation reaction. First, they have essentially no vapor pressure which avoids the problems due to volatility (i.e. safety, losses) faced with conventional organic solvents. Furthermore, they are good solvents for a wide range of both organic and inorganic species without undesirable interactions with the metal centre. Moreover their property to be immiscible with a number of organic solvents makes them very promising solvents to substitute for water in the biphasic hydroformylation of olefins¹.

The first report on the rhodium catalyzed hydroformylation using ionic liquid was proposed by Chauvin *et al.*²: they showed that [Rh(CO)₂(acac)] / PPh₃ in [Bmim][PF₆] was an efficient catalyst system for the hydroformylation of 1-pentene. However, the system suffered from catalyst leaching and so various phosphine ligands were investigated. Immobilization of the catalyst in the IL with sulfonated ligands (i.e. TPPMS, TPPTS) gave better results. Later Favre *et al.*³ reported [Rh(CO)₂(acac)] / TPPTS catalysed hydroformylation of 1-hexene in eight ionic liquids and correlated the observed reaction rates with the solubility of the substrate in ILs.

The use of ionic liquids as solvents to achieve multiphase homogeneous catalysis is here explored following a chemical reaction engineering approach: thermodynamics of multiphase equilibria and reaction kinetics including modelling of the concentration-time profiles of all species. This detailed work is applied to the biphasic hydroformylation of 1-octene using [Bmim][PF₆]/decane emulsion and mainly Rh/TPPTS as catalyst system.

2. Solubility data

As the knowledge of the reactant concentrations in IL phase is required for the interpretation and modelling of the kinetic data, both gas-liquid and liquid-liquid equilibria have been determined for the reaction system.

Solubility of CO and H₂ in [Bmim][PF₆] has been accurately measured at different temperatures (293-373 K) and pressures (up to 25 bar) by a pressure-drop technique⁴. Both gases follow Henry's law, carbon monoxide being more soluble than hydrogen in the investigated range of temperature. As often found in other liquids the effect of temperature on hydrogen solubility is not monotonous like with other gases and shows a maximum. The solubility (per volume) of CO and H₂ is rather low in [Bmim][PF₆] compared to usual organic solvents (around 3 times lower), but higher than in water.

The solubility and partition coefficient of 1-octene and n-nonanal into [Bmim][PF₆] are much more difficult to measure, as routine chromatography or spectroscopy methods are not suitable. For binary mixtures, IL/1-octene and IL/n-nonanal, thermogravimetry analysis can be used due to the non volatile character of the IL. For ternary or

quaternary systems, IL/1-octene/decane/n-nonanal, a more complex technique has been adapted involving multiple headspace gas chromatography in which the liquid sample is heated and only the vapor phase is injected in GC and analyzed. Solubility values obtained by both techniques show a good agreement with low deviations. N-nonanal is found to be much more soluble than 1-octene in [Bmim][PF₆] due to its polar nature. Temperature effect is rather low resulting in less than 35% variation in the considered range (298–353 K). More importantly and as expected, solubility of 1-octene is dramatically higher in [Bmim][PF₆] (1.6 mol % at 298 K) than in water (0.0001 mol %), which confirms the potential performance of such solvent for biphasic catalysis. The presence of decane does not modify the partition of octene or nonanal between organic and IL phases, while n-nonanal still enhances the affinity of 1-octene for the IL phase.

3. Hydroformylation reaction

Experimental: Hydroformylation experiments have been carried out in an autoclave reactor equipped with a gas inducing stirrer. The catalytic complex is synthesized in situ using [Rh(CO)₂(acac)] as precursor and TPPTS as standard ligand, with P/Rh=3 in [Bmim][PF₆] (40 mL) under syngas. The 1-octene substrate dissolved in decane (60 mL) is then added to the reactor. The resulting liquid-liquid system is pressurized with syngas (10 bar) and heated up to desired temperature under low stirring (under self gas induction) to hinder gas-liquid mass transfer. When thermal equilibrium is reached, more gas is introduced until desired pressure and reaction is initiated by increasing the agitation speed to 1200 rpm, enough to ensure kinetic regime is achieved. Initial hydroformylation rate and selectivity towards linear aldehyde are obtained from pressure variations of the ballast feeding the reactor at constant pressure and chromatography analysis of liquid samples (after 1, 3 and 6 hours of reaction) respectively.

Following this procedure, main reaction parameters have been varied: catalyst loading ($2.0\text{--}7.0 \times 10^{-3}$ kmol/m³_{IL}), H₂ and CO pressure separately (5–30 bar), 1-octene concentration ($0.32\text{--}0.97$ kmol/m³_{org}), and temperature (333–353 K). No hydrogenation to octane is detected but significant isomerisation of 1-octene occurs leading further to the branched aldehyde. Concerning the main reaction, Turn Over Frequency is rather high for biphasic catalysis, ranging from 15 to 75 h⁻¹ after 1 hour of reaction. No linear variations are observed except for catalyst loading. Partial orders have been determined for H₂ and 1-octene (0.46 and 0.75 respectively) as well as the usual inhibition by CO, but with a maximum at relatively high CO pressure (about 20 bar). The activation energy is 25.8 kcal/mol.

The n/i ratio decreases all along the reaction course, from about 3 to less than 1 in some cases. Much better results on selectivity can be obtained with sulfoxantphos instead of TPPTS but with lower TOF.

Modelling: The main reaction kinetics of direct hydroformylation has been modelled trying several semi-empirical equations. Following rigorous discrimination

procedure, the best equation is based on a mechanistic model assuming limiting addition of hydrogen in the catalytic cycle.

Then a complete model accounting for octene isomerisation and hydroformylation of 1- and internal octene has been built up and solved thanks to an optimization software using the time variations of the four (lumped) concentrations (1-octene, internal octene, n-nonanal and branched aldehyde) measured in organic phase and recalculated in ionic phase with the equilibrium models. Satisfactory agreement with experimental profiles can be achieved (Fig. 1), but statistical analysis shows broad confidence intervals for some parameters.

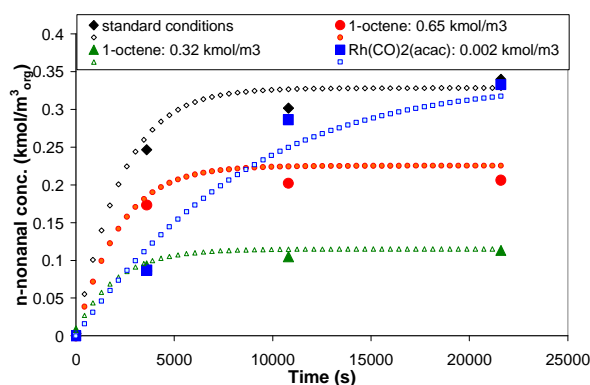


Figure 1 – Time evolution of n-nonanal concentration in the organic phase: exp. (large symbols) and model (small ones). Standard conditions: $Rh(CO)_2(acac): 7.0 \times 10^{-3}$ kmol/m³_{IL}, TPPTS, 1-octene: 0.97 kmol/m³_{org}, $T=353$ K, $P_{CO}=P_{H_2}=20$ bar.

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