

Potential and limits of thermodynamic rate approaches to hydroformylation: A case study for modelling solvent effects on reaction kinetics for gas/liquid reactions

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Highlights

- Prediction of solvent effects on reaction kinetics based on thermodynamic activities
- Calculation of activity coefficients using PC-SAFT equation of state
- Strong agreement between model and experiment for different solvent compositions
- Kinetics of hydroformylation independent from pressure for syngas CO/H₂ = 1/1

1. Introduction

Reaction kinetics are known to depend on the solvent system [1,2]. Thus, kinetic parameters determined for a given reaction can usually not be transferred to other solvent environments. This contribution reports the modelling of reaction kinetics for the homogeneously-catalyzed hydroformylation of long-chain alkenes in different solvent mixtures and operating conditions (Fig. 1) using a thermodynamically consistent activity based approach thus bridging thermodynamics and kinetics.

2. Methods

Kinetic hydroformylation experiments were performed using high-pressure autoclaves of different size with temperature, pressure and stirring variations. Different stirrer types and insets were used to vary gas/liquid mass transfer. Hydroformylation was carried out using long-chain alkene 1-dodecene, syngas (CO/H₂ = 1/1) and catalyst Rh/BIPHEPHOS. Solvent effects on reaction kinetics were investigated for different decane/*N,N*-dimethylformamide (DMF) mixtures. For reaction analysis, liquid samples were analyzed at different times to quantify reactants and products using gas chromatography. To predict solvent effects on hydroformylation kinetics, activity coefficients of reactants and products were calculated using Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state [3]. Therefore, gas-liquid equilibrium (GLE) for CO and H₂ was assumed and experimental time-dependent operation conditions were used to calculate gas and liquid phase composition. For estimating kinetic parameters of hydroformylation and side-reactions a two phase semi-batch reactor model including kinetic rate approaches was implemented in MATLAB[®] [4,5].

3. Results and discussion

Reaction analysis was performed for all kinetic hydroformylation experiments. Mass transfer limitations for CO and H₂ were observed for low pressures and low mass transfer coefficients. Hydroformylation chemo- and regioselectivity was significantly reduced due to a shift into side reactions of isomerization and iso-selective hydroformylation. Thus, mass transfer limitations mask potential solvent effects on hydroformylation kinetics. In addition, the GLE for CO and H₂, an assumption made for calculating activity coefficients using PC-SAFT, cannot be maintained.

To ensure reliable prediction of solvent effects, experiments performed under mass transfer limitations for CO and H₂ were excluded by estimating deviations from GLE for CO and H₂. Therefore, concentrations of dissolved gases CO and H₂ were calculated numerically using a mass transport model based on two-film theory.

To model reaction kinetics of hydroformylation considering predicted solvent effects, a thermodynamically consistent mechanistic kinetic model [4,5] based on thermodynamic activities instead of commonly used concentrations was derived (Fig. 1)

Activity coefficients of reactants were calculated using PC-SAFT equation of state [4]. Analysis of thermodynamic activities of CO and H₂ revealed that both only depend on the composition in the gas phase but not on the total pressure nor on the composition of the liquid reaction system. Activity coefficients of 1-dodecene increase significantly with content of solvent DMF. Using extensive kinetic experiments, the activity-based kinetic model could be parameterized successfully. In addition, it was evaluated in comparison to two concentration-based kinetic models of different complexity.

The thermodynamic consistent model showed strong agreement with the experimental data and confirmed a pressure-independence of the hydroformylation for a syngas mixture CO/H₂ = 1/1. No significant solvent influence of solvent system decane/DMF on yields, selectivities and reaction kinetics of hydroformylation was found. Nevertheless, a thermodynamically consistent kinetic model using thermodynamic activities to account for solvent effects for the complex Rh/BIPHEPHOS-catalyzed hydroformylation of long-chain alkenes could be successfully applied.

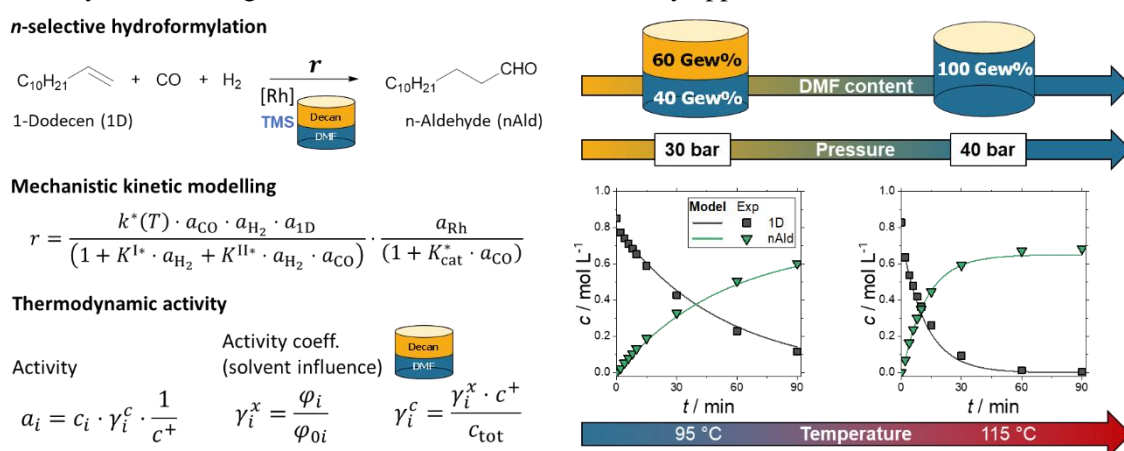


Figure 1. Left: Hydroformylation (n-selective, no other side reactions shown) in different decane/DMF solvent mixtures. Kinetic models are based on detailed reaction mechanisms. Thermodynamic activity coefficients to predict solvent influence on reaction kinetics were calculated by PC-SAFT EOS. Right: Variation of operating conditions in kinetic hydroformylation experiments and agreement to thermodynamically consistent kinetic model.

4. Conclusions

The reaction kinetics of the homogeneously-catalyzed hydroformylation of long-chain alkenes in different solvent mixtures and operating conditions was successfully modelled using a thermodynamically consistent approach based on activities. Thermodynamic solvent-dependent activity coefficients of the alkene obtained from PC-SAFT were used to determine intrinsic solvent-independent kinetic parameters of hydroformylation. Moreover, the analysis of the thermodynamic activities for the gases revealed that for a fixed CO/H₂ ratio, the hydroformylation kinetics do not depend on the total system pressure. The approach is transferable to other gas/liquid reactions and an important tool to reduce experimental efforts for solvent optimization with respect to reaction kinetics.

References

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Keywords

Kinetic modelling; homogenous catalysis; thermodynamic activities; solvent effects