Predicting Solvent Effects on Homogeneity and Reaction Kinetics

A Thermodynamic Approach Using PC-SAFT

Fabian Huxoll, Anna Kampwerth, Thomas Seidensticker, Dieter Vogt, Gabriele Sadowski

Solvents provide the reaction environment of all liquid-phase reactions in the chemical industry and may significantly affect reaction rates and the phase behavior of complex reaction media. Especially, if a reaction is performed in solvent mixtures, a high experimental effort is required to quantify these effects. Within this work, we developed a novel thermodynamic-activity-based approach to predict solvent effects on both reaction rates and phase behavior using the PC-SAFT model. This approach allows gaining in-depth process insights and is applicable to a wide variety of liquid-phase reactions.

Solvents can have an enormous impact on the phase behavior and kinetics of chemical reactions. Knowledge and quantification of these effects are of major importance and need to be known to achieve high selectivities and reaction rates.

In this work, the liquid-liquid equilibrium of a multicomponent reaction system was predicted using PCSAFT. At the same time, solvent effects on the reaction kinetics were estimated. For highest reaction rates we searched for reaction mixtures that lead to the highest thermodynamic activities of the reactants. We applied this workflow to the homogeneously catalyzed reductive amination (RA) of undecanal in a solvent mixture of methanol and *n*-dodecane (DDC). During the reaction, water is formed as a by-product, which may lead to an unwanted phase separation during the reaction. An increasing DDC content in the solvent mixture was predicted to limit the working space for the reaction and also to massively reduce the reaction rate. As a result, DDC should be added only after the reaction to form a second liquid phase, thus enabling an efficient catalyst recycling. Validation experiments were in perfect accordance with the modeling results (Fig.1).

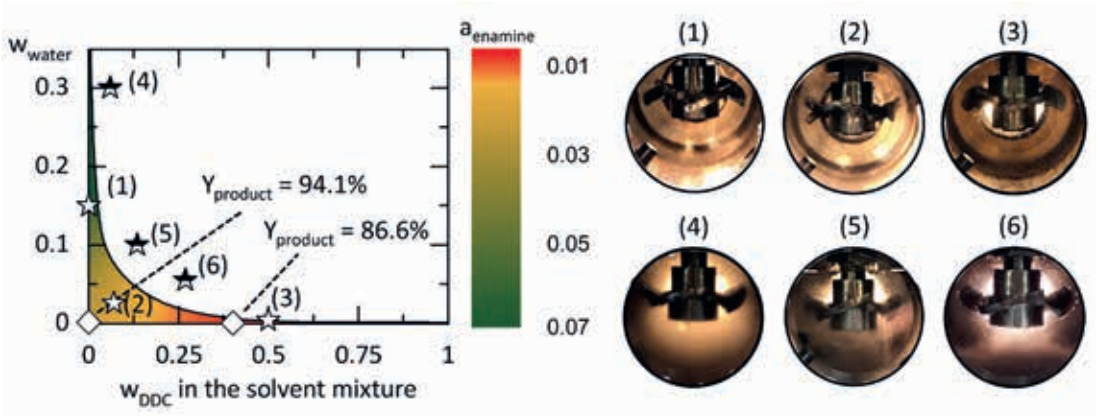

Figure 1: PC-SAFT predictions of enamine thermodynamic activities ($a_{enamine}$) at 373.15 K at 3 MPa as a function of the methanol/DDC solvent composition and the water content in the multicomponent RA reaction mixture (highest $a_{enamine}$ is green; lowest $a_{enamine}$ is red). Homogeneity experiments (1)–(6) and experimental product yield $Y_{product}$ after t = 2 min (diamonds) are compared to the PC-SAFT modeling results. The solid line represents the predicted binodal curve separating the single-phase region (white area) from the two-phase region (colored area). Empty stars denote homogeneous samples; half-filled stars indicate heterogeneous samples.

For samples (1)–(3) indicated as stars in Fig.1, a homogeneous liquid was predicted and also experimentally found at reaction conditions. In contrast, samples (4)–(6) showed strong turbidity caused by the presence of a fine dispersed second liquid phase. The highest product yield $Y_{product}$ = 94.1% was obtained in pure methanol, whereas increasing DDC contents in the solvent mixture resulted in decreasing product yields down to $Y_{product}$ = 86.6 %, confirming the predicted negative effect of DDC on the initial reaction rate.

To conclude, the ability to predict solvent effects on both reaction rates and phase behavior offers the opportunity to identify the most promising solvent compositions for liquid-phase reaction systems while ensuring homogeneous systems during the whole reaction and high reaction rates. As no experimental reaction data is required for the modeling, promising solvent compositions and working spaces are identified fast and reliably, reducing time-consuming experiments to a minimum.

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Contacts:
fabian.huxoll@tu-dortmund.de
anna.kampwerth@tu-dortmund.de
thomas.seidensticker@tu-dortmund.de
dieter.vogt@tu-dortmund.de
gabriele.sadowski@tu-dortmund.de