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Superior catalyst recycling in surfactant based multiphase systems – Quo vadis catalyst complex?

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ABSTRACT

Microemulsion systems are smart solvent systems which can be applied in homogeneous catalysis. We investigate these multiphase systems to exploit their characteristics for catalytic gas/liquid reactions and processes in aqueous media. One critical aspect from an economic perspective is the quantitative recycling of the catalyst complex dissolved in the multiphase system. Therefore, it is important to know the distribution of the catalyst complex in each of the single phases. In this contribution we analyse the different parameters/factors that may have an influence on the distribution of catalyst complexes in microemulsion systems, e.g. temperature, type of ligand, structure of surfactant, and chain length of surfactant. Afterwards, the derived information is used for the design of a real, industry-oriented application: hydroformylation of long chained alkenes. Hereby, special attention is given to the separation step of a process, which is performed after a homogeneously catalyzed reaction step in a microemulsion system. Process and economic constraints are briefly outlined and compared with operation data, aiming for the reuse of the catalyst in the reaction step and reduced leaching into product streams, even in the case of operational disturbances and shifts in the catalyst distribution.

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1. Introduction

Expensive noble metal catalysts are often applied in homogeneous catalysis. The aims hereby are high activity and selectivity at moderate reaction conditions. However, to establish a large-scale process, the quantitative recovery of these catalysts is crucial and should be possible without loss in activity/selectivity. Hence, reaction media that combine the advantages of homogenous catalysis (high turnover frequencies and high selectivity) and two-phase-catalysis (easy separation of catalyst and product) are of great interest. Beside the classical aqueous-organic two-phase systems, i.e. for the hydroformylation of 1-propene to n-butanal in the Ruhrchemie/Rhône-Poulenc Process [1], many new systems have been developed during the last decades. Well known examples are ionic liquids [2,3], supercritical media based on CO_2 [4,5], thermomorphic solvent mixtures [6], supported ionic liquid-phase (SILP) [7], or sol-gel immobilized catalyst systems [8]. An alternative approach is the application of microemulsion systems as tuneable solvents for the recycling of water-soluble catalysts. Microemulsion systems are ternary mixtures consisting of a non-polar compound (oil), a polar compound (water), and a surfactant (often non-ionic surfactants are chosen in this context). They provide a high interfacial area between the polar and non-polar domains during the reaction. Additionally, their phase separation behaviour can be manipulated through temperature changes. However, for the application of microemulsion systems their phase behaviour, which not only depends on temperature but also on their composition and the interaction between the surfactant and the catalyst/reactants, has to be studied in detail [9]. Among the available green solvents, microemulsion systems, easily tuneable by the selection of an appropriate surfactant, show superior characteristics for catalytic reactions and processes in aqueous media. Furthermore, they fulfil all requirements needed for successful and efficient catalyst recycling. Examples for the application of microemulsions as reaction system are the hydrogenation of dimethyl itaconate with Rh/TPPTS [10], the Suzuki coupling of 2-bromobenzonitrile and 4-methylbenzeneboronic acid with Pd/TPPTS [11] and the hydroformylation of 1-dodecene with Rh/SX [12]. For further examples see also [9].

In this contribution we will evaluate and discuss the distribution of homogeneous catalyst complexes in microemulsion

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systems by the variation of different parameters, e.g. temperature, ligand, structure of surfactant, and chain length of surfactant. We will also discuss several aspects which are important for the application of microemulsion systems for a closed recycle catalytic process with respect to the choice of the surfactant. In addition, we will present a case study to design a process for homogeneous catalysis in a microemulsion system with efficient catalyst recycling based on the results of the first part of this contribution.

2. Aqueous surfactant media

Water can act as a solvent for water-soluble catalysts and enables the biphasic extraction of non-polar products as well as the recycling of catalysts. However, in case of hydrophobic reactants it has the disadvantage of poor reactant solubility. The addition of a surfactant increases the solubility of non-polar reactants in the aqueous phase. Generally, there are two different approaches to create aqueous surfactant media for homogeneously catalysed reactions.

The first approach is to create an aqueous–micellar solution by the addition of a surfactant to water, which exceeds the critical micelle concentration (cmc). Micelles are nano-scale aggregates of surfactant monomers, which are able to solubilize organic components in their cores. Since the size of micelles is usually very small, the concentration of substrate in an aqueous–micellar solution is often lower than in conventional organic solvents. The cmc and the size of micelles depend on the type of surfactant. In general, non-ionic surfactants form larger micelles and have a low cmc in comparison to ionic surfactants.

The second approach is the use of microemulsion systems, which are formed at surfactant concentrations much higher than the cmc. By the addition of a non-ionic surfactant of the type C_iE_j to a biphasic mixture of water and oil, usually four different states can be observed that were classified by Winsor (Winsor systems I–IV). In C_iE_j, i is the number of hydrocarbon groups of the surfactant's hydrophobic part, and j is the number of ethoxylate groups of its hydrophilic part. Important parameters to characterize the mixture are the weight fractions α and γ. In Eq. (1) m_{oil} is the mass of oil, m_{water} is the mass of water and m_{surf} is the mass of non-ionic surfactant.

$$\alpha = \frac{m_{oil}}{m_{oil} + m_{water}} \gamma = \frac{m_{surf}}{m_{oil} + m_{water} + m_{surf}} \quad (1)$$

In Fig. 1 the phase behaviour of a ternary mixture of oil, water and non-ionic surfactant is schematically shown for a constant value of α.

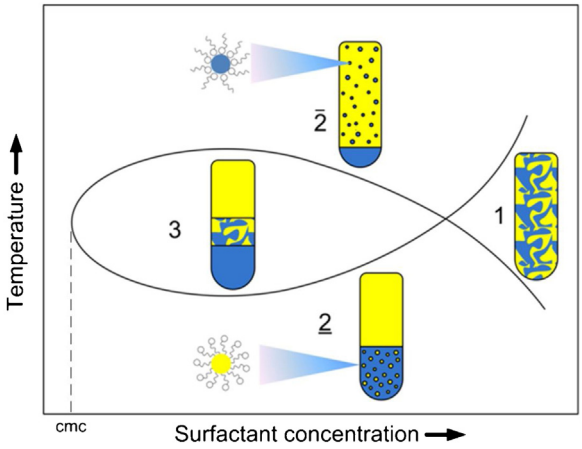

Fig. 1. Phase diagram (commonly called fish-diagram) for a ternary mixture of oil, water, and non-ionic surfactant at a constant ratio of oil and water with normal (bottom) and inverse (top) micelles. The figure has been modified from [13].

At low temperatures the surfactant is mainly solubilized in water, whereas its solubility in oil increases at higher temperatures. Thus, the illustrated sequence of phases as a function of temperature is the result of the gradual change in the surfactant's solubility from hydrophilic to hydrophobic. The phase sequence generally starts at low temperatures with an oil-in-water (o/w) microemulsion (2, Winsor I). This microemulsion consists of oil-bearing micelles in a continuous water phase which is in equilibrium with an organic excess phase. At intermediate temperatures a three-phase region (3, Winsor III) exists, where the surfactant is almost equally soluble in both liquids and forms a surfactant rich microemulsion phase in the middle of two excess phases. For even higher temperatures a water-in-oil (w/o) microemulsion ($\bar{2}$, Winsor II) is formed. Here, water-bearing inverse micelles exist in a continuous oil phase, which is in equilibrium with a water excess phase. If the concentration of surfactant in the ternary mixture is high enough for the complete solubilization of oil and water, a one-phase microemulsion (1, Winsor IV) of the entire volume will be formed, which can be an o/w-, bicontinuous- or w/o-microemulsion depending on the oil content in the mixture.

In general, each of the four Winsor states can be applied as a reaction medium for homogeneous catalysis. Since the phase behaviour of a microemulsion system can be changed as a function of temperature and surfactant concentration, it is possible to adjust the reaction system between different process steps with varying requirements [13]. The choice of the applied surfactant has to be made carefully so that the requirements for a homogenously catalysed reaction with subsequent product separation and catalyst recycling, can be fulfilled. Besides its influence on the phase behaviour, the surfactant will have a strong impact on the distribution of reactants and catalysts between the aqueous and the organic phase. For the quantitative recycling of a homogeneously dissolved catalyst complex from multiphase systems as well as the evaluation of the reaction kinetics it is important to know the distribution of the catalyst complex between the single phases. In general, based on the experience with conventional organic-aqueous two-phase systems, water-soluble catalyst complexes are preferentially dissolved in the aqueous phase (see e.g. the Rh/TPPTS complex in the RCH/RP process) and hydrophobic counterparts are dissolved in the oil phase. For microemulsion systems, the interactions between the surfactant and the catalyst complex can influence the solubility of the latter considerably. In many cases the catalyst follows the surfactant into the corresponding microemulsion phase, which results in different separation tasks for the catalyst recycling during a process step depending on the phase behaviour of the microemulsion system. Therefore, it is necessary to indicate the parameters which are responsible for the catalyst distribution in such surfactant based multiphase systems to select the best surfactant as well as ideal operating conditions that result in a quantitative catalyst recycling and an optimal separation process.

3. Catalyst distribution in multiphase systems

To analyse the effects of the different parameters on the catalyst distribution multiple experiments were carried out. The obtained information from these experiments was then used for an actual industry-oriented application. In the following, details on these experiments as well as the results are presented.

3.1. Experimental

3.1.1. Chemicals

The solvents 1-dodecene (94%), water (HPLC grade), and tetrahydrofuran (THF, 99.5%) were purchased from VWR. The

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