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Determination of phase separation and mass transfer in complex micellar three phase systems

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ABSTRACT

Combining the advantages of the homogeneous and heterogeneous catalysis is the main goal of tunable solvent systems. Homogeneous conditions shall be achieved throughout the reaction period and heterogeneous conditions shall be adjusted within the separation process. Therefore, high and specific reaction rates are coupled with a simplified separation process. For the design of the separation process the phase separation itself and the liquid/liquid mass transfer must be quantified. Therefore, a test cell is designed in this work. For the experimental investigations a model test system was applied (water/1-dodecene/C_4E_2). The separation process of the liquid three phase system was observed by an image analysis. A hysteresis effect was observed which also influenced the separation process. Within the three phase system the coalescence rate is faster than under two phase conditions in the observed temperature range. A diffusion coefficient through the C_4E_2 rich middle phase could be determined experimentally, which was in good agreement with theoretical calculations.

1. Introduction

Tunable solvent systems can be applied to combine the advantages of the homogeneous and heterogeneous catalysis. Mild reaction conditions as well as high and selective yields are combined with a simplified separation processes. In homogeneous systems mass transfer processes can be neglected. Nevertheless, the catalyst/product separation is the great challenge of these systems. Therefore, the main idea of tunable solvent systems is to provide homogeneous conditions for the reaction and heterogeneous conditions for the separation. Liquid/liquid reaction systems are a special type of the homogeneous catalysis. The separation process is simplified in liquid/liquid systems if product and catalyst are solved in different phases. But due to the additional phase transport phenomena must be taken into consideration.

Micellar multiphase systems are examples for tunable solvent systems. These systems fulfill many principles of the green chemistry, e.g., using water as a solvent, reducing waste production, etc. Due to the interfacial active molecules (surfactants) which are used in these systems the phase behaviour is complex [1]. Four different phase conditions are possible for ternary systems of the type water/organic solvent/non-ionic surfactant. These conditions were classified by Winsor [2]:

- Type I consists of an organic and aqueous phase; micelles solubilize oil within the aqueous phase. Therefore, an O/W mircoemuslion occurs [3].
- Type II consists of an organic and aqueous phase; inverse micelles solubilize water in the organic phase; therefore, a W/O microemulsion is created [2].
- Type III consists of three coexisting phases an organic phase, an aqueous phase and a surfactant rich middle phase. Low amounts of water and oil are solubilized within the surfactant rich phase, which is also a microemuslion.
- Type IV: One phase condition. Within these conditions anisotropic structures can be observed at discrete conditions. In these cases micelles agglomerate to large micelle clusters and form liquid crystalline structures [4].

For a clearer understanding only the Winsor III system is called a microemulsion in this paper. The best performance for some reactions and separation processes were achieved under three phase conditions [5]. For some reactions (e.g., the hydroformylation of long chained alkenes) it is beneficial if the catalyst systems are solved within the microemulsion phase [6]. In case of the hydroformylation syngas must be transported into the microemulsion phase [7]. In this phase all other reactants are present; hence,

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mass transfer phenomena must be taken into consideration. Furthermore, the distribution coefficient and the mass transfer of the transferred component must be known to design the separation process. After the reaction the products have to be transported back into the organic phase to realize a simplified separation process. Therefore, the phases need to coalesce in a reasonable period of time. In presence of surfactants the coalescence behavior is mostly hindered due to the adsorption of surfactants at the liquid/liquid interface [8].

This work focuses on the determination of fundamental understanding of the liquid/liquid transport processes in liquid three phase systems which is needed for the design of the separation process. Furthermore, the coalescence must be taken into consideration to understand the separation of these complex systems in detail. Often single drop experiments are carried out to understand transport processes [9] and coalescence processes fundamentally [10].

In the presence of non-ionic surfactants an additional mass transfer resistance was observed. With exceeding the critical micelle concentration (CMC) a change of the phase behavior at the liquid/liquid interface was observed. This lead to an increase of the interfacial viscosity and caused a reduction of the mass transfer rates [11,12]. Especially, for micellar three phase systems these additional mass transfer resistances are expected.

Under micellar three phase conditions single drop experiments fail due to low interfacial tension. Nevertheless, the mass transfer and the distribution coefficients, etc. must be quantified in order to design the extraction process. Different test cells need to be taken into consideration. Stirred test cells are also commonly used to determine mass transfer rates across liquid/liquid interfaces. Here, two phases are overlaid with each other; hence a defined area of contact arises. The first test cell was presented by Lewis [13]. In the “Lewis test cell” the stirrer speed can only be adjusted in both phases equally. This results in different Reynolds numbers in both phases due to different physical properties (density, viscosity). Hence, the fluid dynamic properties within the phases cannot be chosen equally. An improvement of the “Lewis test cell” was achieved by Nitsch [14,15]. In the “Nitsch test cell” both liquid phases are stirred separately. A broad overview of methods determining the liquid/liquid mass transfer is given in [16]. The test cells which are given in this overview were modified throughout the last years and have been adjusted to their applications. Lee and Varma [17] used a stirred cell to quantify the kinetics of a biphasic aldol condensation within the mass transfer controlled regime. In this work low stirrer speeds were applied to ensure a stable interface. Another development is shown in the work of Wang et al. [18]; here the extraction kinetics of Thorium were determined within a constant interfacial area test cell. Two stirrers were applied to stir the phases independently. Nevertheless, these stirrers were installed in a cubic test cell and were not installed above each other. They were installed shifted to ensure a stable interface. Datta and Kumar [19] presented a test cell in which two stirrers were installed above each other, but both were attached to one stirrer shaft. Therefore, both stirrers could not be operated independently and further the interface is disturbed. Bertakis et al. [20] optimized the Nitsch test cell based on the Fisher information matrix to improve the quality of the measurements.

In this work other requirements on the test cell arise. Due to the low interfacial tension the stirring has to be carried out with great care to neither destabilize the interface nor to create an emulsion, which ensures the quantification of the mass transfer across a defined cross section. Therefore, the influence of the amphiphilic molecules can be identified to optimize the extraction process.

2. Materials and methods

2.1. Experimental setup

In Fig. 1 the test cell is shown which was designed to determine the separation process and the mass transfer in liquid three phase systems.

The test cell is designed based on the model of the “Nitsch test cell”. It was modified for the challenges in micellar three phase systems in which very low interfacial tensions occur. A double-walled glass reactor (1) with an inner diameter of D = 65 mm and a planar bottom was applied. Therefore, an optical access and an exact determination of the volume was ensured. Two different stirrers (2/3) were installed to avoid concentration and temperature gradients in the aqueous and organic phase. The microemulsion phase was not stirred. Both stirrers were operated independently to provide similar fluid dynamic conditions in each phase. The volume of each

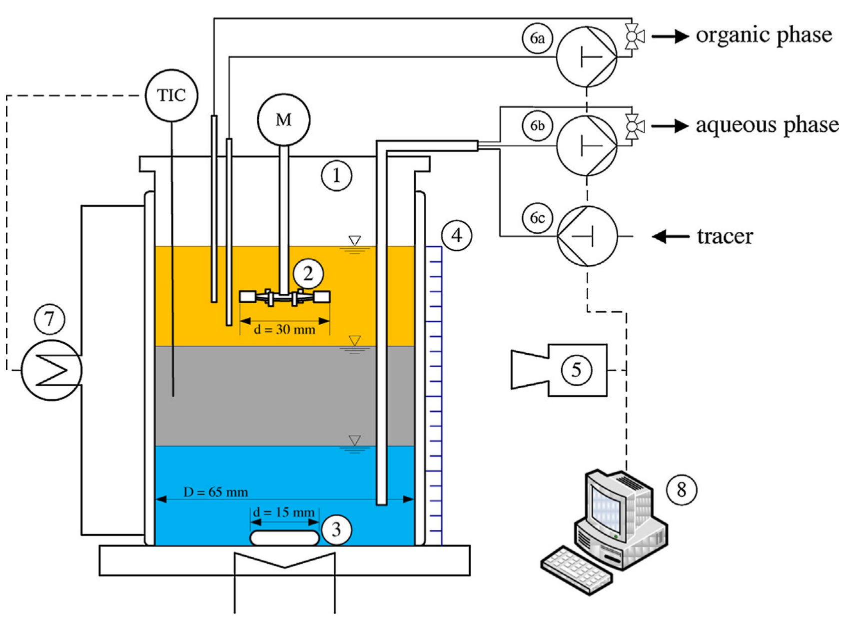

Fig. 1. Experimental setup for the determination of the phase separation and the liquid/liquid mass transfer in micellar three phase systems: 1 double-walled glass reactor; 2 and 3 stirrers; 4 scale; 5 camera; 6a,b,c Hamilton modules PSD/3 with three way valves; 7 Lauda E-200 thermostat; 8 computer.

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