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# Dispersion conditions and drop size distributions in stirred micellar multiphase systems

L. Hohl*, N. Paul, M. Kraume

*Chair of Chemical and Process Engineering, Technische Universität Berlin, Ackerstraße 76, D-13355 Berlin, Germany*

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ABSTRACT

Micellar multiphase systems can be applied to enable reactions like the hydroformylation of long-chained olefins. These liquid/liquid systems combine advantages of homogenous catalysis like high and specific yield or mild reaction conditions with a fast phase separation process. In previous studies highest yields were observed in systems under three phase operation conditions whereby the reaction rate was a function of stirrer speed. Hence, dispersion conditions and drop size distributions need to be taken into consideration. In this study, micellar three phase systems were analysed using an endoscope measurement technique and image analysis in a stirred tank. A methodical approach to identify the respective phases and to clarify the dispersion conditions was found. The mean Sauter diameters were quantified as a function of the system composition. By applying abrupt changes of the stirrer frequency, the dynamic behaviour and coalescence effects were investigated.



## 1. Introduction

The determination of dispersion conditions and drop size distributions is a common method to characterise and optimise processes in liquid/liquid systems. Agitation and separation of systems with partly miscible fluids are major fields of interest in various applications and the analysis of two phase systems has been performed by numerous authors. Different aspects like coalescence effects, drop breakage, stirrer speed or dispersed phase fractions have been taken into consideration in set-ups ranging from stirred tanks to horizontal pipelines and other flow vessels [1–7]. Knowledge of the drop size distribution is used for process monitoring and control or to characterise and improve product quality. Thus, it is possible to enhance the operational capacity of separators and mixers or to intensify e.g. extraction, rectification or polymerisation processes [8–10].

One interesting application for liquid/liquid systems is the hydroformylation of olefins to aldehydes. Common industrial methods like the Ruhrchemie/Rhône-Poulenc process use a water soluble rhodium complex as catalyst. Hence, it can be realised as a homogeneous catalysed reaction under mild conditions with high and specific yield [11,12]. The use of aqueous solvent systems provides economic and ecological advantages. However, the solubility of olefins in water decreases with the chain-length, leading to marginal reaction rates and economically inefficient operation for long-chained alkenes [11–13]. Therefore, the solubilisation of the reactants needs to be enhanced to intensify this process. From the economic point of view the recycling of the catalyst and the separation of the product phase have to be taken into consideration too. In previous studies it was observed that micellar multiphase systems of water, organic solvent and non-ionic surfactants are promising technological approaches to overcome low reaction rates, since they improve the solubility of aqueous and organic phase [12,13].

The phase behaviour of these micellar systems can be regulated by adjusting the temperature and composition (Fig. 1, left). The two most common conditions for systems of water, oil and non-ionic surfactant are oil-in-water (o/w) emulsions with an organic excess phase ($2\Phi$) or water-in-oil (w/o) emulsions with an aqueous excess phase ($\bar{2}\Phi$). At high amounts of surfactant formation of only one phase is observed ($1\Phi$). Under specific operating conditions the systems develop a microemulsion middle phase consisting of water, organic phase and huge amounts of surfactants ($3\Phi$) [12,14,15]. The occurrence of the third phase leads to significantly higher aldehyde yields during the hydroformylation reaction (Fig. 1, right). The reaction mostly occurs in the microemulsion phase where catalyst and reactant are brought in close contact. Additionally it was observed that the reaction rate increases with higher impeller speeds until the formation of fluid spouts deteriorates the process [12,13].

The three phase operation condition enhances mass transport processes during the reaction and provides faster phase

* Corresponding author.
*E-mail address:* Lena.Hohl@tu-berlin.de (L. Hohl).

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**Nomenclature**

*Latin letters*

| | |
|---|---|
| $h_{St}$ | height of stirrer blade, mm |
| $d_{St}$ | stirrer diameter, mm |
| $D$ | inner diameter of tank, mm |
| $d_{32}$ | Sauter mean diameter, μm |
| $h$ | stirrer bottom clearance, mm |
| $H$ | height of fluid level in the tank, mm |
| $Q_0$ | cumulative distribution function of number, – |
| $t$ | time, min |
| $T$ | temperature, °C |
| *MAC* | minimal aggregation concentration mol/L |
| *CMC* | critical micelle concentration, mg/L |
| *aq* | aqueous phase |
| *mi* | microemulsion phase |
| *org* | organic phase |

*Greek letters*

| | |
|---|---|
| $\alpha$ | ratio of organic and aqueous phase, – |
| $\gamma$ | wt-% of surfactant, – |
| $\kappa$ | conductivity, mS/m |
| $\phi$ | phase |

separation compared to micellar two phase systems. Hence, the isolation of the product phase and recycling of the catalyst can be simplified [12,13,16]. In many two phase systems, the dispersion conditions are either predetermined by the task, setup or composition. Otherwise, different methodical approaches like conductivity measurements or selective colouring of the substances have to be applied to identify the continuous and dispersed phase. To determine the drop size distributions, several experimental methods can be utilised [18]. Microscopy is a common technique to analyse drop sizes in stable emulsions [17]. However, to analyse drop sizes of coalescent systems in-situ, other techniques have to be applied. For example, Coulaloglou and Tavlarides [1] used a photo-micrographic probe assembly, whereas Maaß[3,18] and Alban [19] applied an endoscope setup and image analysis to detect drops in two phase dispersions for different agitation speeds and dispersed phase fractions. Other authors combined in-line near-infrared spectroscopy with an endoscope technique or applied a method of extinction profiles [20,21].

The drop size distributions in liquid/liquid systems are influenced by several aspects like stirrer speed, temperature, physical properties or phase volume fractions of the systems [1,3]. The appearance of a third phase leads to different characteristic system properties. A basic approach to understand the complex hydroformylation systems is a simplification to the educts: water, oil and non-ionic surfactant. The composition of the systems can be defined using the mass ratios $\alpha$ and $\gamma$:

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

$$\gamma = \frac{m_{surfactant}}{m_{oil} + m_{water} + m_{surfactant}} \quad (2)$$

In former investigations a three phase system consisting of water, 1-dodecene and non-ionic surfactant was used to enlighten mass transport during the hydroformylation process. A system with a constant composition was analysed using an endoscope measurement technique [13,22]. Two different dispersed phases could be observed, which were either dark and clear or bright and hazy (Fig. 2). Thus, the adhering drops of both dispersed phases were distinguished due to their visual appearance. The continuous phase was identified using conductivity measurements while adding a small amount of potassium chloride without significantly changing the phase behaviour.

The conductivity measurements indicated that the continuous phase was either aqueous or the microemulsion. The authors assumed that the cohesive drop interaction would only occur

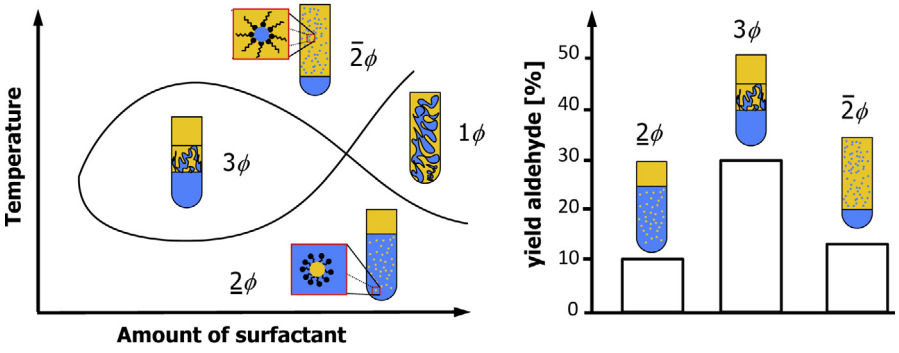


**Fig. 1.** Phase behaviour of micellar systems with a fixed oil to water ratio: o/w emulsion (2̲Φ), w/o emulsion (2̄Φ), one phase system (1Φ) and three phase system (3Φ) (left). Yields of the hydroformylation as a function of the operating conditions (right) [12,13].

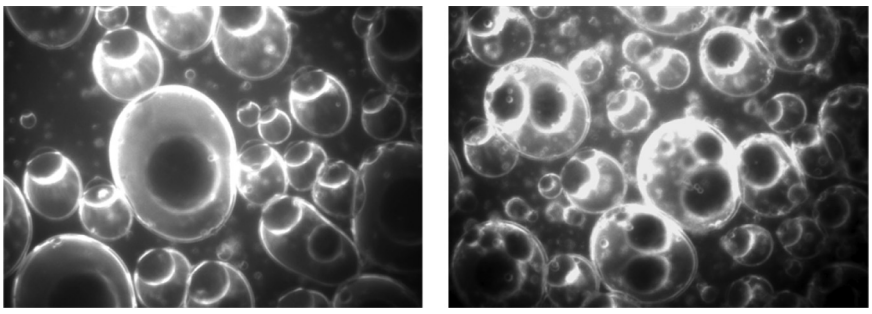

**Fig. 2.** Micellar three phase system consisting of water, 1-dodecen and Marlophen NP7 at 300 rpm (left) and 400 rpm stirrer speed (right) [13].