Extended abstract of the Ph.D. thesis

Summary:

Systems consisting of water, oil and non-ionic surfactants can develop up to three liquid phases as a function of composition and process conditions. These solvent systems are promising reaction media for processes such as the hydroformylation of long-chained olefins. In this work, the influence of the third phase on drop size distributions and phase separation - crucial parameters to achieve high reaction rates and an efficient catalyst recycling - was investigated. A methodology to identify the phases in agitated systems was developed using a combination of different measurement techniques. By analyzing phase behavior and physical properties of the systems in combination with drop size analysis, the influencing factors on the drop size distributions under two and especially three phase conditions were quantified. The prediction of the droplet sizes in three phase systems with population balance equations is a challenging task that was performed for the first time in this work. Due to its complexity, it still mainly works for simple dispersion conditions and in a narrow process condition range. Although the predictive power is not yet satisfactory, this work provides an overview on how a change in process conditions affects all parameters relevant for drop breakage and coalescence. Furthermore, the impact of the dispersion conditions on the phase separation was investigated. Experimental and simulation results indicate that the phase separation process can be modeled successfully. The thesis is based on five publications.

On the following pages, the main characteristics of microemulsion systems and experimental work are presented, since they are crucial to understand the general problems tackled in the thesis. For details concerning the complex modeling of drop size distributions via Population balance equations [1] and of phase separation using a modified model by Henschke [2] in liquid 3ϕ systems, see [3]–[5] .

Problem addressed and applications:

In the Ruhrchemie-Rhône-Poulenc process, short-chained olefins can be converted to aldehydes in two basic process steps [6]. A high interfacial area between an aqueous and organic phase is achieved in a stirred tank reactor, followed by a simple phase separation in a decanter where the very efficient catalyst located in the water phase is recycled (see Figure 1).
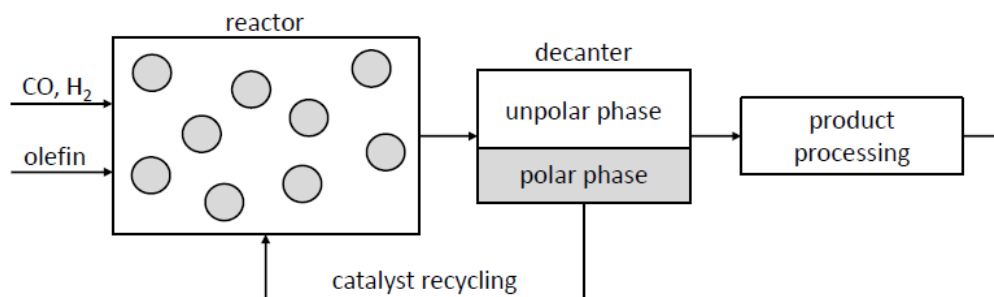

Figure 1: Process concept of the Ruhrchemie-Rhône-Poulenc process used for the hydroformylation of short-chained olefins. The concept can be adjusted by adding non-ionic surfactants to realize the hydroformylation of long-chained olefins [5].

The long-term goal is to apply this process concept using also long-chained olefins from renewable resources. For long-chained olefins, the energy dissipation rates needed to achieve comparable reaction rates are extremely high due to their low solubility in water. This makes the process economically unviable unless the process concept is modified. With non-ionic surfactants, the reduction of interfacial tension between the phases facilitates the dispersion process [7].

The very unique phase behavior and especially a condition with three liquid phases and a high tendency to coalesce offer the possibility for an efficient phase separation despite the presence of high amounts of surfactant usually hindering coalescence [8]. The phases containing surfactant, water and catalyst can thus be recycled and separated from the relatively pure organic product phase. Although dispersion and phase separation processes of liquid multiphase systems are widely performed in industry and investigated by numerous research groups, the impact of a third liquid phase on phenomena such as drop breakage, coalescence or sedimentation is barely understood.

State of the Art:

The different phases developed in systems consisting of water, oil and non-ionic surfactants are shown in Figure 2 (left) as a function of composition and temperature [9]. The phase behavior is caused by a changing solubility of the surfactant which is transferred from the aqueous phase (aq) to the organic phase (org) with rising temperature. At intermediate temperature the surfactant is nearly equally soluble in water and oil and a third liquid phases is formed, which is called a bicontinuous microemulsion (mi). Its inner structure is often described as inter-twinned continuous water and oil phases with a large amount of surfactant or as accumulated swollen micelles so numerous that they touch one another [10], [11]. An important fact about microemulsions and the difference to common (macro)emulsions was summarized by Salager et al. [11]:

> *"It is worth pointing out that the term microemulsion is a misnomer, since […] microemulsions cannot be considered tiny droplets dispersed in a continuous phase, i.e., a microemulsion is not really a special case of a regular emulsion or macroemulsion. In fact, regular emulsions and microemulsions are fundamentally different. […] The most fundamental difference between them is that microemulsions exist in a state of thermodynamic equilibrium. In contrast, macroemulsions are metastable two-phase systems in which the coalesced state is the actual state of equilibrium. Macroemulsions are only kinetically stable, meaning that the kinetics of coalescence is slowed by the presence of a film of surface-active materials at the oil/water interface".*

In Figure 2 (middle) the interfacial tensions between the phases are shown schematically. Within two-phase ($\underline{2\phi}$/$\overline{2}\phi$) conditions, only the aq/org interfacial tension occurs, which undergoes a minimum within the three phase (3ϕ) temperature interval [12]. The interfacial tension aq/mi rises with temperature after formation at T_u due to a decreasing solubility of surfactant in water. The interfacial tension org/mi behaves contrary as the solubility of surfactant in oil rises with temperature. Since more than 5 wt.% of surfactant is usually needed to reach this phase behavior, interfacial tensions are extremely low at all conditions ($\sigma_{i/j} \ll 1$ mN/m). If a 3ϕ system is stirred, an emulsion with two drop populations is created, where drops of both dispersed phases break and coalesce simultaneously.
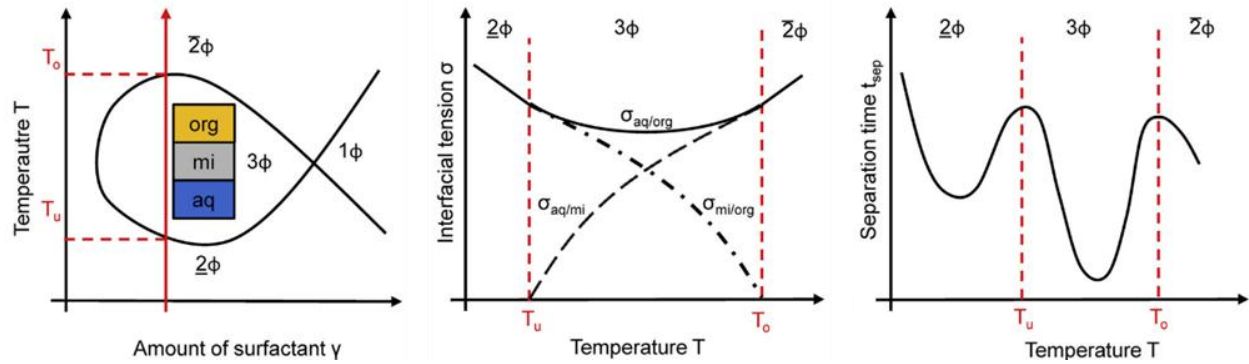
Figure 2: Phase behavior of water/oil/nonionic surfactant systems at constant oil/water ratio α is a function of surfactant mass fraction γ and temperature T. (organic phase "org", aqueous phase "aq" and microemulsion phase "mi") [13]

Phase separation times of the systems can vary by order of magnitudes [14]. A minimum of phase separation time after agitation stop lies within 3ϕ conditions, as indicated schematically in Figure 2 (right). This separation time at this minimum is in the range of 5-10 minutes for many surfactant systems, whereas the separation can take hours if the temperature is varied by only 1-2°C. At other conditions, phase separation takes weeks or month and is, therefore, barely feasible. This can partly be explained by changes in interfacial rigidity affecting drop deformation [15]. Although many studies on phase behavior, the separation time minimum or on the molecular structure of the bicontinuous phase and microemulsions in general are available in literature, these 3ϕ systems have never been applied as reaction media in industrial processes. Furthermore, no in-situ measurements of drop sizes, no analysis of occurring dispersion types and no combination of these experiments with a dynamic phase separation analysis had been performed.

Key innovations of the thesis

To achieve a better fundamental understanding, the following topics were addressed in non-reactive microemulsion systems:

1. Determination of phase behavior and physical properties of all phases for relevant process conditions
2. Development of a method to identify the phases in agitated systems using an in-situ endoscope technique.
3. Analysis of emulsion rheology to determine its possible impact on the process.
4. Combining the previous results with a detailed drop size analysis, the influencing factors on the drop size distributions under two and three phase conditions were quantified.
5. The possibility to predict droplet sizes in three phase systems with population balance equations was evaluated and all relevant parameters needed for the simulation were identified.
6. The impact of dispersion conditions on phase separation was investigated including the case of multiple emulsions. Methods to model the phase separation behavior were evaluated.
7. Key experiments to determine the dispersion type of the agitated system based on simple batch-settling experiments were identified.

Materials & Methods:

The physical properties viscosity, density and interfacial tension of the systems were determined in pure systems, mixtures and in the single phases (aq, mi, org). The rheological behavior of the systems was analyzed using a cone and plate rheometer (MCR 302, Anton Paar GmbH), the density with an oscillating U-tube principle (DSA 5000M, Anton Paar GmbH) or a conical Hubbard pycnometer and interfacial tension was determined using pendant drop method (OCA15, Dataphysics) and spinning drop method (SVT 20, Dataphysics) with temperature regulation [5].
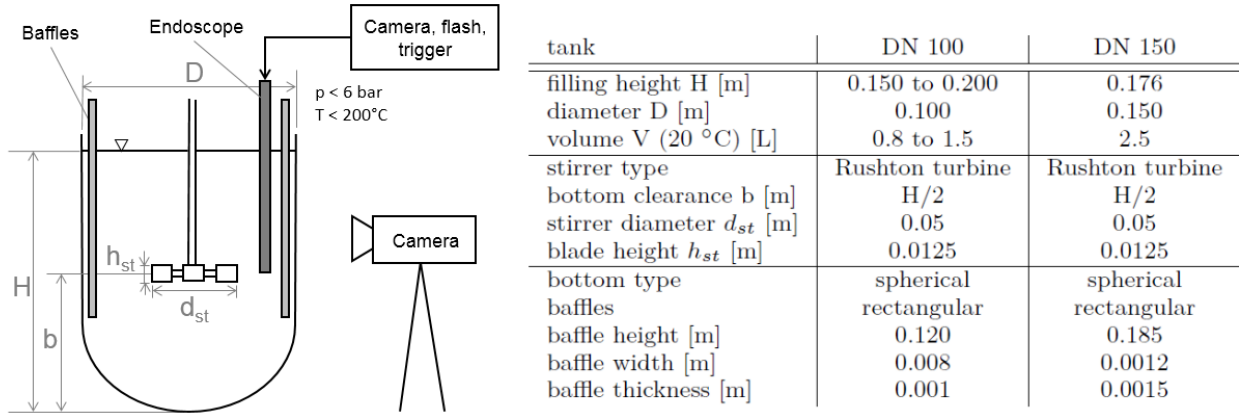
tank	DN 100	DN 150
filling height H [m]	0.150 to 0.200	0.176
diameter D [m]	0.100	0.150
volume V (20 °C) [L]	0.8 to 1.5	2.5
stirrer type	Rushton turbine	Rushton turbine
bottom clearance b [m]	H/2	H/2
stirrer diameter d_{st} [m]	0.05	0.05
blade height h_{st} [m]	0.0125	0.0125
bottom type	spherical	spherical
baffles	rectangular	rectangular
baffle height [m]	0.120	0.185
baffle width [m]	0.008	0.0012
baffle thickness [m]	0.001	0.0015

Figure 3: Stirred tanks for analysis of drop sizes and phase separation [5]

The electrical conductivity of the single phases and stirred multiphase systems was determined using a conductivity probe (Knick). Two different stirred tanks were used to quantify drop size distributions and phase separation (see Figure 3). An in-situ endoscope technique (SOPAT GmbH) was applied, which consisted of two different endoscopes connected to a digital camera (GX 2750, Allied Visions Technology) and an image analysis software (SOPAT GmbH).

Images of the complete vessel were taken by an external camera (CANON EOS 700D) controlled via LabView (National instruments) in defined time steps after the stirrer was stopped. The dynamic phase separation curves were derived from the visible interfaces and dense packed zones between the phases. The phase volume fractions were determined after completed phase separation.

Since drop sizes can be extremely small and separation times extremely long with common non-ionic surfactants, a model system with a short-chained amphiphile was identified that allows a very good measurability over the complete range of process parameters. It was shown that the results can be used to also describe the behavior of classical, longer-chained non-ionic surfactants although the absolute values such as drop sizes and separation time differ.

Selected results

Phase behavior and influence of dispersed phase fraction on the continuous phase

To determine the continuous phase in an agitated 3ϕ system, the temperature is varied from low to high values as indicated by the red arrow cutting through the fish diagram in Figure 2 (left). Depending on the continuous phase, the conductivity is high (aq), nearly zero (org) or reaches an intermediate value (mi).

The phase volume fractions can be controlled by changing the oil/water mass ratio α and/or the surfactant mass fraction γ. Increasing α shifts the ratio of organic to aqueous phase towards larger organic phase fractions, whereas a rising γ increases the volume fraction of the microemulsion phase. These results offer the possibility to directly control which phase becomes the continuous one, even in the more complex continuous process in presence of catalysts. This is very advantageous for the application of 3ϕ systems in a continuous process.

Identification of dispersion types

To identify the different drop phases in agitated systems, a combination of measurement techniques was applied: Conductivity measurements in stirred systems over temperature were performed as described previously to determine which phase is the continuous one. Control of phase volume fractions can be used to deliberately create different emulsion types. Furthermore, the optical analysis of the turbidity of each phase after complete phase separation can be compared to the droplet appearance on in-situ endoscope images. In some cases, it is possible to distinguish between clear droplets and turbid droplets and differentiate the phases. The turbidity thereby also is a function of solubility and, therefore, temperature. Some examples of drop appearance are provided in Figure 4 (left). In many cases, droplet interactions in form of multiple emulsions can be observed.
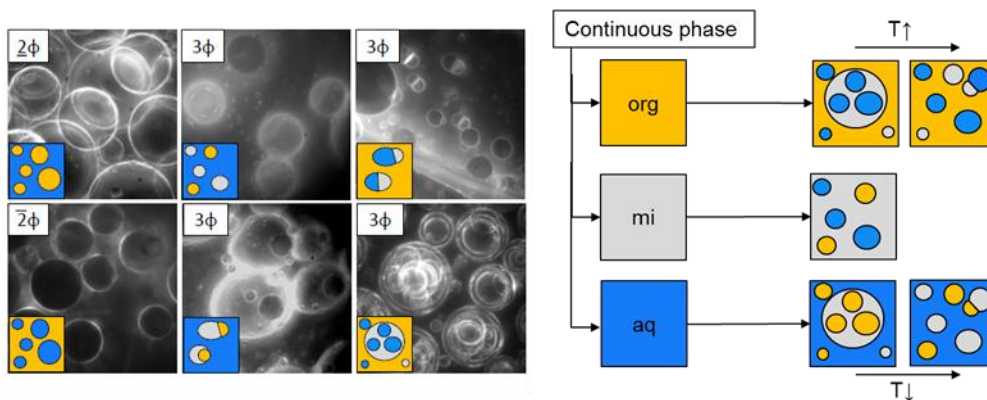

Figure 4: Examples for image quality and droplet appearance using an in-situ measurement technique (left) and observed dispersion types in 3ϕ systems (right) [5], [16], [17].

The type of dispersions that can occur in 3ϕ systems are summarized in Figure 4 (right). If one of the excess phases (aq or org) is continuous, the formation of dimers (droplets attached to each other) or multiple emulsions with a surrounding microemulsion droplet can occur. The formation of these multiple emulsion droplets can reduce the free energy by minimizing interfacial area with high interfacial tension such as the one between the excess phases $\sigma_{aq/org}$ (compare also Figure 2, middle). This is the case if a droplet of the dispersed excess phase is surrounded by a microemulsion droplet. The probability of multiple emulsions, therefore, depends on the ratio of interfacial tensions and is also governed by temperature. The different types of dispersion have a huge impact on drop size distributions and phase separation behavior, as will be discussed in the following.

Analysis of drop sizes in agitated systems

Knowledge of dispersion type and different optical appearance of droplets can be used to analyze the drop sizes of both dispersed phases, as shown in Figure 5. In this case, the microemulsion phase was continuous, and aqueous and organic excess phase were dispersed.
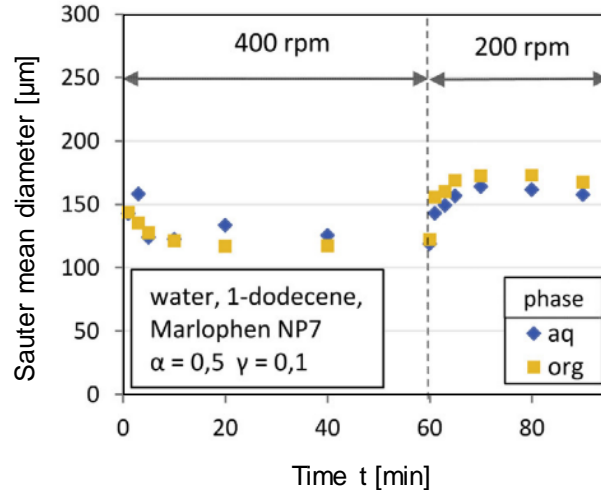

Figure 5: Dynamic changes of Sauter mean diameter after agitation start at t = 0 and after changes in agitation speed (t = 60min), T = 54°C in a system where aqueous and organic phase are dispersed in a microemulsion phase

The droplet sizes are in a very similar size range, which is attributed to the fact that these experiments were performed in the middle of the 3φ temperature interval, where their respective interfacial tensions to the continuous phase $\sigma_{aq/mi}$ and $\sigma_{mi/org}$ are similar (see also Figure 2, middle). The tendency to coalesce can clearly be observed after a change in agitation speed, where droplets of both phases grow until a new steady state is reached.

It should be noted that the differentiation between both droplet populations is not always possible, if the droplet appearance is very similar, drop size are very small or drops overlap due to the usually high dispersed phase fractions of 40-50% and more. In case of multiple emulsions, a differentiation between inner and outer droplets based on the images was sometimes possible, which also allowed for an analysis on how the energy dissipation, temperature and composition affected the number of droplets-per-droplet [13].

Analysis of phase separation behavior

One important aspect for the short separation times in 3φ systems in comparison to 2φ systems also is the simultaneous development of two sedimentation and coalescence curves, which lead to two dense-packed zones and two areas with possible drop/interface coalescence. The multiple emulsions thereby play a crucial role because they can affect the chronological sequence of the phase separation process. In Figure 6 two different cases are compared for systems with the same composition (α = 0.4 γ = 0.2). A schematic representation of the separation process is depicted on the left, while experimental separation curves are shown on the right. The type of dispersion was controlled using the temperature, which affect all physical properties of the phases (density, viscosity, interfacial tension). Aim is not to compare the overall separation times, which clearly can be affected by these parameters, but the sequence of the separation.

a) The organic phase is continuous without multiple emulsions (T = 95°C)

Droplets of both phases sediment towards their continuous phase. Due to their higher density difference to the organic phase and lager drop sizes, the aqueous interface is formed earlier than the microemulsion phase. Two partly overlapping dense-packed zones occur.

b) The organic phase is continuous with multiple emulsions (T = 83°C)

Due to their larger size, multiple emulsion droplets sediment much faster than single droplets. The microemulsion phase is formed quite early and the former inner aqueous droplets are released into the microemulsion phase instead into the organic phase. This leads to an inner aqueous dense-packed zone in the microemulsion phase in combination with overlapping dense-packed zones within the organic phase, formed by slower single and multiple emulsion droplets.
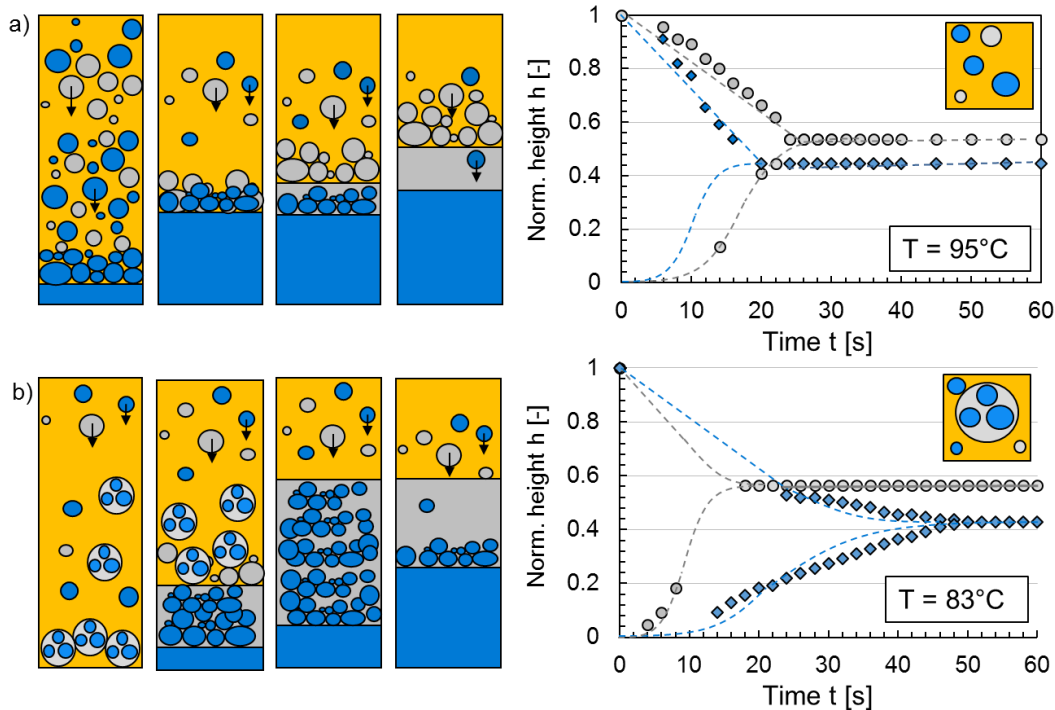

Figure 6: Phase separation of a wWater, 1-dodecene, C4E2 system at two different temperatures within the 3φ state (α = 0.4 γ = 0.2, n = 800 --> 0 rpm) [13]

Concluding remarks:

Although all experiments were performed in simplified, non-reactive systems, the results of this thesis were used to optimize several aspects of the hydroformylation process in a miniplant. Simple batch settling experiments also in the complete reaction systems including catalyst and other additives can be used to determine the initial dispersion type, which often is not easy to determine in-situ in continuous processes at high pressure and temperature. The information on drop sizes and dispersion types and the possibility to control them via composition can also be used to optimize mass transfer routes (liquid/liquid and gas/liquid mass transfer) in reactive microemulsion systems.

References:

[1] L. L. Coulaloglou, C. A., Tavlarides, "Description of interaction processes in agitated liquid-liquid dispersions," *Chem. Eng. Sci.*, vol. 32, pp. 1289–1297, 1977.

[2] M. Henschke, L. H. Schlieper, and A. Pfennig, "Determination of a coalescence parameter from batch-settling experiments," *Chem. Eng. J.*, vol. 85, pp. 369–378, 2002.

[3] L. Hohl, V. Röder, and M. Kraume, "Dispersion and phase separation of water-oil-amphiphile systems in stirred tanks," *Chem. Eng. Technol.*, vol. 42, no. 8, pp. 1574–1586, 2019.

[4] L. Hohl, J. M. Schulz, and M. Kraume, "Towards drop size modeling in three phase microemulsion systems," *J. Chem. Eng. Japan*, vol. 51, no. 4, 2018.

[5] L. Hohl, "Dispersion and phase separation in liquid multiphase systems: Influence of three phase conditions on drop size distributions," Technische Universität Berlin, 2019.

[6] C. W. Kohlpaintner, R. W. Fischer, and B. Cornils, "Aqueous biphasic catalysis - Ruhrchemie-Rhône-Poulenc oxo process," *Appl. Catal. A Gen.*, vol. 221, pp. 219–225, 2001.

[7] A. Rost, M. Müller, T. Hamerla, Y. Kasaka, G. Wozny, and R. Schomäcker, "Development of a continuous process for the hydroformylation of long-chain olefins in aqueous multiphase systems," *Chem. Eng. Process. Process Intensif.*, vol. 67, pp. 130–135, 2013.

[8] T. Pogrzeba *et al.*, "Superior catalyst recycling in surfactant based multiphase systems – Quo vadis catalyst complex?," *Chem. Eng. Process. Process Intensif.*, vol. 99, pp. 155–166, 2016.

[9] M. Kahlweit, R. Strey, P. Firman, J. Jen, and R. Schomäcker, "General patterns of the phase behavior of mixtures of H2O, nonpolar solvents, amphiphiles, and electrolytes. 1," *Langmuir*, vol. 4, pp. 499–511, 1988.

[10] S. Burauer, L. Belkoura, C. Stubenrauch, and R. Strey, "Bicontinuous microemulsions revisited: a new approach to freeze fracture electron microscopy (FFEM)," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 228, pp. 159–170, Nov. 2003.

[11] J.-L. Salager, R. E. Anton, D. A. Sabatini, J. H. Harwell, E. J. Acosta, and L. I. Tolosa, "Enhancing solubilization in microemulsions—State of the art and current trends," *J. Surfactants Deterg.*, vol. 8, no. 1, pp. 3–21, 2005.

[12] M. Kahlweit, R. Strey, D. Haase, and P. Firman, "Properties of the three-phase bodies in H2O-oil-nonionic amphiphile mixturest," *Langmuir*, vol. 4, no. 4, pp. 785–790, 1988.

[13] L. Hohl and M. Kraume, "The formation of complex droplets in liquid three phase systems and their effect on dispersion and phase separation," *Chem. Eng. Res. Des.*, vol. 129, pp. 89–101, 2018.

[14] Y. Kasaka, B. Bibouche, I. Volovych, M. Schwarze, and R. Schomäcker, "Investigation of phase behaviour of selected chemical reaction mixtures in microemulsions for technical applications," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 494, pp. 49–58, 2016.

[15] E. J. Acosta, "The HLD-NAC equation of state for microemulsions formulated with nonionic alcohol ethoxylate and alkylphenol ethoxylate surfactants," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 320, pp. 193–204, 2008.

[16] L. Hohl, M. Knossalla, and M. Kraume, "Influence of dispersion conditions on phase separation in liquid multiphase systems," *Chem. Eng. Sci.*, vol. 171, pp. 76–87, 2017.

[17] L. Hohl, N. Paul, and M. Kraume, "Dispersion conditions and drop size distributions in stirred micellar multiphase systems," *Chem. Eng. Process. Process Intensif.*, vol. 99, pp. 149–154, 2016.