Influence of dispersion conditions on phase separation in liquid multiphase systems

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HIGHLIGHTS

- Separation analysis was performed in liquid two and three phase systems.
- Image analysis of three phase systems is used to determine droplet interactions.
- The character of the phase separation is influenced by the droplet interactions.

ARTICLE INFO

ABSTRACT

The phase separation of liquid/liquid systems consisting of oil, water and amphiphilic molecules is a function of temperature and composition. The phase separation is fastest in liquid three phase systems, where the organic and aqueous excess phases are separated by a microemulsion middle phase. In this work, a detailed analysis of the relevant physical properties (density, rheology, interfacial tension) of the phases in combination with drop size distribution measurements and image analysis of the droplet interactions is performed using an endoscope measurement system. This methodology enables to directly quantify influencing effects of droplet size and droplet interactions on dispersion and phase separation processes. The duration and character of the separation process strongly depends on the droplet interactions (e.g. formation of multiple emulsions) of the dispersed phases.

1. Introduction

Tunable liquid multiphase systems can be applied to enable homogeneous catalysed reactions like the hydroformylation of long-chained olefins including catalyst separation from the product phase (Pogrzeba et al., 2015; Schwarze et al., 2015). Thereby, a catalyst complex is solubilized within a polar liquid phase and needs to be brought in close contact with the nonpolar olefin phase. Since the solubility of water and long-chained olefins is low due to their unequal molecular structures (polarity), tremendous amounts of mechanical energy would be necessary to achieve interfacial areas sufficient for an economically viable reaction process. Therefore, suitable solvent systems need to be identified which enlarge the interfacial area but still allow a fast phase separation with adequate catalyst recycling. Several recent studies investigated the application of either thermomorphic systems, Pickering emulsions or surfactant/microemulsion systems (Pogrzeba et al., 2015; Zagajewski et al., 2014; Zhao et al., 2016;

Schwarze et al., 2015). In comparison, all systems possess specific advantages or disadvantages, e.g., in reaction space-time-yield, sustainability, phase separation or catalyst recycling.

This study will focus on the case of microemulsion systems containing surfactants. Amphiphilic molecules can promote mixing of oil/water systems by reducing the interfacial tension at the liquid/liquid interface. Thereby, a lower energy input (e.g., by stirring) is needed to achieve small droplets sizes and large interfacial areas. The composition of the multiphase systems can be defined using the variables α (mass of oil in relation to oil and water) and γ (weight fraction of surfactant):

$$\alpha = \frac{m_{oil}}{m_{oil} + m_{water}} \tag{1}$$

$$\gamma = \frac{m_{surfactant}}{m_{oil} + m_{water} + m_{surfactant}} \tag{2}$$

The phase behaviour of these systems is a function of temperature and composition (Fig. 1a) and has been investigated in numerous studies (Winsor, 1948; Schrader et al., 2013; Kahlweit et al., 1989a,b; Kiran and Acosta, 2010). The basic types

Nomenclature

Abbreveations

2Φ	lower two phase system
$\bar{2}\Phi$	upper two phase system
3Φ	three phase system
aq	aqueous phase
mi	microemulsion phase
org	organic phase
c	continuous phase
d	dispersed phase
C_4E_2	Diethyleneglycolbutylether
FFEM	freeze fracture electron miscroscopy
HLD-NAC	hydrophilic-lipophilic deviation/net-average curvature model
MAC	minimal aggregation concentration, mol/L
o/w	oil-in-water emulsion
w/o	water-in-oil emulsion
SANS	small angle neutron scattering

Latin letters

d	drop diameter, μm
d_{St}	stirrer diameter, mm
d_{end}	endoscope diameter, mm
d_{32}	Sauter mean diameter, μm

D	inner diameter of tank, mm
h	stirrer bottom clearance, mm
h_{St}	height of stirrer blade, mm
H	height of fluid level in the tank, mm
m_i	mass, kg
n	rotational speed, stirrer speed, rpm
q_0	probability density function of number, 1/μm
Q_0	cumulative distribution function of number, –
t	time, s
t_{sep}	separation time, s
T	temperature, °C
V	volume, L
w_p	velocity, m/s

Greek letters

α	mass fraction of organic phase, –
γ	wt-% of surfactant, –
κ	electric conductivity, μS/cm
ρ	density, [kg/m^3]
η	dynamic viscosity, mPa s
$\dot{\gamma}$	shear rate, 1/s
σ_i	interfacial tension, mN/m
ϕ	dispersed phase fraction, –

are oil-in-water (o/w) microemulsions in equilibirum with an oily excess phase ($\bar{2}\Phi$), water-in-oil (w/o) emulsions in equilibrium with an aqueous excess phase (2Φ), a bicontinuous microemulsion with two excess phases (3Φ) or a single microemulsion phase at high surfactant concentrations (1Φ). The phase behaviour can be used for an optimization of both reaction and separation processes (Schrader et al., 2013): The reaction can be performed at high temperatures in the upper two phase system ($\bar{2}\Phi$) to improve reaction kinetics, whereas the phase separation process is fastest in three phase (3Φ) systems (Kasaka et al., 2016; Müller et al., 2015). Under these conditions, the aqueous (aq) and organic (org) excess phases are separated by a surfactant-rich middle phase which is a thermodynamically stable bicontinuous microemulsion (mi). This third phase occurs in a specific temperature interval and has severe effects on the physical properties, droplet size distributions and separation process (Schwarze et al., 2015; Hamerla et al., 2013; Hohl et al., 2016a). Furthermore, the exact nature of the microemulsion phase has been investigated in various studies (Lee et al., 1990; Krishnan et al., 2002; Ciach and Poniewierski, 1994; Kahlweit et al., 1992; Kiran and Acosta, 2010). The inner structure of the microemulsion phase can be a droplet type or an isotropic bicontinuous type (Kiran and Acosta, 2010; Burauer et al., 2003). The inner droplet size of the microemulsion phase can be predicted using the ratio of the dispersed phase to the mass of surfactant as described by Eastoe et al. (1991a,b, 1992). Another possibility is using the inverse of the average curvature calculated from the hydrophilic-lipophilic deviation/net - average curvature (HLD-NAC) model (Acosta et al., 2003; Acosta, 2008). Kiran and Acosta (2010) also used an extended version of the HLD-NAC model to predict the morphology and viscosity of microemulsions. The predicted shapes of the droplets were used to generate theoretical small angle neutron scattering (SANS) profiles and compared to respective experimental data. Bicontinuous microemulsions usually are described as coexisting, mutually inter-twinned, continuous water and oil sub-phases as was shown for example by Burauer et al. (2003) using freeze fracture electron microscopy (FFEM). All methods are used to predict the inner structure and characteristics of the microemulsion phase.

The schematic separation time of these systems is depicted in Fig. 1(b) for a constant α and γ. Within the lower two phase condition (2Φ) a minimum of separation time can be observed (Kasaka et al., 2016). At the transition from 2Φ to 3Φ condition a significant increase of the separation time occurs whereas a global minimum of separation time appears in the middle of the 3Φ system. At the transition to the upper $\bar{2}\Phi$ system, the separation time increases again. The whole separation process is extremely sensitive to temperature since a variation thereof also influences parameters like the interfacial tension, density and viscosity (Kasaka et al., 2016; Strey, 1994; Kahlweit et al., 1989a,b). One degree Celsius more or less can induce a change of separation time, e.g., from 5 to 10 min to several hours or even days. The general behaviour applies for most non-ionic surfactants but the exact values differ due to the surfactants' molecular structures (e.g., chain length, degree of ethoxylation, surface rigidity).

The study presented here focusses on the macroemulsions that are formed if the excess phases and the microemulsion phase are dispersed. Hence, reffering to droplet sizes in this work does not mean the inner structure or composition of the microemulsion phase or occuring micelles, but the dispersion of the complete system. Amongst others, Acosta et al. (2003) reported that the coalescence of the macroemulsion is a function of the interfacial properties (interfacial thickness, tension and rigidity). They conducted turbidity measurements to analyze the dynamic phase separation process over time after shaking the macroemulsion systems. Using conductivity measurements in their optimum formulations they concluded that the bicontinuous microemulsion phase was the continuous phase and organic and aqueous phase were dispersed in their macroemulsion. Since the turbidity measurements did not allow a direct measurement of droplet sizes, they used an expression described by Fletcher and Morris (1995) to correlate the size and number of droplets to the turbidity while assuming monodisperse droplets. In this study, an in situ measurement technique is used to determine the droplet size distributions and droplet interactions in the dispersed macroemulsion system. The main advantage of this methodology is that these parameters can be determined directly and in situ (Hohl et al., 2016a).