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Effects of phase behaviour on mass transfer in micellar liquid/liquid systems

Niklas Paul [a,*], Philipp Schrader [b], Sabine Enders [b], Matthias Kraume [a]

[a] *Chair of Chemical and Process Engineering, Technische Universität Berlin, Ackerstarße 71-76, 13355 Berlin, Germany*
[b] *Chair of Thermodynamics and Thermal Separation Processes, Technische Universität Berlin, Ernst-Reuter-Platz 1, 10587 Berlin, Germany*

HIGHLIGHTS

- ▸ We studied influences of surfactants on liquid/liquid mass transfer.
- ▸ We determine the phase behaviour of water/1-octanol/Triton X-100.
- ▸ Increasing surfactant concentration leads to a reduction in mass transfer.
- ▸ The reduction of mass transfer cannot be explained by effects from literature.
- ▸ The phase behaviour has to be considered.

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ABSTRACT

Transport limitations often occur in liquid/liquid systems and, for instance, are responsible for low reaction rates in homogeneous catalysed liquid/liquid reactions with water soluble catalysts. By using surfactants the water solubility of the reactants can be increased, which results in an increase of the reaction rate. Surfactants adsorb at liquid/liquid interfaces, but this is the place where the important transport processes occur. Therefore, an influence by surfactant molecules on the transport processes is obvious. In this work the focus lies on the effects of surfactants on liquid/liquid mass transfer. An increase of surfactant concentrations leads to a decrease in the mass transfer rate. In the literature this reduction is described by two effects, but as the experimental results show, the effects describe this reduction of the mass transfer rate incompletely. Furthermore, the effects exerted by the change in phase behaviour must be taken into consideration.

1. Introduction

Liquid/liquid mass transfer plays an important role in many industrial applications such as extraction processes or homogeneous liquid/liquid reactions. At the interface between the two immiscible liquids is the place where the important transport processes occur. Therefore, this area is of special interest for the investigations of mass transfer rates. In many industrial applications interfacial active contaminations (e.g. surfactants) appear or some reactions will not proceed without high surfactant concentrations. In both cases the behaviour of the liquid/liquid interface will change, which affects mass transfer rates. Furthermore, for high surfactant concentrations surfactant molecules will agglomerate to micelles which increase the complexity of the liquid/liquid mass transfer. For the fundamental understanding of mass transfer mechanisms in micellar liquid/liquid systems single droplets are regarded in this fundamental investigation as these are the smallest transfer units and also complex swarm effects can be neglected.

The influence of interfacial active substances on mass transfer rates has been investigated by many authors. In most of the present works only low surfactant concentrations have been applied and there are no consistent results. Most authors found a reduction of liquid/liquid mass transfer rates with an increase of surfactant concentration. In the work of Beitel and Heideger (1971) the mass transfer of methyl carbtiol from the dispersed organic phase into the continuous aqueous phase was observed for various Triton X-100 concentrations. A strong reduction of the mass transfer rate was obtained in presence of the non-ionic surfactant.

Lee (2003) determined mass transfer rates for three different surfactants (SDS, Triton X-100 and DTMAC). The measurements

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* Corresponding author. Tel.: +49 30 314 72687.
E-mail address: n.paul@mailbox.tu-berlin.de (N. Paul).

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were carried out in the test system water–tetrachloromethane. For all three surfactants a reduction of the mass transfer rates was found. With increasing the surfactant concentration the mass transfer rates were reduced constantly until a specific surfactant concentration was reached. For higher surfactant concentrations the mass transfer rate remained constant. For the non-ionic surfactant Trion X-100 a slight increase of the mass transfer was measured.

Wegener and Paschedag (2012) analysed the mass transfer of acetone in the test system water-toluene for various SDS concentrations below the critical micelle concentration (CMC). A reduced mass transfer rate in comparison to the pure system has been observed, but the mass transfer obtained was not as slow as predicted by the models published in literature. From these results it was derived SDS molecules were not able to inhibit Marangoni convection. For low SDS concentrations (10^{-8} mol/L) even an improvement of the mass transfer rate was observed for non spherical droplets. That might be referred to an enhanced Marangoni convection exerted by SDS molecules. When droplets rise in moderately concentrated aqueous surfactant solutions the surfactant molecules will gather at the rear end of the droplet due to the shear stress. Therefore, at the rear end of the droplet a high surfactant concentration will adjust respectively a low interfacial tension which can exert an enhanced Marnagoni stress. Few authors found an improvement of mass transfer rates which was referred to Marangoni convection.

The reduction of the mass transfer rates is always referred to two mechanisms (West et al., 1952; Lindland and Terjesen, 1956; Gibbons et al., 1962; Beitel and Heideger, 1971; Chen and Lee, 2000; Lee, 2003): the change of the fluid dynamics and the formation of an adsorption layer. With the adsorption of surfactant molecules at the liquid/liquid interface the droplet's characteristics change to a rigid particle. Therefore, the inner circulations of the fluid particle are reduced, which will lead to a reduction of the mass transfer rate. Furthermore, the physicochemical effect has to be considered: an additional mass resistance of the adsorption layer is created in the presence of surfactants. One effect which is not taken into account in the literature yet, is the ability of surfactants to change the phase behaviour of ternary systems (Kahlweit and Strey, 1985). At specific compositions of ternary water/oil/surfactant systems the formations of high viscous multiphase systems is possible, or even the formation of liquid crystalline conditions. The change in the phase behaviour results in an extreme mass transport resistance. The formation of multiphase systems or liquid crystalline conditions for high surfactant concentrations is possible. When the interface is regarded as a pseudo phase, in which the surfactant concentration is high the phase behaviour may change.

In this work the effects of the non-ionic surfactant Triton X-100 on liquid/liquid mass transfer is observed. Besides the effects given in the literature responsible for a reduction of mass transfer rates, the phase behaviour of the ternary system is also investigated. Measurements of the composition at the liquid/liquid interface are more or less impossible. To quantify the effects which might be exerted by a change of the phase behaviour, the interfacial rheology is measured by applying the oscillating drop method. Finally, the experimental results of the mass transfer shall be compared to the models given in the literature.

2. Materials and methods

2.1. Materials

For the experimental investigations a test system is used. Due to the highly-sensitive measurements, all components used are at the highest available purity. The regarded system consists of deionised water with a resistance of 18.3 MΩ cm, which is used as the continuous phase; 1-octanol (AppliChem, 99%) is applied as the dispersed phase. To avoid additional transport processes both liquid phases are saturated with each other. The non-ionic surfactant Triton X-100 (Aldrich, 99%) is used. The critical micelle concentration of Triton X-100 is 0.2 mmol/L (Saien and Asadabadi, 2010). Reverse Triton X-100 micelles will not occur. In pure organic solvents reverse micelles are not observed (e.g. Zhu et al., 1992). The preparations of the parent surfactant solutions at 100 mmol/L are carried out by a Satorius balance with an uncertainty of 0.1 mg. Other surfactant concentrations were prepared by a serial dilution. As a model transferred component an azo dye (pyridine-2-azo-dimethylaniline, PADA) is used. Therefore, the dye concentrations are determined by a photometer.

2.2. Experimental setup—mass transfer

Liquid/liquid mass transfer of single droplets is obtained in the experimental setup shown in Fig. 1 and it is already described by Wegener (2007, 2010). The height of the glass column is 1000 mm and its diameter is 75 mm. Due to the similar refraction index to borosilicate glass the surrounding jacket is filled with glycerol. In this work every experiment is carried out at 25 °C; therefore, a thermostat by LAUDA® is installed. A syringe pump (Hamilton® PSD/2 module, 3a in Fig. 1) is used to generate a well defined drop volume. For the drop release a solenoid device is installed; hence the droplets can be released at a specific volume or diameter, respectively.

Due to the use of surfactants the interfacial tension changes; hence different nozzles (see in Table 1) with different diameters can be installed into the column to provide a wide range of different droplet diameters.

For the determination of the liquid/liquid mass transfer coefficient of single droplets, the droplets are collected at the glass funnel's neck (9 in Fig. 1). Here, a small of organic phase is kept so that the droplets are able to coalesce. The diffusive mass transfer into the small dispersed phase at the funnel's neck is neglected. The second Hamilton® PSD/2 module (3b in Fig. 1) is used to take the droplets out of the system. As mentioned above an azo dye (PADA)

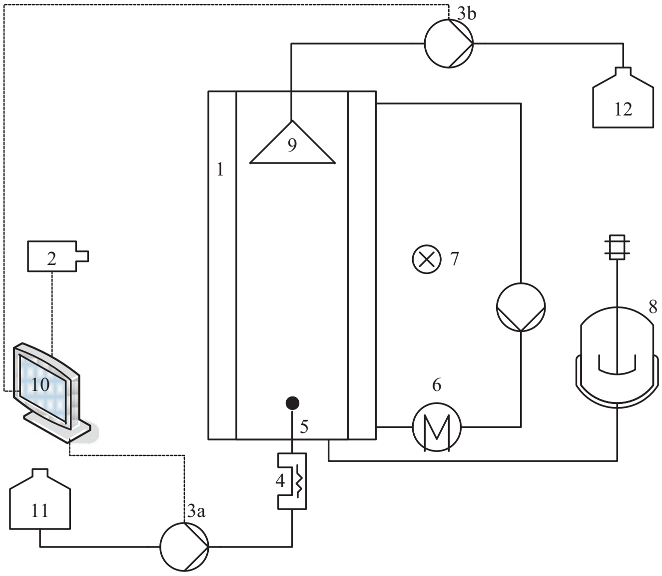

Fig. 1. Experimental setup: (1) 1 glass column; (2) high-speed camera; (3a and 3b) Hamilton® PSD/2 moduls; (4) solenoid device; (5) nozzle; (6) thermostat; (7) illumination; (8) saturation tank; (9) glass funnel; (10) computer; (11) storage tank for dispersed phase; (12) storage tank for samples.

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