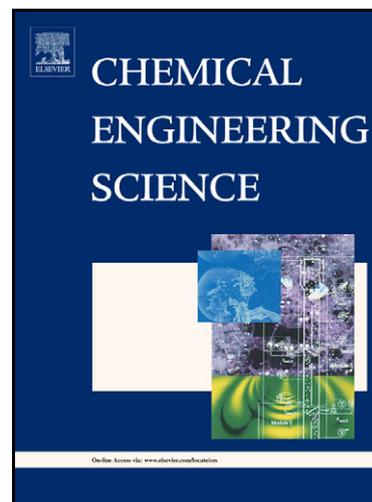


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Effects of phase behaviour on mass transfer in micellar liquid/liquid systems

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Abstract

Transport limitations often occur in liquid/liquid systems and, for instance, are responsible for low reaction rates in homogeneous catalyzed 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.

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Keywords: liquid/liquid mass transfer, phase behaviour, microemulsions, surfactants, micelles, liquid/liquid interfaces

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 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 Marangoni 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 1952, Lindland 1956, Gibbons 1962, Beitel and Heidberger 1971, Chen 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 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 behavior 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.

Materials and Methods

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 M Ω 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 [Saïen 2010]. Reverse Triton X-100 micelles will not occur. In pure organic solvents reverse micelles are not observed [e.g. Zhu 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.

Experimental Setup- Mass transfer

Liquid/liquid mass transfer of single droplets is obtained in the experimental setup shown in Figure 1 and it is already described by Wegener et al [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 Figure 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.

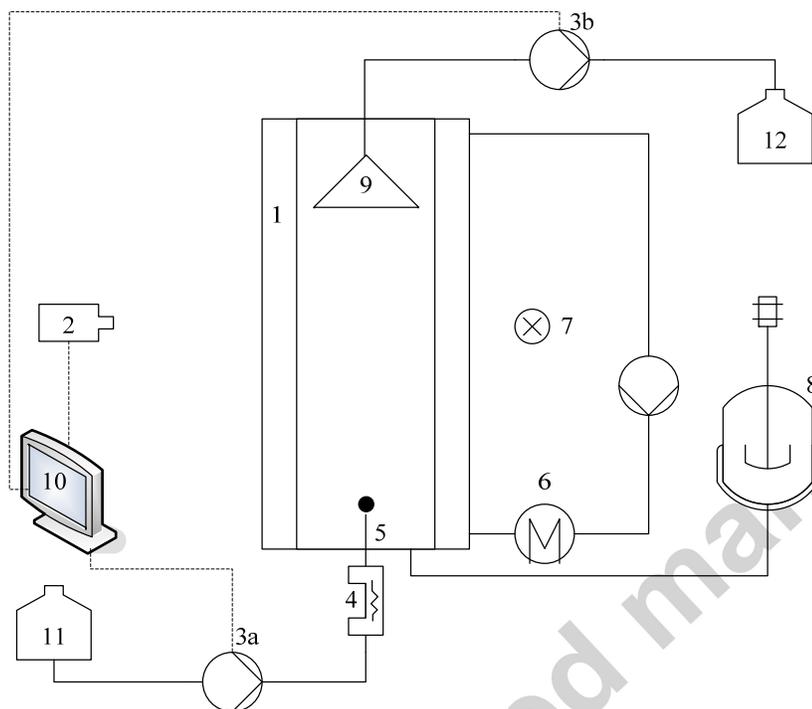


Figure 1: Experimental setup: 1) 1 glass column; 2) high-speed camera; 3a & 3b) Hamilton® PSD/2 moduls; 4) solenoid device; 5) nozzle; 6) thermostat; 7) illumination; 8) saturation tank; 9) glass funnel; 10) computer; 11) storage tank for dispersed phase; 12) storage tank for samples

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

Table 1: Nozzles used for providing a wide range of droplet diameters

	N ₁	N ₂	N ₃	N ₄
OD [mm]	0.5	1	3	5
ID [mm]	0.2	0.42	2	4
Material	borosilicate	Borosilicate	stainless steel	stainless steel

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 Figure 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 Figure 1) is used to take the droplets out of the system. As mentioned above an azo dye (PADA) is used as the transferred component; a Specord 210 photometer by Jena Analytik® is used to analyse the dye concentration.

Furthermore, it is possible to determine the instantaneous drop rise velocity with the experimental setup shown in Figure 1. A high-speed camera (Photonfocus® MV-752-160) is installed perpendicular to the column. The path of a droplet is recorded by this camera. The analysis of the droplet's path is carried out with Image-Pro Plus® 5.1 by Media Cybernetics. As results the vertical and horizontal positions of the droplet are obtained. This information can be used to calculate the instantaneous drop rise velocity. Due to the linkage between mass and momentum transfer, the drop rise velocity is important information for the explanation of the occurring phenomena. In this work the focus lies on the mass transfer.

Experimental Setup – Characteristics of the liquid/liquid interface

The oscillating drop method (ODM) is used to determine the interfacial rheology and the characteristics of the liquid/liquid interface respectively. Therefore, the Data Physics OCA 20 with an oscillating drop module was applied. Information of the interfacial rheology is gained by this method. An aqueous droplet is created at the tip of a nozzle and hangs in the 1-octanol phase. After the interfacial tension approaches a stationary value the droplet is exposed to harmonic oscillations with various frequencies. An amplitude of 10 % was chosen for the interfacial area of the droplet. The progress of the interfacial tension depending on the interfacial area is detected. With these results important information about the interfacial rheology can be determined.

Experimental Setup – Phase behaviour

All samples are prepared in 5 mL glass-flasks, weighed in with a Kern ABJ 220-4M balance and an accuracy of 0.0001 g. After preparation the glass flasks are immediately sealed pressure tight and tempered at 25°C for at least two weeks to reach thermodynamic equilibrium. The equilibrium is

reached when two or three clear phases are in contact. The number of the coexisting phases are detected visually and transmitted in the Gibb's triangle at 25°C.

Results

Phase behaviour

The knowledge of the phase behaviour of the involved substances is fundamental for further investigation e.g., mass transfer. For the determination of the phase behaviour of water/1-octanol in dependence of Triton X-100 concentrations, almost 200 different samples with various compositions were set up. Afterwards, the samples were observed qualitatively for the adjusted thermodynamic equilibria. Four different equilibria were observed (see Figure 2 a-d): two phase systems (Figure 2a), three phase systems (Figure 2b), one phase systems (Figure 2c) and liquid crystalline systems as shown in Figure 2d.

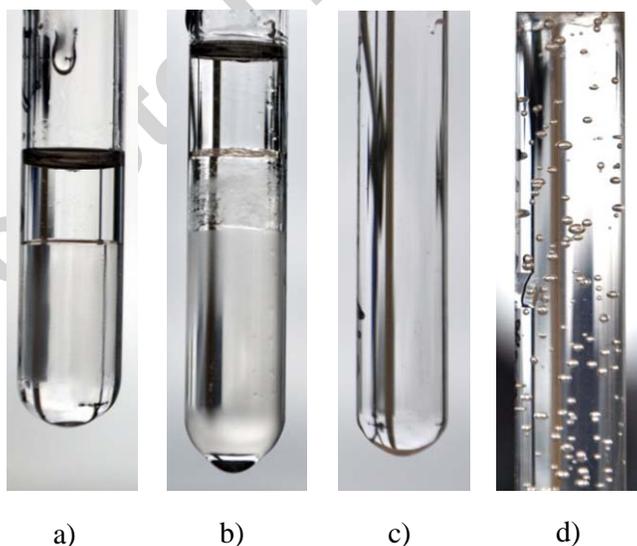


Figure 2: Characteristic examples of the observed phase conditions 2a: bi-continuous; 2b: three-phase system 2c: single phase system; 2d: liquid crystalline condition

These results are transferred into a ternary plot (Figure 3). This phase diagram gives the thermodynamic conditions (shown in Figure 2) for various compositions (mass fraction) of the samples. At low

surfactant concentrations an aqueous phase is in equilibrium with an octanol-rich phase. According to Lawrence [1938, 1939] and Schulman [1943] micelles are formed above the CMC and 1-octanol is solubilised within this micelles.

With increasing the surfactant concentration beyond 12% a third phase is occurring, the microemulsion as the middle phase. The so called microemulsion or Winsor III – System was first described by Winsor [1948]. With a further increased 1-octanol fraction only one phase can be obtained. Furthermore, when Triton X-100 concentration is increased, liquid/crystalline regions can be recognized. Here, surfactant molecules have a certain long range order, which is responsible for the liquid crystal formation. In dependence of surfactant concentration the type of liquid crystal will change [Larson 1989]. The occurrence of liquid crystalline conditions was proofed by using the polarization microscope. The type of liquid crystal was not obtained in this work.

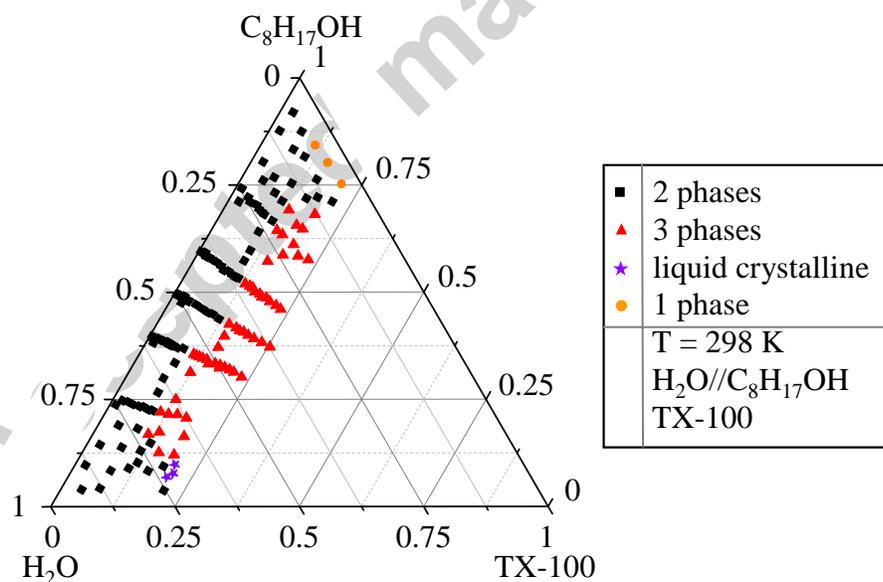


Figure 3: Phase diagram of the ternary system water/1-octanol/ Triton X-100; compositions of the samples are given in mass fraction

Figure 4 shows a comparison between the experimental results from this work with the results from Guo et al [2001]. While in some cases both data agree well with each other, at other compositions different results were obtained. The liquid crystalline conditions appear in both results almost at the same

compositions. Furthermore, the bi-continuous microemulsion requires a three phase region. Starting at the binary subsystem one cannot find a three phase region in the manner it is shown in the results of Guo et al. Also the shape of the microemulsion middle-phase cannot be observed in the way it was suggested by Guo et al [2001] according to Schreinemarkers rule [Schreinemarkers 1911]. Having a look at the binary subsystems the broad miscibility gap between 1-octanol and water can be recognized although the binary subsystem water and 1-octanol does not fit not well [Stoicescu 2011]. But comparing the binary subsystem Triton X-100-water with literature data [Nakagawa 1963, Lee 1995, Sagadina 1991] large deviations become visible. There is no oil in water or water in oil emulsion at the binary subsystem. After all, no measured data points were given for the entire phase-diagram, therefore it is not clear which points were measured in Guo et al. [2001].

In this work three phase systems were found for surfactant concentrations higher than 12%. Higher surfactant concentrations than 26% have not been observed in this work, because concentrations that high were not of interest for the determination of the mass transfer.

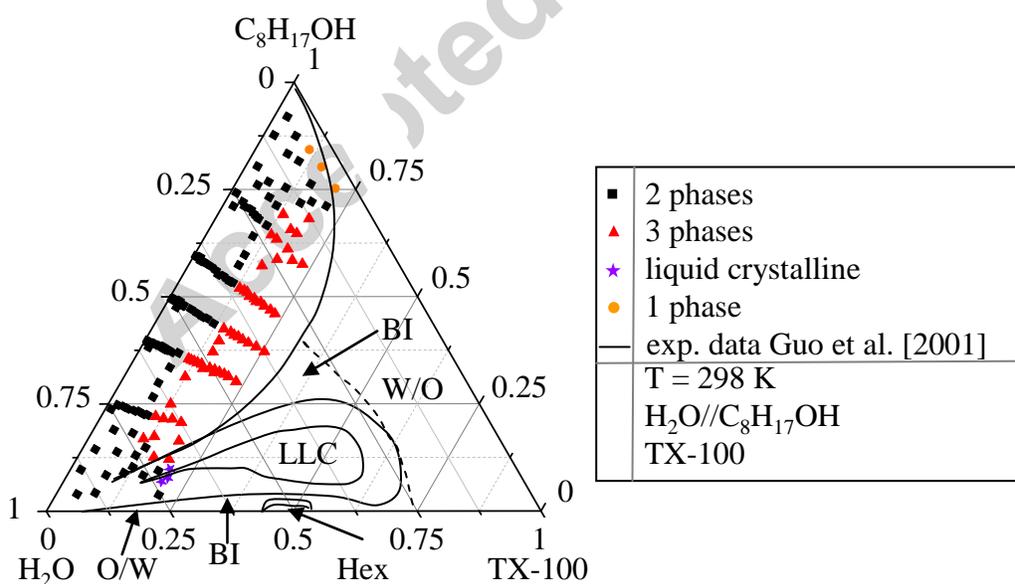


Figure 4: Phase diagram of the ternary system water/1-octanol/Triton X-100 in comparison with experimental results¹ from Guo et al [2001] with BI: bi-continuous region; LLC: liquid/liquid crystal region; Hex: hexagonal crystal region O/W , W/O: microemulsions region

Rheological studies of the liquid/liquid interface

It is impossible to determine the exact composition at the liquid/liquid interface experimentally. Therefore, possible changes in phase behaviour at the interface have to be observed by measuring the interface's characteristics. In this work the characterization of the liquid/liquid interface is carried out by applying the oscillating drop method, which gives important information about the rheology of the interface. An increase in the interface's viscosity or reduction of the interface's elasticity is evidence for the formation of multiphase systems or even liquid crystalline phases at the interface. Figure 5 shows the experimental results gained from the oscillating drop method. Before each measurement is started every droplet is kept for 1200 s in 1-octanol until an equilibrium interfacial tension is reached. Interfacial area amplitudes (ΔA) of 10% at harmonic oscillation frequencies ω between 0.1 Hz and 1 Hz are observed. The results are analysed by using a Fourier transformation [Fainerman 2004]:

$$E^*(i\omega) = A_0 \frac{F|\Delta\gamma|}{F|\Delta A|} . \quad (1)$$

where E^* is visco-elastic modulus, A_0 is the initial drop surface and γ is the interfacial tension.

The visco-elastic modulus E^* for various surfactant concentrations and frequencies is shown in Figure 5a. Besides the elastic characteristics the, visco-elastic modulus exhibits the viscous characteristics of the interface and describes the resistance the interface opposes against deformation. In presence of surfactant molecules the interfacial tension decreases; hence the deformation of droplets is easier and the visco-elastic modulus should decrease. This behaviour is described for the ionic surfactant sodium dodecyl sulphate (SDS) [Rao 2005] and for the non-ionic surfactant $C_{14}EO_8$ [Fainerman 2008] in the literature. This is not observed in this work. For all three frequencies a slight increase of the visco-elastic modulus with an increase of surfactant concentrations is obtained. Therefore, the resistance against deformation of the droplet is increasing, although the interfacial tension is reduced with

increasing surfactant concentration. This is evidence for a change of the characteristics of the liquid/liquid interface and shows that something other than adsorption of Triton X-100 molecules is happening at the interface. Furthermore, the presence of micelles has to be considered. The critical micelle concentration (CMC) of Triton X-100 is 0.2 mmol/L . In presence of micelles the viscous modulus as well as the elastic should decrease. The adsorption of micelles at the interface results in a less densely packed mono layer of surfactant molecules; hence the interactions of surfactant molecules decrease and the elastic modulus reduces [Rao 2005]. Furthermore, the diffusion of micelles is slower than for monomer molecules; hence the viscous modulus decreases as well [Rao 2005]. In contrast both phenomena are not observed in this work. In this work both moduli increase with higher Triton X-100 concentrations, which results in a higher resistance for the drop deformation.

Additionally, the behaviour of the phase angle in dependence of the surfactant concentration shows other results than in a system (air bubble in aqueous $C_{14}EO_8$ solutions) observed by Fainerman et al [2008]. Here, an increase of the surfactant concentration resulted in higher phase angles, which can be explained by the adsorption of the surfactant molecules at the interface. The more surfactant molecules are in the bulk phase the more molecules adsorb at the interface during the increase of the interfacial area. When the interfacial area is reduced less adsorption places exist, surfactant molecules desorb and the interfacial tension increases again; hence a shift between harmonic oscillations of the interfacial area and the interfacial tension is obtained. For the lowest harmonic oscillating frequency (0.1 Hz) applied in this work the phase angle reduces from 60° to 8° with an increase of Triton X-100 concentration. For a surfactant concentration of 0.01 mmol/L the obtained phase angle is 60° , the surfactant molecules adsorb at the interface during the increase of the drop area while these molecules desorb again with the reduction of the interfacial area. This behaviour is as expected. In contrast, at surfactant concentrations of 10 mmol/L phase angles of 8° were found, which implies that the oscillation of interfacial tension is almost congruent with the oscillation of the interfacial area. Therefore, no further molecules adsorb or desorb at the interface during its harmonic oscillation. This shows the interfacial characteristics have

changed, the elastic and the viscous modulus have increased and hence reduced the flexibility of the liquid/liquid interface. That is evidence for a change in phase behaviour at the interface.

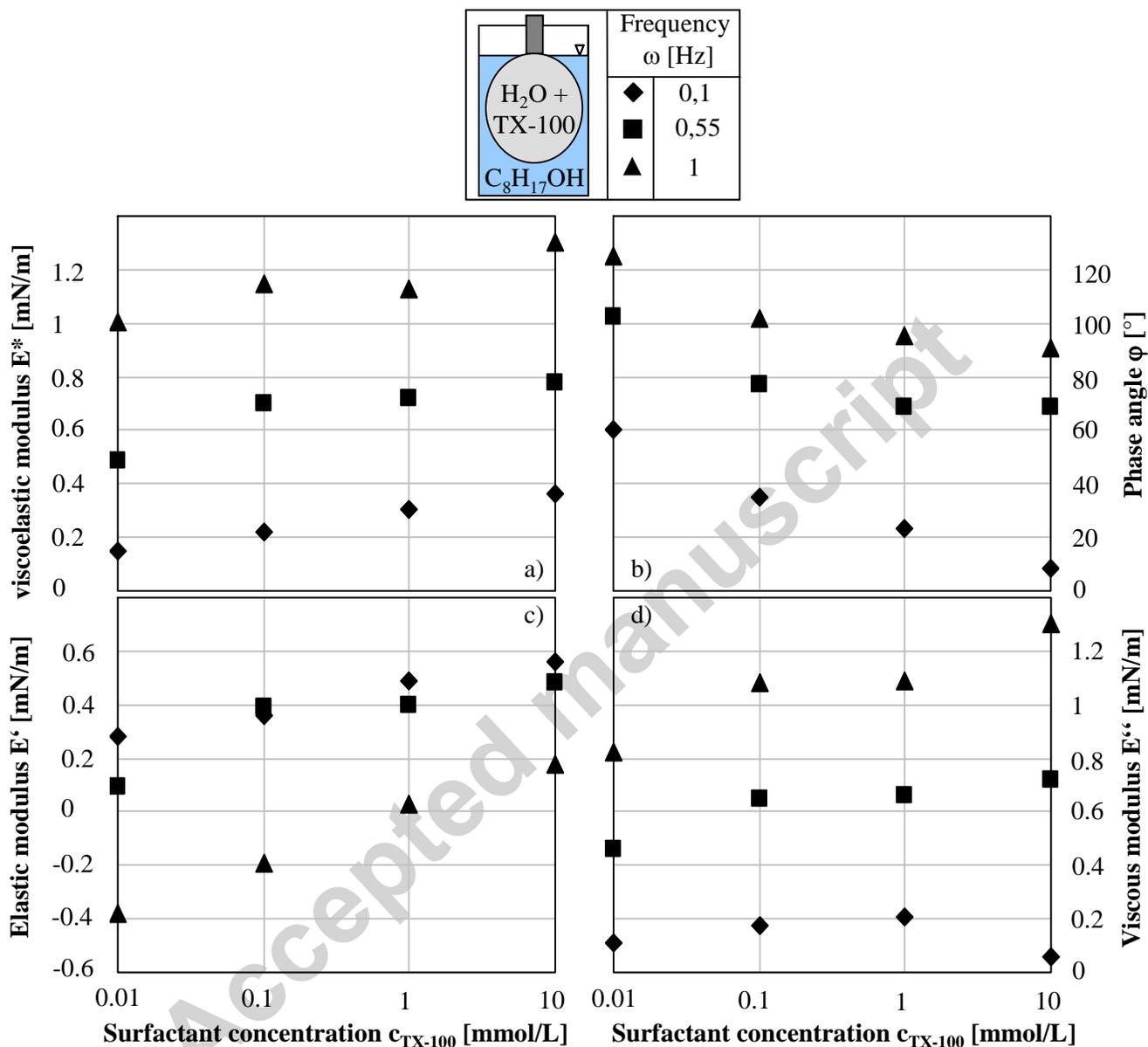


Figure 5: ODM-measurements for various surfactant concentrations and harmonic oscillation frequencies. a) visco-elastic modulu; b) phase angle; c) elastic modulus; d) viscous modulus

Another indicator for the change of the phase behaviour at high surfactant concentrations was obtained during the measurements: All droplets observed during these investigations remained clear while the droplets hung in the 1-octanol phase except the droplets with Triton X-100 concentrations that were higher than 10 mmol/L . These droplets became blurry (see Figure 6). This is also evidence that the

phase behaviour at the interface had changed. Due to the formation of high viscous multiphase systems or even liquid crystalline phases at the interface the liquid/liquid mass transfer decreases; hence an additional mass transfer resistance occurs.

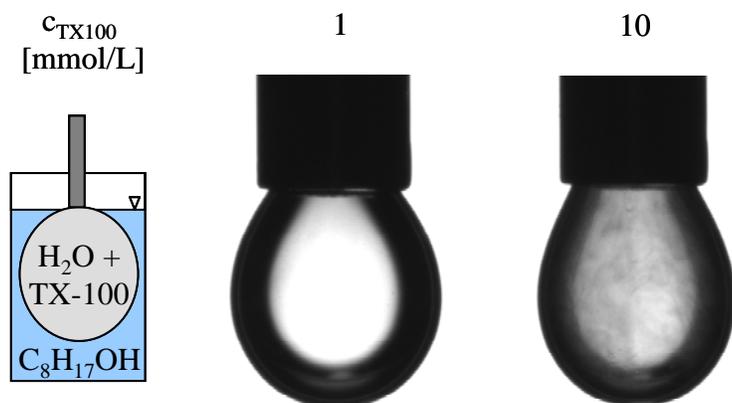


Figure 6: Observations during the ODM-measurements for Triton X-100 concentrations of 1 mmol/L and 10 mmol/L

Mass transfer

Figure 7 shows the unsteady mass transfer for various Triton X-100 concentrations. The transferred component (PADA) was dissolved in the continuous phase. Therefore, the transport direction was from the continuous into the organic dispersed phase. The droplet diameter ($d_p = 2.5 \text{ mm}$) as well as the temperature ($T = 25^\circ\text{C}$) were kept constant. In absence of Triton X-100 a linear increase of the concentration of the transferred component with contact time is observed in Figure 7. During the drop formation a certain amount of transferred component was transported into the drop; hence a linear extrapolation of the experimental results does not go through the origin of the diagram. This result agrees with results that can be found in the literature. Many research groups observed high extraction efficiencies during the drop formation [e.g. West 1951, Nitsch 1965, Liang 1990, Wegener et al. 2009].

In presence of Triton X-100 the mass transfer rates reduce. For concentrations of 0.01 mmol/L of Triton X-100 there is hardly any difference observed in Figure 7. A ten times higher concentration of 0.1

$mmol/L$ make the droplets behave like solid particles. Therefore, the inner circulations of the 1-octanol droplets are reduced which decreases the mass transfer rates. Furthermore, concluding from the change of fluid dynamics a complete coverage of the liquid/liquid interface with surfactant molecules is derived; thus for higher surfactant concentrations than $0.1 mmol/L$ there should not be any further reduction of the mass transfer. The experimental results in Figure 7 display a different situation. Here, for higher surfactant concentrations than $0.1 mmol/L$ the mass transfer rates reduce dramatically, although from the fluid dynamic point of view, a complete coverage is reached under these concentrations. Therefore, an additional mass transfer resistance is responsible for the large decrease in the mass transfer. This resistance is exerted by the change in the phase behaviour and the accompanying change in the interface's characteristics as shown with the ODM-measurements. With both methods an increase in the interface's rigidity was observed.

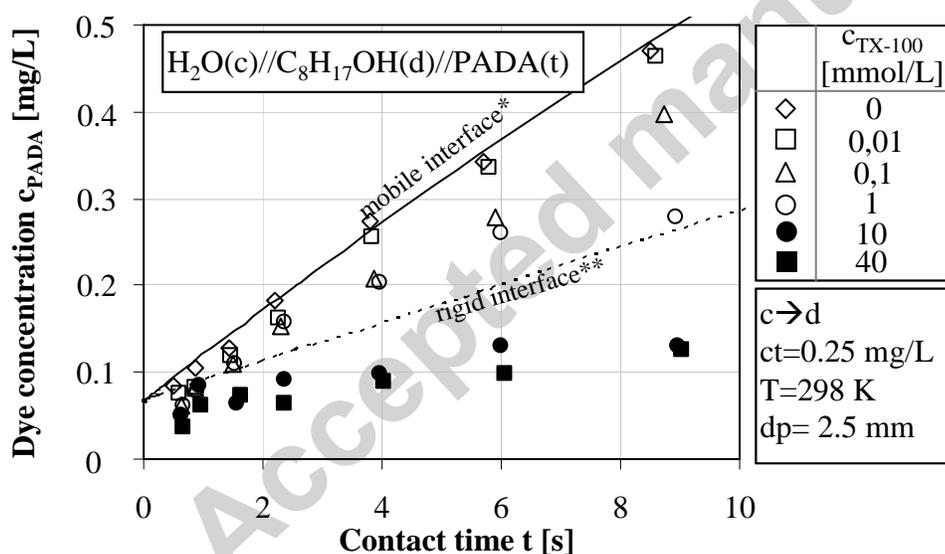


Figure 7: Comparison of the experimental results with results calculated with the given correlations of literature for (*) mobile interfaces [Clift et al 1978] and rigid interfaces (**) [Clift et al 1978, Lochiel and Calderbank 1964]

To compare the experimental results shown in Figure 7 with correlations given in the literature the main mass transfer resistance has to be discovered. Therefore, the diffusion coefficients as well as the partition coefficients have to be determined. The experimental determination of diffusion coefficients is

challenging. Applying the dynamic light scattering (DLS) method allows the calculation of a hydrodynamic radius of a molecule. This information is needed for the Stokes-Einstein equation [Einstein 1905]:

$$D_f = \frac{k_B T}{6\pi\eta R_0} \quad (2)$$

where D_f is the Diffusion coefficient, k_B is the Boltzmann constant, η is the dynamic viscosity of the surrounding fluid and R_0 is the hydrodynamic radius of the solved molecule. For the transferred molecules (PADA) observed in this work the hydrodynamic radius was too small for the determination with the DLS method. Therefore, the diffusion coefficient was calculated by applying the group theory. Nakanishi [1978] developed an equation with parameters derived from experimental data where different interactions between the solvent and the dissolved molecules were taken into account. The parameters were chosen by the functional groups the molecules consist of. The total deviation for 149 data points was 9.1%.

Table 2: Diffusion coefficients for different substances in water at 293 K. Calculated with the group theory [Nakanishi 1978] and compared to experimental determined values from the literature.

	Calculated D_{A,H_2O} [m^2/s] $\cdot 10^{-9}$	Literature [Atkins 2006] D_{A,H_2O} [m^2/s] $\cdot 10^{-9}$
Ethanol	1.21	1.24
Methanol	1.52	1.58
Sucrose	0.61	0.52
Glycin	1.16	1.06
PADA	0.554	
PADA in $C_8H_{17}OH$	0.056	

Table 2 shows the diffusion coefficients for some well known substances from the literature. The deviations between the calculated diffusion coefficients and the experimentally determined coefficients are small. For the transferred component regarded in this work, Pyridin-2-azo-dimethylaniline, the diffusion coefficient was calculated by using the parameter set for the group of compounds for pyridine.

Therefore, the diffusion coefficient calculated for PADA in water is $D_{PADA,H_2O} = 5.54 \cdot 10^{-10} \text{ m}^2 / \text{s}$. The viscosity of 1-octanol is approximately 10 times higher than the viscosity of water; hence the diffusion coefficient in water is one order of magnitude smaller than in water $D_{PADA,C_8H_{17}OH} = 5.6 \cdot 10^{-11} \text{ m}^2 / \text{s}$.

The partition coefficients for PADA in the binary system water/1-octanol were determined by applying the shake-flask method as well as the slow stirring method. A partition coefficient (K_A) of 58 is determined for PADA in the binary system water/1-octanol. The partition coefficient is defined as:

$$K_A = \frac{C_{PADA,org}}{C_{PADA,aq}} . \quad (3)$$

As micelles are able to solubilise the hydrophobic PADA molecules in the aqueous phase, the partition coefficient is a function of Triton X-100 concentration. A decrease of the partition coefficient is expected, because the solubilisation of PADA leads to lower concentrations in the organic phase.

For the ratio of the diffusion coefficients and the high partition coefficient the main mass transfer resistance is located in the continuous phase. Hence, a correlation for calculating the mass transfer for an external problem has to be applied to compare the experimental results of this work. For the mass transfer in a system where the main mass transfer resistance is located in the continuous phase the correlation of Clift et al [1978] can be applied:

$$E = \frac{c(t)}{K_A \cdot c_{A,f}} = 1 - \exp\left(-3Fo \frac{Sh}{2K_A}\right) . \quad (4)$$

where E is the extraction efficiency Fo is the Fourier number, Sh is the Sherwood number and K_A is the partition coefficient. The Sherwood numbers are calculated for the two borderline cases of fluid particles: with and without rigid interfaces. For a fluid particle with a movable interface the following correlation is used to calculate the Sherwood number [Clift et al 1978]:

$$Sh = f \frac{2}{\sqrt{\pi}} Pe^{0.5} \quad (5)$$

where Pe is the Peclet number and f characterizes the moveable interface and can be determined by the ratio of viscosities, which is approximately 10 in this work. The Reynolds number for the droplets observed here is approximately 230. Therefore, f is defined at a value of 0.6. The other borderline case is the fluid particle with a rigid interface; here the Sherwood number can be calculated by using the correlation of Lochiel and Calderbank [1964]:

$$Sh = A \cdot Re^{0.5} \cdot Sc^{0.33} \quad (6)$$

where the exponents are derived from the boundary layer theory. A was chosen at a value of 0.84 as in [Lochiel and Calderbank 1964].

The comparison between experimental data and the mass transfer calculation based on the two boundary cases is given in Fig. 7 also. The mass transfer during the drop formation was found by a linear extrapolation of the experimental results. The mass transfer in a pure system is described well by applying the correlation of Clift [1978]. Also the results calculated for a rigid particle agree satisfactory with the experimental results. The investigations of fluid dynamics [Kraume et al. 2011] have shown that the droplets behave like rigid particles at Triton X-100 concentrations of 1 mmol/L. This is also underlined by the correlation of Clift et al [1978]. But the experiments at higher surfactant concentrations show a further reduction of mass transfer. This is referred to high surfactant concentrations at the liquid/liquid interface which lead to a change in phase behaviour and to an increase in the interface's viscosity and to reduction of the flexibility which ends up in a high mass transfer resistance and to a reduction in mass transfer rates.

Equation 5 gives a correlation of the Sherwood number which is used for the calculation of the mass transfer [Clift et al 1978]. The correction factor f has to be determined graphically [Clift et al. 1978] and is a function of the viscosity ratio and the Reynolds number. Both values are changing in presence of Triton X-100. The drop rise velocity decreases to the velocity of a particle with a rigid interface; hence lower Reynolds numbers occur. Furthermore, the rheological conditions at the interface are changing as observed in Figure 5. Both changes have a huge impact on the correction factor f . Therefore, a new

correlation for f was developed in this work, where the influences of the surfactant molecules are implemented. The correction factor f was fitted to the experimental results given in Figure 7 and the following function was found for f :

$$f^* = \frac{1}{(\eta_p / \eta_c)} + \frac{(\eta_p / \eta_c)^2}{\text{Re}} \cdot \exp\left(\frac{c_{\text{TX-100}}[\text{mol/L}]}{c_{c,\text{PADA},0}[\text{mol/L}] \cdot \text{Re} \cdot (\eta_p / \eta_c)}\right) \quad (7)$$

where f^* is the new correction factor which is a function of the viscosity ratio and the Reynolds number for the pure system. Furthermore, the impact of the surfactant concentration is taken into account. With this new correlation for f^* , the calculation of the mass transfer in micellar liquid/liquid systems could be improved. The results are given in Figure 8.

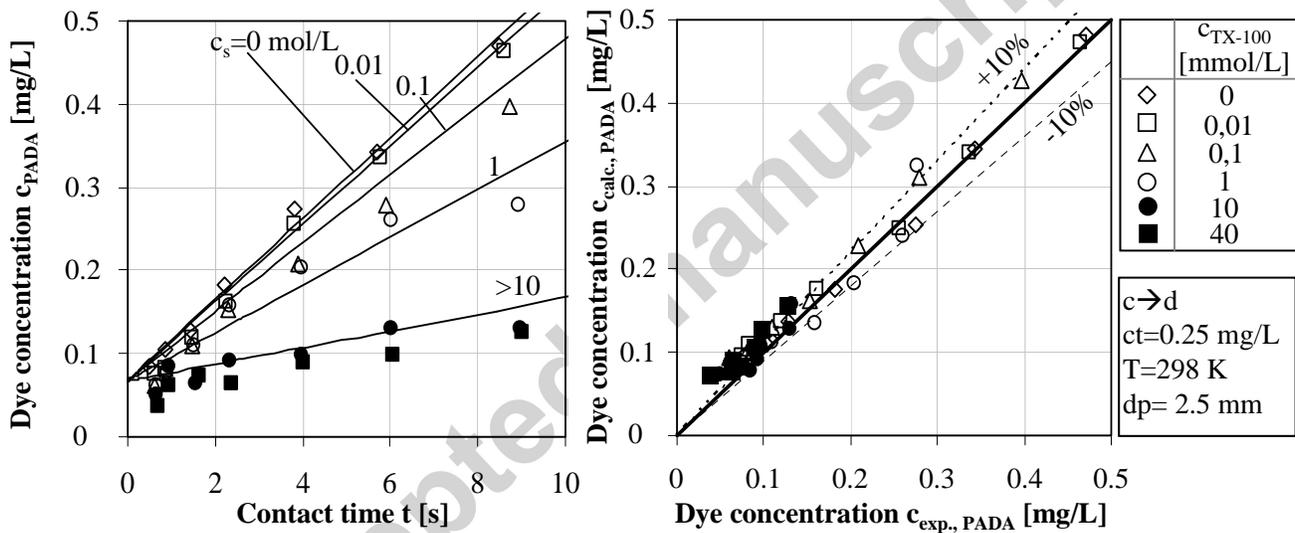


Figure 8: Comparison of the experimental results with results calculated with the given correlations (Equation 4 & 5) of literature [Clift et al 1978] and the improved calculation of the correction factor f^* . The left diagram shows unsteady mass transfer for various Triton X-100 concentrations. Furthermore, it gives the calculated progress of the transferred component concentration with the improved model from this work. A distinctive improvement of the calculated concentration is achieved with this model. This shows the parity diagram on the right hand side. The deviations of the confidence interval ($\pm 10\%$) are rather small for high concentrations of the transferred component. Another advantage of the developed model is that only one Sherwood correlation needs to be applied for various surfactant concentrations. The Sherwood correlations given in Equation 5 and 6 can only be used for the limiting cases of a freely

movable and a rigid interface. With the new extended model it is also possible to calculate the mass transfer for other cases than the limiting cases and furthermore it takes the change of the phase behaviour into account.

Conclusions

In this work the liquid/liquid mass transfer in micellar systems was analysed. First the phase behaviour of the test system was characterised. The experimental results of the phase behaviour show that at high Triton X-100 concentrations the formation of liquid crystalline phases is possible. Furthermore, it is proved that for higher surfactant concentrations than 12%, a Winsor III system is formed which has not been detected in the previous works given in the literature. At the liquid/liquid interface the surfactant concentration is sufficiently high so that the formation of such viscous systems is possible. To identify a change in phase behaviour, oscillating drop method was applied. These results show that an increase in surfactant concentration results in an increase in the interfacial viscosity and a reduction of the flexibility of the liquid/liquid interface. This is evidence for a change in the phase behaviour at the interface. These results are reflected in the experimental results of the liquid/liquid mass transfer. Here, a strong increase of mass transfer resistance is detected at high surfactant concentrations. For Triton X-100 concentrations higher than 10 mmol/L the experimental results of the mass transfer were even lower than the predicted results for a rigid particle. Therefore, the physicochemical effect and the fluid dynamic effect which are given in the literature for the reduction of mass transfer rates due to surfactants describe the situation at high surfactant concentrations incompletely. Additionally, the phase behaviour has to be observed for high surfactant concentrations. With the new experimental results found in this work, the given correlation from the literature was extended to take into account the interfacial phenomena. It was possible to develop an extension of a given correlation which describes the unsteady mass transfer for various surfactant concentrations and which considers the change of the phase behaviour at the liquid/liquid interface.

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Symbols

Notation

A	interfacial area
c	concentration mol/L or mg/L
d	diameter, mm
E^*	visco-elastic modulus, mN/m
E'	elastic modulus, mN/m
E''	viscous modulus
f	correction factor
f^*	correction factor
ID	inner diameter, mm
K	partition coefficient
n	number of ions
N	Nozzle
OD	outer diameter, mm
R	gas constant, J/(mol K)
t	time, s
T	temperature, °C
v	drop rise velocity, mm/s

Greek letters

γ	interfacial tension, mN/m
Γ	interfacial concentration, mol/m ²
μ	chemical potential, J/mol
η	dynamic viscosity, mPas
φ	phase angle, °

Subscripts

0	no surfactant
A	component A
c	continuous phase
cs	surfactant concentration

Max	maximal
p	particle
s	surfactant

Dimensionsless numbers

Fo	Fourier number
Pe	Peclet number
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

Shortcuts

CMC	critical micelle concentration
ODM	Oscillating drop method
SDS	sodium dodecyl sulfate
TX-100	Triton X-100

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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 can't be explained by effects from literature.
- The phase behaviour has to be considered.

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