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INFLUENCE OF NON-IONIC SURFACTANTS ON LIQUID-LIQUID MASS TRANSFER OF SINGLE DROPLETS

WPŁYW NIEJONOWYCH ŚRODKÓW POWIERZCHNIOWO CZYNNYCH NA MASOWE PRZENOSZENIE POJEDYNCZYCH KROPELEK MIĘDZY PŁYNAMI

Abstract

One of the main goals of “green chemistry” is: using water as a solvent. Many substances are hardly soluble in water; hence multiphase reactions will not proceed, for instance. By using surfactants the water solubility of such substances can be increased which ends up in an increase of the reaction rate. Due to their amphiphilic structure surfactants adsorb at interfaces. This is the place where the important transport processes occur. Therefore, an interference of the mass transport by the surfactants is obvious. In previous works a reduction of the mass transfer in the presence of surfactants was observed. Also, in this work the experimental results show a decrease of the mass the transfer, but describing this reduction of the mass transfer with the known phenomena from literature is not enough. Additionally, the phase behaviour has to be taken in account.

Keywords: surfactants, fluid dynamics mass transfer, micellar liquid-liquid systems

Streszczenie

Jednym z podstawowych celów “chemii proekologicznej” jest stosowanie wody w roli rozpuszczalnika. Wielu substancji praktycznie nie da się rozpuścić w wodzie, przez co niemożliwe stają się np. reakcje wielofazowe. Stosowanie środków powierzchniowo czynnych może zwiększyć rozpuszczalność takich substancji w wodzie, a w rezultacie przyspieszyć tempo reakcji. Ze względu na swą tolerancyjną strukturę środki powierzchniowo czynne adsorbują na granicy faz. Jest to miejsce, w którym występują istotne procesy przenoszenia, co wyjaśnia interferencję przenoszenia masy za pomocą środków powierzchniowo czynnych. We wcześniejszych pracach zaobserwowano redukcję przenoszenia masy w obecności środków powierzchniowo czynnych. Wyniki eksperymentów zaprezentowanych w niniejszym artykule wykazują spadek przenoszenia masy. Nie wystarczy jednak opisać go, wykorzystując zjawiska znane z literatury – należy też wziąć pod uwagę zachowania fazowe.

Słowa kluczowe: środki powierzchniowo czynne, masowe przenoszenie dynamiki płynu, systemy micelarne między płynami

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1. Introduction

Homogenous catalyzed reactions fulfill many principles of green chemistry [1, 2]. One field of the homogenous catalysis is liquid-liquid reactions. Here the interface between both immiscible phases plays a main role; hence the important transport processes take place at interfaces which might govern the yield and the selectivity of the reaction. In many industrial applications unwanted interfacial active contaminations (surfactants) occur. For some applications the need of surfactants is indispensable [3]. In both cases the surfactant molecules will adsorb at liquid-liquid interfaces, where they will disturb the transport processes. For fundamental understanding of the surfactants' impact on the transport processes it is of great importance to observe single droplets; thus this is the smallest transfer unit.

By the adsorption of surfactants at liquid-liquid interfaces two phenomena are responsible for the influences on the transport processes. The molecules form a barrier layer at the interface which causes an additional mass transfer resistance [4–7]. Furthermore, the adsorption of the surfactants has an impact on the mobility of the interface; the interface gets less mobile, the drag coefficient increases. The droplet behaves like a rigid particle; hence the inner circulations, which occur in fluid particles, are hindered which also has an effect on the mass transfer [8–11]. Both phenomena described above will lead to a reduction in the mass transfer rate.

In the work of Lee [7], the mass transfer rates decrease drastically in the presence of surfactants. At a certain surfactant concentration the mass transfer rate remains constant although the critical micelle concentration (CMC) is not reached; this implies a complete coverage of the interface. Most authors investigated low surfactant concentrations, but homogenous reactions in micellar systems require high surfactant concentrations so that the reactions will proceed. With increasing the surfactant concentration beyond the CMC the situation gets even more complex. Micelles form and are able to solubilize the transferred component. Furthermore, with the formation of micelles the viscosity of the continuous phase increases dramatically [12, 13], which has an influence on the fluid dynamics. Another phenomenon which has to be considered is the phase behavior that is changed by surfactants [14]. Multiphase systems can be formed with some surfactants at certain concentrations. The interface between two immiscible fluids can be seen as a pseudo-system, in which the surfactant concentration is high compared to the other phases. There is also a certain amount of both other phases the continuous phase and dispersed phase; hence at certain concentrations the formation of high viscose multiphase systems is possible. Also liquid crystals may form at the interface [15]. In both cases a high resistance for the momentum transport and for the mass transport would be the result.

2. Materials and Methods

The experimental investigations are carried out in a testing system, because of the highly-sensitive measurements; all components used were at the highest purity. The regarded system consisted of deionized water with a resistance of 18.3 M Ω -cm, which has been used as the continuous phase; 1-Octanol (Appli. Chemistry, 99%) was used as the dispersed phase Triton X-100 (Aldrich, 99%) was used as a nonionic surfactant. As the transferred component an azo dye (PADA, Aldrich, 99%) was used.

For the determination of the fluid dynamics and the mass transfer of single droplets the same experimental setup was used as described by Wegener [16, 17].

Figure 1 shows a glass column (1) with a height of 1000 mm and a diameter of 75 mm. The surrounding jacket (2) is filled with glycerol, due to the similar refraction index to borosilicate glass. In this work every experiment is carried out at 22°C; therefore, a thermostat by LAUDA® is installed. The Hamilton® PSD/2 module 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 respectively diameter. Four different nozzles, with different diameters are used to provide a wide range of different droplet diameters.

To determine the mass transfer, the droplets are collected at the glass funnel's neck. A tiny dispersed phase is kept so that droplets could coalesce. The second Hamilton PSD/2-module is used to take the drops out of the system. An azo dye is used as a model transferred component; hence a Specord 210 photometer by Jena Analytik® is used to analyse the dye concentration.

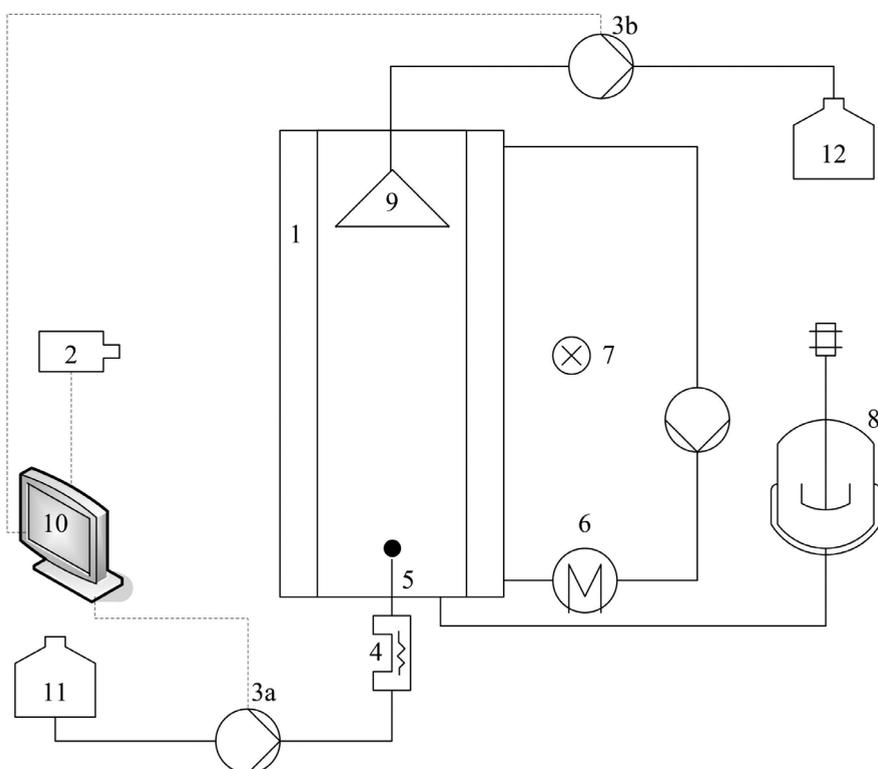


Fig. 1. Experimental setup: (1) Glass column, (2) high speed camera, (3a, 3b) Hamilton PSD/2 module, (4) solenoid device, (5) nozzle, (6) thermostat, (7) illumination, (8) saturation tank, (9) glass funnel, (10) computer control

Rys. 1. Układ doświadczalny: (1) kolumna szklana, (2) kamera szybkobieżna, (3a, 3b) moduł Hamilton PSD/2, (4) cewka, (5) końcówka wylotowa, (6) termostat, (7) oświetlenie, (8) zbiornik saturacyjny, (9) lejek szklany, (10) sterowanie komputerowe

3. Results and discussions

The focus of this work lies on the influence of non-ionic surfactants on liquid-liquid mass transfer. As mentioned above surfactant molecules will adsorb at the interface where these molecules will disturb the momentum and mass transport processes. The influence of the surfactant concentration on the interfacial tension of the liquid-liquid system gives information about the interfacial coverage; hence the exact knowledge of the interfacial tension is of great importance. Also, the fluid dynamics can be used as an important tool for the determination of the interfacial coverage. Therefore, the interfacial tension and the fluid dynamics need to be investigated for the discussion of the influence of non-ionic surfactants on the liquid-liquid mass transfer.

3.1. Interfacial tension

First the critical micelle concentration CMC was determined. Therefore, the interfacial tension at the water/air interface was determined in dependence of the surfactant concentration. The CMC is determined by obtaining the distinctive point of bending in a diagram, where the interfacial tension is plotted in dependence of the logarithmic surfactant concentration. For Triton X-100 a concentration of 0.24 mmol/L was determined for the CMC. This value agrees well with values given in the literature [18].

Knowing the exact relation between interfacial tension in the binary system water/1-octanol and the surfactant concentration is of great importance as mentioned above. Therefore, the dynamic interfacial tension was determined in dependence of the surfactant concentration. Figure 2 shows the unsteady interfacial tension for different Triton X-100 concentrations. For a clearer representation only the average values are shown. The deviations were less than 3%.

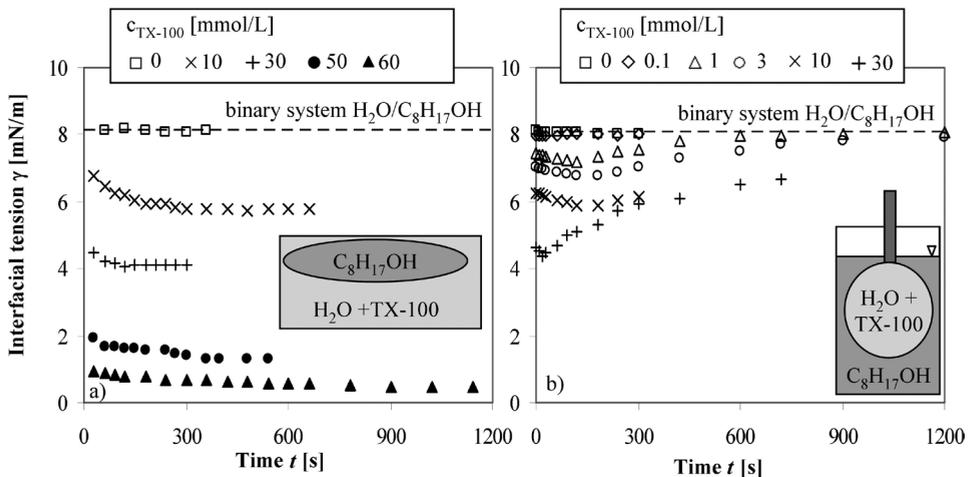


Fig. 2. Dynamic interfacial tension of the binary system water/1-octanol in dependence of Triton X-100 concentration: a) measured by spinning drop method; b) measured by pendant drop method

Rys. 2. Dynamiczne napięcie w obszarze wzajemnego oddziaływania układu binarnego woda/1-oktanol w zależności od stężenia Tritonu X-100: a) mierzone metodą rotacyjną; b) mierzone metodą zwornikową

The interfacial tension of the liquid-liquid system water/1-octanol was determined at 22°C with a value of 8.1 mN/m. For both measurement techniques applied in this work, the value of the interfacial tension of the binary system water/1-octanol agrees with the values given in the literature [19]. While Fig. 2a shows the unsteady interfacial tensions determined with the spinning drop method Fig. 2b shows the interfacial tension measurements carried out with the pendant drop method. For Triton X-100 concentrations lower than the critical micelle concentration (0.2 mmol/L) there is almost no change in the interfacial tension observed. This behavior is unexpected; hence the reduction of the interfacial tension at the liquid/liquid interface should occur at lower concentrations than the CMC concentration measured in the system aqueous-surfactant-solution/air. Exceeding the surfactant beyond 1 mmol/L the unsteady interfacial tension in Fig. 2a progresses as expected. After a certain time the interfacial tension remains constant. Fig. 2b shows a different situation. First the interfacial tension decreases with time. After reaching a minimum the interfacial tension rises again. With increasing surfactant concentration the minima occur earlier and become more distinctive. The surfactant molecules that adsorb at the liquid-liquid interface are transported into the 1-octanol phase [20]. Therefore, the progress of the unsteady interfacial tension depends on the partition coefficient, also. By applying the spinning drop method a 1-octanol droplet is produced in an aqueous-surfactant solution. While, by applying the pendant drop method an aqueous-surfactant solution droplet is produced into a 1-octanol phase. The main difference between both experiments lies in the amount of surfactant molecules that are involved. By applying the pendant drop method the amount of the surfactant molecules is limited. While by applying the spinning drop method the amount of surfactant molecules seems to be infinite [20]. Therefore, the transport of surfactant molecules into the organic phase is taken much more into account by applying the pendant drop method. Evidence that transport processes of surfactant molecules take place is a strong movement of the droplet while measuring. Furthermore, cloudiness was recognized as the measurements proceeded (Fig. 3), although the phases have been saturated.

The occurrence of the cloudiness is evidence that the phase behavior of the system has changed as it is described by Kahlweit [14]. For the ternary system water/1-octanol/Triton X-100 there are many possibilities for a change of the phase behavior [21]. This could also have an effect on the interfacial tension measurements. Fig. 4 shows the influence of the surfactant concentration on the interfacial tension at steady state.

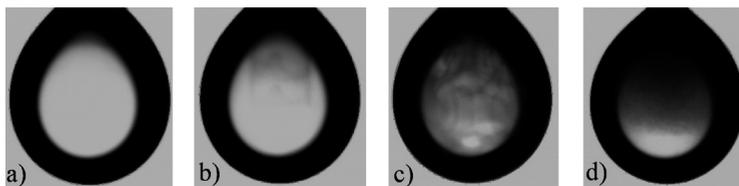


Fig. 3. Water droplet with a Triton X-100 concentration of 3 mmol/L while measuring the interfacial tension by pendant drop method:
a) $t = 0$ s; b) $t = 180$ s; c) $t = 720$ s; d) $t = 1200$ s

Rys. 3. Kropelka wody przy stężeniu Tritonu X-100 3 mmol/L w pomiarze napięcia w obszarze wzajemnego oddziaływania metodą zwornikową:
a) $t = 0$ s; b) $t = 180$ s; c) $t = 720$ s; d) $t = 1,200$ s

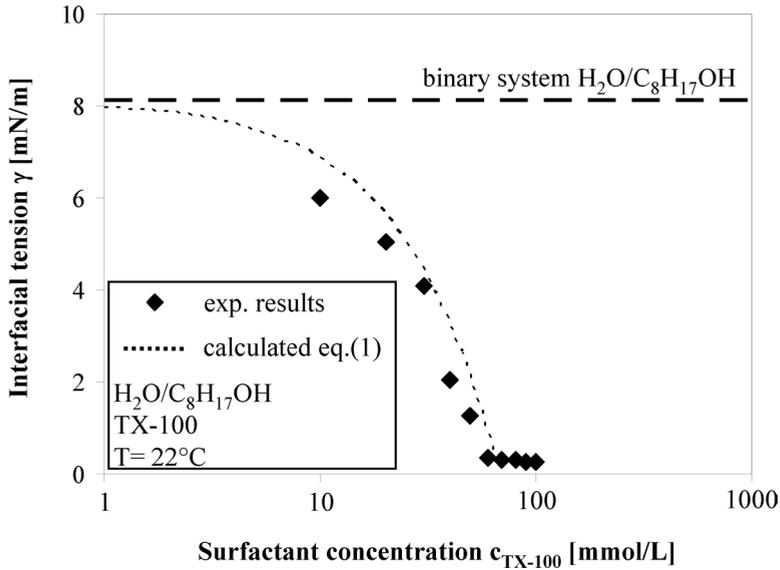


Fig. 4. Interfacial tension depending on surfactant concentration.
Comparison of the experimental and calculated results

Rys. 4. Napięcie w obszarze wzajemnego oddziaływania w zależności od stężenia środka powierzchniowo czynnego. Porównanie wyników eksperymentów i obliczeń

These measurements have been carried out by the spinning drop method (Fig. 2a). Due to the logarithmic scale of the diagram the interfacial tension decreases linearly for concentrations higher than 15 mmol/L. Exceeding a concentration of 70 mmol/L the interfacial tension remains constant, at this distinctive bending point the CMC is determined. Therefore, a huge shift of the CMC is obtained compared to the water/air system (CMC = 0.24 mmol/L). This behavior is unexpected. Furthermore, this diagram shows the calculated behavior of the interfacial tension in dependence of the surfactant concentration. The calculations shown in Figure 4 have been carried out by the Langmuir-Syskowski equation [23]:

$$\gamma = \gamma_0 - nRT\Gamma_{\max} \ln\left(\frac{c}{b} + 1\right) \quad (1)$$

where γ_0 is the interfacial tension of the binary system water/octan-1-ol in absence of Triton X-100, n is the number of ions, Γ_{\max} is the maximal concentration of surfactants at the interface and b is the Langmuir constant representing the ratio of the adsorption and desorption rate. Γ_{\max} and the constant b were determined with the experimental results. For Γ_{\max} a value 35 $\mu\text{mol/L}$ was determined and the ratio between the adsorption and desorption rate b is 0.991. The ratio of almost one between both rates implies that both rates have the same value. This means that other than adsorption is happening at the liquid-liquid interface. At some compounds the formation of high viscose multiphase systems is possible, which affects the measurements. Another helpful tool quantifying the coverage of the liquid-liquid interface with surfactants is the fluid dynamics of single droplets.

3.2. Fluid dynamics

In absence of Triton X-100 the droplet's interface is freely movable. As soon as surfactant molecules adsorb at the interface the mobility of the interface decreases, hence the drag coefficient increases which is reflected in a reduction of the drop rise velocity. When a complete coverage of the interface is reached the interface is immobile and the droplet rises like a particle with a rigid sphere. Fig. 5 shows the drop rise velocity in dependence of the interfacial coverage which is calculated from the experimental results of the interfacial tension measurements. Therefore, the Langmuir isotherm is used:

$$\Phi = \frac{\Gamma_s}{\Gamma_{\max}} \quad \text{and} \quad \Gamma_s = \frac{c_s \cdot \Gamma_{\max}}{c_s + b} \quad (2)$$

Furthermore, the calculated drop rise velocities for the two border cases are plotted in this diagram. On the one hand side the case that the interface is freely movable and on the other hand that the interface of the droplet is rigid. For an interfacial coverage of 0.01 % with Triton X-100 molecules the drop rise velocity is reduced to the velocity value of a droplet with a rigid sphere. This applies for all droplet sizes plotted in Fig. 5. Actually, it was assumed, that for a high interfacial coverage the drop rise velocity of a rigid sphere is obtained as was found for another surfactant (SDS). That could not be confirmed. Therefore, some other phenomena have to be responsible for the reduction of the drop rise velocity. An explanation for the reduction of the drop rise velocity is that at the interface a high viscous multiphase is created [21]; hence the mobility of the interface is reduced which causes a decrease in the drop rise velocity. Furthermore, this will affect the internal flow which will exert a reduction of the mass transfer rate.

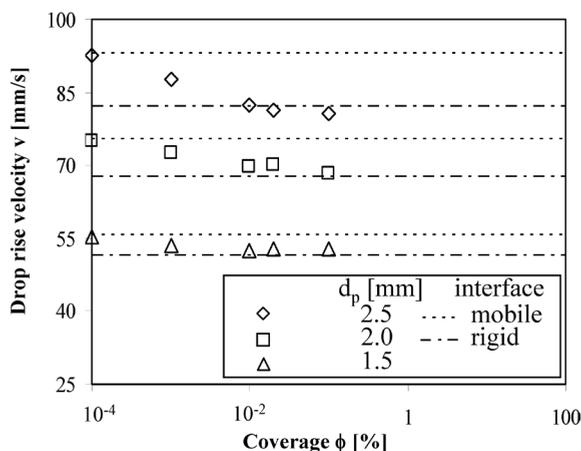


Fig. 5. Drop rise velocity in dependence of the interfacial coverage with Triton X-100 molecules for different drop sizes and calculated values for the drop rise velocities of droplets with rigid and moving interfaces

Rys. 5. Zmiany prędkości w zależności od zasięgu obszaru wzajemnego oddziaływania z molekułami Tritonu X-100 dla różnych zakresów i obliczanych wartości zmiennych prędkości kropelek o sztywnych i ruchomych obszarach wzajemnego oddziaływania

3.3. Influence of non-ionic surfactants on the mass transfer

The impact of Triton X-100 on the mass transfer is shown in Fig. 6. This diagram shows the unsteady PADA concentration for different Triton X-100 concentrations. With an increase of the surfactant concentration the liquid-liquid mass transfer is reduced. In absence of Triton X-100 the concentration of the transferred component increases linearly with time. When Triton X-100 is added to the continuous phase the fluid dynamics of the droplet is changed, as seen above. For Triton X-100 concentrations larger than 0.1 mmol/L the drop behaves like a rigid sphere; hence from the fluid dynamic point of view a further decrease of the mass transfer should not be obtained, but a further significant reduction of the mass transfer is observed. The interfacial tension measurements have shown, that at the concentrations regarded in Fig. 6 coverage of 1% is reached for the highest Triton X-100 concentration; hence the reduction of the mass transfer can not be explained by the coverage of surfactant molecules at the interface. But the phase behaviour of the system changes and multiphase regions are created at the interface. This will act like an additional mass transfer resistance. Furthermore, the influences of micelles have to be considered. Exceeding a concentration of 0.2 mmol/L micelles will occur and solubilize the hydrophobic transferred component (PADA) and might cause another mass transfer resistance. The solubilisation of PADA by micelles is proofed by a change of the light absorption maximum of PADA molecules; due to the solubilisation of PADA molecules by micelles a change of the absorption behaviour is observed.

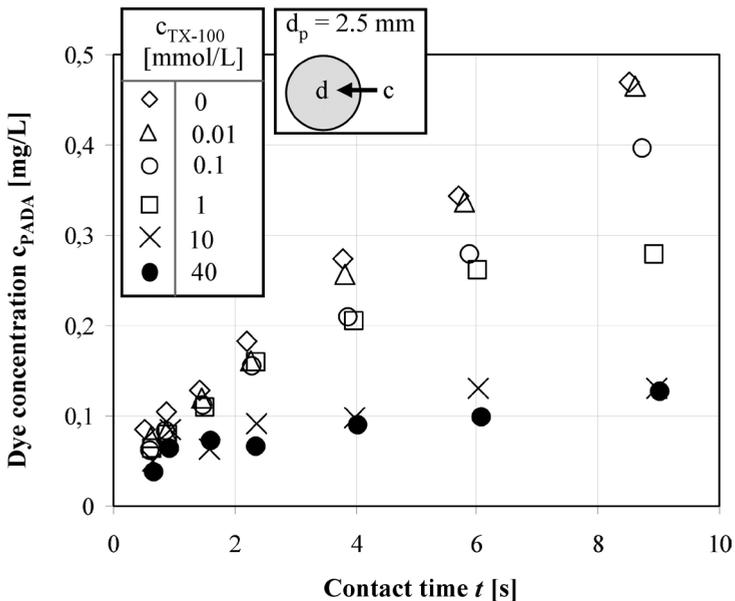


Fig. 6. Unsteady dye concentration depending on Triton X-100 concentration for 2.5 mm droplets: transport direction from continuous phase to dispersed phase

Rys. 6. Niestabilne stężenie barwnika w zależności od stężenia Tritonu X-100 dla kropelek 2,5 mm: kierunek przeniesienia od fazy ciągłej do rozproszonej

4. Summary and conclusion

The goal of this work was identifying the influences of non-ionic surfactants on the liquid-liquid mass transfer of single droplets. There are many influences exerted by surfactants which have to be regarded. By adsorbing at the interface surfactants reduce the interfacial tension. Furthermore, these molecules increase the stiffness of the interface which decreases the drop rise velocity. Besides the adsorption of surfactants at the interface another transport resistance was identified. There were compositions reached at the interface that form a high viscose multiphase interface. These conditions change the fluid dynamics drastically and create an additional mass transfer resistance, which leads to a reduction of liquid-liquid mass transfer.

Symbols

c	–	concentration [mol/L] or [mg/L]
d	–	diameter [mm]
ID	–	inner diameter [mm]
n	–	number of ions [–]
N	–	Nozzle
OD	–	outer diameter [mm]
R	–	Gas constant
t	–	time [s]
T	–	temperature [°C]
V	–	drop rise velocity [mm/s]
γ	–	interfacial tension [mN/m]
Φ	–	coverage at the interface [%]
ρ	–	density
ζ	–	drag coefficient
0	–	no surfactant
s	–	surfactant
cs	–	surfactant concentration
Max	–	maximal
p	–	particle

References

- [1] Anastas P., Warner J., *Green Chemistry: Theory and Practice*, Oxford University Press, New York 1998.
- [2] Rothenberg G., *The best of both worlds*, Nature Chem., 2, 2010, 9-10.
- [3] Oehme G. et al., *Reaktionen in mizellaren Sytsemen*, Angewandte Chemie, 117, 2005, 7338– 7364 (in German).
- [4] West F.B. et *Addition Agents and Interfacial Barriers in Liquid-Liquid Extraction*, Ind. Eng. Chem., 44, 1952, 625.

- [5] Lindland K.P., Terjesen S.G., *The Effect of a Surface-Active Agent on Mass Transfer in Falling Drop*, Chem. Eng. Sci., 5, 1956, 1-12.
- [6] Chen L.H., Lee Y.-L., *Adsorption Behavior of Surfactants and Mass Transfer in Single-Drop Extraction*, AIChE J., 46, 2000, 160-168.
- [7] Lee Y.-L., *Surfactants on Mass Transfer During Drop-Formation and Drop Falling Stages*, AIChE J., 49, 2003, 1859-1869.
- [8] Gibbons J.H., Houghton G., Coull J., *Effect of a Surface Active Agent on the Velocity of Rise of Benzene Drops in Water*, AIChE J., 8, 1962, 274-276.
- [9] Griffith R.M., *The effect of surfactants on the terminal velocity of drops and Bubbles*, Chem. Eng. Sci., 17, 1962, 1057-1070.
- [10] Beitel A., Heideger W.J., *Surfactant effects on mass transfer from drops subject to interfacial instability*, Chem. Eng. Sci., 26, 1971, 711-717.
- [11] Wegener M., Paschedag A.R., *The effect of soluble anionic surfactants on rise velocity and Mass Transfer at Single Droplets in Systems with Marangoni instabilities*, International Journal of Heat and Mass Transfer, 55, 2012, 1561-1573.
- [12] Kern F. et al, *Dynamical Properties of Salt-Free Viscoelastic Micellar solutions*, Langmuir, 10, 1994, 1714-1723.
- [13] Pictuelli L., Ergermayer M., Sjöström J., *Rheology of Mixed Solutions of an Associating Polymer with a Surfactant. Why Are Different Surfactants Different?*, Langmuir, 19, 2003, 3643-3649.
- [14] Kahlweit M., Strey R., *Phasenverhalten ternärer Systeme des Typs H₂O-Öl-nichtionisches Tensid*, Angewandte Chemie, 97, 1997, 655-669 (in German).
- [15] Horvath-Szabo G. et al, *Sandwich Structures at Oil-Water Interfaces under Alkaline Conditions*, Journal of Colloid and Interface Science, 253, 2002, 427-434.
- [16] Wegener M. et al., *Transient rise velocity and mass transfer of a single drop with interfacial instabilities – experimental investigations*, Chem. Eng. Sci., 2007, 2067-2078.
- [17] Wegener M., Kraume M., Paschedag A.R., *Terminal and Transient Drop Rise Velocity of Single Toluene Droplets in Water*, AIChE J., 56, 2-10.
- [18] Saïen J., Asadabadi S., *Adsorption and Interfacial Properties of Individual and Mixtures of Cationic/Nonionic Surfactants in Toluene + Water Chemical Systems*, J. Chem. Eng. Data, June 2010, 3817-3824.
- [19] Villers D., Platten J.K., *Temperature Dependence of the Interfacial Tension between Water and Long-Chain Alcohols*, J. Phys. Chem., March 1988, 4023-4024.
- [20] Miller R. et al., *Messungen der dynamischen Grenzflächenspannung im System wässrige Tensidlösung/ organisches Lösungsmittel*, Chemie Ingenieur Technik, 70, 1998, 89-99.
- [21] Guo R. et al., *The Phase Behaviour and the Structural Properties of Triton X-100/n-C₈H₁₇OH/PEG1000aq Systems*, Journal of Dispersion Science and Technology, 22, 2001, 443-451.
- [22] Atkins P. W., de Paula J., *Physical Chemistry*, Oxford University Press, New York 2006.
- [23] Schwurger M., Findenegg G. et al: *Lehrbuch der Grenzflächenchemie*, Georg Thieme Verlag, Stuttgart 1996 (in German).