Transient Rise Velocity and Mass Transfer of a Single Drop with Interfacial Instabilities - Experimental Investigations

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Abstract

An experimental study of transient drop rise velocities and mass transfer rates was carried out in the system toluene/acetone/water which is known to show interfacial instabilities. The rise velocity of toluene drops was studied without added solute (acetone) in the diameter range 1 to 3 mm and with added solute for 2 mm drops. The initial concentration of the transferred solute was varied from 0 to 30 g/L. The transient drop rise velocities were used to quantify the Marangoni effect since the drag coefficient depends on the strength of the Marangoni convection patterns caused by interfacial tension gradients. In addition, mass transfer measurements were carried out in order to determine the modification of the mass transfer rate due to Marangoni convection. Velocity and mass transfer measurements were then correlated via the contact time. Results reveal the existence of a range in which a critical value for the solute concentration can be defined for Marangoni convection.

Keywords: drop; liquid/liquid extraction; mass transfer; interface; Marangoni; instability

1. Introduction

Mass transfer of a solute between a dispersed and a continuous phase is of high importance in many liquid/liquid processes. In such systems, the interfacial tension is a function of the solute concentration. If the concentration is not uniformly distributed along the interface, interfacial phenomena like the Marangoni convection occur. These effects lead to a strong coupling between concentration and velocity field and can influence the mass transfer rate significantly. This is of great interest for the design and optimization of industrial applications, e.g. extraction columns. But to date, for many systems it is not yet possible to predict interfacial instabilities reliably which results from the fact that these phenomena are not fully understood. One of the problems in industrial practice, e.g. in dispersed liquid/liquid systems, is that the influence of Marangoni convection on mass transfer cannot easily be deduced since too many superimposed effects on the mass transfer rate occur. Therefore, the polydisperse system has to be reduced to single drop experiments which allows to separate the Marangoni effect from others.

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The present study deals with two main questions:

- Is the onset and the end of Marangoni convection predictable?
- Does an intensification of Marangoni convection always lead to an enhanced mass transfer rate?

Experimental studies from the 1960’s reported increased mass transfer rates if interfacial instability occurs (e.g. Maroudas & Sawistowski, 1964; Olander & Reddy, 1964; Bakker et al., 1966; Bakker et al. 1967; Lode & Heideger, 1970). The first efforts to predict theoretically interfacial instability in a liquid/liquid system with a plane interface were made by Sternling & Scriven (1959). More general approaches were developed by Hennenberg et al. (1979), Hennenberg et al. (1980), Nakache et al. (1983), Slavtchev et al. (1998), Slavtchev & Mendes (2004). Slavtchev et al. (2006) show in a linear stability analysis for a system with a planar interface that the onset for temperature driven Marangoni instabilities depends on the three parameters diffusivity ratio, kinematic viscosity ratio and the product of the heat of solution and the thermal interfacial tension coefficient. The predictions are compared with experiments showing both success and failures. Agble & Mendes-Tatis (2001) compared intensely the predictions of Sternling & Scriven, Hennenberg et al. and Nakache et al. with own experimental results. They investigated hanging drops in quiescent surrounding liquid with and without added surfactants using the Schlieren technique, instabilities were observed visually. Results show that none of the criteria predicts instabilities accurately. They define a critical Marangoni coefficient which takes into account the transport of surfactants. For most of the examined systems it predicts the correct tendency of instability. Mendes-Tatis et al. (2002) observed interfacial convection for acetone transferred from toluene drops into water which is contradictory to Sternling & Scriven’s predictions. The addition of ionic surfactants leads to a dampening of interfacial convection. In an isobutanol-water system, interfacial convection is enhanced by ionic surfactant whereas non-ionic surfactants stop interfacial motion (Mendes-Tatis & Agble, 2000). Lee et al. (1998) and Chen & Lee (2000) show in their investigations that mass transfer resistance is increased when selected surfactants are added.

Quite a number of diversified studies concerning the Marangoni effect has been published. Just to mention a few, Molenkamp (1998) investigated in experiments under microgravity conditions the onset of solutal Marangoni convection in different V-shaped containers in the system water/acetone/air. The enhancement of Marangoni convection increases when the mass transfer resistance becomes more or less equal in both phases. Wolf (1998) studied the mass transfer enhancement due to the Marangoni effect in a convection cell under laminar flow conditions. Other researchers performed studies concerning the thermocapillary induced motion of drops.
under low gravity conditions. Halpern et al. (1998) studied theoretically the transport of surfactants into the human lung due to Marangoni induced flow. It should be mentioned that the dampening mechanisms of Marangoni induced flow in gas/liquid systems has to be distinguished from liquid/liquid systems due to the different viscosity ratios.

Concerning moving drops, Steiner et al. (1990) reported that mass transfer enhancement in the toluene/acetone/water system is strongly dependent on the mass transfer direction. Higher rates were obtained if toluene is the dispersed phase. In this configuration, mass transfer is higher if acetone is transferred from the dispersed phase into the continuous phase. Temos et al. (1996) confirmed the enhancement of mass transfer when the solute transfer direction is $d \rightarrow c$. In order to describe the increased mass transfer due to interfacial instabilities, Steiner et al. (1990) introduce an effective diffusivity, Henschke & Pfennig (1999) describe the enhanced mass transfer with an “instability constant” which has to be identified in single-drop experiments. Schulze et al. (2003) confirmed the chaotic flow structure inside drops due to Marangoni convection in decolourization experiments. Brodkorb et al. (2003) investigated the influence of contaminants on the mass transfer rate of rising drops in the same ternary system toluene/acetone/water and compared experimental results with both a solute time-averaged model and a multicomponent non-equilibrium model pointing out that a correct prediction of the mass transfer is currently not possible.

The fluid dynamics of liquid drops moving in another liquid has been investigated since many decades by several research groups (e.g. Clift et al., 1978). The circulation inside drops has a strong influence both on mass transfer and drag coefficient, i.e. terminal drop velocity (e.g. Garner & Skelland, 1955; Calderbank & Korchinski, 1956; Horton et al., 1965). Correlations for terminal drop velocities were published by several research groups (e.g. Hu & Kintner, 1955; Klee & Treybal, 1956), but the correlations were obtained with unpurified systems. Winnikow & Chao (1966); Thorsen et al. (1968) and Edge & Grant (1971) reported terminal velocities well above the predictions using purified systems. The terminal and interfacial velocity is reduced if the liquid contains impurities or surfactants (e.g. Griffith, 1962; Edge & Grant, 1972; Levan & Newman, 1976; Hatanaka et al., 1988; Li et al., 2003). Some authors propose a stagnant cap model in order to describe the blockage effect of the interface through contaminants (e.g. Griffith, 1962; Levan & Newman, 1976; Hatanaka et al., 1988 for drops and e.g. Alves et al., 2005 for gas bubbles). Schulze & Kraume (2001) and Henschke (2004) report that the drop velocity can also be reduced by Marangoni convection. They both observed a reacceleration of the drops when mass transfer is completed.
The objective of this study is to present an experimental method to detect a critical concentration range for the onset or end of Marangoni convection in the system toluene/acetone/water. Thereto, the transient drop rise velocity of toluene drops with simultaneous mass transfer of acetone into water (section 3.2) are correlated with the mean concentration of acetone (section 3.3) via the contact time. In addition, the results will reveal to what extent the mass transfer rate is enhanced or dampened when the initial solute concentration is changed.

As mentioned above, the system toluene/acetone/water shows significant interfacial instabilities resulting in a strong coupling between flow and concentration field. In a system without Marangoni convection, the relative velocity between drop and surrounding fluid generates one toroidal circulation inside the moving drop due to the non-slip condition at the interface (see Fig. 1, left). Interfacial tension gradients lead to convection patterns which disturb this structure and thereby globally reduce the relative velocity between drop and surrounding fluid (see Fig. 1, right). The drop rise velocity is lower than in the case with constant interfacial tension because of a higher drag coefficient. Additionally, the structured internal circulation disappears completely when Marangoni convection patterns are strong, passing over to a chaotic flow structure inside the drop. This inevitably leads to different mass transfer rates. Later on, when the Marangoni effect gets weaker due to smaller concentrations and concentration gradients of the transferred solute, the internal circulation restarts leading to a reacceleration of the drop. The presented data will show that the reacceleration is linked with the mean solute concentration at a certain time. Therefore, mass transfer measurements were made varying the initial solute concentration and contact time.

2. Materials and methods

The effect of Marangoni convection on momentum and mass transfer can be identified measuring the transient drop rise velocity and the mean solute concentration inside the droplet as a function of contact time and initial solute concentration. The standard test system toluene/acetone/water proposed by the European Federation of Chemical Engineering EFCE (Misek et al., 1985) was used for all experiments. Toluene and acetone are of analysis quality provided by MERCK®. The continuous phase is deionized water of high purity in all experiments, the dispersed phase is toluene. Toluene and water are mutually saturated in order to avoid additional mass transfer. Table 1 summarizes the physical parameters of the system.

Position of Fig. 1.

Position of Table 1.
2.1 Experimental setup

The velocity measurements and the mass transfer experiments were carried out in the same laboratory scale column (see (1) in Fig. 2) made of borosilicate glass. The inner diameter is 75 mm and the height 1000 mm. The column is equipped with a jacket (2) filled with anhydrous glycerol in order to minimize optical distortion effects due to the curvature of the column. The refraction index of glycerol is near to that of borosilicate glass. The temperature of the system is adjusted by circulating glycerol of 25°C with a gear pump (4). A RK 20 thermostat by LAUDA® (5) has been used for temperature control. The drops are dosed by a precision syringe HAMILTON® pump (7a) (PSD/2 module). If a drop of a certain volume has been formed, it does not detach automatically from the nozzle tip (6). Therefore, a thrust type solenoid (8) by KUHNKE® linked with the nozzle device is used to generate a quick impulse downwards detaching the droplet from the nozzle tip. This is done automatically to allow for detaching time control. Before each run, the organic and the aqueous phase are mutually saturated in a stirred tank (9) in order to avoid additional mass transfer of toluene and water. Because of the sensitivity of the system to impurities only glass, PTFE and stainless steel have been used as materials for the experimental device. In order to guarantee the cleanliness of the system, a precise cleaning procedure has been accomplished. Therefore, all materials getting in contact either with the continuous phase or the dispersed phase sample (e.g. saturation tank, column, tubes, syringes, funnel etc.) were cleaned several times mechanically and rinsed with toluene and water of the quality described above.

Position of Fig. 2

2.2 Velocity measurements

Before each run, the cleanliness of the system was checked. Thereto, the terminal velocity of pure toluene drops ($d_p = 2$ mm) was determined at 25°C. As mentioned above, small amounts of surfactants or impurities can change the drag coefficient and hence the terminal velocity dramatically. Nevertheless, the terminal velocity of an ideally clean and spherical toluene drop in water can be calculated with numerical methods (see Fig. 5 & 8). These figures show excellent agreement between numerical solution and our experimental data.

The instantaneous drop rise velocity was filmed with a high-speed camera [10] (Photonfocus® MV-752-160, 2/3”-CMOS sensor with a maximum spatial resolution of 752x582 pixels and a corresponding maximum frame rate of 350 Hz). For our experiments, a spatial resolution of 640x480 pixels and a frame rate of 50 Hz were found to be sufficient. In order to provide a sufficient light intensity during the shutter time, a gas discharge lamp
has been used. The camera position is perpendicular to the column, the distance between camera and column has been chosen in such a way that the whole column height can be represented. The focus of the camera is set to the middle of the column and the scale can be determined. From the moment when the drop is detached by the solenoid device, it is filmed by the high-speed camera. The recorded sequence is stored via the framegrabber on the RAM and from there on the hard disk of the computer. The sequences were analyzed with the image processing tool IMAGE-PRO PLUS® 5.1 by MEDIA CYBERNETICS, INC. In order to track the drop's path through the column, a reference image is subtracted from each image of the sequence. Then, image binarization is used applying a threshold value on the resulting image. A track objects tool in IMAGE-PRO PLUS® identifies the drop as an object. Applied to the whole sequence, the drop path can be detected. The result is a file where the x,y-coordinates of the object’s center are written for each frame in pixels. With knowledge of the frame rate and the object scale, the instantaneous velocity of the drop can finally be calculated from the raw data.

2.3 Mass transfer measurements

The mass transfer experiments are carried out in the same column. The cleanliness of the system is checked in the same manner as for the velocity measurements. In order to collect the drops, a funnel sampling device (11) has been constructed. The position of the funnel device inside the column is adjustable. The funnel is made of glass with an inner maximum diameter of 70 mm, thus only drops moving near the column wall pass the funnel without being collected. Inside the funnel, a small volume of dispersed phase is kept just above the funnel neck in order to allow for drop coalescence. With a second precision syringe pump (7b) the dispersed phase is withdrawn. Before each measurement, the phase volume is exchanged twice generating drops of a given initial concentration to remove the material created during the last run. The actual drop phase is then collected (3b). 200 µL are needed for one gas chromatography analysis. For concentration analysis, a HEWLETT PACKARD 5890 gas chromatograph (GC) was used. Fig. 3 shows the calibration curve performed in the concentration range between 0.03 g/L and 30 g/L. The accuracy of the GC measurements is ± 5-8 %. A quasi-linear power law function can be found between the integrator peak area and the sample acetone concentration in toluene.

Position of Fig. 3

The sample collection procedure is then repeated for another contact time. This is realized by adapting the position of the funnel device. 10 different contact times have been realized for each initial solute concentration.
The continuous phase was changed if 1% of the initial solute concentration have been transferred from the dispersed to the continuous phase.

3. Results and discussion

At first, velocity measurement results for drops without acetone are presented for different drop diameters. The acceleration behaviour and the terminal drop rise velocity are shown; the latter is compared with literature data.

Then, the results for instantaneous drop rise velocity with accompanied mass transfer are presented for different initial solute concentrations. The drop diameter here is $d_P = 2$ mm. In section 3.3, the mass transfer measurements are presented, using the same initial concentrations as for the velocity measurements. In section 3.4, velocity and concentration results are correlated via the contact time.

3.1 Velocity measurements without mass transfer

Five different drop diameters from 1 to 3 mm in 0.5 mm steps have been investigated. For each diameter, at least 10 sequences have been considered for statistical evidence. If the drop is detached from the nozzle tip, the drop shape is oscillating in the vertical direction. Fig. 4 shows an example of a 3 mm drop which detaches from the nozzle tip and deforms from oblate to prolate shape. The lower the drop diameter is, the faster the shape oscillation is dampened by the surrounding fluid.

**Position of Fig. 4**

For velocity measurements without mass transfer, the terminal drop rise velocity is reached within short time (< 1 s). Fig. 5 shows the transient drop rise velocity as a function of time for different drop diameters. The figure shows excellent reproducibility for all diameters since 10 sequences have been plotted per diameter. Drops up to 2 mm accelerate immediately to a constant terminal velocity. These drops have nearly spherical shape. Drops larger than 2 mm accelerate to a certain pseudo-terminal velocity, but then start to deform. This deformation leads to a higher drag coefficient, the velocity is reduced and oscillates around a lower velocity value. Later on, the drops collide with the column wall because they leave the vertical pathway due to deformation. Additionally, Fig. 5 compares the transient drop velocity of the five different drop sizes with the calculated values from the equation of motion. For unsteady motion, the force balance equation is

$$ F_I = F_G - F_B - F_D, $$

(1)
where \( F_I \) is the inertia term, \( F_G \) the gravity force, \( F_B \) the buoyancy force and \( F_D \) the drag force. Equation (1) leads to a differential equation for the relative velocity \( v_P \) between drop and fluid with the drag coefficient \( C_D \), a coefficient \( \alpha \) which takes into account the acceleration of surrounding fluid (virtual mass force), the densities of both phases and the drop diameter \( d_P \) as parameters:

\[
\frac{dv_P}{dt} = \frac{\Delta \rho \cdot g}{\rho_p + \alpha \rho_\infty} - C_D \frac{\rho_d}{\rho_p + \alpha \rho_\infty} \frac{3}{4} \frac{v_P^2}{d_P} 
\]

Equation (2) is solved numerically using the drag coefficient model by Hamielec et al. (1963):

\[
C_D = \frac{3.05 \left( 783 \mu^* + 2142 \mu^* + 1080 \right)}{\left( 60 + 29 \mu^* \right) \left( 4 + 3 \mu^* \right) \cdot Re^{0.74}}
\]

with \( 4 \leq Re \leq 100 \) and the viscosity ratio \( \mu^* \). Of course, the model originally predicts the drag coefficient in steady state and was not intended to be used for unsteady motion. Nevertheless, there is excellent agreement between experiments and numerical solution. For the 1 and 1.5 mm drops, the Reynolds number is below 100, but the corresponding Reynolds number of larger drops exceeds the proposed limit by Hamielec et al. Anyhow, the data show good agreement for the acceleration period for the whole diameter range. When the acceleration is over, the oscillation influences significantly the drag coefficient of larger drops \( (d_P > 2 \text{ mm}) \), and the velocity decreases to a lower value. In this period, the terminal velocity is not accurately predicted by the model.

**Position of Fig. 5**

The drag coefficients corresponding to the terminal velocity are plotted in Fig. 6 as a function of Reynolds number. For comparison, experimental data from Keith & Hixson (1955) and Modigell (1981) are also plotted in the figure. The drag coefficient of drops with liquid/liquid interface should lie between the two limiting curves

a) for rigid particles (Brauer & Mewes, 1972), \( \mu^* \to \infty \)

\[
C_D = \frac{24}{Re} + \frac{4}{Re^{0.5}} + 0.4
\]

b) for spherical bubbles (Brauer, 1979), \( \mu^* \to 0 \)
Position of Fig. 6

Fig. 6 shows that the experimental data of this study fulfill the condition. The data from Keith & Hixson show higher values for the drag coefficient and therefore lower terminal velocities compared to our results. Modiegell’s data show even higher values for the drag coefficient: they lie on the curve for a rigid sphere. This leads to the assumption that both systems might have been impure. Impurities decrease the mobility of the interface. The inner circulation gets weaker or disappears, the interfacial velocity decreases and therefore the drag coefficient increases. The comparison shows the need for avoiding impurities of all kind in the system. The Marangoni effect is an interfacial phenomenon which results from convection patterns due to interfacial tension gradients. A reduced mobility of the interface caused by impurities falsifies the effect of Marangoni convection. The detection of a reacceleration (see next section) would not be possible because an impure drop will accelerate only to the terminal velocity of a rigid sphere.

3.2 Velocity measurements with mass transfer

Different amounts of solute were added to the toluene drops. Six different initial solute concentrations have been realized ($c_{A0} = 30, 15, 7.5, 3.75, 1.8, 0.9 \text{ g/L}$). The drop diameter for all measurements was 2 mm. As the study from the previous section shows, effects of drop deformation on the velocity are negligible for this diameter. The general data acquisition procedure is the same as in the last section. Fig. 7 shows two pathways of a 2 mm drop, on the left side without acetone, on the right side with an initial concentration of 30 g/L acetone. Whereas an unloaded drop rises vertically on a straight line, the effect of Marangoni convection on the drop path when acetone is added can clearly be seen: the drop oscillates around its vertical rise axis on small length scale right from the start.

Position of Fig. 7

In addition to that, the transient vertical velocities show concentration dependent behaviour as can be seen in Fig. 8 where the vertical drop velocities are plotted as a function of time for different initial solute concentrations. For

$$C_D = \frac{16}{Re} + 14.9 Re^{-0.78} \left( \frac{1}{1+10 Re^{-0.6}} \right). \quad (5)$$
convenience, only one sequence for each initial solute concentration has been plotted. Similar to the velocity of unloaded drops (see Fig. 5), the behaviour was reproducible in all sequences. For comparison, a sequence for a drop without added solute ($c_{\text{A,0}} = 0$ g/L) and the terminal velocities for a rigid sphere and a spherical drop with freely moving interface obtained from own CFD simulations are given in the figure as well.

**Position of Fig. 8**

For concentrations larger than 1.8 g/L, the drops accelerate in a first step to the terminal velocity of a rigid sphere with identical physical parameters (which is approximately 56 mm/s). Following the discussion of Fig. 1, this is due to interfacial convection patterns – the Marangoni effect is strong and dominating. The relative velocity between drop and continuous phase is reduced, the inner circulation is displaced by the flow patterns induced by Marangoni convection. When acetone is transferred to the surrounding fluid and its concentration in the drop and along the interface is reduced, the Marangoni effect becomes weaker, the internal circulation restarts and so the drop reaccelerates. The point of reacceleration is the earlier the lower the initial solute concentration is. For 1.8 g/L, the Marangoni effect is not strong enough to reduce the velocity to the value of a rigid sphere. For 0.9 g/L, the drop accelerates to an even higher velocity, but the value of a drop with freely moving interface is not reached. This behaviour cannot be explained without taking into account the solute concentration inside the drop for a given contact time (see section 3.3). The reason why the velocities after reacceleration in Fig. 8 do not reach the value of a drop without added solute is another interesting effect: when the reacceleration begins, the drops leave their vertical axis, break out and – later – collide with the column wall. Henschke (2004) likewise observed drop-wall collisions in his experiments after strong transverse motions of rising toluene drops with simultaneous mass transfer.

The breakout effect is shown quantitatively in Fig. 9 where the horizontal drop position $y$ is plotted as a function of time. For convenience, only one sequence per initial concentration has been plotted. The breakout direction is randomly, the paths plotted in Fig. 9 have been chosen arbitrarily. Corresponding to the reacceleration time, the breakout is the earlier the lower the initial concentration is. Obviously, the point of reacceleration indicates the beginning of the end of Marangoni convection dominance. The inner circulation restarts inside the drop. Apparently, the location where the inner circulation begins is arbitrary, i.e. that in one part of the drop the inner circulation is still blocked whereas in another part it can redevelop freely. This leads to a pressure gradient around the drop interface and the drop breaks out from its axial pathway. The breakout time is highly
reproducible, i.e. the breakout point lies within a small time range, see Fig. 10. Additionally, the drop breaks out to the left as often as to the right (breakout in z-direction could not be quantified because only one camera has been used).

**Position of Fig. 9**

**Position of Fig. 10**

### 3.3 Mass transfer measurements

Fig. 11 shows the dimensionless mean concentration $c^* = \frac{c_A}{c_{A,0}}$ of acetone in toluene as a function of the Fourier number. The Fourier number is calculated with the contact time $t$. The contact time $t$ is the sum of the drop formation time $t_f = 0.84$ s, the holding time $t_h$ (time between end of formation and detachment, $t_h = 0.2$ s) and the drop rising time $t_r$. Acetone is transported from the drop to the surrounding fluid, therefore the mean drop concentration decreases when the Fourier number increases. The first measurement point represents a funnel distance of 25 mm from the nozzle tip which is 2.5 % of the column height, but more than 50 % of mass transfer is completed. Lower distances of the funnel device from the nozzle tip are technically not feasible. The curve of an initial solute concentration of 30 g/L shows the fastest mass transfer velocity. If the initial solute concentration is decreased to 15 g/L, 7.5 g/L and then 3.75 g/L respectively, the mass transfer velocity decreases continuously. This is apparently due to Marangoni convection which is more pronounced when the initial concentration is high. But surprisingly, if the initial solute concentration is reduced to 1.8 g/L, the mass transfer velocity increases again. The mass transfer rate is even higher than for 7.5 g/L and after $F_o = 1.6 \cdot 10^{-2}$ even higher than for 30 g/L. If the initial solute concentration is reduced to 0.9 g/L, the effect is even more pronounced.

In Fig. 11, results from CFD simulations by Schulze et al. (2003) in the same system but with constant interfacial tension are given for comparison. In this case, the dimensionless mean concentration is independent from the concentration gradient at the interface, i.e. the curves for different initial solute concentrations would coincide. The interesting conclusion which can be drawn from Fig. 11 is, that in comparison with the numerical data the mass transfer in the real system is – due to Marangoni convection – always enhanced for all investigated initial solute concentrations.

**Position of Fig. 11**
Fig. 12 highlights the dependence of the mass transfer rate on the initial solute concentration: the Fourier number at which 90% of the mass transfer is completed, $Fo_{90}$, is plotted as a function of the initial solute concentration $c_{A0}$. Linking Fig. 8 with Fig. 11, the following explanation is proposed: if the initial concentration is relatively low ($c_{A0} \leq 1.8 \text{ g/L}$), the drop accelerates to a higher velocity compared to a rigid sphere but to a lower velocity compared to a drop with freely moving interface. This could be a hint that there is both: Marangoni convection patterns and some kind of internal circulation. Obviously, this configuration does not reduce the mass transfer rate. If the initial solute concentration is higher ($1.8 \text{ g/L} < c_{A0} < 15 \text{ g/L}$), the Marangoni convection increases which leads to interfacial velocity vectors opposite to the external flow. This movement of the interface reduces on one hand the drop rise velocity, and on the other hand it hinders the internal circulation. This blockage effect obviously decreases the mass transfer rate, $Fo_{90}$ has a local maximum. If Marangoni convection is so strong that the hindered internal circulation is overcompensated, $Fo_{90}$ decreases again. Now, only the chaotic flow structures induced by interfacial instability influence the mass transfer. We suppose that the mass transfer rate is even more enhanced if the initial solute concentration is increased to values above $30 \text{ g/L}$. If the initial solute concentration tends to zero, we expect that $Fo_{90}$ tends to a certain constant value. But experiments with very low initial concentrations are bounded by the measurement range of the gas chromatography analysis.

The numerical results for the same system but with constant interfacial tension by Schulze et al. (2003) are also given for comparison in Fig. 12. In this case, $Fo_{90}$ is more than two times higher than for the experiments, i.e. the mass transfer rate in the system with Marangoni convection is more than twice as fast as for the system with constant interfacial tension.

Position of Fig. 12

3.4 Correlation of drop velocity and mass transfer

The results from the two previous sections can now be correlated. The drop velocity, the breakout event and the solute mean concentration are expressed as a function of contact time. We suppose that the Marangoni convection dominated regime ends if a certain critical mean concentration of acetone in the toluene drop is reached, regardless of the initial solute concentration. We locate the end of the Marangoni convection dominated regime between the reacceleration and the breakout event. For both events, a respective mean solute concentration can be found. The general procedure is shown in Fig. 13 exemplarily for one drop sequence. The time $t_v$ indicates the point of reacceleration from the velocity plot. $t_y$ is the time when the drop breaks out from the vertical axis. $c_v(t_v)$ and $c_y(t_y)$ are the corresponding mean concentrations. Since multiple sequences of drop
paths have been recorded to determine the instantaneous velocity for every initial solute concentration, the procedure described above is repeated correspondingly.

**Position of Fig. 13**

$c_i(t_i)$ and $c_j(t_j)$ are plotted as a function of the initial solute concentration $c_{A,0}$ in Fig. 14. The figure shows that most of the data can be found in the concentration range $c_{A,cr} = 0.5 \text{ g/L} \pm 0.2 \text{ g/L}$. Only the data for $c_{A,0} = 1.8 \text{ g/L}$ are significantly higher and nearly completely outside of $c_{A,cr}$. This is probably due to the fact that the determination of the reacceleration time was quite difficult (see Fig. 8) and the breakout effect takes place nearly immediately after the detachment. However, for the lower initial concentration $c_{A,0} = 0.9 \text{ g/L}$, the same concentration range $c_{A,cr} = 0.5 \text{ g/L} \pm 0.2 \text{ g/L}$ can be found. In this case, it should be mentioned that $c_i(t_i)$ is always higher than the correspondent $c_j(t_j)$ value, i.e. the breakout effect takes place earlier than the reacceleration which is not the case for all other initial solute concentrations. Again, the determination of the reacceleration was quite difficult. Anyway, the detection of the breakout effect was more distinct in most of the cases compared to the identification of the reacceleration.

The result in Fig. 14 can be interpreted as follows: if the initial concentration is higher than the critical value $c_{A,cr}$ Marangoni convection is not dampened and strong enough to develop. The drop velocity is reduced and the mass transfer behaviour is according to Fig. 11. When the mean solute concentration decreases to $c_{A,cr}$, the Marangoni convection gets weaker, the drop can reaccelerate and finally breaks out. If the initial concentration is smaller than $c_{A,cr}$, the Marangoni effect is probably so weak that it will presumably have no significant effect on the drop rise velocity. Concerning the mass transfer rate in this case, Fig. 12 suggests that Marangoni convection still has enough influence even if the solute mean concentration is below $c_{A,cr}$, and the mass transfer rate is comparable to relatively high initial solute concentrations.

**Position of Fig. 14**

4. Conclusions

An intense study of transient drop rise velocity and mass transfer has been carried out for the system toluene/acetone/water. Measurements of the rise velocity of toluene drops without added surfactants or solute in a diameter range of 1 - 3 mm were made using a high-speed camera. Results show that drops with a diameter up
to 2 mm accelerate to a constant terminal drop rise velocity. The results are in excellent agreement with the numerical solution of the equation of motion using the drag coefficient model of Hamielec et al. (1963). Larger drops show different behaviour: after acceleration to a pseudo-terminal velocity which is well predicted by the equation of motion, the velocity decreases and oscillates around a lower value until the drops collide with the column wall. The terminal velocities and with that the drag coefficients were compared with literature data. Results reveal that the terminal velocity can be used to verify if the system is contaminated since impurities are able to decrease the terminal velocity to that of a comparable rigid sphere.

The behaviour of the system changes dramatically when a solute is added to the toluene phase. In this study, acetone is used. For higher initial solute concentrations, the drops accelerate to a pseudo-terminal velocity which is typical for rigid spheres. This is due to the Marangoni effect, i.e. the motion of the interface tends to minimize interfacial tension gradients which reduces the overall relative velocity between drop and surrounding fluid. When Marangoni convection gets weaker due to the transfer of acetone into water, the drops reaccelerate because internal circulation restarts. Immediately after reacceleration, the drops break out from their vertical path due to a pressure gradient resulting from an asymmetric initialization of internal circulation.

Comparisons of our concentration measurements with CFD simulations by Schulze et al. (2003) in an analogous system but with constant interfacial tension show that the mass transfer in the real system is generally enhanced due to Marangoni convection. Further on, the mass transfer measurements indicate that the mass transfer rate for lower initial solute concentrations can be as high as for higher initial solute concentrations. For higher concentrations the mass transfer is dominated by Marangoni convection patterns, for lower concentrations, mass transfer is dominated by both, internal circulation and Marangoni convection. In the transition region, the mass transfer rate shows a minimum.

The results of mass transfer and velocity measurements are then correlated via the contact time of the drops with the continuous phase. It can be shown that the end of Marangoni convection dominance starts for the investigated system when the remaining mean solute concentration reaches a critical concentration range of $c_{Acet} = 0.5 \text{ g/L} \pm 0.2 \text{ g/L}.$

The present paper shows that our method is principally useful to determine a critical concentration range where Marangoni convection does play a significant role in the mass transfer process. Future objectives will be to
generalize the dependencies of the mass transfer rate on Marangoni effects. Thereto it is planned to change the parameters drop diameter, viscosity ratio and mass transfer direction.

5. Nomenclature

\( c_{A,0} \) initial solute concentration (g/L)

\( \bar{c}_A \) solute mean concentration (g/L)

\( c^* \) related concentration \( \bar{c}_A/c_{A,0} \) (-)

\( C_D \) drag coefficient (-)

\( d_P \) drop diameter (mm)

\( D_{ad} \) diffusion coefficient in dispersed phase (m²/s)

\( F \) force (N)

\( g \) acceleration of gravity (m/s²)

\( R \) drop radius (m)

\( t \) time (s)

\( v_P \) relative velocity (m/s)

\( \alpha \) acceleration factor

\( \vartheta \) temperature (°C)

\( \mu \) dynamic viscosity (Pa s)

\( \mu^* \) viscosity ratio \( \mu_P/\mu_c \) (Pa s)

\( \rho \) density (kg/m³)

\( \Delta \rho \) density difference (kg/m³)

**Greek**

\( \alpha \) acceleration factor

\( \vartheta \) temperature (°C)

\( \mu \) dynamic viscosity (Pa s)

\( \mu^* \) viscosity ratio \( \mu_P/\mu_c \) (Pa s)

\( \rho \) density (kg/m³)

\( \Delta \rho \) density difference (kg/m³)

**Dimensionless numbers**

\( Fo \) Fourier number \( Fo = t D_{ad}/R^2 \)

\( Re \) Reynolds number \( Re = (v_P d_P \rho_*)/\mu_c \)

**Subscripts**

\( A \) solute
6. Acknowledgement

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7. References


Bakker, C.A.P., Fentener van Vlissingen, F.H. & Beek, W.J. (1967). The influence of the driving force in liquid-liquid extraction - a study of mass transfer with and without interfacial turbulence under well-defined conditions. Chemical Engineering Science, 22(10), 1349-1355


**Figure captions**

Fig. 1: Drop with toroidal internal circulation (left), principle of development of Marangoni convection patterns (right).

Fig. 2: Experimental setup for velocity and concentration measurements of single rising drops. (1) column, (2) jacket, (3a, b) dispersed phase sample, (4) gear pump, (5) thermostat, (6) glass nozzle, (7a, b) Hamilton pumps, (8) solenoid device, (9) saturation tank, (10) high speed camera, (11) funnel device, (12a, b) computer for control

Fig. 3: Calibration curve for concentration measurements. GC peak area as a function of acetone concentration in toluene.

Fig. 4: Detachment of a toluene drop from the nozzle tip.
   a: drop at resting nozzle tip
   b: drop elongation whilst nozzle is pulled downwards
   c: oscillation, oblate spheroid
   d: oscillation, prolate spheroid

Fig. 5: Rise velocity of pure toluene drops in water as a function of time for different drop diameters. Comparison of experimental results (●), 10 sequences per diameter, with equation of motion (— - -), Equation (2) with $\alpha = 0.75$.

Fig. 6: Drag coefficient $C_D$ of pure toluene drops as a function of Reynolds number. Comparison of own experimental values with data of Modigliani (1981) and Keith & Hixson (1955).

Fig. 7: Effect of Marangoni convection on vertical pathway of toluene drops in water ($d_P = 2$ mm). Straight pathway when no solute is added (left), small length-scale oscillation when $c_{A,0} = 30$ g/L (right).

Fig. 8: Drop rise velocity of toluene drops in water as a function of time for different initial solute concentrations ($d_P = 2$ mm). The terminal drop rise velocities of a rigid sphere and a spherical drop with freely moving interface obtained from own CFD simulations are given for comparison.
Fig. 9: Breakout effect of rising toluene drops in water for different initial solute concentrations \((d_P = 2 \text{ mm})\). Deviation from column axis is expressed in \(y\)-position as a function of time according to the coordinate system in Fig. 2.

Fig. 10: Reproducibility of breakout effect, 15 paths of toluene drops with \(d_P = 2 \text{ mm}\) and \(c_{A,0} = 7.5 \text{ g/L}\). Deviation from column axis is expressed in \(y\)-position as a function of time according to the coordinate system in Fig. 2.

Fig. 11: Dimensionless mean solute concentration \(c^*\) as a function of Fourier number for different initial solute concentrations \((d_P = 2 \text{ mm}, \text{ mass transfer direction } d \rightarrow c)\). CFD results by Schulze et al. (2003) for the system toluene/acetone/water with constant interfacial tension are given for comparison.

Fig. 12: The Fourier number indicating that 90% of mass transfer is completed, \(F_{90}\) as a function of initial solute concentration \(c_{A,0}\). The corresponding CFD results by Schulze et al. (2003) for the system toluene/acetone/water with constant interfacial tension are given for comparison.

Fig. 13: Scheme for the correlation of transient drop rise velocity and \(y\)-position with the solute mean concentration \(\bar{c}_A(t)\).

Fig. 14: Critical concentration range as a function of initial solute concentration. \(c_v\): concentration at time \(t_v\), i.e. when drop reacceleration begins. \(c_y\): concentration at time \(t_y\), i.e. when drop breaks out from vertical axis.

**Table caption**

Table 1

Physical parameters for \(\vartheta = 25^\circ C\)
<table>
<thead>
<tr>
<th>Substance</th>
<th>ρ [kg/m³]</th>
<th>η [10⁻⁴Pa s]</th>
<th>Dₐ [10⁻⁹m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>862.3</td>
<td>5.52</td>
<td>2.9</td>
</tr>
<tr>
<td>water</td>
<td>997.02</td>
<td>8.903</td>
<td>1.25</td>
</tr>
<tr>
<td>acetone</td>
<td>784.4</td>
<td>3.04</td>
<td>–</td>
</tr>
</tbody>
</table>
internal circulation

Marangoni convection patterns

Fig. 1
Figure

Fig. 2
Fig. 3
Fig. 4
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Fig. 5
Figure

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This figure illustrates the drag coefficient $C_D$ as a function of $Re$. The graph shows data points for different values of $d_p$ (mm) and author contributions:
- $2, 2.5, \ldots, 4$ by Modigell
- $1.5, 2, \ldots, 4$ by Keith & Hixson
- $1, 1.5, \ldots, 3$ for this study

The equation $C_D \rightarrow 0$ as $Re \rightarrow \infty$ is indicated by Eq. 3.

Fig. 6
\[ c_{A,0} = 30 \text{ g/L} \]

\[ x = 40 \text{ mm} \]

\[ x = 0 \]

Fig. 7
Fig. 8
Figure

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$c_{A,0} = 0.9 \text{ g/L}$

$d_P = 2 \text{ mm}$
$d_p = 2\, \text{mm},$

$c_{A,0} = 7.5\, \text{g/L}$
Fo = $t \frac{D_{Ad}}{R^2}$

cA,0 = 0.9 g/L

cA,0 = 1.8 g/L

90% mass transfer completed

CFD, $\sigma$ = const. (Schulze et al., 2003)

Fig. 11
Figure

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![Graph showing Fourier number $F_{O90}$ vs. initial solute concentration $c_{A,0}$ [g/L]. The graph includes a dotted line for CFD, $\sigma = $ const. (Schulze et al., 2003).]

Fig. 12
Fig. 13
Figure

Fig. 14