Sedimentation Behavior of Droplets for the Reactive Extraction of Zinc with D2EHPA

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The sedimentation characteristics of the reactive standard test system zinc + D2EHPA are investigated in this work. Experiments with single droplets rising in a stagnant continuous phase have been carried out. The concentration of D2EHPA, zinc, and sulfuric acid as well as the diameter of the droplets are varied. The velocity of droplets is observed to be transient for several seconds. High mass-transfer rates increase the velocity of single droplets for the case of reactive extraction whereas for physical systems contrary behavior is observed. Therefore, droplets seem to behave principally different in reactive and physical extraction. This is explained by the interfacially active properties of D2EHPA. © 2009 American Institute of Chemical Engineers *AIChE J*, 56: 160–167, 2010
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Introduction

Process intensification has been of great industrial interest in recent years. An example already frequently applied in industry for metal refining is reactive extraction.[1] Adding a reaction to an extraction process leads to an increased selectivity and, therefore, to an increased efficiency of the overall process. Columns, centrifuges, or mixer-settlers are used in industrial applications.[2] The design of industrial-scale columns can be successfully achieved by a newly developed method based on simple lab-scale experiments.[3–6] In these experiments, all phenomena acting on each droplet in a real column are individually investigated in corresponding small laboratory cells: sedimentation, mass transfer, drop breakage,

and coalescence. As a key variable the sedimentation velocity determines the residence time of the droplets in the column and is, therefore, an important factor for the performance of the column and its accurate modeling. In the literature, many models are available for the calculation of the velocity of single droplets. They are mostly of empirical character. Kumar has collected most of the correlations relevant for solvent extraction.[7] Nevertheless, these models often neglect the influence of contaminants while it is known that these components change the properties of the interface. Thereby the contaminants influence the internal circulation of the droplet which in turn has a strong influence on the sedimentation velocity. Even experiments with identical systems from different authors can, therefore, be hardly compared, since usually different impurities were present.

Standard test systems for solvent extraction as proposed by the European Federation of Chemical Engineering

(EFCE) will be used here to investigate the sedimentation behavior.[8] The sedimentation behavior of the physical standard test systems has been investigated in detail.[4,9–11] Hence, it is surprising that there are only few data available in the literature for the reactive standard test system.[12] The aqueous phase of the reactive test system consists of water, zinc sulfate, and sulfuric acid whereas the solvent isododecane and the cation exchanger D2EHPA (di(2-ethylhexyl) phosphoric acid) form the organic phase. D2EHPA is a surface-active component and extracts zinc via an interfacial reaction[12–15]:

$$Zn^{2+} + 1.5\ \overline{R_2H_2} \leftrightarrow \overline{ZnR_2RH} + 2H^+ \tag{1}$$
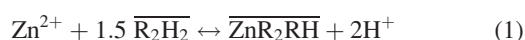
Here the bars indicate components in the organic phase. To the author's knowledge, Mack is the only one who has measured sedimentation velocities for the reactive standard test system.[16] He measured the velocity of the droplets in a conical cell with a counter-flow of continuous phase. When the counter flow balances the sedimentation velocity, the droplet levitates. Measuring the overall flow rate of the continuous phase and dividing this by the area of the cell in the levitating position, the author calculated the velocity. However, he did not account for the velocity profile of the continuous phase in the cell. Thus, his values can only indicate the order of magnitude and the relative order of sedimentation velocities at different conditions.

Thus, the goal of this research work was to investigate the sedimentation behavior of droplets of the reactive standard test system, to provide an experimental database for further simulations and to study, if there are principal differences between the fluid dynamics of single droplets in physical and reactive extraction systems. By doing this, it can be better understood what is going on in the droplets and at their interface. Comparison to a suitable model will allow systematic discussion of variations. Also the model results will give other researchers the opportunity to simulate drop behavior of the reactive standard test system without doing experiments themselves.

Modeling the Sedimentation of Single Droplets

Depending on their diameter, droplets show different behavior while rising in a continuous phase (Figure 1). Drops with a small diameter behave like rigid spheres (I). With increasing diameter the shear force at the interface increases and a circulation inside the drop is induced (II) which leads to an increased velocity as compared to rigid drops. If the diameter rises further, the droplets start to visibly loose their spherical shape. Simultaneously, the drops start to oscillate (III). Finally, the region of deformed drops is reached where drops move wobbling through the continuous phase (IV).

Especially, the transition between regions I and II is strongly influenced by impurities present in the system as well as the intensity of mass transfer.[4] For typical extraction systems these effects are most pronounced in range of drop diameters around 2 to 3 mm. This is exactly the region, which is recommended for optimal performance of extraction columns.[17] As a consequence, it is highly important to catch these effects when modeling sedimentation as a basis for column design. From this discussion it is also clear that
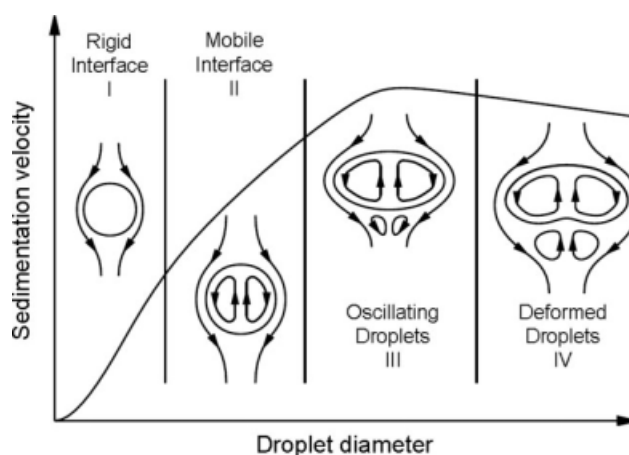

Figure 1. Drop behavior as a function of drop diameter.

any column design requires experiments to catch these effects. Actually it is generally desired to mimic the technical extraction system as closely as possible in the sedimentation experiments. It is also obvious that models used for describing drop sedimentation are required to contain suitable parameters if these effects are to be captured.

As mentioned earlier, there are many empirical relationships to calculate the velocity of droplets. Most of the models do not have any adjustable parameters and do not include the effect of mass transfer. Henschke as well as Wegener et al. have independently investigated the influence of mass transfer on the sedimentation velocity of a single droplet.[4,18] Henschke observed that mass transfer decreases the sedimentation velocity as shown in Figure 2.[4] His results indicate that mass transfer leads to a partial reduction of the internal circulation so that the drops slow down. Therefore, Henschke developed his own model, which will be further used to correlate the experimental results. Thus, this model shall be presented in slightly more detail, also because it has until now only been published in German. Henschke's idea is to use different models for spherical, oscillating, and deformed droplets and to combine them by appropriate crossover functions into a single model which is applicable over the entire diameter range.

For the regions I and II in Figure 1, the behavior of spherical drops is represented by the two limits of a sphere with rigid interface and ideally mobile interface. In case of a rigid sphere, a simple force balance yields the following dimensionless equation[4]:

$$Ar = \frac{3}{4} Re_{rigid}^2 c_w \tag{2}$$

where the two dimensionless numbers are the Archimedes number Ar and the Reynolds number Re:

$$Ar = \frac{\rho_c \Delta\rho g d^3}{\eta_c^2} \tag{3}$$

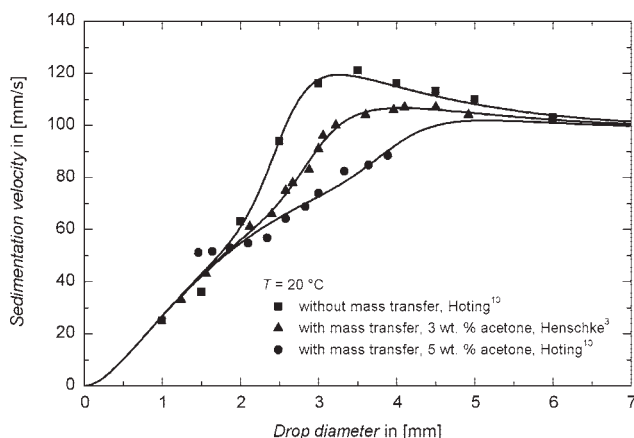$$Re_{rigid} = \frac{\rho_c v_{rigid} d}{\eta_c} \tag{4}$$

Figure 2. Influence of mass transfer in a physical extraction system.

Henschke et al. express c_w as function of the Archimedes number[19]:

$$c_w = \frac{432}{Ar} + \frac{20}{Ar^{1/3}} + \frac{0.51 Ar^{1/3}}{140 + Ar^{1/3}} \quad \text{for } 0 < Re < 3 \times 10^5 \quad (5)$$

For the calculation of the sedimentation velocity for drops with an ideally mobile interface, Henschke uses the following equation[4]:

$$Re_{\infty,\text{ideallymobile}} = \frac{Ar}{12(0.065 Ar + 1)^{1/6}} \quad (6)$$

From Eqs. 5 and 9 Henschke derives an equation covering both regions I and II where the crossover is mainly determined by the diameter d_{sw} which corresponds to the diameter where the drop behavior switches from rigid to circulating.

$$Re_{\infty,\text{spherical}} = (1 - f_1^*) Re_{\infty,\text{rigid}} + f_1^* Re_{\infty,\text{ideally mobile}} \quad (7)$$

The crossover factor f_1^* is calculated with a modified Hadamard-Rybczynksi factor K_{HR}^*[20]:

$$f_1^* = 2(K_{HR}^* - 1) \quad (8)$$

with

$$K_{HR}^* = \frac{3(\eta_c + \eta_d/f_2)}{2\eta_c + 3\eta_d/f_2} \quad (9)$$

and

$$f_2 = 1 - \frac{1}{1 + (d/d_{sw})^{\alpha_{sw}}} \quad (10)$$

Henschke finds that the value of α_{sw} which scales the steepness of the cross over can be set constant to 10. The parameter d_{sw} has to be fitted to experimental sedimentation data. With the limits of $d_{sw} \to \infty$ and $d_{sw} \to 0$ the ideal limits of a rigid and

of an ideally mobile interface are retained, respectively. With the Reynolds number for a spherical droplet, the velocity can be calculated from:

$$v_{\text{spherical}} = \frac{Re_{\infty,\text{spherical}} \eta_c}{\rho_c d} \quad (11)$$

In the region of deformed droplets, Henschke uses an empirical approach which is given by Clift et al.[21]:

$$v_{\text{deformed}} = \sqrt{\frac{\Delta \rho g d}{2\rho_c}} \quad (12)$$

A theoretically founded correlation is again used for the region III.

$$v_{\text{oscillating}} = \sqrt{\frac{2 a_{os} \sigma}{\rho_c d}} \quad (13)$$

This approach has also been used by Maneri and contains the parameter a_{os} which has to be fitted to experimental data.[22] A smooth transition from oscillating to deformed droplets is realized by Henschke with[4]:

$$v_{\text{oscillating or deformed}} = \left(v_{\text{oscillating}}^8 + v_{\text{deformed}}^8 \right)^{\frac{1}{8}} \quad (14)$$

The following final equation for the calculation of the sedimentation velocity of a droplet over the entire range of diameter is then used:

$$v_\infty = \frac{v_{\text{oscillating or deformed}} v_{\text{spherical}}}{\left(v_{\text{oscillating or deformed}}^{a_{\text{tot}}} + v_{\text{spherical}}^{a_{\text{tot}}} \right)^{\frac{1}{a_{\text{tot}}}}} \quad (15)$$

This smooth function contains the last parameter of the model, a_{tot}, which characterizes the sharpness of the transition between the velocities of spherical and nonspherical drops. In summary, this model contains three adjustable parameters which all have a clear physical interpretation. For the details of the model and for its detailed derivation, the interested reader is referred to Henschke.[4] In order to fit the model parameters to experimental data, the physical properties of the phases of the reactive standard test system are required, which here have been determined with the correlations given by Bart.[15] The parameters of the model are fitted to the results of sedimentation velocity as a function of drop diameter for each set of experimental condition as collected in Table 1.

Materials

Deionized water has been used for the continuous phase. The water quality has been checked with conductivity measurements and it was taken care that the conductivity is in the range of 0.1–3.0 μS/cm. The conductivity was checked with a conductimeter (Product SA, Wilhelm Werner GmbH, Germany). Zinc sulfate monohydrate (extra pure, $\geq$99 wt %, main contaminants: chloride, $\leq$0.005 wt %; arsenic, $\leq$0.0003 wt %; iron, $\leq$0.003 wt %; and alkali and alkaline earth metals as sulfates, $\leq$0.5 wt %) and sulfuric acid ($\geq$98

Table 1. Experimental Conditions and Parameters Fitted to Experimental Results ($\alpha_{sw} = 2$)

Experimental Settings				Model Results		
Zinc (mmol/L)	sulfuric acid (mmol/L)	pH	D2EHPA (wt %)	d_{sw} (mm)	a_{os}	a_{tot}
30	0	4.7	1	5.87	2.27	4.84
30	0	4.7	5	6.57	2.37	4.12
30	0	4.7	10	4.72	2.33	4.41
30	0	4.7	20	3.06	2.32	4.69
10	5	2.2	1	5.65	2.33	5.79
10	5	2.2	5	3.72	2.43	4.31
10	5	2.2	10	2.56	2.42	4.37
10	10	1.95	1	7.46	2.37	7.02
10	10	1.95	5	2.04	2.43	4.03
10	10	1.95	10	2.00	2.46	4.07
0	5	2.05	1	5.95	2.44	4.07
0	5	2.05	5	4.45	2.58	5.53
0	5	2.05	10	2.94	2.60	5.79
0	10	1.8	1	12.02	2.41	10.38
0	10	1.8	5	4.11	2.62	4.67
0	10	1.8	10	3.32	2.70	4.78

wt %, main contaminants: ammonium, ≤ 0.0002 wt % and selenic, ≤ 0.0001 wt %) have been purchased from Merck. D2EHPA (Baysolvex p.a.) and isododecane (technically pure) have been kindly donated by Bayer AG and by EC Erdölchemie, respectively. Solutions with the desired concentration of zinc and sulfuric acid in the continuous phase and of D2EHPA in the dispersed phase have been prepared by weight. Although the solubility of water in isododecane and vice versa is insignificant, it was taken care that the water had been saturated with isododecane and that, conversely, the isododecane saturated with water.

The aqueous zinc concentration was analyzed by titration with EDTA (ethylenediaminetetraacetate, Merck). The procedure is described by Klocker.[23] With this method, zinc concentrations can be determined with an accuracy of $\pm 2\%$. The pH in the aqueous phase was measured by a pH meter model E520 (Metrohm Herisau, Switzerland). The error in the pH measurements was 0.05 pH units.

In previous work it has been shown that a very strong test for constant system purity is a settling experiment.[17,24] Thus, to generate reproducible data, settling experiments with deionized water and isododecane have been carried out in a washing bottle with a diameter of 50 mm. One hundred fifty milliliters of the water and 75 mL of isododecane have been filled into the bottle. The bottle has been shaken for 10 s and, because of the phase ratio, isododecane was dispersed in water. Then the bottle has been placed on a table and the time was measured until only half of the interface remained occupied with drops. This settling time of water and isododecane has been determined to be between 14 and 18 s. These measurements directly indicate the impact of impurities and have been carried out weekly to maintain same quality of the material system. Whenever values outside the range indicated were observed, a fresh system has been produced.

Experimental Procedure

The sedimentation velocity of single droplets has been determined in two laboratory cells. Before the start of

experiments, the sedimentation cell in use is filled with the continuous phase. With the help of the temperature jacket, the temperature in the cell is kept constant at 20°C.

For the first experiments with 30 mmol/L zinc, a cell with a diameter of 200 mm and a total height of 900 mm was used. This shorter cell is divided in four zones, a first section with a length of 50 mm and three following sections with 100 mm in length. The first zone of 50 mm is not considered for the determination of sedimentation velocities, in order to exclude the influence of acceleration effects of the droplet formation.

It was observed that the sedimentation velocity changes with contact time between the phases. Therefore, a second, longer cell with a diameter of 150 mm and a total height of 1350 mm was used for further experiments (Figure 3). The longer cell is divided into nine sections. The first four
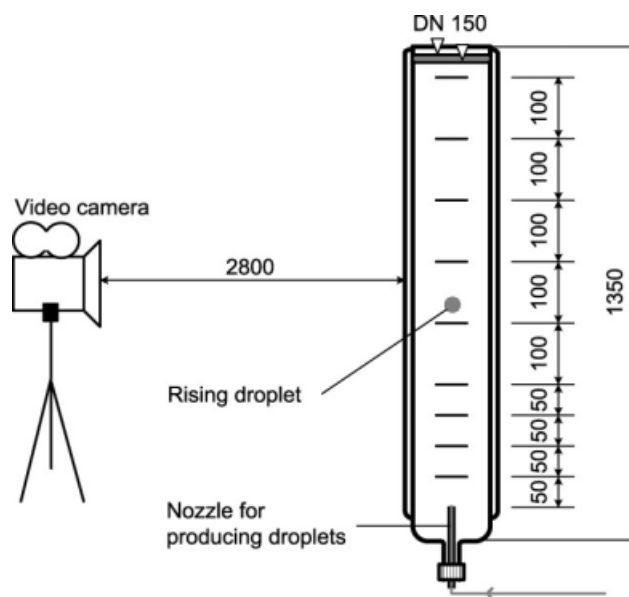
Figure 3. Sketch of the sedimentation cell.

sections have a height of 50 mm, the subsequent five parts each have a height of 100 mm. Also here the first section is not included in the analysis.

The droplets are generated with a Hamilton precision syringe drive (type Microlab M, Hamilton, Switzerland) and a glass nozzle which is inserted into the cell from below. The operation of the syringe is controlled by a personal computer with the software Visual Designer from Intelligent Instrumentation. With this device it is possible to form single droplets with an exact volume and without any secondary-droplet formation. The relative maximum error in the drop volume is 1.5% due to the manufacturers' instructions. To create different droplet diameters different nozzles with different internal diameters are necessary.

The rising of the droplets is recorded with a video camera (F10 Mark II, Panasonic, Japan) thus it is possible to determine the sedimentation velocity of the droplet in each section of the cell by evaluating the video on a frame-by-frame basis. The free software VirtualDub was used to quantify the time entering into a section and leaving a section for each drop. By dividing the height of each section by the determined time, the sedimentation velocity of the drop is calculated. For every section, at least 15 droplets have been evaluated. Droplets colliding with the wall have been explicitly noted and are excluded from the analysis. The accuracy of the determined sedimentation velocity is ± 1 mm/s.

The distance between camera and cell was 3.5 m or 2.8 m, respectively. For the longer cell, the camera was positioned at three different vertical positions, in order to minimize the distortion in determining the position of the droplets. All experimental values with 10 mmol/L zinc are obtained in the longer cell. The major dimensions of this cell can be seen in Figure 3.

Although the concentration in the continuous phase does not change significantly due to the large volume ratio of continuous phase to droplet volume, the concentration in the continuous phase was checked at the end of each series of experiments in order to be sure that the zinc concentration had not changed. As soon as the zinc concentration differed more than 3% from the target concentration the continuous phase was replaced.
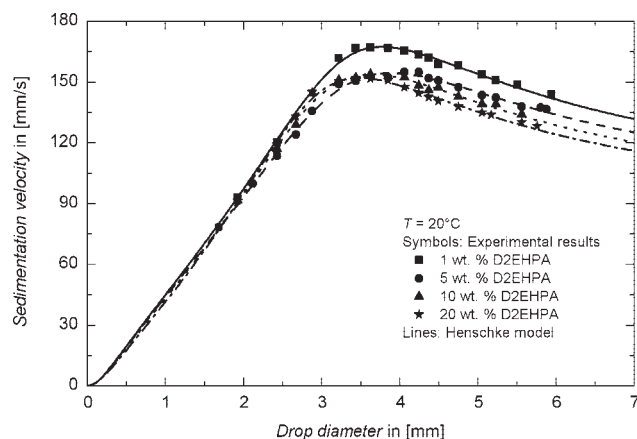

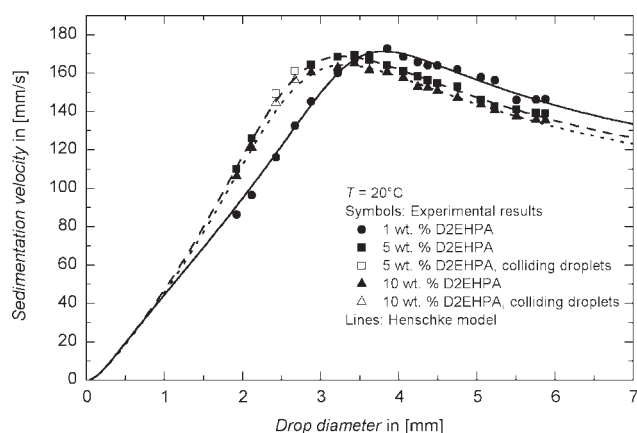**Figure 5. Sedimentation velocities for 10 mmol/L zinc.**

Modeling and Experimental Results

First the average velocities determined over the entire cell height are presented here. For both initial zinc concentrations, 10 and 30 mmol/L respectively, the influence of the D2EHPA concentration is shown in Figures 4 and 5. The symbols are experimental values whereas lines represent the model of Henschke with different parameters for each composition combination (see Table 1). The open symbols in Figure 5 represent experiments in which the droplets always collide with the wall. In the shorter cell, this phenomenon was not observed. In order to be sure that the reason is not a defect nozzle, different nozzles have been used but this left the effect unchanged. Experiments without any mass transfer do not show this behavior: All droplets (without any exception!) rise on straight paths in the cell. Therefore, this effect can be clearly attributed to mass transfer which apparently induces secondary convections inducing a horizontal component in the drop velocity.[25–27]

The experimental results show that for smaller diameters there is no systematic dependence of the sedimentation velocity on the D2EHPA concentration. For droplets in the region of oscillating or deformed drops, the sedimentation
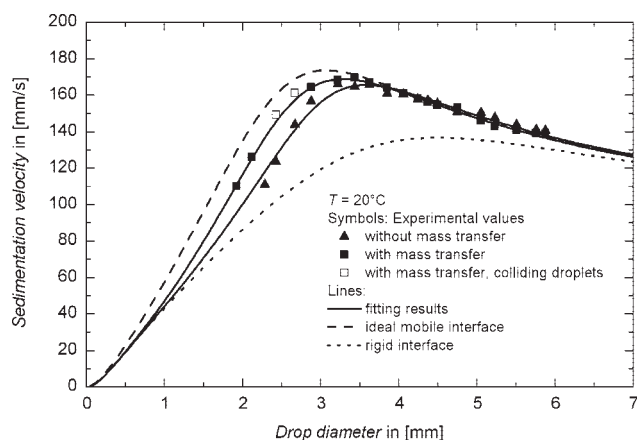

Figure 4. Sedimentation velocities for 30 mmol/L zinc.

Figure 6. Influence of reactive mass transfer on sedimentation behavior.

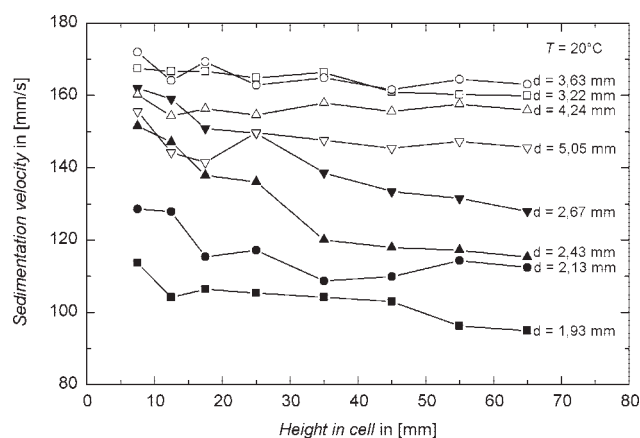**Figure 7. Transient sedimentation velocities with the drop diameter as parameter.**

Figure 8. Change in the sedimentation velocity with the drop diameter as parameter.

velocity increases with decreasing D2EHPA concentration. An explanation for this observation will follow in the further part of the article.

Experimental results have been fitted with the model of Henschke. Fitting results with α_{um} of 10 for the reactive systems did not lead to good agreement with the experimental results. Therefore, after brief analysis the value of α_{um}, it was set to 2, which leads to a smoother the transition between the rigid droplets and the droplets with internal circulation. The average deviation with the fitted Henschke model shown is less than 1%.

As mentioned in the introduction, it is known for physical extraction that mass transfer decreases the sedimentation velocity. In Figure 6 the influence of reactive mass transfer on the drop velocity can be seen. Experimental results for 0 and 10 mmol/L zinc are compared. For comparison, the curves for a drop with a rigid and an ideally mobile interface are included.

Reactive mass transfer increases the velocity of droplets for a certain range of drop diameter. Thus, the range of diameter has to be divided into two main parts: In the region II where the inner circulation plays an important role, mass transfer increases the sedimentation velocity of a single droplet. For the regions III and IV (Figure 1) where the velocity is mainly determined by physical properties, the presence of mass transfer does not significantly change the drop velocity. Compared to physical extraction (Figure 2), reactive mass transfer appears to induce different phenomena at the interface. While for physical extraction mass transfer decreases the velocity of drops, in case of reactive extraction it accelerates them in certain regions. The explication of Henschke that mass transfer reduces the inner circulation of the droplet by interfacial turbulences and, therefore, decreases also the velocity of the droplet does not explain the observations for the system zinc + D2EHPA. Thus, the behavior of the interface has to be discussed in more detail. To gain a better understanding of this effect is especially important, since drops in technical extraction processes are usually in the range of diameters where the influence on sedimentation velocity and thus residence time in an apparatus is influenced most.
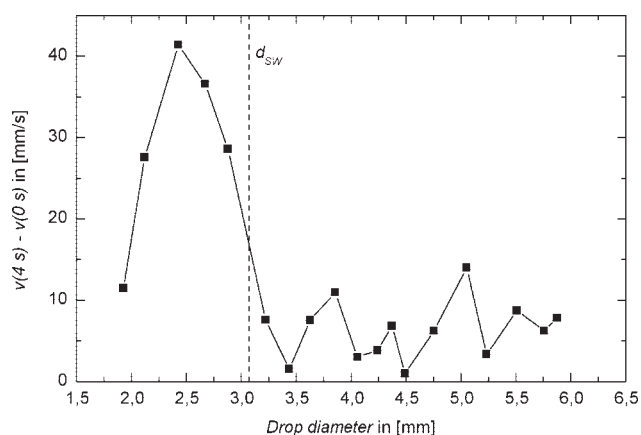
The reactive system contains already a surface-active component D2EHPA which takes part in the reaction. For the case of missing mass transfer D2EHPA will accumulate at the interface. According to the usual interpretation, the drop will have the tendency to show rigid behavior. Thus, the drop will move more slow. If zinc ions are present in the continuous phase, D2EHPA will react at the interface. At a larger part of the interface, the concentration of surfactant will be reduced and consequently a larger part of the interface will be free to transfer momentum from the continuous to the dispersed phase more easily. Therefore, an inner circulation is induced in a larger part of the droplet and the drop becomes faster. This explanation is also consistent with the model limits of drops with a rigid and an ideally mobile interface, respectively. When the drops undergo a chemical reaction, their behavior approaches that of a drop with an ideally mobile interface.

Up to here, only average velocities of the drops have been regarded. During the analysis of the sedimentation velocities, it was observed that the drop velocity changes as a function of height in the sedimentation cell. Figure 7 illustrates this behavior for 10 mmol/L zinc and 5 mmol/L sulfuric acid in
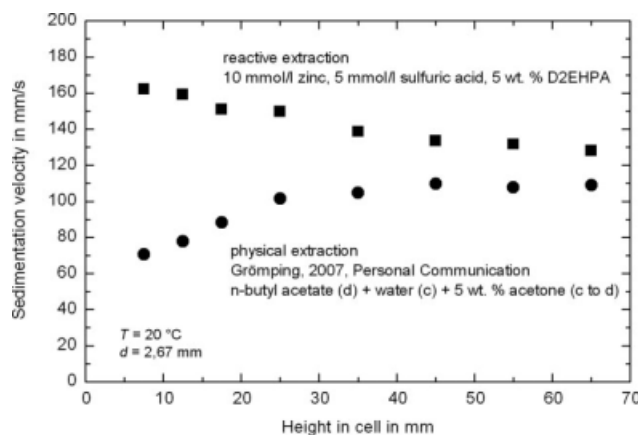

Figure 9. Transient sedimentation in a physical and reactive system.

the continuous phase. The weight fraction of D2EHPA is 5%. The height in cell is defined as the medium height of the sections in Figure 3 over which the velocity has been determined.

For all diameters, the drops slow down with increasing contact time with the continuous phase. Especially for diameters between 2 and 3 mm, the change in sedimentation velocity is significant. For other diameters, the drop velocity does not undergo a remarkable change. To better illustrate this dependency, the sedimentation velocities after 4 s are compared to the extrapolated initial velocity at time 0. This initial velocity is obtained by taking the velocities in the first three sections of the cell and extrapolating them to the height of 0. Figure 8 shows these sedimentation velocity differences for 10 mmol/L zinc, 5 mmol/L sulfuric acid, and 5 wt % D2EHPA as a function of the drop diameter. It can be clearly seen that the sedimentation velocity for drop diameters between 2 and 3 mm is significantly decreasing during the first 4 s of drop lifetime. Interestingly, this region corresponds exactly to the drop diameters, where mass transfer changes the velocity of single droplets (see Figure 6). For other diameters, this change is less than 5%. The drop diameter of 3 mm at which the change in behavior occurs corresponds to the diameter d_{sw} below which the drop is essentially rigid. This means that in agreement to the above arguments the rigid interface becomes mobile as mass transfer takes place in the reactive system. In comparison to experiments without mass transfer it could be verified that this is purely an effect of mass transfer. All drop diameters colliding with the wall have been excluded from this evaluation.

If the position-dependent velocities are directly recorded in Figure 8 for drops with mass transfer, it can be seen that with increasing contact time the drops slow down. At the begin of its rising the drops show a high mass-transfer rate, the concentration of free D2EHPA at the interface is thus reduced as discussed and so the drops rise faster. With increasing contact time, the mass-transfer rate reduces, the D2EHPA concentration at the interface increases, and as a result, the sedimentation velocity is reduced. This interpretation is again in accordance with the overall behavior of the drops. Also it is again another striking difference to physical extraction. Grömping found in measurements with the physical test system n-butyl-acetate + water + acetone that drops are accelerating with increasing contact time (Grömping, 2007, Personal Communication). In his system, n-butyl-acetate drops are rising in water while extracting the transfer component acetone. In Figure 9 it is shown for a drop diameter of 2.67 mm how drops dynamically change their velocity for a physical as compared to a reactive system. This shows again the principal difference between these two systems consistent with the above interpretation.

Conclusion

The sedimentation characteristics of the reactive standard test system zinc + D2EHPA have been investigated. The velocity of drops changes with mass transfer and shows transient behavior. While comparing reactive extraction to physical extraction, droplets behave strongly differently, regarding their transient behavior as well as the effect of present mass transfer. In the case of reactive extraction with a surface-active component taking part in the surface reaction, present mass transfer accelerates drops and they become slower with time as the mass-transfer rate decays. These observations can be explained by the properties of the surface-active component D2EHPA. As soon as mass transfer is present, the concentration of the D2EHPA at the interface will decrease so that the drops will rise faster. For physical extraction systems, mass transfer inhibits marangoni-convections which destroy the internal circulation of the drop and thus slow the droplets down.

Notation

a_i = model parameter
Ar = Archimedes number
c_w = drag coefficient
d = diameter, m
f_1^* = crossover function
K_{HR}^* = modified Hadamard-Rybczynksi factor
Re = Reynolds number
T = temperature, °C
v = sedimentation velocity, m/s

Greek letters

α = exponent
Δ = difference
ε = average relative deviation
η = dynamic viscosity, Pa s
σ = interfacial tension, N/m
ρ = density, kg/m^3

Subscripts

∞ = in infinitely extended fluid
c = continuous phase
d = dispersed phase
os = oscillating
sw = passing from rigid to circulating drop
tot = total

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