Influence of Marangoni convection on mass transfer at non-spherical droplets

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In the present study, mass transfer at single droplets with simultaneous Marangoni convection is systematically investigated in the ternary toluene/acetone/water system. The investigated key parameter are the initial solute concentration $c_{A,0}$ and the drop diameter d_P. Mass transfer is increased for higher initial concentrations and smaller droplet sizes. For non-spherical droplets, relatively good agreement is found with the Handlos & Baron model for high initial concentrations, and it can be assumed that internal circulation in deformed droplets in combination with Marangoni convection is of turbulent structure.

1. Introduction

A single droplet is the smallest mass transfer unit in extraction devices and therefore of fundamental interest. The transfer of a solute out of or into a fluid particle mainly depends on the complex fluid dynamic behaviour caused by the movable interface. In surfactant-free systems, internal toroidal circulation appears in droplets induced by the tangential shear forces at the interface due to the relative motion between dispersed and continuous phase. With the additional convection, mass transfer is increased compared to rigid particles, and matter is transported perpendicular to the streamlines of Hadamard type by molecular diffusion (Kronig and Brink, 1950). Above a certain critical Weber number, We ≈ 4 (Krishna et al., 1959; Winnikow and Chao, 1966), droplet shape deforms significantly and more or less vigorous oscillations may appear (e.g. Rose and Kintner, 1966), affecting drop rise velocity and surface area (e.g. Al-Hassan et al., 1992). The internal circulation is replaced by irregular flows provoking a random mixing and thus higher mass transfer coefficients (e.g. Schroeder and Kintner, 1965). In many systems, the mass transfer of a solute affects the local interfacial tension and additional tangential shear forces may appear (Marangoni effect). Marangoni instabilities can promote significantly internal mixing and influence droplet motion which leads to notable mass transfer enhancement (e.g. Steiner et al., 1990; Wegener et al. 2007). The considerations above are only valid for clean systems without surfactants which would hinder interfacial motion.

The Marangoni effect in combination with shape deformations leads to an even more complex fluid dynamic behaviour which is far from being understood. Thus, more experimental investigations are needed than published in literature so far. Some aspects of unsteady mass transfer at deformable toluene droplets rising in water with simultaneous Marangoni convection are highlighted in the present paper.

2. Experimental setup

The setup used for the experiments is shown in Fig. 1. The column (1) ($H = 1000$ mm, $Ø_i = 75$ mm) is equipped with a jacket (2) used for temperature control (3) ($\vartheta = 25°C$). Drops of a specified volume are generated with a Hamilton® PSD/2 precision module (5) at a nozzle (6). Drop release is accomplished automatically using a solenoid device (7). Before each run, organic and aqueous phase were mutually saturated in a stirred tank (10) in order to avoid additional mass transfer. The drops are collected with a movable funnel (8) at different drop travel heights h_t and withdrawn by a second pump. For the analysis of the mean solute concentration gas chromatography has been used.

The system is highly sensitive to impurities and to the quality of the chemicals, thus only chemicals of high purity have been used (analytical grade toluene and acetone by Merck®, deionized water of high purity). For physical properties see Misek et al. (1985). Additionally, only the materials PTFE, glass and stainless steel were used. A distinct cleaning procedure has been accomplished. Before each experiment, system purity has been carefully checked.

mass transfer direction: *dispers → continuous*
droplet diameter: $d_P = 2 \dots 6$ mm
initial concentration: $c_0 = 1 \dots 60$ g/L

Fig. 1: Experimental setup. (1) column, (2) jacket, (3) thermostat, (4) dispersed phase, (5) precision dosing pumps, (6) nozzle, (7) solenoid device, (8) funnel, (9) dispersed phase sample, (10) saturation tank, (11) computer control

3. Results and discussion

Fig. 2 shows the relative droplet mean concentration $c^* = \overline{c}\,(t)/c_0$ as a function of contact time (time from the beginning of drop formation until the drop is collected in the funnel) for different droplet diameters. The initial solute concentration c_0 is fixed to 30 g/L. For comparison, the curves of the Kronig & Brink model are given. The model assumes internal circulation of the type described by Hadamard (1911), i.e. Re << 1, higher time required for diffusion than that for fluid circulation, and negligible mass transfer resistance in the continuous phase. From Fig. 2 it is obvious that the smaller the diameter is, the faster the mean concentration decreases which is mainly due to the higher surface to volume ratio of the smaller droplets. Time of diffusion increases with the square of the droplet diameter, circulation time however increases with d_P (Kronig & Brink, 1950). The comparison with the Kronig & Brink model shows that mass transfer is significantly enhanced by Marangoni convection (factor 5 for 2 *mm* droplets, up to factor 10 for 6 *mm* droplets at $c^* = 0.3$, see dotted line in Fig. 2). Obviously, toroidal flow structures from the Hadamard type assumed in the model do not exist, and vigorous internal circulations must appear promoting axial mixing and thus convective mass transfer. This may be due to Marangoni induced flows as well as due to internal motion induced by surface deformations. Apparently, the mass transfer enhancement is significantly higher for more deformed droplets, possibly because deformation induced flows become more developed than in smaller particles. Note that in Fig. 2 the slopes of the experimental curves are much higher than predicted by the Kronig & Brink model.
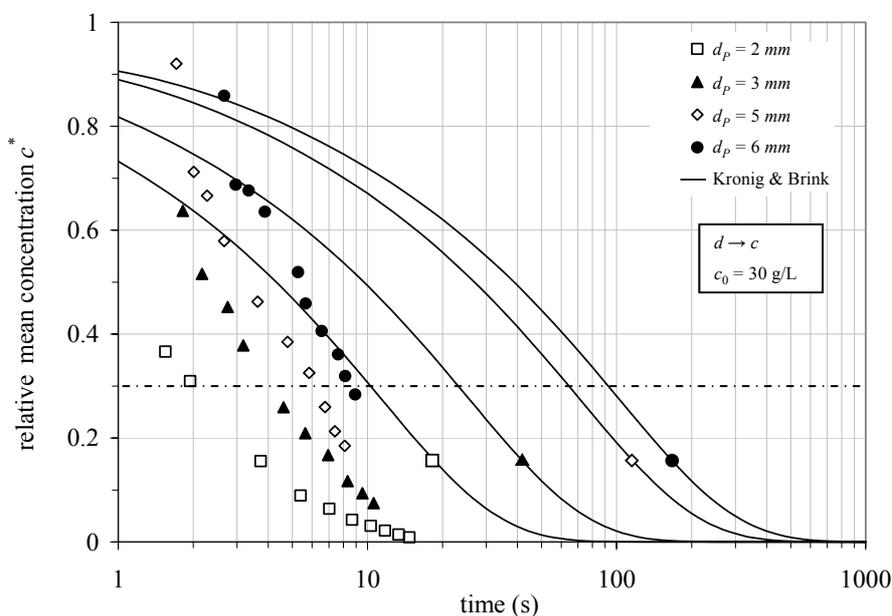

Fig. 2: Relative mean concentration c^* as a function of time for different drop diameters. Initial solute concentration 30 g/L, mass transfer direction d→c. The corresponding curves of the Kronig & Brink model are given for comparison.

Fig. 3 shows the influence of Marangoni convection on the mean solute concentration of 5 *mm* droplets. Parameter is the initial solute concentration c_0, varying from 1 to 60 g/L, to accentuate the strength of Marangoni convection. The relative mean concentration c^* is plotted versus the Fourier number $Fo = tD_A/R^2$ (D_A diffusion coefficient, t time, R droplet radius). With increasing c_0, the curves for c^* are shifted to the left which means faster mass transfer. Higher initial solute concentrations induce stronger Marangoni flows due to higher concentration gradients and thus promote radial mixing. Half of the mass transfer is completed for 60 g/L 1.7 times earlier than for 1 g/L. In Fig. 3, two curves for the Handlos & Baron model are given for comparison. This model was derived for vigorously circulating spherical droplets, assuming some kind of turbulent mechanism in which random radial motion is superimposed on internal circulation, resistance in the continuous phase is neglected. In the model equation, the terminal drop rise velocity v_t or respectively the Péclet number $v_t d_P/D_A$ has to be considered. But Marangoni convection influences drop rise velocity, depending on the instantaneous solute concentration, thus drop rise velocity is transient. The higher the concentration is, the more the droplet is retarded, the limiting case is the velocity of a rigid particle (Linde & Sehrt, 1966; Wegener et al., 2007). The dotted line represents the model with a Péclet number based on the terminal rise velocity of an drop without retardation, the continuous line the Péclet number based on the retarded drop, both values were determined experimentally. The agreement of the latter is quite good compared with the 60 g/L experiments, the mean deviation is about 15%. Note that the slope of the model curves are comparable to the experimental data.
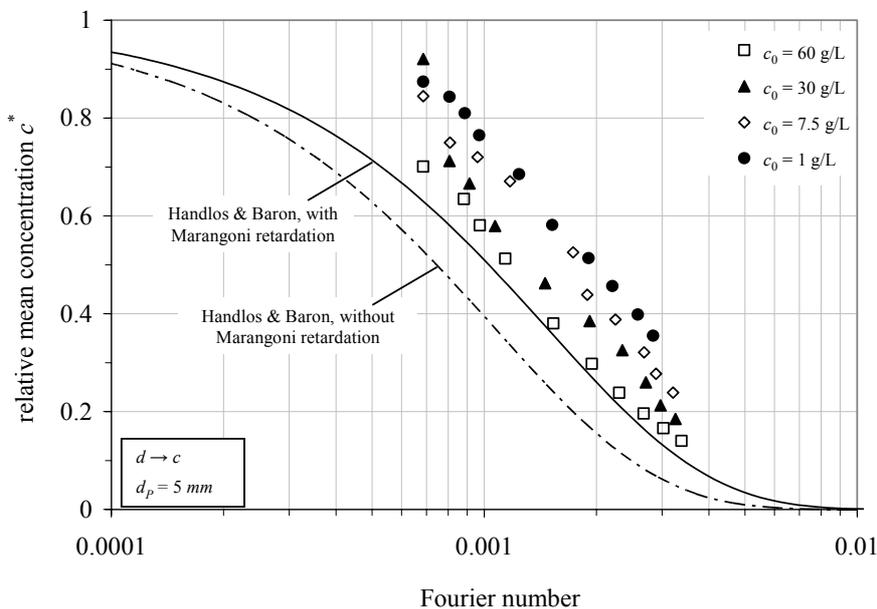

Fig. 3: c^* as a function of Fourier number for different solute concentrations for 5 mm droplets, mass transfer direction d → c. The Handlos & Baron model with/without consideration of Marangoni retardation is given for comparison.

If the initial solute concentration is high, Marangoni convection is strong and dominant. The better the radial mixing is promoted by Marangoni flows, the more the assumption of turbulent mixing in the Handlos & Baron model is fulfilled.

In Fig. 4, the relative mean concentration c^* is plotted versus the Fourier number Fo for different drop sizes. Each figure represents a distinct initial solute concentration $c_{A,0}$. The dotted line is a simple exponential function $f(Fo)=A \cdot exp(-\lambda Fo)$ with adjusted parameters A and λ to quantify how the mass transfer depends on the initial solute concentration. Analogous to the results shown above, the mean concentration c^* decreases faster for higher initial solute concentrations and thus stronger Marangoni convection (parameter λ increases). Compared with Fig. 2, Fig. 4 reveals one essentially new aspect. In all three cases, the experimental data for the non-spherical 5 and 6 *mm* droplets fall into one single curve when c^* is expressed as a function of the Fourier number, i.e. when contact time t is related to the square of the droplet radius R^2. This is not the case for the nearly spherical 2 *mm* droplets, the corresponding curves are shifted to the right. One possible conclusion could be that in the regime where droplets are strongly deformed, mass transfer and fluid dynamic mechanisms are in some way equivalent and scale with droplet size. In a c^*-Fo-diagram, the parameter d_P can be eliminated which could be advantageous for the development of mass transfer models with simultaneous Marangoni convection. For smaller droplets, the interaction and mutual coupling of mass transfer and drop rise velocity is different and has been investigated elsewhere (Wegener et al., 2007).
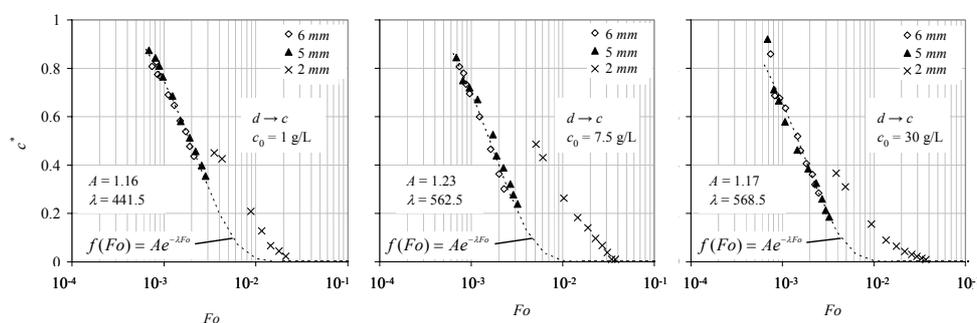

Fig. 4: c^* as a function of Fourier number Fo for different drop diameters. Initial solute concentration 1 g/L (left), 7.5 g/L (middle), 30 g/L (right).

4. Conclusion

Mass transfer measurements in the toluene/acetone/water system were conducted in an extraction column for different drop sizes covering the spherical and non-spherical regime, and for different initial solute concentrations to investigate the effect of Marangoni convection on the mass transfer. In all experiments, the mass transfer was directed from the dispersed to the continuous phase. For a given initial solute concentration, mass transfer is faster for smaller droplets, but compared to the Kronig & Brink model, mass transfer enhancement is twice as effective for bigger droplets,

probably due to the more vigorous internal circulation patterns. Experiments for bigger droplets showed that the higher the initial concentration was, the better the experimental data correspond to the Handlos & Baron assumption of perfect internal mixing due to higher gradients of interfacial tension and thus stronger Marangoni effects promoting radial mixing. Mass transfer data of non-spherical droplets fall into one single curve when expressed in non-dimensional form, indicating comparable mechanisms scaling with the square of droplet size.

Future experimental studies should include additional drop sizes than those investigated here. Especially the transition regime around the critical diameter (which is around 4.4 *mm* in the toluene/water system, see e.g. Klee and Treybal, 1956), where droplets change from spherical to non-spherical shape, should be focussed on.

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