

# **EXPERIMENTAL AND NUMERICAL INVESTIGATIONS OF MASS TRANSFER IN LIQUID-LIQUID EXTRACTION WITH SUPERPOSED MARANGONI CONVECTION**

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The design of extraction columns requires reliable correlations for the prediction of mass transfer coefficients. In the last decades many authors published mass transfer rates on single drops for very simplified cases - for instance the mass transfer resistance was neglected either in the continuous or in the dispersed phase. As the consideration of both resistances cannot be solved analytically one has to revert to numerical solutions. Such numerical results were presented recently e.g. by Piarah<sup>1</sup>. The goal of further investigations is to enhance the validity of the used mass transfer model for more practical conditions, for example deformable drop shapes, multi-component mass transfer or the consideration of surface active agents. This work deals with the experimental and numerical investigation of the influence of superposed interface convections (Marangoni convection), which are present in many practical applications. This convection is caused by differences of interface tensions over the drop surface, where the differences results from different concentrations on the interface due to the mass transfer process.

The strategy to be presented is to adapt the model equations on the mentioned mass transfer problem. The numerical results will then be compared with experimental data for validation.

The experimental determination of mass fluxes through the drop interface is carried out with the aid of a special mass transfer cell where the mean concentration of the transferred component could be measured as a function of mass transfer time. The drop is introduced by means of a glass capillary. After its formation the drop rises up and is held in place by a counter current flow of the continuous phase. After a predetermined mass transfer time the counter current flow is stopped, the drop rises further and is then collected in a funnel. From there it is taken to chemical analysis. Mass transfer during drop formation or during the residence time in the funnel can be neglected for the considered systems and initial concentration differences.



Fig. 1: Neutralisation front of acetic acid with Marangoni convection (right) and without Marangoni convection (left)

In addition to the determination of mean concentration differences also concentration profiles inside of the drop were visualised by using a decolorisation method. For this purpose the physical mass transfer was superposed by an acid/base neutralisation, changing the pH of the dispersed phase. Depending on the used pH indicator one iso-concentration can be detected for different mass transfer times.

Another relevant information for comparisons with numerical data can be obtained by the determination of drop rise or fall velocities. This is done by using a vertical glass tube, filled with the continuous phase. The glass tube is equipped with a rectangular heat jacket to ensure constant temperatures and undistorted view on the drop. The drop can be introduced again by a glass capillary. After its formation, the drop is followed by a video camera. To ensure a constant distance between the camera and the drop, the camera is mounted on a traversing saddle. The position of the drop is detected once every second to determine the mean velocity in this interval. Then results can be compared with numerical data for drops with moving interface. Surface active agents lead to a reduction of the rise velocity compared to the pure system. During drop rise surface active agents accumulate on the liquid/liquid interface and create a partially rigid surface. This behaviour gives information about the purity of the system.

At first experimental results will be presented for the system cyclohexanol (continuous phase), acetic acid (transferred component) and water (drop phase). The results show the decrease of the concentration difference as a function of the mass transfer time. Good agreement was found with numerical results by using a mass transfer model without consideration of Marangoni convection. This observation can be explained by the high viscosity of cyclohexanol (12 mPas) and the moderate concentration of acetic acid chosen. The influence of Marangoni convection can be neglected in this case. This was also confirmed by the analysis of the concentration profiles using the decolorisation method. For this purpose a very small amount of sodium hydroxide and phenol red was added to the dispersed phase to observe the neutralisation front of acetic acid. The shape of a torus as shown in Fig. 1 is in good agreement with the predicted CFD result.

The results regarding the settling velocity of the water drop are also in agreement with the predicted CFD velocities and remain constant over time.

The investigation of mass transfer with superposed Marangoni convection is carried out with four systems. Toluene and butylacetate, respectively is used as dispersed phase with water as the continuous phase and acetone as the transferred component. These two systems were applied by many authors because of its recommendation by the European Federation of Chemical Engineering (EFCE) with a detailed data collection published by Misek<sup>2</sup>

In addition, investigations are carried out with water as the dispersed phase and toluene and butylacetate, respectively as the continuous phase. In this case acetic acid is chosen as transferred component.

For all physical systems, experimental mass transfer rates are significantly higher than predicted by CFD calculations without the consideration of Marangoni convection. Furthermore, all systems showed a strong dependency of the drop velocity on mass transfer time. By exceeding a certain initial concentration difference, the drop moves with the velocity of a rigid sphere. Depending on the initial concentration, after a certain duration of mass transfer the drop accelerates to its maximum speed. The maximum speed is in agreement with the numerical results. It can be shown that the transition between the two velocities occurs always at the same concentration difference.

Experiments with simultaneous decolorisation, analogous to the system cyclohexanol/acetic acid/water showed that the mentioned torus shape of the concentration field was completely

disturbed by superposed Marangoni convections (Fig.1, right). While without Marangoni convection diffusion perpendicular to the iso-concentration lines is limiting the mass transfer process, the stochastic movements on the interface cause additional convections in the direction of the torus centre. This additional convection term results in increased mass transfer rates. As a second conclusion it can be assumed that the mentioned stochastic interface movements interact with the surrounding velocity field and therefore influence the drop velocities.

More general numerical calculations regarding the influence of Marangoni convection on the velocity and concentration field in liquid-liquid systems were carried out for the system toluene/acetic acid/water in a flat flow channel. For this systems detailed experimental data from Tokarz<sup>3</sup> are available (LDA measurements, concentration profiles). To get these detailed information for single drop systems, unreasonable effort would be necessary. Additionally, in this case it was sufficient to describe the geometry by using a 2-dimensional grid. For this simplified case the numerical effort regarding the solution of the mass transfer problem is not too excessive and therefore suitable for some principal investigations.

It can be shown that by exceeding a certain concentration difference, deformed roll cells can be observed strongly influencing the concentration profile. These cells also influence the interfacial velocity. The averaged velocity of the entire interface converges towards a rigid interface. The achieved numerical results will be discussed and compared with the experimental observations.

## REFERENCES

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