Epilogue

In this epilogue, a summary of the results presented in this thesis is given with the intention to discuss its implications, and suggest topics for further research.

Marangoni convection and experiments in microgravity

In chapter 2, results from a microgravity experiment were presented and compared to experiments performed in a normal gravity environment. The goal of the experiments was to learn about the relationship between Marangoni convection and mass transfer. The reason for performing the experiments in microgravity was that Rayleigh and Marangoni convection interfere with each other in thicker liquid layers. No experimental technique is presently available that can resolve flow patterns in liquid layers of 1 mm and less. And these are the layers that are of interest to the chemical engineer that intends to study relationships between mass transfer and the Marangoni effect in industrial equipment. The particular geometry chosen also rendered microgravity imperative, as the concave and convex containers could only be filled properly in the absence of gravity.

The experiment revealed the way the flow behaved over extended times, and showed that flow patterns ultimately strongly resemble each other, whatever the geometry. The major difference between the flow observed in the various containers could be observed in the beginning of the experiments. In containers which induce macroconvection a two roll cell pattern almost immediately forms, while in containers without asymmetry a four roll cell pattern forms after several seconds. The four roll cell pattern ultimately evolves into a two roll cell pattern with the transition time depending on the size and the precise form of the container.

The experiment was intended to study flow development and translate the information obtained in such a way that predictions could be made about flow development in thin liquid layers. To do this, a numerical model was constructed in chapter 3 that describes the evolution of flow and concentration patterns in V-shaped containers. The results of this model were compared with the results of the microgravity experiments.

A quite good match was obtained between experiments and numerical model. Qualitatively, the results were very similar, and clear conclusions on Marangoni flow patterns could be drawn. However, quantitatively a mismatch was obtained between the experimental Marangoni number and the model Marangoni number necessary to represent the experiments best. Several causes for this discrepancy were proposed. Some of the discrepancy is due to non-idealities in the experimental situation, and some of the discrepancy is due to simplifications in the numerical model that can be improved upon relatively straightforward, especially with computing capacity and numerical tools improving continuously.

Some of the discrepancy, however, is difficult to capture, unless interfacial phenomena are more accurately described, such as the effect of Gibbs adsorption, interfacial viscosity, and the Plateau-Marangoni-Gibbs effect. And especially these phenomena become increasingly important when the model is used to describe flow patterns in thin films. That is, for a better quantitative understanding of phenomena occurring in thin liquid films, it is not possible to translate results obtained for thick liquid layers. This renders the use of microgravity experiments for this particular line of research redundant. Other experimental techniques should be improved first, and a more accurate modelling of interfacial phenomena should be pursued.

Again, the experiments have shown that the Plateau-Marangoni-Gibbs effect is an important, but difficult to quantify, phenomenon. Small traces of pollution can increase stability and decrease flow intensity. In the past this has impeded the exact determination of the onset of Marangoni convection and the value of the critical Marangoni number. In retrospect, it might have been better to choose a model system which is less sensitive to pollution than the acetone-water system.

Modelling Marangoni convection

In chapter 3, Marangoni flows in V-shaped containers have been modelled numerically, and in chapter 4, the model was used to predict mass transfer characteristics of the system. Several important conclusions could be drawn with respect to this model. It proved to be very important to model both the liquid and the gas phase in order to accurately describe the phenomena occurring in the experiments. Furthermore, certain mass transfer characteristics could only be captured because the flow and concentration patterns in the gas phase were modelled as well. In particular, the phenomenon that mass transfer is enhanced most by Marangoni convection for intermediate Biot numbers can not be resolved from the model if only one phase is taken into account.

The model developed in this thesis only provided the results it did, because a completely implicit numerical technique was chosen. Furthermore, the use of an elegant preconditioning technique to treat the large Jacobian matrix that needed to be solved every Newton iteration proved to be indispensable.

Future work in this field could be directed to the incorporation of more interfacial physics into the model, such as Gibbs adsorption, the Plateau-Marangoni-Gibbs effect and interfacial viscosity. However, to characterise the extent of the most important effect, the Plateau-Marangoni-Gibbs effect, it is necessary to identify the type of surface active substance and to determine its concentration and properties. This might prove to be very difficult in most practical cases.

Marangoni convection and mass transfer

In chapter 4, the influence of Marangoni convection on the mass transfer coefficient was discussed. The model developed in chapter 3 was used to investigate the influence of surface tension gradients on mass transfer from convex containers systematically. The convex container was chosen, because the flow in these containers represents the flow in systems in which microconvection is important. Microconvection is likely to be the more important mechanism occurring in thin films.

Apart from depending on the value of the Marangoni number, the enhancement of mass transfer proved to be strongly dependent on the Biot and Schmidt numbers as well. Enhancement was found to be largest for intermediate Biot numbers. Qualitatively, this can be easily understood: if mass transfer resistance is located exclusively in one phase, mass transfer in the other phase cancels out concentration gradients at the interface. Results were discussed and compared to experimental work described in literature, and especially to a semi-quantitative model, which was developed by Golovin to explain the various experimental results found in literature. Despite the elegance of Golovins model, some inconsistencies were identified, and a qualitative model was proposed to explain the effect of the Biot number on the enhancement of mass transfer by the Marangoni effect.

The research described in chapters 2, 3, and 4 followed a clearly defined route. Firstly, it was experimentally established how solutal Marangoni convection evolves when acetone is desorbed from a relatively thick liquid layer. In order to do this, microgravity experiments were necessary. The results from these experiments were compared to a numerical model. This model was adapted to include a representative part of the gas phase in order to be able to compare the results to the experiments favourably. Some quantitative discrepancy remained, however. Finally, the model was used to predict mass transfer characteristics in mass transfer systems in general. The model was able to predict some effects successfully. In the end, therefore, the chosen route delivered some valuable results.

Quite a large part of the quantitative discrepancy between the final model and experimental results for mass transfer in thin liquid layers (wetted wall columns) published in literature is, again, due to the omission of the Plateau-Marangoni-Gibbs effect in the model. And, although the research described in this thesis can be very helpful to explain effects found in mass transfer equipment, precisely this effect prevents the use of relationships derived from such studies in the design of industrial mass transfer equipment. For, if such relationships are used to calculate a mass transfer coefficient, this mass transfer coefficient might prove to be overestimated if the Plateau-Marangoni-Gibbs effect plays a significant role. The latter effect is hard to predict, because small traces of pollution might set the effect into action.

In some cases, the Marangoni effect enhances mass transfer significantly, also in industrial equipment. However, the effect is difficult to predict, and is almost impossible to control. One way to control the effect to some extent is to provoke it artificially, as exemplified in the series of papers by Lu et al. [1, 2, 3] for mass transfer, and in other papers in the case of heat transfer [4, 5, 6]. It is not always possible, though, to add an additional component to a system in order to enhance mass transfer.

Possibly, a more promising way to use interfacial instability to enhance mass transfer is to use the effect non-uniform electric fields can have on interfaces. The electrocapillary-related spraying effect can strongly enhance mass transfer [7, 8], and the effect can be controlled by manipulating the intensity and the non-uniformity of the electric field. The effect is only operative in case polarisable liquids are used, but when it is operative, mass transfer can be enhanced severalfold.

Marangoni convection and protein crystallisation

The study described in chapter 5 was a first effort to assess the possibility of the Marangoni effect occurring in protein crystallisation systems. The experimental study described in this chapter suffered from the fact that the optical magnification of the droplet was too small to observe some of the flows that might occur in these droplets, as some microscope studies in the laboratory and in literature [9, 10] have demonstrated.

The analysis in chapter 5, however, also showed that Marangoni convection intensities are probably very small for most protein crystallisation systems some time after creating the gas-liquid interface. Moreover, conclusions for one protein crystallisation system are not necessarily valid for another protein crystallisation system, even if differences between the systems are very small, as they are in the cases of orthorhombic and tetragonal lysozyme.

Whether or not Marangoni convection is significant enough to disturb the growth of protein crystals, can only be assessed if experimental techniques for observing protein crystallisation systems improve, and some effort is currently being made to implement this improvement. In a recent study, protein crystal growth in microgravity was observed over extended times, and some movement of the crystals was found, possibly as a result of thermocapillarity, possibly also a result of solutal Marangoni convection initiated by the presence of concentration halos around growing crystals [11]. If, for some protein crystallisation systems, the Marangoni effect is found to be responsible for imperfecting protein crystal growth, its influence could quite easily be eliminated by choosing the dialysis crystallisation system, rather than the vapour diffusion crystallisation system [12].

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