

## Summary

Apart from a general introduction in chapter 1, this thesis consists of two distinct parts. In the first part, which includes chapter 2, 3, and 4, a study is described which intends to reveal aspects of mass transfer enhancement due to the Marangoni effect with the help of microgravity experiments. In chapter 5, which is the second part, a study to the possible influence of the Marangoni effect during the crystallisation of proteins is presented.

### *The Marangoni effect*

The phenomenon that liquid flows along a gas-liquid or a liquid-liquid interface from areas having low surface tension to areas having higher surface tension is named the Marangoni effect, after an Italian physicist living in the nineteenth century. Solutal Marangoni convection is flow caused by surface tension gradients originating from concentration gradients, while thermocapillarity is flow caused by surface tension gradients originating from temperature gradients. Two types of convection can be distinguished: macroconvection and microconvection. Marangoni flow is labelled macroconvection when the gradient in interfacial tension is imposed on the system by an asymmetry, while flow is labelled microconvection when the flow is caused by a disturbance that is amplified in time (an instability).

Apart from the Marangoni effect described above, also the Plateau-Marangoni-Gibbs effect plays an important role in this thesis. This effect sets itself into action when an interface contains (traces of) surface active substances. When, for any reason, an interface expands locally, these surface active solutes are swept outward with the movement, creating a gradient in concentration of these surface active substances. This concentration gradient implies a surface tension gradient which acts opposite to the movement. The interfacial movement is therefore damped and this effect is labelled the Plateau-Marangoni-Gibbs effect.

Solutal Marangoni convection which is caused by mass transfer across a gas-liquid interface is the subject of the first part of this thesis. This type of convection is expected to enhance the mass transfer coefficient, and the wish to describe the extent of this enhancement is the original reason for carrying out the research described in this thesis.

### *Microgravity experiments*

The concentration gradients responsible for solutal Marangoni convection can also contribute to density-driven Rayleigh convection, or buoyancy. If it is desired to study the Marangoni effect separately, either very thin liquid films (< 1 mm) should be chosen, or gravity should be reduced substantially. Although these thin liquid films are interesting for the chemical engineer that wants to study the influence of Marangoni convection on mass transfer, since these thin films often occur in mass transfer equipment, it is experimentally nearly impossible to study liquid flow in such thin films. For this study, therefore, it was decided to conduct

experiments in the microgravity environment provided for by sounding rockets. The mass transfer of acetone from water into air was studied in various geometries. These geometries were called V-shaped containers. The V-shaped containers were constructed in such a way that both micro- and macroconvection could be studied. Both concentration and flow fields were monitored during the experiments which are described in chapter 2 of this thesis.

The final roll cell patterns in all containers, in which flow was not inhibited by the Plateau-Marangoni-Gibbs effect, consisted of two roll cells of approximately equal size. These roll cells turned in such a way that liquid from the bulk was transported to the interface through the middle of the container, while liquid from the interface was transported into the bulk along the solid side walls. Although the final roll cell patterns were similar, initial flow patterns differed. In containers where the flow was driven predominantly by an asymmetrical concentration distribution, two roll cells almost immediately arose as a result of this asymmetry (macroconvection). In the other containers, flow originated from random disturbances which were amplified in all cases to a four roll cell pattern (microconvection). This four roll cell pattern transitioned into the two roll cell pattern after a certain time, this time being larger for larger containers.

These results were discussed in chapter 2, and explanations were forwarded for the fact that roll cell patterns with flow coming from the bulk along the rigid side walls to the interface were not observed, and the fact that the two roll cells in the final pattern were approximately equally large. Results were also compared to results under normal gravity conditions. The most important difference with the microgravity experiments could be observed in the concentration distribution. Heavy liquid sank to the bottom of the containers during normal gravity, which resulted ultimately in an inversion of the concentration distribution compared to the microgravity experiments.

### *Model of Marangoni flow in V-shaped containers*

Chapter 3 of this thesis was focused on modelling the flow and concentration distribution in the V-shaped containers, with the objective of obtaining as good a match as possible. In order to do this, the Navier-Stokes equation, the convection-diffusion equation, and the continuity equation had to be solved together with the appropriate boundary conditions. These equations were solved numerically, using a fully implicit finite difference method. Two types of containers were modelled, in order to study the difference between microconvection (convex container) and macroconvection (triangular container).

It proved to be important to include a representative part of the gas phase in the model, as otherwise flow patterns in the simulations did not resemble the experiments. Qualitatively, a good agreement between model and experiment was obtained. A quantitative mismatch remained, in the sense that Marangoni numbers used in the model to obtain a quantitative match with the experiments were smaller than the experimental ones. Some explanations for this discrepancy were proposed, of which the absence of the Plateau-Marangoni-Gibbs effect in the model is one the most important ones.

### *Marangoni flow and the enhancement of mass transfer*

In chapter 4, the model developed in chapter 3 was used to study the enhancement of the mass transfer coefficient by the Marangoni effect in gas-liquid systems. Only the model for the convex container was used. Several parameters were varied, such as the Marangoni number, the gas and liquid phase diffusivities, and the distribution coefficient of the transferring solute. An extra convection-diffusion equation was modelled to study the simultaneous transfer of a tracer component from the gas to the liquid phase. A tracer component is characterised by having no influence on the surface tension, and its low solubility in the liquid.

The results of this study showed that the enhancement of Marangoni convection is largest for systems in which the liquid phase mass transfer resistance is approximately equal to the gas phase mass transfer resistance, i.e. the Biot number is close to 1. This is qualitatively easy to understand, for if the resistance to mass transfer is located exclusively in one of the phases, mass transfer in the other phase cancels out all concentration gradients at the interface. A semi-quantitative model was developed to support these results.

A comparison was made between the results in this chapter, and experimental and theoretical results described in the literature, and some causes for discrepancy between all these results were proposed. Especially the work of Golovin, who developed an elegant model to describe the influence of the Marangoni number on the enhancement of mass transfer, was discussed intensively. Some omissions in his work were identified.

Chapter 4 demonstrated again that it is important to model both liquid and gas phase when one intends to study the effect of Marangoni convection on mass transfer.

### *The Marangoni effect during protein crystallisation*

The last chapter of this thesis describes a study to the possible influence of the Marangoni effect on protein crystallisation. Protein crystallisation is an important step in the determination of the three-dimensional structure of proteins, and it is the step which is most likely to fail. Several reasons have been forwarded for the failure to grow perfect crystals, one of them being the detrimental effect convection can have on the growth of crystals. Convection during protein crystal growth can occur as a consequence of density variations within the liquid, and therefore many crystal growers conduct microgravity experiments to avoid buoyancy. However, Marangoni convection might still occur during microgravity.

A microgravity experiment was conducted in order to study possible Marangoni effects in vapour diffusion protein crystallisation hardware. This sounding rocket experiment showed that some convection can occur during protein crystallisation, but results were inconclusive.

This was mainly due to the limited possibility to study convection in the vapour diffusion set-up, the most notable limitation being the small magnification with which the droplets in the set-up could be examined.

Some microscope studies in the laboratory showed that Marangoni effects can occur during protein crystallisation, most likely in those systems that use an organic solvent as a precipitant. Also, a qualitative and semi-quantitative study presented in the same chapter arrives to this conclusion. In most protein crystallisation systems, however, and especially in those systems that use salt as a precipitant, the Marangoni effect is expected to be negligible some short time after the start of the experiment. This is mainly due to the inclination of proteins to form a rigid layer of denatured proteins at interfaces, and the presence of surface active substances that set the Plateau-Marangoni-Gibbs effect into action.