A numerical parameter study on the impact of Marangoni convection on the mass transfer at buoyancy-driven single droplets

M. Wegener *

Chair of Chemical and Process Engineering, Ackerstraße 71-76, D-13355 Berlin, Germany

ARTICLE INFO

ABSTRACT

Based on earlier successful validations of 3D simulations with experiments in a Marangoni dominated liquid/liquid system, this paper presents a numerical parameter study which investigates the effect of droplet diameter, kinematic viscosity ratio, interfacial tension gradient, and partition coefficient on the mass transfer of a solute via the Marangoni induced flow patterns. Simulation results exhibit a strong influence of droplet size on the mass transfer performance and reasonable agreement with experiments in the spherical droplet shape regime. In contrast to predictions based on the linear stability theory, the Marangoni convection was found to be unimpressed by a change in the kinematic viscosity ratio. For all kinematic viscosity ratios studied here, the mass transfer was significantly faster than in the system with constant interfacial tension (i.e. no Marangoni convection). The same is true for the interfacial tension gradient, which is the main driving force for Marangoni flow. Even if the gradient is decreased by a factor of 100, mass transfer enhancement factors >2 were found. Only an increase in the partition coefficient to a value of 10, and therewith a respective decrease in the concentration gradient at the interface, ended the dominion of the Marangoni effect on the mass transfer rate.

1. Introduction

The solutal Marangoni convection plays an important role for the fluid dynamics and the mass transfer of a solute across the interface of single droplets freely rising in an ambient liquid. The Marangoni effect in moving droplets is a complex phenomenon which eludes stubbornly an analytical description, mostly due to the fact that the Marangoni convection is a chaotic and inherently three-dimensional phenomenon which affects and is affected by various parameters and properties of the system under consideration. Moreover, the Marangoni convection is an utterly time-dependent and temporary process. It needs a certain time to develop its flow patterns, becomes dominant and eventually dies away in the later stages of the process [9].

Fig. 1 shows the main stages of Marangoni convection patterns in and around rising droplets. The upper row shows schematics, whereas the lower row displays results from numerical simulations [22]. The convection originates from tangential shear stresses at the interface which in turn result from local gradients of interfacial tension around the droplet surface. In the early stage of mass transfer, the concentration gradient is large and the shear stresses at the interface are strong. The adjacent fluid layers are accelerated by momentum transfer and result in vortex structures on a sub-drop scale level and increasing radial displacement (or mixing) within the droplet (Fig. 1(a)). Strong Marangoni convection at the interface increases the drag coefficient and reduces the drop rise velocity temporarily. The maximum level of reduction is reached when the rise velocity fluctuates around the terminal velocity of a comparable rigid sphere. Hence, Reynolds and Peclet number are not constant and vary with time.

In the middle stage of the mass transfer process, the influence of interfacial tension induced shear stresses starts to weaken. The drag decreases, and eventually a more regular internal circulation establishes in an asymmetric manner (Fig. 1(b)). In this stage, experiments showed that the rise velocity increases and the droplet breaks out from its vertical path due to the asymmetric onset of internal circulation [25]. In the later stage of the process, the influence of Marangoni convection becomes insignificant. The droplet shows the well known toroidal flow pattern which is now completely axisymmetric (Fig. 1(c)). The drag reduces and the droplet approaches its terminal velocity.

Is it of particular interest – especially from a practical point of view – to be able to estimate the impact of Marangoni convection on the mass transfer performance, e.g. in liquid/liquid extraction processes. For those processes, the single droplet is an important test case as it can be regarded as the smallest mass transfer unit in extraction columns, stirred tanks or likewise. Empirical mass transfer correlations developed to describe the complex droplet swarm behaviour in contact apparatuses are based on single

* Tel.: +49 30 314 23701.
E-mail address: mirco.wegener@alumni.tu-berlin.de

Nomenclature

Latin letters

c_s	concentration of solute s, g/L
$c_{s,0}$	initial concentration of solute s, g/L
c^*	related concentration of solute s $c^* = c_s/c_{s,0}$
d_{cr}	critical droplet diameter (Eq. 14), m
d_P	droplet diameter, m
$D_{s,c}$	diffusion coefficient of component s in continuous phase, m^2/s
$D_{s,d}$	diffusion coefficient of component s in dispersed phase, m^2/s
D^*	ratio of diffusion coefficients $D^* = D_{s,d}/D_{s,c}$
E	enhancement factor, Eq. 13
g	gravitational acceleration, m^2/s
H^*	partition coefficient
L	characteristic length, m
p	pressure, Pa
r	radial coordinate, m
R	droplet radius, m
t	time, s
u	velocity, m/s

Greek letters

β	mass transfer coefficient, m/s
ϑ	temperature, °C
θ	azimuth angle, rad
μ	dynamic viscosity, Pa s

μ^*	ratio of dynamic viscosities $\mu^* = \mu_d/\mu_c$
v	kinematic viscosity, m^2/s
v^*	ratio of kinematic viscosities $v^* = v_d/v_c$
ρ	density, kg/m^3
σ	surface tension, N/m
φ	polar angle, rad

Subscripts

0	initial, at $t = 0$
1, 2	phase 1, phase 2
c	continuous phase
$c \to d$	mass transfer direction from continuous phase to droplet
d	dispersed phase
$d \to c$	mass transfer direction from droplet to continuous phase
P	droplet
s	soluble component
TAW	toluene/acetone/water

Dimensionless numbers

Ma	Marangoni number, $Ma = (\partial\sigma/\partial c)(\Delta c\, L)/(\mu D)$
Pe	Peclet number, $Pe = Re \cdot Sc$
Re	Reynolds number, $Re = u\, d_P\, \rho_c/\mu_c$
Sc_c	continuous phase Schmidt number, $Sc_c = v_c/D_{s,c}$
Sc_d	dispersed phase Schmidt number, $Sc_d = v_d/D_{s,d}$
Sh_d	dispersed phase Sherwood number, $Sh_d = \beta\, d_P/D_{s,d}$

droplet experiments. The Marangoni effect may increase the extraction efficiency substantially [15,19], whereas its absence may lead to relatively lower mass transfer coefficients.

Consequently, the question arises under which conditions a system will exhibit noticeable Marangoni instabilities? This question

Fig. 1. Main stages of Marangoni convection flow pattern in a rising droplet. Upper row: Schematics. Lower row: Concentration field obtained by numerical simulation of a acetone laden 2 mm toluene droplet rising in water [22]. (a) Early stage in the process, large concentration gradients, strong Marangoni convection, enhanced radial mixing and fast mass transfer, (b) middle stage, decreasing strength of Marangoni convection, asymmetric onset of internal circulation, (c) later stage, no Marangoni convection, symmetric toroidal internal flow field. Blue: low concentration, red: high concentration. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

is even more interesting for rising droplets as the local Sherwood number (and hence the local concentration) changes with the polar angle [3,5] which means that concentration gradients (and hence interfacial tension gradients) are always present. But it was observed that in some systems Marangoni effects are strong and last long, whereas in other systems, interfacial effects develop only for a short time or cannot be observed at all. Thus, a certain combination of factors may lead to the promotion of Marangoni instabilities, whereas there may be others for which instabilities die away before they have been noticed. In case of noticeable Marangoni instabilities, the next questions are: for how long and to which extent do they exist?

Despite all efforts, to the author's best knowledge, there seems to be no reliable analytical description available to take the impact of the Marangoni convection on fluid dynamics and mass transfer at single droplets into account. Hence, first and foremost carefully conducted experimental investigations may elucidate the underlying phenomena in such liquid/liquid systems, but the number of possible experiments is usually limited due to time and budget constraints. In this regard, direct numerical simulations offer to access a broader parameter range and to investigate the dynamic influence of single parameters on the unsteady mass transfer with simultaneous Marangoni convection.

Theoretical considerations by Sternling and Scriven [20] – considering two immiscible semi-infinite quiescent fluid phases in contact along a plane surface – and later Sawistowski [14] identified four primary factors to be decisive for the appearance of instabilities (a discussion of different aspects of Marangoni phenomena in solvent extraction can be found in [12]):

1. the mass transfer direction (a system can be stable for mass transfer in one direction but instable for the opposite direction),
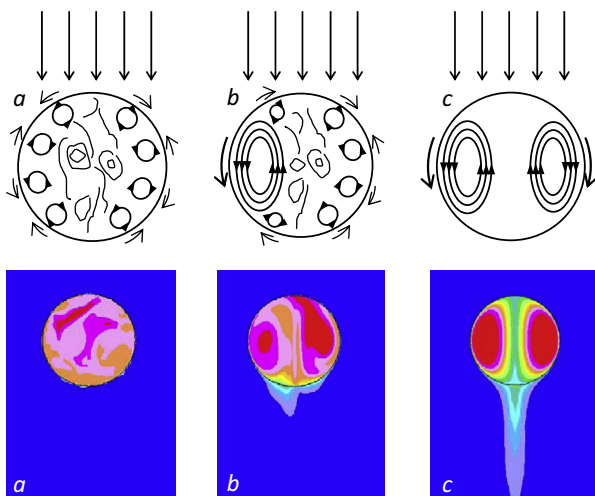2. the sign of the interfacial tension gradient $\partial\sigma/\partial c$ (which is usually negative for liquid/liquid systems),