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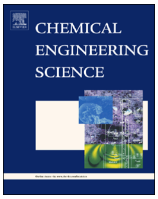

Influence of Marangoni convection on mass transfer in the *n*-propyl acetate/acetic acid/water system

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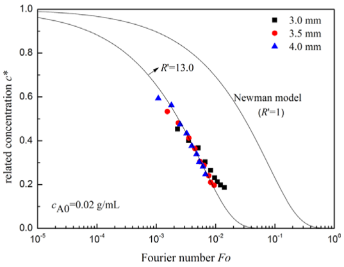
HIGHLIGHTS

- First known study of Marangoni convection in *n*-propyl acetate/acetic acid/water.
- Behavior of Marangoni convection shows similarities to other extraction systems.
- A parameter reflecting the impact of Marangoni convection is introduced in the model.
- A maximum mass transfer rate exists in the range of the investigated concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

An experimental study of the mass transfer rates in single drops with simultaneous Marangoni convection was carried out, using a system in which acetic acid was transferred from water to *n*-propyl acetate. In all experimental trials, high purity deionized water was employed as the continuous phase while *n*-propyl acetate served as the dispersed phase. The effects of both the drop diameter and the initial solute concentration in the continuous phase on the mass transfer were examined. The results demonstrated that mass transfer is increased as the drop size decreases and exhibits a maximum at an acetic acid concentration in the aqueous solution of 0.15 g/ml which reveals the competing mechanisms between reduction of velocity and mass transfer enhancement due to Marangoni effects. All current models, including the Newman (1931) model, do not account for the influence of the initial solute concentration, and thus a correction factor, α, was introduced to obtain the factor, R', by which the effective diffusivity is enhanced, based on Steiner's (1986) modified Newman model. This α factor is a function of the initial difference in solute concentration. The mass transfer rates predicted by our modified Newman model were in good agreement with the experimental data obtained in the present study.

1. Introduction

The single drop is the smallest mass transfer unit in extraction devices and therefore of fundamental interest (Wegener et al., 2009d). Such drops may experience three stages during an extraction process: (1) formation and acceleration, (2) free falling or rising and (3) coalescence with the bulk phase. It is necessary to have a good understanding of the mass transfer mechanism between the drop and the continuous phase to fully optimize the operating characteristics, design and scale-up of an extraction apparatus (Lu et al., 2010).

The transfer of a solute into or out of a fluid particle is primarily affected by the complex fluid dynamic behavior at the movable interface. Marangoni convection occurs when the interfacial

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tension varies along the drop surface due to concentration gradients. Provided the surface is not contaminated with surfactants which hinder interfacial motion (Agble and Mendes-Tatsis, 2000; Wegener and Paschedag, 2012), an interfacial flow is induced as the system attempts to minimize its free energy in expanding regions of low interfacial tension. This in turn affects both phases adjacent to the interface (Sternling and Scriven, 1959). Complex chaotic flow structures develop inside the drop and promote radial mixing and thus mass transfer. This process differs from the toroidal flow in moving droplet systems without Marangoni convection (Clift et al., 1978; Magarvey and Kalejs, 1963). The velocity field both inside the drop and in the immediate vicinity is influenced by these instabilities and therefore the concentration field is coupled with the velocity field via the convective terms in Marangoni convection dominated systems. As a consequence, the variation in mass transfer affects the local solute concentration at the interface and thus the interfacial tension gradient (Wegener et al., 2009b). Velocity and mass transfer measurements were correlated via the contact time, and it has been demonstrated that there seems to exist a concentration range in which a critical value for the solute concentration can be defined to indicate the end of Marangoni convection (Wegener et al., 2007, 2009a). In addition, when the droplets are sufficiently large, instabilities are superimposed with shape deformations and oscillations. Mass transfer measurements in a toluene/acetone/water system (Wegener et al., 2009d) within an extraction column using different drop sizes have shown that mass transfer is significantly enhanced in the case of larger droplets which undergo deformation and oscillation, likely due to the generation of more vigorous internal circulation patterns.

Numerous mass transfer models have been developed which consider solely the mass transfer resistance inside the droplets. The Newman (1931) model is applicable for rigid spheres with no internal calculation. Kronig and Brink (1951) derived a model based on droplets with internal circulation described by Hadamard (1911) flow patterns derived from equations of motion simplified for the Stokes flow regime ($Re < 1$). The model of Handlos and Baron (1957) assumes that internal mixing can be considered complete following a single hypothetical laminar inner circulation, equivalent to random radial convection superimposed on the mass transfer. Though handicapped by unrealistic assumptions (Hubis and Hartland, 1986), the Handlos and Baron model actually describes experimental data fairly well and is still frequently used to predict the mass transfer rates associated with both single drops and collections of drops (Steiner et al., 1990). Nevertheless, Henschke and Pfennig (1999) advanced a different view suggesting that the circulation period cannot be adequately calculated because such mixing completely suppresses circulation inside the drop, and drops in which turbulent internal momentum transfer occurs should not settle noticeably faster than solid spheres, which contradicts experimental findings. Finally, based on their investigations of an *n*-butyl acetate/acetone/water system, Henschke and Pfennig proposed that the turbulence inside a drop is induced only by mass transfer and not by the hydrodynamic conditions. Their model introduces a turbulent transfer coefficient based on diffusion and turbulence induced by mass transfer, incorporating an instability constant, C_{IP}, which may be adjusted to fit experimental data. Other models and modifications (Rose and Kintner, 1966; Wegener and Paschedag, 2012) describing the turbulence induced by random radial motions have also been developed, but they are only valid in special cases. In the case of deformed or oscillating droplets with simultaneous Marangoni convection, however, no reliable models have been reported in the literature. Thus it remains necessary to establish a model of mass transfer which incorporates local interfacial instabilities or Marangoni convection. Based on suggestions by Sherwood et al. (1939), molecular diffusivity in the Newman (1931) model was replaced by an experimentally determined parameter termed effective diffusivity to predict mass transfer rate for drops considered as rigid spheres. Steiner (1986) verified this approach using numerous data sets and correlated the effective diffusivity with the properties of various systems. In this paper, we present a modified Newman model to allow the prediction of mass transfer rates in the *n*-propyl acetate/acetic acid/water system.

The *n*-propyl acetate/acetic acid/water system has been widely used in chemical industry, such as in the recovery of high purity acetic acid from dilute aqueous acetic acid solutions in various chemical processes. An improved understanding of this system is consequently very important in terms of its theoretical significance and also its potentially valuable applications. Recent investigations presented in the literature focus on the toluene/acetone/water system, which is a high interfacial tension system. By contrast, investigations on low or medium interfacial tension systems are rare. To our knowledge, no investigations on the influence of Marangoni convection on mass transfer in the *n*-propyl acetate/acetic acid/water system – representing a medium interfacial tension system – have been reported so far.

The aim of the work presented herein was to use time-resolved measurements to examine the influence of Marangoni convection on mass transfer during the drop free rising in the aqueous phase of an *n*-propyl acetate/acetic acid/water system. During all the experimental trials in this study, the direction of mass transfer was from the continuous phase to the dispersed phase. The effects of the drop diameter (focusing on large drops with diameters ≥ 3 mm) and the initial solute concentration in the continuous phase on the mass transfer rate were examined. All current models, including the Newman (1931) model, did not account for the influence of the initial solute concentration. We subsequently introduced a new correction factor, α, that varies with the initial solute concentration, into the Newman model previously modified by Steiner (1986). Lastly, the experimental data resulting from such trials were correlated with the modified Newman model proposed in this paper.

2. Experimental investigations

The extraction system used for mass transfer measurements in our experimental trials was composed of *n*-propyl acetate (the dispersed phase), acetic acid (the solute) and water (the continuous phase). Since the system was sensitive to contaminants, only high-purity chemicals were used: *n*-propyl acetate p.a. $\geq$ 99.0% (Aladdin), acetic acid p.a. $\geq$ 99.5% (National Medicine Group Chemical Reagent Co., Ltd.) and highly purified deionized water with a specific resistance of 18.25 MΩ cm. Prior to each run, the organic and aqueous phases were mutually saturated in a stirred vessel to avoid mass transfer between phases. The physical parameters of the chemical system at 30 °C are given in Table 1. Densities were calculated according to the individual densities of the pure components (Lu, 1982), viscosities were measured using a

Table 1
Physical parameters of the chemical system for 30 °C. ρ: density. μ: dynamic viscosity. σ: interfacial tension. D_A: diffusion coefficient. Subscript A refers to the transfer component.

Phase	ρ (kg/m^3)	μ (10^{-3} Pa s)	σ (10^{-3} N/m)	D_A (10^{-9} m^2/s)
Continuous[a]	997.6–1005.9	0.839–1.057	6.71–3.18	2.25–3.25
Dispersed[b]	877.2	0.521		3.76

[a] The solute concentration in the continuous phase c_{A0} is between 0.05 and 0.25 g/ml.

[b] The solute concentration in the dispersed phase c_{A0} is zero.