Effect of channel size on mass transfer during liquid–liquid plug flow in small scale extractors

CrossMark

Dimitrios Tsaoulidis, Panagiota Angeli *

Department of Chemical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

A R T I C L E   I N F O

A B S T R A C T

In this paper the effect of channel size on the mass transfer characteristics of liquid–liquid plug flow was investigated for capillaries with internal diameter ranging from 0.5 to 2 mm. The extraction of $\{UO_2\}^{2+}$ ions from nitric acid solutions into TBP/IL mixtures, relevant to spent nuclear fuel reprocessing, was studied for different residence times, dispersed phase fractions, and mixture velocities. It was found that extraction efficiencies increased as the channel size decreased. For a given channel length and for all channel sizes, an increase in mixture velocity decreased the extraction efficiency. The overall mass transfer coefficients ($k_L\alpha$) for all channels varied between 0.049 and 0.29 s^{-1} and decreased as the channel size increased. The evolution of the $k_L\alpha$ along the extraction channel showed a decreasing trend for all the channel sizes. The experimentally obtained mass transfer coefficients were compared with existing models for liquid–liquid and gas–liquid segmented flows from the literature. The results showed good agreement with the empirical correlation proposed for a liquid–liquid system. A finite element model was developed that solved the velocity and concentration fields in the channel for both phases considering a unit cell (one plug and one slug) with periodic boundary conditions at the inlet and the outlet. The model used experimental data for the geometric characteristics of the plug flow and predicted reasonably well the experimentally measured extraction efficiencies (with mean relative error of 11%).

1. Introduction

Two-phase, liquid–liquid systems find many applications in the process and chemical industries including solvent extraction, catalysis, polymerization, and nitration [1]. Solvent extraction in particular is one of the main processes in reprocessing of the spent fuel from a nuclear reactor. Commonly, uranium(VI) (and plutonium(IV)) are recovered from nitric acid solutions of the spent nuclear fuel through the PUREX process, with mixtures of organic solvents with tributylphosphate (TBP) as extractant [2]. Organic solvents, however, are flammable, volatile, and suffer from radiolysis, thus posing problems to the plants and threats to the

environment. Ionic liquids are considered as alternative candidates to conventional organic solvents and have found applications in catalytic reactions, separation processes, and synthesis [3]. In general, ionic liquids are salts composed from ions that have low melting points (below 100 °C), while many of them are liquid even at room temperature [4]. They have very good physical characteristics such as, negligible vapour pressure and high thermal stability in normal operating conditions, while their high resistance to radiation makes them suitable for spent nuclear fuel reprocessing. A popular anion choice for synthesizing hydrophobic ionic liquids that are chemically and thermally more stable and of lower viscosity compared to the majority of ionic liquids, is the bis(trifluoromethylsulfonyl)imide anion $[(CF_3SO_2)_2N]^-$ (abbreviated to $[Tf_2N]^-$) [5]. The production of the ionic liquids can be expensive though, and thus prevent their extensive use in large-scale

---

Nomenclature

A	cross sectional area [m^2]
$[C]_{aq,init}$	initial concentration of dioxouranium(VI) in aqueous phase [mol L^{-1}]
$[C]_{aq,fin}$	final concentration of dioxouranium(VI) in aqueous phase [mol L^{-1}]
$[C]_{aq,eq}$	concentration of dioxouranium(VI) in aqueous phase at equilibrium [mol L^{-1}]
D	diffusion coefficient [m^2 s^{-1}]
E_{eff}	extraction efficiency [%]
ID	internal diameter of the microchannel [m]
K_U	distribution coefficient of dioxouranium(VI) [dimensionless]
k_L	overall mass-transfer coefficient [m s^{-1}]
$k_L\alpha$	overall volumetric mass transfer coefficient [s^{-1}]
L	length [m]
Q	volumetric flow rate of fluid [m^3 s^{-1}]
t	residence time [s], $t = u_p/L_{ch}$
u	velocity [m s^{-1}]
V	volume [m^3]
w	width [m]

Greek letters

α	specific interfacial area [m^2 m^{-3}]
δ	film thickness [μm]
ε	volume fraction [dimensionless]
μ	dynamic viscosity [kg m^{-1} s^{-1}]
ρ	density [kg m^{-3}]
τ	residence time [s], $\tau = V_{ch}/Q_{mix}$

Subscripts

c	continuous
cap	cap
ch	channel
d	dispersed phase
eff	efficiency
film	film
g	gas
mix	mixture
IL	ionic liquid
p	plug
UC	unit cell

---

systems. The application of intensified small scale units in extraction processes would reduce the amount of solvent required and associated costs, and would make economically viable the use of ionic liquids.

Mixing and mass transfer are significantly enhanced in small scale two-phase contactors, despite the absence of turbulence, as a result of high specific interfacial areas, increased molecular diffusion through the thin fluid layers, improved radial mixing due to recirculation within phases [6], convection induced by surface tension gradients, and flow instabilities between the two immiscible phases [7]. The increased importance of interfacial and viscous forces in small channels, however, results in different patterns to those encountered in large scale systems [5], whose characteristics need to be studied as they affect mass transfer. One of the most common configurations in liquid–liquid flows is the plug (segmented) flow pattern, where drops of one liquid (plugs), with diameter larger than the channel diameter, are formed within the other liquid, while a thin film separates the plugs from the channel wall.

Operating small scale contactors with the high viscosity ionic liquids would bring in a number of challenges. In plug flow the size of the segments is among others an important parameter since it affects the interfacial area available for mass transfer and the intensity of the circulation patterns, and subsequently the heat and mass transfer rates. In small-channel flows, both the dispersed and the continuous phase properties influence the formation of the plug. Studies on the effect viscosity on the formation of the plugs and on the mixing inside the segments has been performed both numerically [8,9] and experimentally [10–12], however the results are limited and not conclusive. The use of high viscous liquids as continuous phase is also expected to affect the magnitude of the film that surrounds the dispersed plug, which is related to the Ca number, and the internal circulation within the dispersed plug which is affected by the shear stress induced by the liquid film. Studies on internal circulation in liquid–liquid systems that involve ionic liquids have been limited so far. Using numerical simulations, Kashid et al. [13], showed that the circulation patterns in the two phases are independent of viscosity. Dore et al. [6,14] investigated the mixing patterns in aqueous-ionic liquid systems and the internal circulation within the continuous or dispersed

aqueous phase in plug flow, using micro-Particle Image Velocimetry (μ-PIV). It was found that the circulation within the aqueous segments is strongly related to the flow rates and the size of the segments. Scheiff et al. [15] studied the internal circulation within ionic liquid segments in an organic-ionic liquid two-phase flow. They found that the internal circulation within the ionic liquid segments is slower than in aqueous segments by a factor of 2–10. Moreover, they showed that circulation velocity was higher when the ionic liquid was the continuous phase than when it was the dispersed.

To evaluate the performance of two-phase small scale separators (gas–liquid or liquid–liquid) the mass transfer coefficients need to be known. A number of models have been developed for gas–liquid Taylor bubble (plug) flow based on both empirical correlations, and on film and penetration theory. These models provide estimates of the mass transfer coefficient in the continuous liquid phase, while the mass transfer resistance in the gas phase is considered negligible. The individual contributions of the caps of the bubbles and of the fully developed film separating the bubbles from the channel wall are estimated. Bercic and Pintar [16] proposed a model for the calculation of the mass transfer coefficient in small channels (Eq. (1)), that includes only the contribution of the caps because of the rapid saturation of the film.

$$k_L\alpha = \frac{0.111 u_p^{1.19}}{((1-\varepsilon_d)L_{UC})^{0.57}} \tag{1}$$

However, the absence of any parameter related to the channel size limits the application of the model to different two-phase systems.

Van Baten and Krishna [17] and Irandoust and Anderson [18] included in their models the contributions of both bubble caps and film (Eq. (2)). Van Baten and Krishna [17] evaluated the contribution of the caps (Eq. (3)) according to the Higbie penetration theory, whilst the transfer through the film (Eqs. (4) or (5)) was obtained based on mass transfer in a falling film in laminar flow. The mass transfer rates predicted by the correlations agreed well with the results from CFD (computational fluid dynamics) simulations.

$$k_L\alpha = k_{L,cap}\alpha_{cap} + k_{L,film}\alpha_{film} \tag{2}$$