Chemical Engineering Journal 235 (2014) 109–123

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Electrically induced liquid–liquid extraction from organic mixtures with the use of ionic liquids

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HIGHLIGHTS

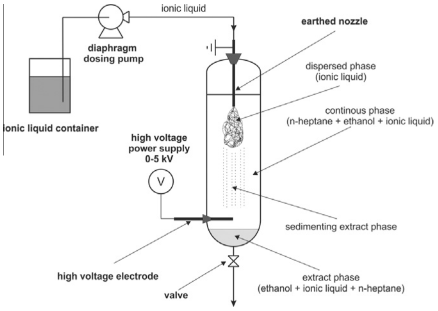
- Novel azeotrope breakage using an electrostatically dispersed ionic liquid is shown.
- A highly efficient, low energy attractive technique for enhancing mass transfer and liquid–liquid contact is demonstrated.
- Voltage–current critical problem for the electrically enhanced liquid–liquid contactor is solved.
- A simulation method was demonstrated for predicting all important time dependent phenomena.

ARTICLE INFO

Article history:
Received 4 July 2013
Received in revised form 30 August 2013
Accepted 3 September 2013
Available online 13 September 2013

Keywords:
Liquid–liquid extraction
Charged drops of ionic liquid
PDA analysis
Electric current characteristics
Finite element analysis

GRAPHICAL ABSTRACT



ABSTRACT

An innovative methodology for a liquid–liquid extraction process is presented based on an electrically induced emulsion of an ionic liquid as the extracting solvent dispersed in an organic mixture. As an example 1-butyl-3-methyl-imidazolium methylsulfate [bmim][$MeSO_4$] was applied for extraction of ethanol from a mixture with *n*-heptane, which forms an azeotrope at a composition of 50 wt.%. Liquid–liquid extraction provides an environmentally friendly process as an alternative to azeotropic distillation, pervaporation and reverse osmosis because these procedures require the use of large amounts of energy, volatile organic compounds, or high pressures.

The diameters of the dispersed droplets in the emulsion were controlled by the voltage between the nozzle and another electrode situated near the bottom of the liquid–liquid contactor. For better understanding of the electro-emulsion mechanism, a series of experiments using phase Doppler anemometry were performed for evaluating the relationship between the applied electrical voltage, droplet diameter and velocity distribution. Due to the highly developed interfacial area during the motion of the droplet phase towards the bottom electrode, the extraction process was sufficiently fast for the system to approach equilibrium. The solvent was then separated from the organic mixture for recovery of ethanol by distillation which is extremely easy due to the very low vapor pressure of the ionic liquid. On the other hand the remaining concentration of ethanol in the organic mixture was measured by the use of gas chromatography.

Special attention was paid to the electric current characteristics of the system which may influence the feasibility of an otherwise excellent extraction process. The problem of possible excessive current variations was addressed and a method for solving this is described in the paper.

Additionally, the whole process was illustrated by numerical simulation with the use of our own simulation software based on the finite element method.

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http://dx.doi.org/10.1016/j.cej.2013.09.019

Nomenclature

a_d	specific interface area (m^2/m^3)
c_D	drag coefficient ($kg/(m^3\ s)$)
$\mathbf{D}$	rate of deformation tensor (1/s)
D_c	continuous phase diffusion coefficient (m^2/s)
D_d	dispersed phase diffusion coefficient (m^2/s)
d	droplet diameter (m)
$\mathbf{E}$	electric field strength (V/m)
F_B	buoyancy force for single particle (N)
F_D	drag force for single particle (N)
F_{EP}	electrophoresis force (N)
f_c	volume fraction of continuous phase (–)
f_d	volume fraction of dispersed phase (–)
K_{tot}	total mass transfer coefficient ($kg/(m^2\ s)$)
k_c	mass transport coefficient in continuous phase (m/s)
k_d	mass transport coefficient in dispersed phase (m/s)
k_e	liquid–liquid distribution coefficient at the equilibrium (–)
g	gravity (m/s^2)
m_d	mass of droplet that represents a cloud of droplets of the same diameter (kg)
n_d	droplet number density distribution ($1/m^3$)
p	pressure (Pa)
q	electric charge of the particle/droplet (C)
r	correlation coefficient (–)
r_M	mass transfer rate ($kg/(m^2\ s)$)
t	time (s)
$\mathbf{u}_d$	dispersed phase velocity (m/s)
$\mathbf{v}$	local velocity of liquid (m/s)
v_{rel}	relative (slip) velocity between phases (m/s)
x_{Et}	mass fraction of ethanol in the raffinate (–)
$x_{Et,i}$	mass fraction of ethanol in the raffinate at the interface (–)
$x_{Et,e}$	equilibrium value of mass fraction of ethanol in the raffinate corresponding to y_{Et} (–)
y_{Et}	mass fraction of ethanol in the extract (–)
$y_{Et,i}$	mass fraction of ethanol in the extract at the interface (–)

Greek symbols

ε_r	relative permittivity of materials (–)
λ	relaxation time of the dielectric liquid (s)
μ	bulk viscosity (Pa s)
μ_c	continuous phase viscosity (Pa s)
ρ	bulk density (kg/m^3)
ρ_c	continuous phase density (kg/m^3)
ρ_d	continuous phase density (kg/m^3)
ρ_{Ec}	electric space charge density (C/m^3)
σ	electric conductivity (S/m)
Φ	electric potential (V)

1. Introduction

This paper is concerned with the novel application of electrostatic spraying techniques to the intensification of mass transfer in a liquid–liquid system comprising an ionic liquid and a second liquid phase, an azeotropic mixture of ethanol in *n*-heptane. The main focus of the paper is the experimental measurement and simulation of droplet behavior and mass transfer in a batch extraction column in which the ethanol-*n*-heptane azeotrope is "broken" by the extraction of ethanol into the ionic liquid, butyl-methyl-imidizolium methylsulfate $[bmim]^+$–$[MeSO_4]^-$.

Liquid–liquid extraction is one of the basic unit operations employed in the chemical process industries for product separation and purification. The extraction rate is determined by the mass transfer coefficient, the interfacial area and the concentration difference between the phases. Since in most cases the diffusivities of liquids are small, a significant energy input must be provided to force mass transfer rate to occur at an acceptable rate. In practice, mechanical energy is introduced in well known devices such as pulsed plate columns, mechanical agitators, rotating discs, and centrifugal contactors [1]. Such devices represent inefficient use of energy because only a small percentage of the applied energy is actually utilized for the mass transfer enhancement and the majority is dissipated either as heat or as mechanical vibration. In addition, conventional extraction techniques are not well suited to handling viscous extractants such as ionic liquids. Another liquid–liquid process of relevance here in addition to solvent extraction is phase transfer catalysis using an immiscible solvent either as a reaction medium or as a means of delivering substrate to a reaction medium [2]. Droplet size and volumetric hold-up of the dispersed phase are fundamental parameters which control the effective interfacial area for mass transfer and reaction. In addition, in liquid–liquid contacting the extent and nature of secondary flows in the continuous phase can strongly influence the mixing and residence time distribution and thus overall performance [3,4].

The ability of superimposed electric fields to improve liquid–liquid processes has been well known for many years [5,6]. Over the past few decades an extensive effort has been directed to finding new applications of electrical energy in the field of mass-transfer operations, mainly solvent extraction [7,8]. The direct utilization of electrical energy offers several advantages, especially in multiphase systems [9]. The electrical energy supplied interacts selectively with an interface and, to a lesser degree, with the bulk. This interaction may lead to increased rates of heat or mass transfer across the interface.

Electric fields improve both factors influencing mass transfer rate: (a) the mass transfer coefficient; (b) the interfacial liquid–liquid surface area. In both cases the main mechanisms promoting interfacial phenomena in the presence of an electric field are: (a) higher terminal droplet velocities resulting from electrical field forces on the charged drops in the direction of motion (b) generation of electrically induced circulatory flows in the neighborhood of the interface (c) interfacial-tension-induced surface flows (Marangoni effects) due to the presence of electric charges at the liquid–liquid interface. It has been amply demonstrated that electrostatic spraying produces substantial reductions in drop size thus enhancing interfacial area per unit volume, accelerates dispersion of drops though a second immiscible liquid, thus improving mass transfer rate, enhances overall mixing, and can result in more effective coalescence which is important for product and solvent recovery [10–12].

Ionic liquid solvents are a family of novel inorganic designer solvents which exhibit a high degree of catalytic activity and multiple options for chemical and physical structure. They are excellent solvents for separations and as reaction media, offering a real alternative to conventional organic solvents and their associated emission constraints [13–16]. Ionic liquids are salts that are liquid at ambient temperatures. The well documented features of ionic liquids (ILs) includes: low melting organic salts (−60 C); a stable liquid range of over 300 K; very low vapor pressure at room temperature; selective solubility of water and organics; low solubility