A state-of-the-art review on single drop study in liquid-liquid extraction: Experiments and simulations

Jiyizhe Zhang¹, Yundong Wang^{1,*}, Geoffrey W Stevens², Weiyang Fei¹

¹*The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*

²*Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia*

Abstract: The experimental and numerical investigations of single drop in liquid/liquid extraction system have been reviewed with particular focus on experimental techniques and computational fluid dynamic simulation approaches. Comprehensive surveys of available experimental techniques and numerical approaches for single drop rising and falling were given. Subsequently, single drop mass transfer was also reviewed both experimentally and numerically. Additionally, single drop breakage and coalescence process and the influencing factors were summarized and compared, so as to establish sub-models for population balance model. Future directions on single drop mass transfer, drop breakage and coalescence were suggested. It is believed that the single drop is a powerful tool to assist extraction process design from lab-scale to pilot-scale.

Key words: Solvent extraction; mass transfer; single drop; drop breakage and coalescence; computational fluid dynamic simulation; population balance model

1. Introduction

Liquid-liquid extraction processes are well suited to industries which need to separate heat-sensitive, relatively nonvolatile or high value liquid feeds [1]. They are widely used in hydrometallurgical, petrochemical, pharmaceutical, environmental and nuclear fuel reprocessing industries. Liquid-liquid extraction is based on the partial miscibility of liquids and used to separate a dissolved component from its solvent by mass transfer to a second solvent. Typical industrial application includes recovery of metals such as copper, cobalt, nickel and rare earth elements from acidic leach liquors, extraction of aliphatic aromatic and naphthenic chemicals, refining of uranium, plutonium and other radioactive isotopes from spent fuel elements, extraction of antibiotics and separation from fermentation broth, recovery of vegetable oil from natural substrates, etc.

Extractors are usually classified according to the ways of inter-dispersing the phases and producing the countercurrent flow pattern, namely, mixer-settler, column and centrifugal contactors [2]. Mixer-settlers are widely used when a process requires longer residence times and when the solutions are easily separated by gravity. But they also require a large facility area and high capital cost. Therefore, mixer-settlers are commonly applied in nuclear industry, hydrometallurgy, as well as rare earth separation [3, 4]. Extraction columns have many types, including rotating disc contactor column (RDC), pulsed column, packed column, sieve tray column and so on [5]. Centrifugal extractors employ a spinning rotor that intensively mixes the two phases and separates the two phase inside the rotor, resulting in efficient and fast phase separation [6]. It is obvious that centrifugal extractors can treat systems with low density difference and systems with short contact time. They

are inevitably high capital, operation and maintenance cost.

Despite years of study, the design of extraction equipment still relies on pilot-scale experiments to realize a full-scale design for a new process. The pilot-scale experiments usually cause most of the costs and time, which is difficult for the chemical companies to catch up with the rapid changing market. On the basis of these experiments, models are derived for the scale-up design, like stage-wise models, dispersion or back-mixing model. These models are mainly based on experiences and far from optimum due to oversimplified assumptions. Moreover, the extraction process is very complicated because various interactions between droplets and the two phases influence the overall conditions. Interactions like drop rising or falling, breakage and coalescence, as well as mass transfer [7] coupled with different time and length scales make the scale-up design difficult to handle. Although the rapid progress has been made in various simulation methods provides a detailed insight into the transport phenomena which can be applied as a useful design tool, it is still difficult to perform exact simulation of the extraction process and describe the above interactions.

Fig. 1. Complex interactions within extraction column

Therefore, people are searching a more scientific way to reduce the effort of pilot-scale experiments and avoid previous experience and oversimplified models. Single drop experiments consume less chemicals to obtain design parameters which seems to be a good choice. In this case, hydrodynamic and mass transfer behavior, like drop terminal velocity, coalescence probability, mass transfer coefficient could be determined in a lab-scale unit. Several advantages are summarized below:

- Reduce the complexity of the drop swarm to single drops, which makes it easier for study;
- Diminish the number of influencing factors of the extraction process and identify separately;
- Small amount of liquid is used to save cost with considerable effort;
- Easy to control and analyze;

Fig. 2. Single drop study to breakdown the complexity

But it is obvious that there is a big gap between single drop to the whole extraction process, therefore, accurate and reliable models are required to predict droplets behaviors with various time and length scale. A promising approach to contain the complex droplet interactions is the population balance model (PBM). Within the model, characteristic features of droplet, such as terminal velocities, breakage and coalescence behavior and mass transfer mechanisms are described as sub-models or parameters, which could be measured from single drop experiment. By establishing more accurate sub-models and connecting them together, it is possible to predict the drop size distribution (DSD) as fundamentals for the scale-up process. In this way, PBM builds a bridge between single drop study and scale-up design and offers a more rational and efficient way for industrial application. Except for experimental methods, simulation is likely to provide basic information in the sub-models, since more details in single drop behaviors can be derived which are not accessible by observation. Furthermore, computational fluid dynamic (CFD) simulation couple with PBM are able to predict the DSD and the fluid flow structure simultaneously, which is more desirable for the scale-up design.

The present paper attempts to review some researches from fundamental single drop perspective for deep understanding liquid-liquid extraction process. Firstly, basic hydrodynamic behavior of rising and falling are introduced, where the terminal velocity is mainly discussed. Next, single drop mass transfer is reviewed in the second part, which is of major importance and can be influenced dramatically by various factors. Then, interactions between drops as coalescence and breakage are considered. These two situations are studied because they are closely related to drop size distribution (DSD), and eventually influence the mass transfer rate and the operational conditions. Both experimental techniques and simulation methods are summarized in the above three sections. Finally, several prospects of the single drop studies are suggested.

2. Single drop rising and falling

Although single drop rising and falling in an ambient quiescent liquid rarely occur in extraction column for several reasons such as different flow patterns, swarm effect, mass transfer or column internals, it is one of the most fundamental cases for further studying and modelling of two-phase flow in an extraction unit.

For single drop rising without heat and mass transfer, drops with different diameters have

different corresponding terminal velocities. Fig.3 shows the relationship between the drop terminal velocity with its diameters when rising or falling in a continuous phase [8]. Four sections are involved, namely, rigid, circulating, oscillating and deformed drops. When the diameter is very small, drops can be modelled as rigid particles (A) with immobile interface. As shear force at the interface increases with the drop diameters and the internal circulation is induced, terminal velocities increase for circulating drops (B), therefore, a mobile interface has to be taken into account. As the drop diameter increased further, the drop cannot maintain its spherical shape and start to become oblate ellipsoidal and oscillate periodically (C). In the last stage, drops are deformed and are likely to wobble through the continuous phase (D).

Fig. 3. Drop behavior as a function of drop diameter (adapted from [8])

Single drop rising or falling is governed by physical properties of dispersed and continuous phases, as well as properties of the interface. With the help of single drop experiment and simulation, the above influencing factors can be identified and even quantified by correlations and models. The most prominent case is to determine the terminal velocity as a function of drop diameter, which can be derived from the Navier-Stokes equations. However, the analytical solution for the equations have been only derived for creeping flow by Hadamard [9] and Rybczynski [10]. For higher Reynolds number, terminal velocity can be calculated in three ways [11]:

- Indirect calculation by so-called standard drag curve. The drag coefficient was plotted as a function of Reynolds number. To predict terminal velocity, an iteration procedure was needed since Reynolds number contains terminal velocity as well as drop diameter. Many correlations were available in literatures such as Hamielec [12], Feng and Michaelides [13] and so on. However, these correlations are restricted to certain range of Reynolds number. Some of the correlations are summarized in Table 1.

Table 1 Drag coefficient correlations in literature

Authors	Year	Correlations	Range of Reynold number	Application area
---------	------	--------------	-------------------------	------------------

Rybszynski [10]	1911	$C_D = \frac{24}{Re} \frac{2/3 + \mu^*}{1 + \mu^*} \quad (1)$	$Re \ll 1$	Drop
Rivkind <i>et. al</i> [14]	2001	$C_D = \frac{1}{1 + \mu^*} \left[\mu^* \left(\frac{24}{Re} + \frac{4}{Re^{1/3}} \right) + \frac{14.9}{Re^{0.78}} \right] \quad (2)$	$10 \leq Re < 100$	Drop
Hamielec <i>et. al</i> [12]	1963	$C_D = \frac{3.05(783\mu^{*2} + 2142\mu^* + 1080)}{(60 + 29\mu^*)(4 + 3\mu^*)Re^{0.74}} \quad (3)$	$4 < Re < 100$	Drop
Saboni <i>et. al</i> [15]	2002	$C_D = \frac{\left[\mu^* \left(\frac{24}{Re} + \frac{4}{Re^{1/3}} \right) + \frac{14.9}{Re^{0.78}} \right] Re^2 + 40 \frac{3\mu^{*2} + 2}{Re} + 15\mu^* + 10}{(1 + \mu^*)(5 + Re^2)} \quad (4)$	$0.01 \leq Re < 400$	Drop, bubble and solid particle
Brauer [16]	1973	$C_D = \frac{16}{Re} + \frac{14.9}{Re^{0.78}} \left(\frac{1}{1 + 10Re^{-0.6}} \right) \quad (5)$	$Re < 3 \times 10^5$	Drop and bubble
Polyanin <i>et. al</i> [17]	1994	$C_D = \frac{1}{1 + \mu^*} \left(\frac{16}{Re} + \frac{32}{Re + 32} \right) \frac{\mu^*}{1 + \mu^*} \frac{24}{Re} (1 + 1.5Re^{0.678}) \quad (6)$	$0 \leq Re \leq 100$	Drop
		$C_D = \frac{26.5}{Re^{0.78}} \left[\frac{(1.3 + \mu^*)^2 - 0.5}{(1.3 + \mu^*)(2 + \mu^*)} \right] \quad (7)$	$Re \leq 5$	
Feng <i>et. al</i> [13]	2001	$C_D = \frac{2 - \mu^*}{2} \left[\frac{48}{Re} \left(1 + \frac{2.21}{Re^{1/2}} - \frac{2.14}{Re} \right) + \frac{4\mu^*}{6 + \mu^*} (17 \times Re^{-2/3}) \right] \quad (8)$	$0.1 < Re < 10$	Drop

- Use of generalized graphical correlation of Reynolds number versus Eotvös number. Proposed by Clift *et al.* [18], the diagram was given in double logarithmic scale covering spherical, ellipsoidal, wobbling and some other regimes. But it should not be applied to systems with extreme continuous and dispersed phase density or viscosity ratios.
- Explicit correlation of terminal velocity against drop diameter. These correlations were semi-empirical in most cases. For example, correlation by Grace *et al.* [19] permitted to predict terminal velocity in contaminated systems by using a correction function. Another widely used model proposed by Henschke [20] needs to be fitted by experimental data.

2.1 Experimental studies

As summarized in Table 2, different models and correlations for single drop rising/falling were tested or extended and the application scopes were determined. Different test systems were used and were kept extremely pure with special caution. Experimental setups were considerably simple and mostly in extraction columns filled with continuous phase liquid. Then the dispersed phase was injected from the bottom or released from the top of the column. Earlier studies [21-25] measured terminal velocity of a variety of liquid drops immersed in water, covering a wide range of physical properties. Drop size was measured by drawing a specific volume with capillary tube or burette, or by counting the number of drops produced by a given volume of dispersed liquid. These methods

required careful operations and were sometimes tedious. The terminal velocities were measured by timing method, i.e. measuring the time when droplets pass through a certain distance. The passage of the drops should ensure the terminal velocities are reached and also avoid the end effects. Transient velocities were difficult to obtain with this method.

Generalized curve obtained by Hu *et al.* [21] could be used directly to predict terminal velocity, drag coefficient and Reynolds and Weber numbers for any given drop size. Klee *et al.* [22] proposed two correlations for terminal velocity and studied the eccentricity of drops. Since oscillation of drops were very complex, and has been paid much attention by many researchers. Oscillation frequencies and amplitudes of nineteen pure systems were measured by Schroeder *et al.* [23]. Empirical equation of terminal velocity for circulating and oscillating drops were derived by Thorsen *et al.* [24] from seven high interfacial tension systems. Additionally, oscillation frequency and terminal velocity of oscillation drops were proposed by Edge *et al.* [25]. A transition from non-oscillating to oscillating drop was found at a break when plotting a modified Weber number against a modified Ohnesorge number.

Table 2 Single drop free rising/falling experimental studies

Authors	Year	System	Drop motion	Drop diameter range (mm)	Objectives
Hu <i>et al.</i> [21]	1955	Ten organic liquids/water	Falling	5.11-15.37	Terminal velocity Drag coefficient
Klee <i>et al.</i> [22]	1956	Eleven organic liquids/water	Rising Falling	No exact range	Terminal velocity Drag coefficient Frequencies
Schroeder <i>et al.</i> [23]	1965	Nineteen pure system	Falling	No exact range	Amplitudes of oscillations
Thorsen <i>et al.</i> [24]	1968	Carbon tetrachloride/water Ethylene bromide/water Methylene bromide/water Bromoform/water Tetrabromoethane/water Ethyl bromide/water O-Dichlorobenzene/water Chlorobenzene/water 1,2 dichloroethane/water	Falling	0.6-3.16	Terminal velocity
Edge <i>et al.</i> [25]	1971	Ethyl-bromide/water Sys-tetrachloroethane/water 1,2 dibromoethane/water	Falling	1.62-8.82	Terminal velocity Frequency of oscillation
Yamaguchi <i>et al.</i> [26]	1975	Benzene/water Glycerine/carbon tetrachloride	Rising Falling	3.03-8.09	Terminal velocity
Wegener <i>et al.</i> [27]	2009	Toluene/water	Rising	1-7	Terminal velocity

Baümler <i>et al.</i> [28]	2011	Toluene/water	Rising	1-7	Terminal velocity
		<i>N</i> -butyl acetate/water		1-4.5	Aspect ratio
		<i>N</i> -butanol/water		1-4	

Recently, with the help of photographic technique, the configuration and trajectory of single drop rising/falling can be recorded by camera. Drop with certain diameter can be obtained by either precision dosing pump, or via image processing. The latter is done through commercial software to know the pixel length and then convert them into actual length. High speed camera always set perpendicularly to the column and to record the entire or part of the path. After image processing, the velocities could be calculated by vertical position of the mass center of the drop for each frame. In this way, both transient velocities and terminal velocities can be measured accurately and reduce the operational errors.

Wegener *et al.* [27] presented single drop experiment to study toluene droplets rising in water ranging from 1.0 to 7.0 mm. A semiempirical correlation to predict the single drop rising/falling terminal velocity based on experimental data was presented. Interestingly, for 3mm droplets, a bifurcation velocity was observed, which two distinct terminal rise velocities were observed, as shown in Fig.4. Different interfacial tension standard systems were investigated by Baümler *et al.* [28]. Comparisons between different systems were presented and terminal rise velocity, aspect ratio, and the onset of shape oscillation were determined. However, they found that investigated correlations lost accuracy with the decrease of interfacial tension.

Fig. 4. Experimental result of toluene-water system [27].

((a) terminal velocity as a function of drop diameter and (b) drop rise bifurcation velocity)

(Reprinted from AIChE Journal, 56, M. Wegener, M. Kraume, A. R. Paschedag, 1-9, Copyright (2019), with permission from John Wiley and Sons)

Although the test systems were retained extreme clean, contaminations or surfactants inevitably existed in real situation. These factors would block the mobility of the drop surface and thus slowed down the velocity [29-32].

2.2 Simulation studies

To reduce time and effort to precisely control the purity and to have an in-depth insight into the transport phenomena, computational fluid dynamic (CFD) simulation provides an efficient way. The simulation of single drops in a continuous liquid phase reveals a more detailed look on time

and length scales where experiments are not accessible, and can be served as a validation of the experimental data. Unlike solid particles, droplets move with topological changes, along with mass transfer and surfactant which largely influence the structure of the interface. Thus, one of the main issues in simulation is to describe the interface changes exactly with low cost. Generally, methods to deal with interface change are summarized in Fig. 5. Moving mesh method and fixed mesh method are widely used in most cases. Diffuse interface method and Lattice Boltzmann method also provide a feasible way. Several options for fixed mesh methods, e.g. front-capturing method, front-tracking method and hybrid the previous methods. Interfacial forces are also crucial when describe the interface. In this case, continuous surface stress (CSS) model, continuum surface force (CSF) model and ghost fluid method (GFM) most widely-used.

Several representative studies were listed in Table 3. For moving mesh method, as the name suggested, a moving mesh is used to track the interface. As the topology of the interface changes, the nodes are moving in accordance with the change, allowing direct implementation of boundary conditions at the interface. This results in a very exact and sharp representation of the interface, but is limited to moderately deformed interface without significant topological changes, i.e. droplet coalescence or breakup. Bäumlér *et al.* [28] investigated three standard test systems suggested by EFCE [33] with no mass transfer experimentally and numerically. The simulation was performed by the academic code NAVIER with mesh moving method to feature the interface. The numerical results were in excellent agreement with experiments results in all three test systems.

Fig. 5. Different simulation methods for single drop study

Fixed mesh method, obviously, use a fixed mesh with different approaches to locate the interface between the phases, including front-capturing method, front-tracking method and hybrid capturing and tracking method. These methods are able to describe large deformation of the interface. But the main difficulty arises in maintaining a sharp interface between phases.

Front-capturing method represents the interface by using special markers or indicator functions in an implicit way, which can be categorized in point-based or marker-based, surface capturing and volume capturing method. Marker-based method is one of the oldest methods where massless marker particles are used to identify each fluid and thus the motion of the interface. Although it is easy to be implemented, it fails to describe large deformation due to the necessity of redistributing the markers. Another well-known method is volume capturing method, e.g. volume of fluid (VOF)[34] method. The basic idea is to use a volume fraction function to describe the phases and the interface. The method is capable of handling problems with significant interface topology deformation and does not suffer from mass losses, however, these are usually come at a high

computational cost. Surface-capturing method offers another more accurate option, like the level-set[35] method. In this method, the topology changes of the interface are fully described by the zero-level set function. The method is more accurate and is easy to be implemented in three-dimensional calculation. However, the main drawback is the possible loss of mass for significant deformed topology. Several representative work will be briefly reviewed here. Bertakis *et al.* [36] utilized level-set function for capturing the interface movement to simulate *n*-butanol droplets freely sediment in water. The finite-element and the extended finite-element methods were implemented and evaluated. Compared to the traditional method, the extended method provided more accurate results and a wide spectrum of droplet diameters that also covers the oscillating region. In the study of Engberg *et al.* [37], level-set code was developed for simulate single drop rising in three standard test systems. Interfacial force is described by both continuum surface force (CSF) model and the ghost fluid method (GFM) to prevent volume (or mass) loss during the reinitialization of the level set function. Simulation results were in accordance with experimental results and the onset of oscillations was correctly predicted. Huang *et al.* [38] applied VOF method in conjunction with the CSF model to investigate the effects of physical properties on the drop rising behaviors. The simulation results showed a good agreement with experiments.

Front-tracking method, on the other hand, tracks the interface explicitly as the interface moves. This approach is extremely accurate and robust yet rather complex to implement. Dijkhuizen *et al.*[39] studied the air bubble or toluene drop rising in water by 3D front-tracking model. Drag coefficients and lift forces were computed with a high accuracy. Recent years, hybrid capturing and tracking method[40] is proposed to combine the advantages and eliminate the weakness of the previous two methods. Normally, a stationary grid is used for fluid flow and the interface is tracked by a separate grid, but is rather complex.

Other methods like diffuse interface method does not require any explicit interface treatments. The interface changes naturally based on the thermodynamics of the model. The method provides a feasible way to run simulations of large-scale three-dimensional system and with significant topological deformation of the interface, but may not be accurate enough since the width of the interface is enlarged to allow easier computations. Another method as LBM was used in Komrakova *et al.* [41]to study the motion of *n*-butanol drop in water. Space and time are discrete in LBM method and identical particles of equal mass populate at each lattice. It is able to capture the drop shape especially in the oscillating regime was demonstrated. The results were compared to experimental and numerical ones and to semi-empirical correlations.

Table 3 Single drop free rising/falling simulation studies

Authors	Year	System	Moving Interface Method	Dimensional
Waheed <i>et al.</i> [42]	2004	/	/	2D
Dijkhuizen <i>et al.</i> [39]	2005	Air bubble/water Toluene/water	Front-tracking method	3D

Bertakis <i>et al.</i> [36]	2010	<i>N</i> -butanol/water	Level-set	3D
Eiswirth <i>et al.</i> [43]	2011	Toluene/water	Level-set	2D
Bäumler <i>et al.</i> [28]	2011	Toluene/water <i>N</i> -butyl acetate/water <i>N</i> -butanol/water	Mesh moving method	2D
Komrakova <i>et al.</i> [41]	2013	<i>N</i> -butanol/ water	LBM	3D
Engberg <i>et al.</i> [37]	2014	Toluene/water <i>N</i> -butyl acetate/water <i>N</i> -butanol/water	Level-set	2D
Engberg <i>et al.</i> [44]	2015	Toluene/water	Level-set	3D
Huang <i>et al.</i> [38]	2018	Toluene/water	VOF	2D

3. Single drop mass transfer

Single drop with mass transfer is a relatively complex situation compared to drop rising or falling in a quiescent liquid. A third or more component [45] is added and could be transfer from one phase to another across the interface by different solubilities. As the most crucial part influencing the whole extraction performance, mass transfer should be analyzed in details and decomposed to single drop mass transfer behavior foremost.

3.1 Experimental studies

To study mass transfer performance for single drop in a lab-scale test cell, two types of cells are mainly used. One is the traditional drop rising column with a funnel on the top to collect the dispersed phase, which is easy to operate. However, the total length of the column should be high enough to have the long residence time. Another type of cell is like a conical venturi tube as Fig.6 shows, in which the drop firstly rising for a distance and then suspend for a while when the continuous phase begins to flow in an opposite direction. In both cases, the direction of mass transfer occurs from either continuous to disperse phase (c→d) or disperse to continuous (d→c).

Fig. 6. Schematic of single drop mass transfer cell

(a) single drop rising column and (b) conical venturi tube for single drop mass transfer

Mass transfer resistance lies in three cases: inside the droplet only (internal problem) ,outside the droplet only (external problem), or in both phases (conjugate problem) [11]. During the mass transfer process, various phenomena are involved, namely, the shift of moving trajectory, interfacial instability and turbulence, or the contamination may affect the mass transfer rate. Several representative studies were listed in Table 4. Perspectives of these studies related to mass transfer can be categorized as [46]: hydrodynamic change, interfacial instability, contamination and some other factors.

Table 4 Single drop mass transfer experimental study

Authors	Year	System	Size of column (mm)	Mass transfer direction	Resistance
Sherwood <i>et al.</i> [47]	1939	Water/Acetic acid/MIBK Benzene/acetic acid/water	1.74 inches×60 inches tall	d-c	Inside drop
West <i>et al.</i> [48]	1951	Benzene/acetic acid/water Water/ethyl acetate	44×1520	d-c	Inside drop
Skelland <i>et al.</i> [49]	1964	Ethyl acetoacetate/water Glycol diacetate/water Glyceryl triacetate/water	75×140,280,540,780,1030	d-c	Inside drop
Yamaguchi <i>et al.</i> [26]	1975	Water(glycerine solution)/iodine/benzene Water(glycerine solution)/iodine/CCl ₄	70×800 70×1000	d-c	Aqueous phase
Slater <i>et al.</i> [50]	1988	Iso-propyl benzene/acetic acid/water	152×400	d-c	Inside drop
Steiner <i>et al.</i> [51]	1990	Toluene/water	50×1000	c-d d-c	Both phases

Hassan <i>et al.</i> [52]	1992	Toluene/acetone/water <i>N</i> -heptane/acetone/water	50×1000	d-c	/
Temos <i>et al.</i> [46]	1995	MIBK/water/acetic acid	38×1220	c-d d-c	Both phases
Henschke <i>et al.</i> [20]	1999	<i>N</i> -butyl acetate/acetone/water	Conical test cell	c-d	Both phases
Henschke <i>et al.</i> [53]	2002	Toluene/acetone/water <i>N</i> -butyl acetate/acetone/water	Conical test cell with sieve trays	c-d	Inside drop
Lee <i>et al.</i> [54]	2003	Carbon tetrachloride/acetic acid/water	/	d-c	/
Wegener <i>et al.</i> [55]	2009	Toluene/acetone/water	75×1000	d-c	Inside drop
Wegener <i>et al.</i> [56]	2009	Toluene/acetone/water	50×150	c-d d-c	/
Azizi <i>et al.</i> [57]	2010	Toluene/acetic acid/water	72×650	d-c	Inside drop
Wegener <i>et al.</i> [58]	2011	Toluene/acetone/water	75×1000	c-d d-c	Inside drop
Wegener <i>et al.</i> [59]	2012	Toluene/acetone/water	75×1000	c-d d-c	Inside drop
Zheng <i>et al.</i> [60]	2014	<i>N</i> -propyl acetate/acetic/water	40×100,200,300,400,500	c-d	Inside drop
Huang <i>et al.</i> [61]	2016	Chloroform/ethanol/water	38×200 38×500	d-c	Both phases
Azizi <i>et al.</i> [62]	2016	Toluene/acetone/water	100×480	d-c	Inside drop

3.1.1 Hydrodynamic factors

Considering single drop moving in a quiescent liquid, it experiences three stages during its life: drop formation, rising or falling as well as coalescence at the end of bulk interface. The fulfillment of mass transfer in the above stages are different.

■ Drop formation

As the initial stage, drop formation plays an important role as to determine the primitive drop size, initial velocity and mass transfer condition for the following process [63]. Some [64-67] even proved that around 3-50% of the mass transfer was completed in formation stage, which should not be neglected. Especially during the drop formation stage, the concentration gradient is relatively high which will cause strongly Marangoni effect (will be discussed later). In this case, influencing factors involving drop diameter, initial solute concentration and mass transfer directions were discussed by Wegener *et al.* [56] to account for the impact of Marangoni effect on mass transfer during formation. A correlation by taking initial solute concentration into account was proposed to predict extraction efficiency with reasonable accuracy. However, difficulties arise due to short time and length scales between drop formation and finalized at the Teflon tip and the role of coalescence

at the tip remains unclear.

■ Drop rising or falling

Most of the single drop mass transfer studies are concerning with drop free rising or falling stage. As mentioned in section 2.1, single drop experiences internal circulation, oscillation or deformation, which thus eventually affects mass transfer. Models of mass transfer coefficient or Sherwood number were obtained for each occasion with different application scopes, as summarized in Table 5.

Table 5 Mass transfer correlations for different drop behavior

Drop behavior	Model	Expression
Rigid drops	Newman model [68]	$k_d = -\frac{d}{6t} \ln \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left[\frac{1}{n^2} \exp \left(-\frac{n^2 D_L \pi^2 t}{(d/2)^2} \right) \right] \quad (9)$
Inner circulation drop	Kronig and Brink model [69]	$k_d = -\frac{d}{6t} \ln \frac{3}{8} \sum_{n=1}^{\infty} \left[B_n \exp \left(-\lambda_n \frac{16 D_L t}{\left(\frac{d}{2}\right)^2} \right) \right] \quad (10)$
Oscillating drop	Handlos and Baron model [70]	$k_d = -\frac{d}{6t} \ln 2 \sum_{n=1}^{\infty} \left[B_n \exp \left(-\frac{16 \lambda_n D_L t N_{Pe'}}{2048 d^2} \right) \right] \quad (11)$

The first reported study of this type was that of Sherwood *et al.* [47], who investigated acetic acid transfer from drop of benzene and methyl isobutyl ketone to water. The results indicated that the interior of the drop was not stagnant but rather agitated. Extraction coefficients were calculated by comparison in spray and packed columns. However, West *et al.* [48] found that the results were different as much as fivefold from Sherwood's, which was likely caused by the difference in purity of the benzene used in experiment. More recently, Huang *et al.* [61] presented mass transfer study along single drop rising in a system with high density difference, and specific cleaning procedure was performed before each experiment run. Different influencing factors were involved. To predict mass transfer coefficient, a mass transfer enhancement factor was introduced to modify the model, which showed a good accordance with experimental results.

For larger drops, mass transfer is superposed by oscillation and shape deformation. Yamaguchi *et al.* [26] measured mass transfer rate on single drop rising or falling with oscillation. Frequency and amplitude of oscillation were investigated by high-speed camera. An empirical equation was proposed for predicting mass transfer coefficient as well as for the critical drop diameter of oscillation onset. Hassan *et al.* [52] improved the models for larger droplets with size range from 5 to 10mm. Mass transfer coefficient of dispersed phase was obtained by dimensional analysis. For deformed drops, strong interfacial instabilities coupled with mass transfer make it difficult to exactly describe the correlations. With a slight parameter modification to the Handlos and Baron model, the mean droplet concentration of the transferred component was successfully modelled as a function of Fourier number [51]. In comparison with droplets with only slight deformations, the fluid dynamic behavior of oscillating or deformed droplets is substantially different and less predictable, which is due to the unsteady drop shape change.

■ Drop coalescence at the bulk interface

Generally, drop formation and terminal coalescence are eliminated by mass transfer experiments with drop free rising or falling. An inverted funnel locates at the top of the column is always with narrow channel and proper extraction rate of dispersed phase to avoid additional mass transfer. Li *et al.* [71, 72] designed a novel totally-closed extraction column to minimizing the terminal effect of drop coalescence on the accuracy of mass transfer measurements. Two liquid-liquid systems were tested and focused on the effect coalescing interface area on the mass transfer measurements. It showed that failing to minimize the terminal effects would lead to poor repeatability of experimental data. Thus, it is necessary to design the experiments with high rates of drop phase injection as well as withdrawal for the mass transfer study.

3.1.2 Interfacial instability

Mass transfer of a solute between two liquid phases is mainly influenced by the complicated fluid dynamic behavior caused by movable interface. In this case, local interfacial tension and additional tangential shear forces may occur due to solute transfer, which will trigger interfacial instabilities like Marangoni effect as a result. Marangoni convection occurs when there is an interfacial tension gradient, which accounts for the phenomena so-called “tears of wine”. As shown in many studies [67, 73], Marangoni convection can improve internal mixing within droplets and lead to significant mass transfer enhancement. Due to the complexity of these interfacial instabilities with mass transfer, single drop as the basic mass transfer unit are of great interest.

Fig. 7. Schematic of flow patterns in rising drops. [11]

(a) without Marangoni convection and (b) with Marangoni convection

(Reprinted from International Journal of Heat and Mass Transfer, 71, M. Wegener, N. Paul, M. Kraume, 475-495, Copyright (2019), with permission from Elsevier)

Henschke *et al.* [20] proposed an instability constant C_{IP} to describe nonstationary mass transfer in test system. The parameter characterizes the instability at the interface specific to the system. Wegner *et al.* [55], investigated simultaneous Marangoni convection in toluene-acetone-water system. Key parameters such as initial solute concentration and drop diameter were discussed. It was found that mass transfer increased for higher initial concentrations as well as smaller drop diameter. Later in the same test system, Wegner *et al.* [59] studied the effect of soluble anionic surfactants on hydrodynamic and mass transfer behaviors of single droplet with Marangoni instabilities. It was found that mass transfer was still greatly improved by Marangoni convection though high surfactant concentration was believed to slow down interfacial movement. In a recent

study in the system of *n*-propyl acetate/ acetic acid/ water by Zheng *et al.* [60], for a single rising droplet with given diameter, there was a competing mechanism between reduction of velocity and mass transfer enhancement due to Marangoni effect. To date, the Marangoni effect is not fully elucidated. Additional flow patterns generated by Marangoni effect resulting complex interactions between flow and concentration field. Therefore, on the one hand, further work should be done in the clean single drop systems; on the other hand, contaminations like surfactants interact with Marangoni effect should be paid more attention.

3.1.3 Contamination

In general, contamination of the interface by surfactants will reduce the mass transfer rate. One reason is that the adsorbed surfactant may form an interfacial barrier layer on the interface which hinders the transfer of solute. It is so-called the physicochemical effect [54, 74-77]. Another reason from hydrodynamic perspective that the adsorbed surfactants may reduce the internal circulation of droplet and thus decrease the terminal velocity or damping the oscillation and inhibit the interfacial turbulence [78-80]. Therefore, some studies showed pronounced reduction in mass transfer caused by surfactants contamination. For instance, by adding surfactants, Skelland *et al.* [81] found mass transfer reduction to 10% of that in pure system, while Steiner *et al.* [51] found mass transfer slowed down 30 and 70 times due to contamination. Taking contamination caused by surfactant into account, a new model was proposed by Slater [50] to determine mass transfer coefficients for a wide range of drop diameters. Although the influences caused by contaminations have been studied intensively, it is still difficult to describe the degree of contamination to quantify its influence on overall mass transfer.

3.1.4 Other factors

Despite the above factors, others like physical properties of the system (e.g. viscosity, temperature, pH) and outside intensification (e.g. column internals, ultrasonic waves) also play important role to mass transfer. Recent years, considering there will be a change in extraction column feeding to renewable biological origin with high viscosity and low vapor pressure in the future, Donni Adinata [82] investigated single drop behavior in high viscosity system. By increasing viscosity either in the continuous phase (water) or in the dispersed phase (toluene), the mass transfer rate was strongly affected by the viscosity change of continuous phase. Influence of temperature was studied by Saïen *et al.* [83] in toluene/acetic acid/water system within a range of 15-40°C. Results showed that mass transfer rate was significantly enhanced by average 93.6% by elevating thermostat temperature. In addition, the influence of aqueous phase pH was also investigated by the same group [84]. It was found that mass transfer was inhibited with increasing pH from 5 to 8, which may be attributed to the adsorption of the hydroxyl ions in the interface due to NaOH addition to increase pH. The reduction in mass transfer was more obvious for small drop size.

Internals are widely used as a simple method to intensify mass transfer. Concerning this factor, Azizi *et al.* [57] compared random and structured packings in spray and packed columns. Results demonstrated that the structured ones have a positive effect on mass transfer and improve mass transfer coefficient. Different sets of structure packing and their location heights in columns were detailed studied in their later study [62]. However, Slater *et al.* [50] found in their studies that Raschig ring packings slowed down the drop velocity and consequently reduced the mass transfer coefficient. For ultrasonic wave intensification of liquid-liquid extraction, Saïen *et al.* [85]

investigated the effect of ultrasonic waves on single drop mass transfer, where mass transfer could be improved by this method.

In real industrial process, liquid-liquid extraction is performed under the various influencing factors and operating conditions. It is necessary to explore the influences of these factors on mass transfer primarily in a single drop way.

3.2 Simulation studies

Strong coupling between momentum and mass transfer makes it difficult to simulate mass transfer behavior. Despite solving the continuity equation and Navier-Stokes equations, the mass balance equations should be coupled and solved at the same time [86-90]. Due to mass transfer, the concentration exhibits a step change at the interface, since the interface is deforming, resulting a challenging task. Simulation method should ensure an accurate estimate of the interfacial movement as well as concentration change. An ideal case is to assume the droplets as rigid sphere with constant shape during mass transfer process[82, 86, 87, 91-93].

Fig. 8. Streamlines from simulation by level-set method [94].

(a) without Marangoni convection and (b) with Marangoni convection

(Reprinted from Chemical Engineering Science, 117, R.F. Engberg, M. Wegener, E. Y. Kenig, 114-124, Copyright (2019), with permission from Elsevier)

Another difficulty is concerning with the Marangoni effects. Generally, Marangoni effects are highly non-linear and evolve during the mass transfer [63, 94, 95]. Additional flow patterns are generated and result in complicated interactions between flow and concentration field. In this context, a link describing the influence of the solute concentration on the interfacial tension is necessary. In general, Marangoni effects are strongest in the drop formation stage due to high interfacial gradient. Later, when mass transfer begins, Marangoni effect decreases and resulting a reacceleration of droplet [94].

Despite of the above difficulties, mass transfer simulation have been fulfilled by various interface description methods, e.g. VOF [96] and level-set method [89, 90, 94, 95, 97, 98] as described in section 2.2. Part of or the whole lifetime of a droplet motion can be investigated, including drop formation [63, 98], internal circulation [92], oscillating [94, 95] and deformed [97, 99] and then validated with the experimental results.

Table 6 Single drop mass transfer simulation study

Authors	Year	State	Interface Treatment	Dimensional
---------	------	-------	---------------------	-------------

Waheed <i>et al.</i> [86]	2001	Unsteady	Spherical particle	2D
Piarah <i>et al.</i> [87]	2001	Steady	Spherical particle	2D
Mao <i>et al.</i> [88]	2001	Steady	Distortion function	2D
Mao <i>et al.</i> [91]	2004	Unsteady	Spherical particle	2D
Burghoff <i>et al.</i> [100]	2005	Steady	Moving mesh method	2D
Deshpande <i>et al.</i> [89]	2006	Unsteady	Level-set	2D
Wang <i>et al.</i> [90]	2008	Unsteady	Level-set	2D
Bäumler <i>et al.</i> [99]	2009	Unsteady	Moving mesh method	2D
Wegener <i>et al.</i> [93]	2009	Unsteady	Spherical particle	3D
Lu <i>et al.</i> [98]	2010	Unsteady	Level-set	2D
Ubal <i>et al.</i> [92]	2010	Unsteady	Spherical particle	2D
Wang <i>et al.</i> [63]	2013	Unsteady	Level-set	2D
Engberg <i>et al.</i> [94]	2014	Steady	Level-set	3D
Engberg <i>et al.</i> [95]	2014	Unsteady	Level-set	3D
Wegener <i>et al.</i> [82]	2014	Unsteady	Spherical particle	3D

Several representative studies are listed in Table 6. Wegener *et al.* [82] performed a detailed numerical parameter study of the physical properties on the temporal evolution of the Marangoni convection in freely single rising drops. Full three-dimensional simulations were achieved but restricted to a spherical drop. Furthermore, in the study of Engberg *et al.* [94], deformable and oscillating droplets with simultaneous interfacial phenomena were simulated rather than spherical particles. CFD code based on the level set method was implemented and showed good accordance with experimental measurements. To detailed investigate the Marangoni effect, Mao *et al.* [91] solved the coupled fluid flow and solute mass transfer equations in an axisymmetric boundary-fitted coordinate system at the same time. It was found that the Marangoni convection does not necessarily results in mass transfer enhancement but above a certain critical value. Proposed by Wegener *et al.* [82] the Marangoni stress was implemented via the shear stress balance at the interface. Above all, simulation provides a powerful tool to quantitative and qualitative single drop mass transfer behavior. It is more accurate to track the position of the interface by various methods mentioned before and then solve the convection–diffusion equations in order to study mass transfer across the interface. Furthermore, it is necessary to develop fully three-dimensional simulations for Marangoni effects in order to investigate the effects on momentum and mass transfer.

4. Single drop breakage and coalescence

Drop-size distribution (DSD) is a main influencing factor for liquid-liquid extraction, which will determine the overall process efficiency and operating conditions. From microscopic perspective, DSD is influenced by various parameters concerning drop swarm and interactions, like drop breakage and coalescence, which have not been fully understood yet. From macroscopic aspect, in general, a constant DSD is expected when scaling up an extraction process. Most of the previous models rely on geometric similarity or constant power input, thus to overcome these problems. Investigators turn to the mechanism models. Population balance model (PBM) is one of the powerful tools to realize it. By using fundamental breakage and coalescence sub-models, which could be

obtained from single drop experiment and solved numerically, PBM can provide DSD of the system. In this way, PBM connects both microscopic of single drop to the macroscopic behavior of drop swarms, which seems to be a “bottom-up” approach [101], as is shown in Fig.9. Factors influencing DSD are decoupled to sub-models, which could be studied by small scale single drop experiment individually. The sub-models then are integrated together to predict droplet swarm behaviors and are verified by lab-scale experiment.

Fig. 9. From single drop study to DSD prediction (adapted from [102])

4.1 Population balance model (PBM)

Population balance model (PBM) is a powerful modeling approach to predict time dependent DSD by considering negative (death) and positive (birth) source terms for drop breakage and coalescence, respectively. First proposed by Hulburt and Katz [103], the number density transport equation, often referred to as the population balance equation [104, 105], can be written as:

$$\frac{\partial n(V_i, x, t)}{\partial t} + \nabla_x \cdot (u(V_i, x, t) \cdot n(V_i, x, t)) = S_{ph} + S_b + S_c \quad (12)$$

where S_b and S_c represent source term for number density generated by coalescence and breakage, respectively. S_{ph} is the source term caused by phase change. Furthermore, in the absence of phase change like evaporation or dissolution and considering the flow as uniform, the equation can be simplified to:

$$\frac{\partial n(V_i, x, t)}{\partial t} = S_b + S_c \quad (13)$$

To close the problem, one of the key challenges associated with the formulation of predictive PBM is to develop reliable drop breakage and coalescence functions as source terms S_b , S_c in the model.

$$S_b = \int_{V_i}^{\infty} m(V_i) \beta(V_i, V) \Omega(V) n(V, t) d(V) - \Omega(V_i) n(V_i, t) \quad (14)$$

$$S_c = \int_0^{V_i} \lambda(V_i - V, V) h(V_i - V, V) n(V_i - V, t) n(V, t) d(V) -$$

$$n(V_i, t) \int_0^{V_i} \lambda(V_i, V) h(V_i, V) n(V, t) d(V) \quad (15)$$

In this case, details of droplet coalescence and breakage should be carefully studied. Over the past decades, a variety of models have been proposed for the breakage frequency $\Omega(V_i)$ and daughter size distribution $\beta(V_i, V)$ function in the breakage model, coalescence frequency $\lambda(V_i - V, V)$ and efficiency $h(V_i - V, V)$ in the coalescence one. For liquid-liquid extraction, Valentas *et al.* [106] presented the first PBM applied to model drop breakage in 1966. Once the population balance equation has been set up and each source term has been determined separately, the equations can be solved by various methods, for example, method of moments, method of characteristics, Monto Carlo simulation, finite difference method and differential maximum entropy method. Detailed reviews on different solution approaches referred to [5, 107-109]. In terms of liquid-liquid system, population balance equations were solved for mixer-settler [110, 111], rotating disc column [112-115], Kühni column [116, 117], pulsed column [118] and so on.

4.2 Experimental studies

To study breakage and coalescence in lab-scale, experimental setup is more complex than single drop rising or mass transfer test cell. As seen in Fig. 10, for drop breakage, in general, external energy was needed, such as stirring, pulsation, rotation and so on [119, 120]. For drop coalescence, it is considered more complicated than drop breakage since several steps as collision, contact and deformation, film drainage and coalescence are involved. Experimental setups for coalescence can be distinguished into static drop contacts or dynamic drop collisions. In the static drop contact case, drops are produced and fixed on nozzles or lying on the top or next to each other where film drainage and liquid bridge can be observed in detail [121]. However, during extraction process, drop coalescence is a dynamic behavior influenced by droplet movement. Thus, coalescence under dynamic conditions is of special interest. In general, one drop is free moving while the other one is fixed [122]. In order to maintain the repeatability of the experiment, great effort should be done to precisely control the flow rate or keep extreme cleanness without any contamination. Several typical studies are summarized in Table 7.

Fig. 10. Lab-scale test cells for single drop study

((a),(b) test cell for breakage; (c),(d) test cell for coalescence)

Generally, parameters of sub-models concerning breakage and coalescence are determined by statistical measurements. In such experiments, a large number of droplets are recorded by high-speed camera due to high spatial and temporal resolution, aiming to determine the breakage time, breakage probability, number of daughter drop fragments for breakage and coalescence time, coalescence probability for coalescence. Based on this, parameters of sub-models are fitted and then applied to PBM equations. Reviews of numerous breakage and coalescence sub-models are available

in [7, 104, 105]. In the following section, only pure system is involved. For system in presence of contaminants, breakage and coalescence models can be found in [123]. Several representative studies are listed in Table 7.

4.2.1 Breakage

Drop breakage can be induced by various factors, namely, the collision of drops with internals of turbulent eddies and shear forces within the continuous phase. Therefore, the process of breakage is dependent on the size of the drop, the physico-chemical properties of the liquids (i.e. density, viscosity, interfacial tension) as well as the local energy dissipation. In most cases, breakage mechanism can be expressed as a force balance between external stress from the continuous phase which intends to destroy the droplet, and the surface and viscous stress of the droplet to restore the change [104]. When the disruptive stress become dominating, the droplet starts to stretch and deform, leading to formation of a neck that subsequently contracts, and finally forms two or more fragments. For single drop breakage study, some [124, 125] suggest to determine the single drop breakage event as breakage event as “entire breakup cascade” which is more meaningful, rather than only consider the “initial breakup”. But in most of the studies, a binary breakage event is usually assumed, which is a rough assessment of the physical truth.

Fig. 11. Definition of single drop breakage event

Galinat *et al.* [126] performed single drop breakage experiment in turbulent pipe flow in a vertical column. Breakage probability, mean number of fragments and daughter drop distribution were obtained for identifying different breakage mechanisms. After the statistical analysis of single drop breakage, the sub-model was implemented in a simple global PBM to predict the DSD. A similar study [127] was carried out in another *n*-heptane-water-glycerin solution system.

Breakage mostly occurs in a system with a stirrer for mixing. In this case, Maaß *et al.* investigated and modelled the breakage phenomena in a stirred tank. Improved models as daughter drop size distribution [128] and breakage time [129] were proposed, by taking the property influence of viscosity or interfacial tension into account, which result in better predictions. In the study of Solsvik *et al.* [130], single drop experiments were carried out in four oil-in-water systems. It was noticeable that the multiple breakage events were more frequently observed than binary breakage and breakage time was defined as finishing “entire breakup cascade”. Single drop breakage was also investigated in a rotor-stator mixer [131], the result revealed when, where and how the droplets break inside the mixer. It was suggested that turbulent vortices whose size was close to the mother droplet controlled the breakage process. More work should be done to understand how the different scales of turbulence influence the process better.

For extraction columns with mechanical agitators, study of single drop breakage has been

shown in Karr columns [132], Kühni columns [119, 133-135], pulsed disc and doughnut column, rotating disc contactor (RDC) columns [136] and so on. It was noteworthy to mention that in the study of Korb [119], a reactive extraction system $\text{ZnSO}_4/\text{D}_2\text{EHPA}$ was selected for single drop breakage in a lab scale Kühni column. Several existing correlations and kernels for drop breakage probability and daughter DSD were validated. A new unified breakage correlation was proposed and would be further proved.

A relatively small test cell for single drop breakage was also designed for study [127, 137]. The cell consists of a rectangular channel with a fixed single blade representative for a section of a Rushton turbine. Breakage events occurred in the vicinity of the stirrer blade were recorded by high-speed imaging. In this case [137], the influence of droplet substance and diameter were determined.

4.2.2 Coalescence

Coalescence is rather complicated than breakage. On one hand, the coalescence process can be divided into several stages and numerous influencing factors are involved. Additionally, as coalescence is inherently determined by interfacial properties, small amount of impurities as well as mass transfer can change the process dramatically. In general, coalescence process involves approach of drops, contact and deformation, film drainage and coalescence or repulsion [101]. When the two interfaces of drops come to near each other, a thin film of surrounding continuous phase has to drain between the interfaces. When a certain critical distance between the interfaces is reached, coalescence happens [102]. However, the collision of drops may not result in coalescence necessarily, but may also end in repulsion. Plenty of factors affect this process due to coalescence is an interfacial phenomenon. Physico-chemical properties of the continuous and dispersed system (i.e. viscosity, density, ionic strength), especially the interface (i.e. mass transfer, surface active components) between them, as well as the environmental conditions (i.e. temperature, pressure, geometry, electrostatic field, microwaves, ultrasound) may have impact on coalescence, as shown in Fig.12. As a consequence, it is a challenging task to perform the experiment precisely and repeatedly.

Fig. 12. Influencing factors on coalescence probability. (adapted from [101])

Influence of ions on single droplet coalescence was studied in [138-140]. Dynamic coalescence process was analyzed systematically by Villwock *et al.* [140] with the standard test system of toluene/water. Influencing factors like salt concentration and drop size ratio on coalescence probability were investigated. The results showed that coalescence inhibition occurred due to high

concentration of ions while no clear impact of drop size ratio was observed. Later, influence of ions on film drainage and coalescence time were analyzed by the same group [138]. Ion concentration, ion species and equivalent drop size were varied in single drop coalescence experimental study. An increased equivalent drop diameter leads to higher coalescence probability in spite of an increase in the coalescence time. As a result, an empirical correlation was proposed to account for the influence of equivalent droplet diameter and ion concentration on the coalescence time. Kopriwa *et al.* [139]. provided an option to perform single drop coalescence in a sedimentation cell. In this way, coalescence behavior of a system could be characterized by fitting a system-specific parameter to the sedimentation and the coalescence curves as well as the settling time of the system. Thus, the coalescence time of two drops could be calculated.

Influence of drop size and superimposed mass transfer on coalescence was evaluated in toluene/acetone/water test system by Kamp *et al.* [122]. Results showed that the drop size ratio seems to be interfered by the different relative velocities of the drops. Significant influence of superimposed mass transfer on coalescence was observed, which mass transfer from disperse to continuous phase led to coalescence while the opposite transfer directions retarded the coalescence almost completely.

Table 7 Single drop breakage and coalescence experimental study

Authors	Time	Topic	System	Parameters from single drop exp.	Experimental setup
Jares <i>et al.</i> [132]	1987	Breakage	Water/1,2-dichloroethane Water/toluene Water/ <i>n</i> -butanol	Breakage probability Daughter drop size distribution	Karr reciprocating plate column
Cabassud <i>et al.</i> [133]	1990	Breakage	Water/acetone/toluene Water/succinic acid/ <i>n</i> -butanol	Breakage probability Daughter drop population	Kühni column
Gourdon <i>et al.</i> [134]	1991	Breakage	Water/acetone/toluene	Mean drop residence time, breakage probability, breakage rate, number of daughter drops, daughter drop size distribution	Kühni column Pulsed sieve-plate column
Bahmanyar <i>et al.</i> [136]	1991	Breakage	<i>N</i> -butanol/water Cumene/isobutyric acid/water	Breakage probability, mean number of daughter drop	Rotating disc contactor

Fang <i>et al.</i> [135]	1995	Breakage	Water/toluene	Breakage probabilities, characteristic velocity	Kühni column
			Water/acetone/toluene		
			Water/ <i>n</i> -butanol		
			Water/succinic acid/ <i>n</i> -butanol		
			Water/cumene		
			Water/hexane		
			23wt% sucrose/cumene		
			23wt% sucrose/hexane		
Galinat <i>et al.</i> [126]	2005	Breakage	Water/cyclohexane	Breakage probability, mean number of fragments, daughter drop distribution	Pipe flow
			<i>N</i> -heptane/water		
			<i>N</i> -heptane with red Dye(surfactant)/water		
Andersson <i>et al.</i> [141]	2006	Breakage	Air/water	Breakage time, deformation velocity, number of fragments, daughter size distribution	Reactor
			Dodecane/water		
			Octanol/water		
Galinat <i>et al.</i> [127]	2007	Breakage	<i>N</i> -heptane/water/glycerin solution	Breakage probability, mean number of fragments, daughter drop Sauter diameter	Pipe flow
Maaß <i>et al.</i> [128]	2007	Breakage	Toluene/water	Breakage probability, daughter drop population	Stirred tank Drop breakage cell
Maaß <i>et al.</i> [129]	2012	breakage	Petroleum/water Toluene/water	Breakage probability, breakage time	Stirred tank
Nachtigall <i>et al.</i> [137]	2012	breakage	Petroleum/water Toluene/water Paraffin oil/water	Breakage probability, breakage time, breakage location	Drop breakage cell

Villwock <i>et al.</i> [122]	2014	Coalescence	Toluene/water	Coalescence probability, contact time	Single droplet testing cell
Kamp <i>et al.</i> [122]	2014	Coalescence	Toluene/acetone/water	Relative velocity, contact and coalescence time, droplet deformation and coalescence probability	Single droplet testing cell
Solsvik <i>et al.</i> [130]	2015	breakage	Toluene/water Petroleum/water <i>N</i> -dodecane/water Octanol/water	Breakage time, number of daughter drops	Stirred tank
Gebauer <i>et al.</i> [138]	2016	Coalescence	Toluene/water	Coalescence time, coalescence probability	Single droplet testing cell
Liu <i>et al.</i> [120]	2016	breakage	Kerosene/water	Breakup frequency function, daughter droplet size distribution	Pulsed disc and doughnut column
Kopriwa <i>et al.</i> [139]	2016	Coalescence	Toluene/water MIBK/water <i>N</i> -butanol/water	Coalescence time	settler
Korb <i>et al.</i> [119]	2017	breakage	ZnSO ₄ /D ₂ EHPA	Breakage probability, average number of daughter drops, daughter droplet size distribution	Kühni column
Ashar <i>et al.</i> [131]	2018	breakage	Rapeseed oil/water	Deformation time, number of fragments, breakage probability	Rotor-stator mixer

4.3 Simulation studies

Numerical study can also be divided into two types. Similar to single drop rising, simulation can be done to investigate the detailed knowledge of breakage or coalescence by varying operating conditions. Apart from this, simulation can be serve as an aid to single drop experiments to determine some important parameters as turbulent kinetic energy, shear stresses etc., which are difficult to obtain from experiments.

4.3.1 Fundamental simulation of breakage and coalescence regime

Usually, drop breakage and coalescence occur in an extreme short period of time, which presents challenges in determining the start and over time by means of experimental methods.

However, computational fluid dynamics (CFD) can provide local spatial and time resolved information about the breakage and coalescence. It also shows reproducible results which make up the shortcomings of experimental studies. In some occasions, dynamic mesh in vicinity of the interfaces should be refined [142] to fully describe the interface behavior.

Eiswirth *et al.* [143] considered a binary coalescence situation consisting of two rising toluene droplets with different diameter that coalesce in surrounding water. With the help of COMSOL software and level-set capturing method, it was found that the liquid bridge growing between the two drops during coalescence was of the inertial regime and the bridge radius grew in proportion to the square root of time. The simulation results were in a good agreement with the experimental data. Gebauer *et al.* [142] performed CFD simulations with VOF method to study single drop coalescence interactions to further reveal the hydrodynamics and film drainage. The simulations were performed for the interaction of two differently sized droplets at industrial relevant impact velocities. An algorithm based on experimental studies was implemented to account for the contact time and the dimple formation. Also, by utilizing VOF method, a multi-scale simulation method was used to investigate the coalescence behaviour of droplets undergoing a symmetric binary collision [144]. A subgrid-scale model was involved to describe thin-film drainage due to the computational difficulty of capturing all length scales involved with a single discretisation mesh. Combined by large eddy simulations (LES), VOF method was also implemented in simulating droplet breakage in order to reveal the mechanism of breakage in turbulent flows [145]. Simulation results showed that the size of the turbulent vortices was contributed to the breakage and more energy needed to be transferred from the vortices at the final stage for breakage occur.

4.3.2 CFD aided single drop investigation

Despite of fundamental simulation for breakage and coalescence process, CFD can also provide more information of local turbulent kinetic energy, shear stress or other fluid parameters, which can serve as supplement to the previous single drop experimental study.

As in the study of droplet breakage in stirred tank by Maaß *et al.* [137], CFD was used to give the opportunity to control the local dissipation rate of turbulent kinetic energy in the breakage cell. Regions with highest energy dissipation rates and the velocity field were found to be the drop breakage location. Based on drop diameter and physical properties of the test systems, different breakage mechanism can be derived. Drop breakage in a square-sectioned pulsed disc and doughnut column was investigated by Liu *et al.* [120]. Three breakup patterns were observed and shear stress was the dominant factor in common. However, shear stress is hard to determined by experimental study, so that it is calculated based on the simulation. After that, breakage submodels were correlated with the shear stress and finally applied in a simplified PBM to predict DSD. Single droplet breakup in a rotor-stator mixer was investigated by Ashar *et al.* [131]. Turbulent inertial stress induced droplets breakup at different operating conditions were studied. CFD simulations was applied to predict the flow field and turbulent kinetic energy dissipation rate to explain the the tendency of droplet breakup at different locations in the rotor-stator.

5. Outlook

Single droplet in liquid-liquid extraction system has been detailed investigated over the last decades. For about 50 years, efforts have been made to describe the behavior of single droplet and

interfaces. Based on these fundamental knowledges, attempts have been tried to utilize basic sub-models to predict the behavior of extraction columns. For recent 10 years, with the development of computer science, simulations were set up with improving accuracy [7]. Research method, experimental as well as simulation techniques are becoming more and more mature and systematical. On the basis of previous studies, several possible directions in the future are suggested.

5.1 Fundamental study for novel extraction system

In most of the tradition extraction techniques, volatile organic compounds (VOCs) including halogenated hydrocarbons, aliphatic and aromatic hydrocarbons, some esters, alcohols, ethers, aldehydes and ketones are the most commonly used organic solvents [146]. However, as an increasing attention is paid on environmental protection and sustainable development, application of these toxic and highly flammable organic solvents are restricted. In these cases, it is necessary to develop novel sustainable solvents which accord with “green chemistry” concept. Meanwhile, another alternative is to intensify the present extraction process as to promote extraction efficiency as well as reduce the organic solvent use. Previous study of single drop are mainly in common organic-water system, fundamental analysis of novel system are not much.

5.1.1 Reactive ionic liquid system

Room temperature ionic liquids is a new emerging solvents which are salts with melting temperatures below 100°C and are composed of large amount of ions. They are generally called “designer solvents” because various cation/anion combinations enable them with tunable properties [147, 148]. As a salt, they have negligible volatility, high thermal stability, non-flammable and usually of high viscosity [149], which seems to be a potential alternative. For extraction application, ion exchange process by ionic liquids allows extraction of specific anions, cations and even neutral compounds. Despite of these advantages, ionic liquids now is a relative novel solvent resulting in comparably high costs. Therefore, single drop experiments provide a convenient approach for ionic liquids with limit amount and low cost for design and scale-up.

Buchbender *et al.* [150] performed single drop sedimentation experiment with heptane (c)-toluene-[3-mebupy][DCA] (d) to acquire parameters so as to fit sedimentation models. Involving drop breakage and influence of internals, models were simulated by “ReDrop” to obtain hydrodynamic parameters such as hold-up and Sauter mean diameter, which are in a good agreement with the experimental data. In the work of Badié [151] ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIMPF₆) was chosen as a disperse phase to extract acetone from water. Although a relatively high viscosity with HMIMPF₆, the single-drop experiments showed that the mass transfer was not as slow as expected. The Henschke model was applied to this novel system with good accuracy.

5.1.2 Aqueous two-phase system

The extraction of value-added compounds from natural sources exhibit great potential in the future, especially in biotechnology as separation of antibodies, proteins, antibiotics and natural plant ingredients [152]. As these components are mostly heat-sensitive and easily deactivated by organic solvents, the aqueous two-phase system (ATPS) provide an alternative to realize. The aqueous two-phase systems form when two incompatible polymers or a polymer and a salt, detailed types of system can refer to [153]. Generally, the aqueous two phase systems is of high viscosity, low

difference in density and low interfacial tension, which may result in low mass transfer rate [154]. Several extraction trials have been performed in mixer-settler, spray column, perforated rotating disk contactor, pulsed cap column and so on [155]. But it is still far from practical use due to lack of feasible predictive performance models and guidelines for design and scale-up. Thus, detailed investigations should be made from single drop study.

Sawant *et al.* [156] intended to isolate and purify BSA (Bovine Serum Albumin) by using two-phase aqueous system polyethylene glycol (PEG) and dextran in a spray column. Single drop experiment was used to measure overall mass transfer coefficient. Bhawsar *et al.* [157] investigated the extraction of α -amylglucosidase in a sieve plate column. The aqueous two-phase system was formed by sodium sulphate-polyethylene glycol (PEG)-water and the solute was dissolved in PEG-rich phase. Hydrodynamic parameter like terminal velocity and mass transfer coefficient was determined by single drop experiment. Correlations were proposed for true mass transfer coefficients. Srinivas *et al.* [158] dealt with the extraction of horseradish peroxidase using a PEG/salt ATPS in a simple spray column. It was shown that mass transfer rate increased in the presence of NaCl, but the detailed mechanism required further study. Concerning drop formation, an attempt was made by Barhate *et al.* [159] to develop a model for drop formation in ATPSs. By using polyethylene glycol (PEG)/salt systems of different phase compositions at various flow rates, models were developed and compared with experimental results. In consideration of high viscosity with ATPS, Quaresima *et al.* [160] used PEG/salt system with protein albumin as mass transfer component from continuous phase to PEG-rich droplet phase. Single drop experiment results served as the basis of the models introduced to “ReDrop”. It was concluded that mass transfer was strongly influenced by the viscosity of both phases as well as the molecular size of the transferred component.

5.1.3 Nanofluid intensification of extraction

Nanofluids have attracted great attention as effective working fluids in heat and mass transfer enhancement. It is found that the addition of a small amount of nanoparticles exert considerable impact on the hydrodynamic and mass transfer performance of solvent extraction processes [161, 162]. Although it has a prosperous future in process intensification, limited attempts are made in liquid-liquid extraction. In terms of single drop studies, some of the fundamental work are summarized in Table 8.

Table 8 Single drop with addition of nanoparticles experimental studies

Authors	Year	System	Particle size/mm	concentration
Saien <i>et al.</i> [163]	2012	Toluene (+Fe ₃ O ₄ /Al ₂ O ₃)/acetic acid/water	5-150	0.0005–0.005 wt%
Mirzazadeh <i>et al.</i> [164]	2014	<i>N</i> -butanol/succinic acid/water(+ZnO/TiO ₂ /CNT)	<100	0.025–0.1 wt%
Saien <i>et al.</i> [165]	2015	Toluene (+Fe ₃ O ₄)/acetic acid/water	12	0.0005–0.005 wt%
Goodarzi <i>et al.</i> [166]	2016	Toluene/acetic acid/water(+SiO ₂)	7-13	0.005–0.1 vol%
Vahedi <i>et al.</i> [167]	2016	Toluene (+Fe ₃ O ₄)/acetic acid/water	28.8	0.001–0.005 wt%
Saien <i>et al.</i>	2017	Toluene(+SiO ₂)/acetic acid/water	11-14	0.0005–0.005 wt%

[168]		20-30		
		60-70		
Hatami <i>et al.</i>	2017	Toluene(+TiO ₂)/acetic acid/water	25	0.001–0.005 wt. %
[169]				

In terms of hydrodynamic behavior, a reduction in terminal velocity with addition of nanoparticles was observed in most cases. Influencing factors as types of nanoparticle [163, 164], size distribution [168], addition amount [163-169] and their addition in continuous or disperse phase [166] were systematically investigated. For mass transfer investigation, it is interesting to find that mass transfer rate increased as more nanoparticles were added. However, after reaching an optimum point, a decreasing variation was observed [163]. It might be attributed to Brownian motion of nanoparticles and subsequent micro-convection or aggregation and clustering of nanoparticles [169].

Fig. 13. Addition of nanoparticles.

Other factors as temperature [165] and in presence of magnetic field [167] were taken into consideration. For the purpose of industrial use, a great deal of work remains to be done concerning simulation or downstream separation process for recycling the nanoparticles as well as solvent.

5.2 Detailed analysis of single drop interfacial behaviors

As mentioned above, interfacial behaviors like Marangoni effect or contaminations make it much more complicated for liquid-liquid extraction system. Drop swarms with many interactions may not be the suitable test system, in this case, single drop system tends to be a more appropriate one to break down the complexity. For Marangoni effect, as it is reviewed in previous section 3.1, it is a three-dimensional behavior coupling with mass transfer. On the one hand, in experimental studies, effort should be made in building up mechanism models to predict the onset and end point of Marangoni effect and determining quantitative and qualitative influences made by it. Additionally, single droplet with variable interfacial tension and Marangoni effect should be further simulated in a 3D way to visualize the process [11].

Contamination is one of the crucial factors influencing the extraction equipment performance and their actual industrial utilization. It is because contaminations may slow down the terminal velocity, moderate mass transfer rate and hinder droplets from coalescence. Further work should be done in terms of quantify these factors and predict the extraction performance with higher accuracy.

5.3 Coupled CFD-PBM simulation

Starting from single drop extraction concept and combining with population balance models, a bottom-up method can provide a guideline for industry, as it eliminates pilot plant trials and saves both money and efforts. Up to now, several studies have realized this approach. Kamp *et al.* [102] designed a scale-up study considering the influence of collision velocity and drop size on coalescence probability. Parameters of coalescence efficiency can be obtained from single drop experiments. Based on the derived parameters, it is possible to utilize PBM equations to predict the DSD in dispersions. In this case, a sound scale-up is possible by population balance equation simulations. A simulation tool called “ReDrop” was designed by Pfennig *et al.* [170] for the design of extraction columns based on single-drop experiments. Input data containing the properties of the system, operating conditions, and the geometry of the internal were loaded into the program together with the system-specific parameters of the models from single drop experiments. Simulation was carried out by Monte-Carlo method until steady-state conditions were reached. Extraction performances, fluid dynamic behavior, and flooding limits could be predicted. To solve the population balance equations, an algorithm was developed and implemented via a computer program called liquid–liquid extraction column module (LLECMOD) for hydrodynamics simulation of liquid–liquid extraction columns by Bart *et al.* [171, 172]. Sub-models in the population balance equations were determined by single drop experiments. The simulation process showed a flexible way that allows the user to define the breakage and coalescence frequencies, droplet terminal velocity, and the other internal geometrical details of the column. More recently, Attarakih *et al.* [173, 174] presented a new population balance based module so called “PPBLab” for modelling the hydrodynamics and mass transfer processes. Different types of extraction columns like Kühni column [173] as well as pulsed packed bed column [174] were simulated and tested. In future, it is a tendency to link PBM with CFD for high precision engineering and a direct modelling of industrial scale extraction equipment design [175]. With this coupled method, detailed information about the flow fields, turbulent energy dissipation and their influences on drop breakage, coalescence and mass transfer could be determined. Attempts have been made in CFD-PBE simulations [111, 118, 176], models utilized in PBM are either embedded in commercial software or from literature. Considering the differences in test systems, models based on single drop experiment will provide more solid and reasonable predictions for extraction performance.

6. Conclusion

To simplify the complexity of the liquid-liquid extraction separation process, single drop is considered to be an investigation object in order to reduce time and efforts. Single drop rising and falling are the most basic phenomena influenced by physical properties of the binary system. The terminal velocities of single drop with various diameters are obtained experimentally and numerically. Then the correlations and models are compared to the derived results. As the most crucial part of liquid-liquid extraction, mass transfer studies in single drops are interesting. In general, the influence of mass transfer direction, solute concentration and system properties are investigated. In addition, the induced Marangoni convection will cause significant effect on mass transfer, which could not be neglected.

For drop-drop interactions, breakage and coalescence are considered as two fundamental

factors for they will affect mass transfer area consequently. These two processes are more complicated due to high time and spatial resolution. In this case, high speed camera is commonly used to visualize the interactions. Simulation is also used as an assistant tool to reveal the whole process.

In conclusion, single drop investigations have become a trend to study the complex process of liquid-liquid extraction. Future studies could be carried on such as, the mass transfer with Marangoni convection, ion influence on breakage and coalescence, quantify the contaminants effect and so on. More novel systems should be investigated to broaden the study on standard system. Based on the single drop experimental and numerical study, the scale-up design of extraction unit will be more efficient and accurate in future.

Nomenclatures and abbreviations

B_n	Coefficients in series expansion
β	Daughter droplet size distribution
C_D	Drag coefficient
d	Diameter of droplet, m
D_L	Molecular diffusivity of solute in dispersed phase, sq. cm/sec
h	Collision frequency, m^3s^{-1}
k_d	Observed dispersed phase mass transfer coefficient
λ	Coalescence efficiency, s^{-1}
n	Droplet number density
μ^*	Viscosity ratio
$N_{Pe'}$	Modified Peclet group
Ω	Breakage frequency, s^{-1}
Re	Reynold number
t	Time, s
S_{ph}	Source terms caused by phase change
S_b	Source terms caused by droplet breakage
S_c	Source terms caused by droplet coalescence
V_i	Droplet volume, m^3
ATPS	Aqueous two-phase system
BSA	Bovine Serum Albumin
CSF	Continuum surface force
DSD	Drop size distribution
GFM	Ghost fluid method
LES	Large eddy simulation
PEG	Polyethylene glycol
VOF	Volume of fraction

Acknowledgements

This research was carried out under the National Natural Science Foundation of China (21636004), the National Safety Academy Foundation (U1530107), the National Key Basic Research Program of China (No.2012CBA01203) in the State Key Laboratory of Chemical Engineering of Tsinghua University, Beijing, China. The authors gratefully acknowledge these grants.

References

- [1] E. Müller, R. Berger, E. Blass, D. Sluyts, A. Pfennig, Liquid–liquid extraction. Ullmann's Encyclopedia of Industrial Chemistry, 2002.
- [2] J.D. Law, T.A. Todd, Liquid-Liquid Extraction Equipment, *Hydrometallurgy*, 42(3) (2008) 1247-1252.
- [3] S.S. Ye, Q. Tang, J.S. Qiao, Y.D. Wang, Physical properties measurements and CFD simulations in settler of different P507-kerosene systems, *CIESC J.* 67(2) (2016) 458-468. (in Chinese)
- [4] Y. Zou, Y.D. Wang, W.Y. Fei, Research progress of mixer-settler extractor, *Process Equip. Piping.* 51(5) (2014) 40-46.(in Chinese)
- [5] S. Mohanty, Modeling of liquid-liquid extraction column: A review, *Rev. Chem. Eng.* 16(3) (2000) 199-248.
- [6] K. E. Wardle, T. R. Allen, R. Swaney, CFD simulation of the separation zone of an annular centrifugal contactor, *Sep. Sci. Technol.* 44(3) (2009) 517-542.
- [7] N. Kopriwa, F. Buchbender, J. Ayesterán, M. Kalem, A. Pfennig, A critical review of the application of drop-population balances for the design of solvent extraction columns: I. Concept of solving drop-population balances and modelling breakage and coalescence, *Solvent Extr. Ion Exch.* 30(7) (2012) 683-723.
- [8] D. Adinata, Single-drop based modelling of solvent extraction in high-viscosity systems, Ph. D. Thesis, RWTH Aachen Univ., Germany, 2011.
- [9] J. S. Hadamard, Mouvement permanent lent d'une sphere liquide et visqueuse dans un liquide visqueux, *Acad. Sci.* 152 (1911) 1735–1738. (in French)
- [10] W. Rybczynski, Über die fortschreitende Bewegung einer flüssigen Kugel in einem zähen Medium, *Acad. Sci.* 1 (1911) 40–46. (in German)
- [11] M. Wegener, N. Paul, and M. Kraume, Fluid dynamics and mass transfer at single droplets in liquid/liquid systems, *Int. J. Heat Mass Transfer* 71 (2014) 475-495.
- [12] A. E. Hamielec, S. H. Storey, J. Whitehead, Viscous flow around fluid spheres at intermediate Reynolds numbers (II), *Can. J. Chem. Eng.* 41(6) (1963) 246-251.
- [13] Z. G. Feng, E. E. Michaelides, Drag Coefficients of Viscous Spheres at Intermediate and High Reynolds Numbers, *J. Fluids Eng.* 123(4) (2001) 841-849.
- [14] V. Y. Rivkind, G. M. Ryskin, Flow structure in motion of a spherical drop in a fluid medium at intermediate Reynolds numbers, *Fluid Dynamics.* 11(1) (1976) 5-12.
- [15] A. Saboni, S. Alexandrova, Numerical study of the drag on a fluid sphere, *AIChE J.* 48(12) (2002) 2992-2994.
- [16] H. Brauer, Particle/fluid transport processes, in: Fortschritte in der Verfahrenstechnik, VDI, Verlag, Düsseldorf, 1979. Band 17.
- [17] A. D. Polyinin, V. V. Dilman, Methods of modeling equations and analogies in chemical engineering, City: CRC Pr I Llc, 1994.
- [18] R. Clift, J. R. Grace, M. E. Weber, Bubbles, drops, and particles, Academic Press, 1978.

- [19] J. R. Grace, Shapes and velocities of single drops and bubbles moving freely through immiscible liquids, *Chem. Eng. Res. Des.* 54 (1976) 167-173.
- [20] M. Henschke, A. Pfennig, Mass-transfer enhancement in single-drop extraction experiments, *AIChE J.* 45(10), (1999) 2079-2086.
- [21] S. Hu, R. C. Kinter, The fall of single liquid drops through water, *AIChE J.* 1(1) (1955) 42-48.
- [22] A. J. Klee, R. E. Treybal, Rate of rise or fall of liquid drops, *AIChE J.* 2(4), (1956) 444-447.
- [23] R. R. Schroeder, R. C. Kintner, Oscillations of drops falling in a liquid field, *AIChE J.* 11(1) (1965) 5-8.
- [24] G. Thorsen, R. M. Stordalen, S. G. Terjesen, On the terminal velocity of circulating and oscillating liquid drops, *Chem. Eng. Sci.* 23(5) (1968) 413-426.
- [25] R. M. Edge, C. D. Grant, The terminal velocity and frequency of oscillation of drops in pure systems, *Chem. Eng. Sci.* 26(7) (1971) 1001-1012.
- [26] M. Yamaguchi, T. Fujimoto, T. Katayama, Experimental studies of mass transfer rate in the dispersed phase and moving behavior for single oscillating drops in liquid-liquid systems. *J. Chem. Eng. Jpn.* 8(5) (1975) 361-366.
- [27] M. Wegener, M. Kraume, A. R. Paschedag, Terminal and transient drop rise velocity of single toluene droplets in water, *AIChE J.* 56(1) (2010) 2-10.
- [28] K. Bäuml, M. Wegener, A. R. Paschedag, E. Bänsch, Drop rise velocities and fluid dynamic behavior in standard test systems for liquid/liquid extraction-experimental and numerical investigations, *Chem. Eng. Sci.* 66(3) (2011) 426-439.
- [29] R. M. Griffith, The effect of surfactants on the terminal velocity of drops and bubbles, *Chem. Eng. Sci.* 17(12) (1962) 1057-1070.
- [30] R. M. Edge, C. D. Grant, The motion of drops in water contaminated with a surface-active agent, *Chem. Eng. Sci.* 27(9) (1972) 1709-1721.
- [31] M. D. Leven, J. Newman, The effect of surfactant on the terminal and interfacial velocities of a bubble or drop, *AIChE J.* 22(4) (1976) 695-701.
- [32] X. J. Li, Z. S. Mao, W. Fei, Effects of surface-active agents on mass transfer of a solute into single buoyancy driven drops in solvent extraction systems, *Chem. Eng. Sci.* 58(16) (2003) 3793-3806.
- [33] T. Misek, R. Berger, J. Schröter, Standard test systems for liquid extraction studies, EFCE Publ. Ser, 1985.
- [34] C. W. Hirt, B. D. Nichols, Volume of fluid (VOF) method for the dynamics of free boundaries, *J. Comput. Phys.* 39(1) (1981) 201-225.
- [35] S. Osher, J. A. Sethian, Fronts propagating with curvature-dependent speed: algorithms based on Hamilton-Jacobi formulations, *J. Comput. Phys.* 79(1) (1988) 12-49.
- [36] E. Bertakis, S. Groß, J. Grande, O. Fortmeier, A. Reusken, A. Pfennig, Validated simulation of droplet sedimentation with finite-element and level-set methods, *Chem. Eng. Sci.* 65(6) (2010) 2037-2051.
- [37] R. F. Engberg, E. Y. Kenig, Numerical simulation of rising droplets in liquid-liquid systems: A comparison of continuous and sharp interfacial force models, *Int. J. Heat Fluid Flow.* 50 (2014) 16-26.
- [38] Z. Q. Huang, H. Wang, VOF Simulation Studies on Single Droplet Fluid Dynamic Behavior in Liquid-Liquid Flow Process[J], *J. Chem. Eng. Jpn.* 51(1) (2018) 33-48.
- [39] W. Dijkhuizen, M. van Sint Annaland, H. Kuipers, Numerical investigation of closures for interface forces in dispersed flows using a 3D front tracking model, Fourth International Conference on CFD in the Oil and Gas, Metallurgical & Process Industries, Trondheim, Norway, 2005.
- [40] G. Tryggvason, B. Bunner, A. Esmaeili, D. Juric, N. Al-Rawahi, W. Tauber, A front-tracking method for the computations of multiphase flow. *J. Comput. Phys.* 169(2) (2001) 708-759.

- [41] A. E. Komrakova, D. Eskin, J. J. Derksen, Lattice Boltzmann simulations of a single *n*-butanol drop rising in water, *Phys. Fluids*. 25(4) (2013) 042102.
- [42] M. Adekojo Waheed, M. Henschke, A. Pfennig, Simulating sedimentation of liquid drops, *Int. J. Numer. Methods Eng.* 59(14) (2004) 1821-1837.
- [43] R. T. Eisinger, H. J. Bart, T. Atmakidis, E. Y. Kenig, Experimental and numerical investigation of a free rising droplet, *Chem. Eng. Process.* 50(7) (2011) 718-727.
- [44] R. F. Engberg, E. Y. Kenig, An investigation of the influence of initial deformation on fluid dynamics of toluene droplets in water, *Int. J. Multiphase Flow*. 76 (2015) 144-157.
- [45] M. J. Brodkorb, D. Bosse, C. Von Reden, A. Gorak, M. J. Slater, Single drop mass transfer in ternary and quaternary liquid-liquid extraction systems, *Chem. Eng. Process: Process Intensification*. 42(11) (2003) 825-840.
- [46] J. Temos, H. R. C. Pratt, G. W. Stevens, Mass transfer to freely-moving drops, *Chem. Eng. Sci.* 51(1) (1996) 27-36.
- [47] T. K. Sherwood, J. E. Evans, J. V. A. Longcor, Extraction in spray and packed columns, *Ind. Eng. Chem.* 31(9) (1939) 1144-1150.
- [48] F. B. West, P. A. Robinson, A. C. Morgenthaler, T. R. Beck, D. K. McGregor, Liquid-liquid extraction from single drops, *Ind. Eng. Chem.* 43(1) (1951) 234-238.
- [49] A. H. P. Skelland, R. M. Wellek, Resistance to mass transfer inside droplets, *AIChE J.* 10(4) (1964) 491-496.
- [50] M. J. Slater, M. H. I. Baird, T. B. Liang, Drop phase mass transfer coefficients for liquid-liquid systems and the influence of packings, *Chem. Eng. Sci.* 43(2) (1988) 233-245.
- [51] L. Steiner, G. Oezdemir, S. Hartland, Single-drop mass transfer in the water-toluene-acetone system, *Ind. Eng. Chem. Res.* 29(7) (1990) 1313-1318.
- [52] T. Al-Hassan, C. J. Mumford, G. V. Jeffreys, A study of mass transfer from single large oscillating drops, *Chem. Eng. Technol.* 15(3) (1992) 186-192.
- [53] M. Henschke, A. Pfennig, A. Influence of sieve trays on the mass transfer of single drops, *AIChE J.* 48(2) (2002) 227-234.
- [54] Y. L. Lee Surfactants effects on mass transfer during drop-formation and drop falling stages, *AIChE J.* 49(7) (2003) 1859-1869.
- [55] M. Wegener, M. Kraume, A. R. Paschedag, Influence of Marangoni convection on mass transfer at non-spherical droplets, *Chem. Eng. Trans.* 17 (2009) 525-530.
- [56] M. Wegener, A. R. Paschedag, M. Kraume, Mass transfer enhancement through Marangoni instabilities during single drop formation, *Int. J. Heat Mass Transfer*. 52(11-12) (2009) 2673-2677.
- [57] Z. Azizi, A. Rahbar, H. Bahmanyar, Investigation of packing effect on mass transfer coefficient in a single drop liquid extraction column, *Iran. J. Chem. Chem. Eng.* 7(4) (2010) 3-11.
- [58] M. Wegener, A.R. Paschedag, Mass transfer enhancement at deformable droplets due to Marangoni convection, *Int. J. Multiphase Flow*. 37(1) (2011) 76-83.
- [59] M. Wegener, A. R. Paschedag, The effect of soluble anionic surfactants on rise velocity and mass transfer at single droplets in systems with Marangoni instabilities, *Int. J. Heat Mass Transfer*. 55(5-6) (2012) 1561-1573.
- [60] H. Zheng, W. Ren, K. Chen, Y. Gu, Z. Bai, S. Zhao, Influence of Marangoni convection on mass transfer in the *n*-propyl acetate/acetic acid/water system, *Chem. Eng. Sci.* 111 (2014) 278-285.
- [61] Z. Huang, C. Ye, L. Li, X. Zhang, T. Qiu, Measurement and Correlation of the Mass Transfer Coefficient for a Liquid-Liquid System with High Density Difference, *Braz. J. Chem. Eng.* 33(4) (2016) 897-906.
- [62] Z. Azizi, M. Rezaeimanesh, Packing effect on mass transfer and hydrodynamics of rising toluene drops in stagnant liquid, *Chem. Eng. Res. Des.* 115 (2016) 44-52.

- [63] Z. Wang, P. Lu, Y. Wang, C. Yang, Z. S. Mao, Experimental investigation and numerical simulation of Marangoni effect induced by mass transfer during drop formation, *AIChE J.* 59(11) (2013) 4424-4439.
- [64] A. T. Popovich, R. E. Jervis, O. Trass, Mass transfer during single drop formation, *Chem. Eng. Sci.* 19(5) (1964) 357-365.
- [65] A. H. P. Skelland, S. S. Minhas, Dispersed phase mass transfer during drop formation and coalescence in liquid-liquid extraction, *AIChE J.* 17(6) (1971) 1316-1324.
- [66] Y. L. Lee, Surfactants effects on mass transfer during drop-formation and drop falling stages, *AIChE J.* 49(7) (2003) 1859-1869.
- [67] J. D. Thornton, T. J. Anderson, K. H. Javed, S. K. Achwal, Surface phenomena and mass transfer interactions in liquid-liquid systems, *AIChE J.* 31(7) (1985) 1069-1076.
- [68] A.B. Newman, The drying of porous solid: Diffusion and surface emission effects, *Trans. AIChE*, 27 (1931) 203-216.
- [69] R. Kronig, J. C. Brink, On the theory of extraction from falling droplets, *Appl. Sci. Res.* 2(1) (1951) 142.
- [70] A. E. Handlos, T. Baron, Mass and heat transfer from drops in liquid-liquid extraction, *AIChE J.* 3(1) (1957) 127-136.
- [71] T.W. Li, Z. S. Mao, J.Y. Chen, W.Y. Fei, Terminal effect of drop coalescence on single drop mass transfer measurements and its minimization, *Chinese J. of Chem. Eng.* 9(2) (2001) 204-207.
- [72] T.W. Li, Experimental and simulation study of steady mass transfer in single drop at medium Reynolds number, Ph. D. Thesis, Institute of Chemical Metallurgy Chinese Academy of Sciences, China, 1998. (in Chinese)
- [73] K. H. Javed, J. D. Thornton, T. J. Anderson, Surface phenomena and mass transfer rates in liquid-liquid systems: Part 2, *AIChE J.* 35(7) (1989) 1125-1136.
- [74] K. P. Lindland, S. G. Terjesen, The effect of a surface-active agent on mass transfer in falling drop extraction, *Chem. Eng. Sci.* 5(1) (1956) 1-12.
- [75] W. S. Huang, R. C. Kintner, Effects of surfactants on mass transfer inside drops, *AIChE J.* 15(5) (1969) 735-744.
- [76] L. H. Chen, Y. L. Lee, Adsorption behavior of surfactants and mass transfer in single-drop extraction, *AIChE J.* 46(1) (2000) 160-168.
- [77] L. K. Mudge, W. J. Heideger, The effect of surface active agents on liquid-liquid mass transfer rates, *AIChE J.* (1970) 602-608.
- [78] F. H. Garner, A. H. P. Skelland, Effects of surface active agents on extraction from droplets, *Ind. Eng. Chem.* 48(1) (1956) 51-58.
- [79] C. A. P. Bakker, F. F. Van Vlassingen, W. J. Beek, The influence of the driving force in liquid—liquid extraction—a study of mass transfer with and without interfacial turbulence under well-defined conditions, *Chem. Eng. Sci.* 22(10) (1967) 1349-1355.
- [80] A. Beitel, W. J. Heideger, Surfactant effects on mass transfer from drops subject to interfacial instability, *Chem. Eng. Sci.* 26(5) (1971) 711-717.
- [81] A. H. P. Skelland, C. L. Caenepeel, Effects of surface active agents on mass transfer during droplet formation, fall, and coalescence, *AIChE J.* 18(6) (1972) 1154-1163.
- [82] M. Wegener, A numerical parameter study on the impact of Marangoni convection on the mass transfer at buoyancy-driven single droplets, *Int. J. Heat Mass Transfer.* 71(2014) 769-778.
- [83] J. Saien, S. Daliri, Mass transfer from single drops and the influence of temperature, *Ind. Eng. Chem. Res.* 51(21) (2012) 7364-7372.
- [84] J. Saien, S. Daliri, Mass transfer coefficient in liquid– liquid extraction and the influence of aqueous phase pH, *Ind. Eng. Chem. Res.* 47(1) (2008) 171-175.

- [85] J. Saien, S. Daneshamoz, Experimental studies on the effect of ultrasonic waves on single drop liquid–liquid extraction, *Ultrason. Sonochem.* 40 (2018) 11-16.
- [86] M. A. Waheed, M. Henschke, A. Pfennig, Mass transfer by free and forced convection from single spherical liquid drops, *Int. J. Heat Mass Transfer.* 45(22) (2002) 4507-4514.
- [87] W. H. Piarah, A. Paschedag, M. Kraume, Numerical simulation of mass transfer between a single drop and an ambient flow, *AIChE J.* 47(7) (2001) 1701-1704.
- [88] Z. S. Mao, T. W. Li, J. Y. Chen, Numerical simulation of steady and transient mass transfer to a single drop dominated by external resistance, *Int. J. Heat Mass Transfer.* 44(6) (2001) 1235-1247.
- [89] K.B. Deshpande, W.B. Zimmerman, Simulation of interfacial mass transfer by droplet dynamics using the level set method, *Chem. Eng. Sci.* 61(19) (2006) 6486-6498.
- [90] J. Wang, , P. Lu, Z. Wang, C. Yang, Z. S. Mao, Numerical simulation of unsteady mass transfer by the level set method, *Chem. Eng. Sci.* 63(12) (2008) 3141-3151.
- [91] Z. S. Mao, J. Y. Chen, Numerical simulation of the Marangoni effect on mass transfer to single slowly moving drops in the liquid–liquid system, *Chem. Eng. Sci.* 59(8-9) (2004) 1815-1828.
- [92] S. Ubal, C. H. Harrison, P. Grassia, W. J. Korchinsky, Numerical simulation of mass transfer in circulating drops, *Chem. Eng. Sci.* 65(10) (2010) 2934-2956.
- [93] M. Wegener, T. Eppinger, K. Bäuml, M. Kraume, A. R. Paschedag, E. Bänsch, Transient rise velocity and mass transfer of a single drop with interfacial instabilities—numerical investigations, *Chem. Eng. Sci.* 64(23) (2009) 4835-4845.
- [94] R.F. Engberg, M. Wegener, E.Y. Kenig, The influence of Marangoni convection on fluid dynamics of oscillating single rising droplets, *Chem. Eng. Sci.* 117(2014) 114-124.
- [95] R. F. Engberg, M. Wegener, E. Y. Kenig, A numerical investigation of the impact of Marangoni convection on oscillating rising droplets in liquid/liquid systems, International Solvent Extraction Conference, Wurzburg, Germany, 2014.
- [96] M. R. Davidson, M. Rudman, Volume-of-fluid calculation of heat or mass transfer across deforming interfaces in two-fluid flow, *Numer. Heat Transfer, Part B.* 41(3-4) (2002) 291-308.
- [97] J. F. Wang, C. Yang, Z. S. Mao, Numerical simulation of Marangoni effect in single droplet mass transfer by level-set method, *Sci. China (Ser. A: Chem).* 38(2) (2008) 150-160. (in Chinese)
- [98] P. Lu, Z. Wang, C. Yang, Z. S. Mao, Experimental investigation and numerical simulation of mass transfer during drop formation, *Chem. Eng. Sci.* 65(20) (2010) 5517-5526.
- [99] K. Bäuml, M. Wegener, E. Bänsch, A. R. Paschedag, 2D simulations of interfacial instabilities at deformable single droplets, Seventh International Conference on Computational Fluid Dynamics in the Minerals and Process Industries, Melbourne, Australia, 2009.
- [100] S. Burghoff, E. Y. Kenig, CFD modelling of mass transfer and interfacial phenomena on single droplets, *AIChE J.* 20 (2005) 103-108.
- [101] J. Kamp, J. Villwock, M. Kraume, Drop coalescence in technical liquid/liquid applications: a review on experimental techniques and modeling approaches, *Rev. Chem. Eng.* 33(1) (2017) 1-47.
- [102] J. Kamp, M. Kraume, From single drop coalescence to droplet swarms – Scale-up considering the influence of collision velocity and drop size on coalescence probability, *Chem. Eng. Sci.* 156 (2016) 162-177.
- [103] H. M. Hulburt, S. Katz, Some problems in particle technology: A statistical mechanical formulation, *Chem. Eng. Sci.* 19(8) (1964) 555-574.
- [104] Y. Liao, D. Lucas, A literature review of theoretical models for drop and bubble breakup in turbulent dispersions, *Chem. Eng. Sci.* 64(15) (2009) 3389-3406.

- [105] Y. Liao, D. Lucas, A literature review on mechanisms and models for the coalescence process of fluid particles, *Chem. Eng. Sci.* 65(10)(2010) 2851-2864.
- [106] K. J. Valentas, O. Bilous, N. R. Amundson, Analysis of breakage in dispersed phase systems, *Ind. Eng. Chem. Fundam.* 5(2) (1966) 271-279.
- [107] M. Attarakih, Solution methodologies for the population balance equations describing the hydrodynamics of liquid-liquid extraction contactors, Ph. D. Thesis, T. U. Kaiserslautern, Germany 2004.
- [108] D. Ramkrishna, Population balances: Theory and applications to particulate systems in engineering, Elsevier, 1975.
- [109] M. Goodson, M. Kraft, Simulation of coalescence and breakage: an assessment of two stochastic methods suitable for simulating liquid-liquid extraction, *Chem. Eng. Sci.* 59(18) (2004) 3865-3881.
- [110] E.W. Barega, E. Zondervan, A.B. de Haan, A combined lossy capacitor population balance model (LCPBM) for calculating the influence of frequency on electric field enhanced coalescence in a static-mixer settler setup, *Chem. Eng. Sci.* 104 (2013) 727-741.
- [111] A. Misra, L. G. M. de Souza, M. Illner, L. Hohl, M. Kraume, J. U. Repke, D. Thévenin, Simulating separation of a multiphase liquid-liquid system in a horizontal settler by CFD, *Chem. Eng. Sci.* 167 (2017) 242-250.
- [112] A. Vikhansky, M. Kraft, Modelling of a RDC using a combined CFD-population balance approach, *Chem. Eng. Sci.* 59(13) (2004) 2597-2606.
- [113] M. Jaradat, M. Attarakih, H. J. Bart, Effect of phase dispersion and mass transfer direction on steady state RDC performance using population balance modelling, *Chem. Eng. J.* 165(2) (2010) 379-387.
- [114] S. Alzyod, M. Attarakih, H. J. Bart, The Sectional Quadrature Method of Moments (SQMOM): An extension to nonhomogeneous bivariate population balances, *Chem. Eng. Res. Des.* 115(2016) 195-203.
- [115] H. Chen, Z. Sun, X. Song, J. Yu, A pseudo-3D model with 3D accuracy and 2D cost for the CFD-PBM simulation of a pilot-scale rotating disc contactor, *Chem. Eng. Sci.* 139 (2016) 27-40.
- [116] S. Alzyod, M. Attarakih, A. Hasseine, H. J. Bart, Steady state modeling of Kühni liquid extraction column using the Spatially Mixed Sectional Quadrature Method of Moments (SM-SQMOM), *Chem. Eng. Res. Des.* 117 (2017) 549-556.
- [117] A. P. Neto, M.B. Mansur, Transient modeling of zinc extraction with D2EHPA in a Kühni column, *Chem. Eng. Res. Des.* 91(12) (2013) 2323-2332.
- [118] A. Amokrane, S. Charton, N. Sheibat-Othman, J. Becker, J. P. Klein, F. Puel, Development of a CFD-PBE coupled model for the simulation of the drops behaviour in a pulsed column, *Can. J. Chem. Eng.* 92(2) (2014) 220-233.
- [119] C. Korb, H.J. Bart, Solvent extraction in columns in a droplet breakage domain, *Hydrometallurgy.* 173 (2017) 71-79.
- [120] H. Q. Liu, S. Jing, Q. Fang, S. W. Li, Droplet breakup in a square-sectioned pulsed disc and doughnut column, *Ind. Eng. Chem. Res.* 55(7) (2016) 2242-2251.
- [121] L. Peng, Z. Luo, Y. Y. Zuo, G. Yan, B. Bai, Pinch-off of liquid bridge during droplet coalescence under constrained condition, *Chem. Eng. Sci.* 177 (2018) 471-480.
- [122] J. Kamp, M. Kraume, Influence of drop size and superimposed mass transfer on coalescence in liquid/liquid dispersions -Test cell design for single drop investigations, *Chem. Eng. Res. Des.* 92(4) (2014) 635-643.
- [123] S. Falzone, A. Buffo, M. Vanni, D. L. Marchisio, Simulation of Turbulent Coalescence and Breakage of Bubbles and Droplets in the Presence of Surfactants, Salts, and Contaminants, *Adv. Chem. Eng.* 52(2018) 125-188.

- [124] S. Maaß, Experimental analysis, modeling and simulation of drop breakage in agitated turbulent liquid/liquid-dispersions, Ph. D. Thesis, T. U. Berlin, Germany, 2011.
- [125] J. Solsvik, S. Maaß, H.A. Jakobsen, Definition of the Single Drop Breakup Event, *Ind. Eng. Chem. Res.* 55(10) (2016) 2872-2882.
- [126] S. Galinat, O. Masbernat, P. Guiraud, C. Dalmazzone, , & C. Noik, Drop break-up in turbulent pipe flow downstream of a restriction, *Chem. Eng. Sci.* 60(23) (2005) 6511-6528.
- [127] S. Galinat, L. G. Torres, O. Masbernat, P. Guiraud, F. Risso, C. Dalmazzone, , C. Noik, Breakup of a drop in a liquid–liquid pipe flow through an orifice, *AIChE J.* 53(1) (2007) 56-68.
- [128] S. Maaß, A. Gäbler, A. Zaccone, A. R. Paschedag, M. Kraume, Experimental investigations and modelling of breakage phenomena in stirred liquid/liquid systems, *Chem. Eng. Res. Des.* 85(5) (2007) 703-709.
- [129] S. Maaß, M. Kraume, Determination of breakage rates using single drop experiments, *Chem. Eng. Sci.* 70 (2012) 146-164.
- [130] J. Solsvik, H.A. Jakobsen, Single drop breakup experiments in stirred liquid–liquid tank, *Chem. Eng. Sci.* 131 (2015) 219-234.
- [131] M. Ashar, D. Arlov, F. Carlsson, F. Innings, R. Andersson, Single droplet breakup in a rotor-stator mixer, *Chem. Eng. Sci.* 181 (2018) 186-198.
- [132] J. Jareš, J. Prochazka, Break-up of droplets in Karr reciprocating plate extraction column, *Chem. Eng. Sci.* 42(2) (1987) 283-292.
- [133] M. Cabassud, C. Gourdon, G. Casamatta, Single drop break-up in a kühni column. *Chem. Eng. J.* 44(1) (1990) 27-41.
- [134] C. Gourdon, G. Casamatta, H. Angelino, Single drop experiments with liquid test systems: a way of comparing two types of mechanically agitated extraction columns, *Chem. Eng. J.* 46(3) (1991) 137-148.
- [135] J. Fang, J. C. Godfrey, Z. Q. Mao, M. J. Slater, C. Gourdon, Single liquid drop breakage probabilities and characteristic velocities in Kühni columns, *Chem. Eng. Technol.* 18(1) (1995) 41-48.
- [136] H. Bahmanyar, M. J. Slater, Studies of drop break-up in liquid-liquid systems in a rotating disc contactor. Part I: Conditions of no mass transfer, *Chem. Eng. Technol.* 14(2) (1991) 79-89.
- [137] S. Nachtigall, D. Zedel, S. Maaß, A. Walle, M. Schäfer, M. Kraume, Determination of drop breakage mechanisms by experimental and numerical investigations of single drop breakages, 14th European Conference on Mixing, Warszawa, Poland, 2012.
- [138] F. Gebauer, J. Villwock, M. Kraume, H. J. Bart, Detailed analysis of single drop coalescence-Influence of ions on film drainage and coalescence time, *Chem. Eng. Res. Des.* 115 (2016) 282-291.
- [139] N. Kopriwa, A. Pfennig, Characterization of Coalescence in Extraction Equipment Based on Lab-Scale Experiments, *Solvent Extr. Ion Exch.* 34(7)(2016) 622-642.
- [140] J. Villwock, F. Gebauer, J. Kamp, H. J. Bart, M. Kraume, Systematic analysis of single droplet coalescence, *Chem. Eng. Technol.* 37(7) (2014) 1103-1111.
- [141] R. Andersson, B. Andersson, On the breakup of fluid particles in turbulent flows, *AIChE J.* 52(6) (2006) 2020-2030.
- [142] F. Gebauer, M.W. Hlawitschka, H. J. Bart, CFD aided investigation of single droplet coalescence, *Chin. J. Chem. Eng.* 24(2) (2016) 249-252.
- [143] R. T. Eiswirth, H. J. Bart, A. A. Ganguli, E. Y. Kenig, Experimental and numerical investigation of binary coalescence: Liquid bridge building and internal flow fields, *Phys. Fluids.* 24(6) (2012) 062108.
- [144] L. R. Mason, G. W. Stevens, D. J. Harvie, Multi-scale volume of fluid modelling of droplet coalescence, 9th International Conference on CFD in the Minerals and Process Industries, Melbourne, Australia, 2012.

- [145] R. Andersson, A. Helmi, Computational fluid dynamics simulation of fluid particle fragmentation in turbulent flows, *Appl. Math. Modell.* 38(17-18)(2014) 4186-4196.
- [146] J. Płotka-Wasyłka, M. Rutkowska, K. Owczarek, M. Tobiszewski, J. Namieśnik, Extraction with environmentally friendly solvents, *TrAC, Trends Anal. Chem.* 91 (2017) 12-25.
- [147] S. H. Ha, N. L. Mai, Y. M. Koo, Butanol recovery from aqueous solution into ionic liquids by liquid–liquid extraction, *Process Biochem.* 45(12) (2010) 1899-1903.
- [148] H. Passos, M.G. Freire, J.A. Coutinho, Ionic liquid solutions as extractive solvents for value-added compounds from biomass, *Green Chem.* 16(12) (2014) 4786-4815.
- [149] H. J. Bart, C. Drumm, M. M. Attarakih, Process intensification with reactive extraction columns, *Chem. Eng. Process: Process Intensification.* 47(5) (2008) 745-754.
- [150] F. Buchbender, F. Onink, W. Meindersma, A. de Haan, A. Pfennig, Simulation of aromatics extraction with an ionic liquid in a pilot-plant Kühni extractor based on single-drop experiments, *Chem. Eng. Sci.* 82 (2012) 167-176.
- [151] M. M. S. Badieh, M. C. Quaresima, A. Pfennig, J. Saien, Performance study of ionic liquid in extraction based on single-drop experiments, *Solvent Extr. Ion Exch.* 35(7) (2017) 563-572.
- [152] A. G. Teixeira, R. Agarwal, K. R. Ko, J. Grant-Burt, B. M. Leung, J. P. Frampton, Emerging Biotechnology Applications of Aqueous Two-Phase Systems, *Adv. Healthcare Mater.* 7(6) (2018) 1701036.
- [153] M. Iqbal, Y. Tao, S. Xie, Y. Zhu, D. Chen, X. Wang, H. I. Hussain, Aqueous two-phase system (ATPS): an overview and advances in its applications, *Biol. Proced. Online.* 18(1) (2016) 18.
- [154] M.E. Silva, T.T. Franco, Liquid-liquid extraction of biomolecules in downstream processing - A review paper, *Braz. J. Chem. Eng.* 17(1)(2000) 1-17.
- [155] E. Espitia-Saloma, P. Vázquez-Villegas, O. Aguilar, M. Rito-Palomares, Continuous aqueous two-phase systems devices for the recovery of biological products, *Food Bioprod. Process.* 92(2) (2014) 101-112.
- [156] S. B. Sawant, S. K. Sikdar, J. B. Joshi, Hydrodynamics and mass transfer in two-phase aqueous extraction using spray columns, *Biotechnol. Bioeng.* 36(2) (1990) 109-115.
- [157] P. C. Bhawsar, A. B. Pandit, S. B. Sawant, J. B. Joshi, Enzyme mass transfer coefficient in a sieve plate extraction column, *Chem. Eng. J., Biochem. Eng. J.* 55(1-2) (1994) B1-B17.
- [158] N. D. Srinivas, A. V. Narayan, K. S. M. S. Raghavarao, Mass transfer in a spray column during two-phase extraction of horseradish peroxidase, *Process Biochem.* 38(3) (2002) 387-391.
- [159] R. S. Barhate, G. Patil, N. D. Srinivas, K. S. M. S. Raghavarao, Drop formation in aqueous two-phase systems, *J. Chromatogr. A.* 1023(2) (2004) 197-206.
- [160] M. C. Quaresima, M. Schmidt, A. Pfennig, Solvent Extraction Design for Highly Viscous Systems, The 21st International Solvent Extraction Conference, Miyazaki, Japan, 2017.
- [161] P. Amani, M. Amani, G. Ahmadi, O. Mahian, S. Wongwises, A critical review on the use of nanoparticles in liquid–liquid extraction, *Chem. Eng. Sci.* 183 (2018) 148-176.
- [162] J. K. Lee, J. Koo, H. Hong, Y. T. Kang, The effects of nanoparticles on absorption heat and mass transfer performance in NH₃/H₂O binary nanofluids, *Int. J. Refrig.* 33(2) (2010) 269-275.
- [163] J. Saien, H. Bamdadi, Mass Transfer from Nanofluid Single Drops in Liquid–Liquid Extraction Process, *Ind. Eng. Chem. Res.* 51(14) (2012) 5157-5166.
- [164] A. M. Ghanadi, A. H. Nasab, D. Bastani, A. A. S. Kordi, The effect of nanoparticles on the mass transfer in liquid–liquid extraction, *Chem. Eng. Commun.* 202(5) (2015) 600-605.
- [165] J. Saien, M. Zardoshti, Mass transfer intensification of nanofluid single drops with effect of temperature, *Korean J. Chem. Eng.* 32(11) (2015) 2311-2318.

- [166] H. H. Goodarzi, M. N. Esfahany, Experimental investigation of the effects of the hydrophilic silica nanoparticles on mass transfer and hydrodynamics of single drop extraction, *Sep. Purif. Technol.* 170 (2016) 130-137.
- [167] A. Vahedi, A.M. Dehkordi, F. Fadaei, Mass transfer enhancement in single drop extraction in the presence of magnetic nanoparticles and magnetic field, *AIChE J.* 62(12) (2016) 4466-4479.
- [168] J. Saien, R. Hasani, Hydrodynamics and mass transfer characteristics of circulating single drops with effect of different size nanoparticles, *Sep. Purif. Technol.* 175 (2017) 298-304.
- [169] A. Hatami, D. Bastani, F. Najafi, Investigation the effect of super hydrophobic titania nanoparticles on the mass transfer performance of single drop liquid-liquid extraction process, *Sep. Purif. Technol.* 176 (2017) 107-119.
- [170] J. Ayesterán, N. Kopriwa, F. Buchbender, M. Kalem, A. Pfennig, ReDrop—A Simulation Tool for the Design of Extraction Columns Based on Single-Drop Experiments, *Chem. Eng. Technol.* 38(10) (2015) 1894-1900.
- [171] M. M. Attarakih, H. J. Bart, T. Steinmetz, M. Dietzen, N. M. Faqir, LLECMOD: A bivariate population Balance simulation tool for liquid-liquid extraction columns, *Open Chem. Eng. J.* 2 (2008) 10-34
- [172] M. M. Attarakih, H. J. Bart, L. Lagar, N. M. Faqir. LLECMOD: A Windows-based program for hydrodynamics simulation of liquid-liquid extraction columns, *Chem. Eng. Process: Process Intensification.* 45(2) (2006) 113-123.
- [173] M. Attarakih, S. Al-Zyod, M. Abu-Khader, H. J. Bart, PPBLAB: A new multivariate population balance environment for particulate system modelling and simulation, *Procedia Eng.* 42 (2012) 1445-1462.
- [174] M. Attarakih, S. Alzyod, A. Fricke, Population balance modelling of pulsed packed bed extraction columns using PPBLab software, *Comput. Aided Chem. Eng.* 40 (2017) 67-72.
- [175] M. W. Hlawitschka, M. M. Attarakih, S. S. Alzyod, H. J. Bart, CFD based extraction column design - chances and challenges, *Chin. J. Chem. Eng.* 24(2) (2016) 259-263.
- [176] A. Amokrane, S. Maaß, F. Lamadie, F. Puel, S. Charton, On droplets size distribution in a pulsed column. Part I: In-situ measurements and corresponding CFD-PBE simulations, *Chem. Eng. J.* 296 (2016) 366-376.

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Zhang, J;Wang, Y;Stevens, GW;Fei, W

Title:

A state-of-the-art review on single drop study in liquid–liquid extraction: Experiments and simulations

Date:

2019-12

Citation:

Zhang, J., Wang, Y., Stevens, G. W. & Fei, W. (2019). A state-of-the-art review on single drop study in liquid–liquid extraction: Experiments and simulations. Chinese Journal of Chemical Engineering, 27 (12), pp.2857-2875. <https://doi.org/10.1016/j.cjche.2019.03.025>.

Persistent Link:

<http://hdl.handle.net/11343/241452>