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Validation of Single-Drop Cell by the study of Mass Transfer Kinetics for n-Butyl Acetate, Water and Acetone

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Diplôme : Master : ingénieur civil en chimie et science des matériaux, à finalité spécialisée en Advanced Materials - Innovative Recycling
Année académique : 2022-2023
URI/URL : http://hdl.handle.net/2268.2/18365

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Cristian David Gómez Lozano

Liège, August 2023

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Validation of Single Drop Cell by the study of Mass Transfer Kinetics for n-Butyl Acetate, Water and Acetone.

Master-Thesis

to obtain the academic degree of

Master of Science

in

Chemical Engineering

submitted to

Université de Liège

supervisor:

Prof. Dr.-Ing., Andreas Pfennig

Université de Liège

Liège, August 2023

Master-Thesis
for
Mr. Cristian David Gómez Lozano

Validation of Single Drop Cell by the study of Mass Transfer Kinetics for n-Butyl Acetate, Water and Acetone.

Project Description

In the realm of sustainable resource utilization, the recovery of valuable metals from electronic scrap has emerged as a crucial endeavor. Among these valuable materials, rare-earth and precious metals present in electronic waste can be efficiently recovered through acid leaching and subsequent solvent extraction processes. The effective application of these methods hinges on an in-depth understanding of mass-transfer kinetics, a pivotal parameter for modelling extraction performance.

The primary goal of this master's thesis project is to undertake a comprehensive study of mass-transfer kinetics employing a known material system, already explored by colleagues, to validate the prepared equipment. This system involves the transfer of acetone from the aqueous phase (water) to the organic phase (n-butyl acetate). The acquired data will be compared with existing literature and prior results to validate the experimental procedure.

Equipment Preparation and Protocols: The project commences with the setup and calibration of a vital piece of equipment for mass-transfer kinetics a single-drop cell and a Protocols for utilizing these apparatuses will be established to ensure accurate and reproducible experimental procedures.

Literature Review: A thorough literature search will be conducted to gather existing knowledge on mass-transfer kinetic models and experimental findings pertinent to the systems under investigation.

Scientific Contribution: The culmination of this project will be a comprehensive report, detailing the entire research process, from equipment setup to experimental results and model development. This report is envisioned to contribute significantly to the scientific understanding of mass-transfer kinetics in the context of reactive extraction processes.

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Abstract

Liquid-Liquid Extraction (LLE) serves as a pivotal technique in the recovery, purification, and isolation of essential components, making it indispensable for recycling critical raw materials, notably rare earth elements. This engineering master thesis underscores the significance of LLE within the context of recycling and resource recovery.

The dissertation commences with a comprehensive literature review, elucidating the core principles governing LLE. The discussion extends to an exploration of diverse equipment types employed for this technique, particularly extraction columns. Central to this exploration is the elucidation of the underlying fundamentals that define the operation of extraction columns, a framework applicable across all variants. Notably, the ubiquity of mass-transfer with single drops as the primary driver of phenomena across equipment types is highlighted.

Presently, the field is marked by a heightened interest in scrutinizing the behavior of individual droplets, particularly within counter-current LLE columns. A comprehensive modeling approach capturing the intricate interplay of various phenomena within these columns is imperative for accurate description and modeling. In this context, ReDrop (Representative Drops) emerges as a viable modeling tool, integrating all pertinent phenomena to track drop behavior throughout the extraction column.

Laboratory-scale experiments with single drops offer advantages in terms of reduced dimensions and lower liquid volumes, drastically cutting experimental time and associated costs. This thesis delves into the validation of the University of Liège's single-drop cell, a crucial precursor for subsequent experimentation. The validation process encompasses a comparison of mass transfer rates with literature and models established through the literature review.

An in-depth analysis of operational challenges encountered during experimentation is presented, accompanied by an operational manual for the single-drop cell. The validation procedure, conducted with meticulous care, yields positive results, affirming the reliability of the experimental setup. With this validation in place, the groundwork is laid for the next phase of the project.

Table of Content

1 Introduction

The European Union (EU) aims to achieve climate neutrality by 2050. This requires developing and deploying sustainable clean energy and mobility solutions. In the last few decades, many green energy technologies have been developed, and electrification has increased. (Gaus *et al.*, 2021) However, the energy transition requires massive amounts of raw materials. Electric motors that convert electric energy into motion are essential for these applications. The most energy-efficient electric motors and generators contain rare earth permanent magnets. Although EU companies are leaders in electric motor manufacturing, they depend on imports for the entire value chain of rare earth magnet materials.

Rare earth elements (REE) are therefore in the Critical Raw Materials List, both for the EU (Grohol *et al.*, 2023) and United States (Fortier *et al.*, 2021). It is therefore a growing need to develop recycling processes that can recover materials such as neodymium, praseodymium and dysprosium from highly diluted sources as can be the waste of electric and electronical equipment (WEEE), electric vehicles (EVs) and generators used in some green energy applications (IEA, 2021).

As mentioned before, REE are found in WEEE and according to (Adrian *et al.*, 2020) it a growing problematic due to the massive generation. According to (Luis Stephens, 2023) rare earth metals are among the metals with lowest recycling rates, and according to (Gregoir, 2022) the need for them will grow from 7 to 13% annually from 2020 to 2030. Therefore, technically efficient improvements are needed to improve both the collection and processing.

Is here where hydrometallurgy plays a key role by providing the platform in which these complex materials can be processed. LLE is one of the techniques that has been widely used in the industry for the recovery of valuable metals from acid solutions.

Several authors have developed processes and techniques for the deployment of the technology, (Abreu and Morais, 2014; Xie *et al.*, 2014; Kumari *et al.*, 2015; Mohammadi *et al.*, 2015; Jha *et al.*, 2016; Yoon *et al.*, 2016; Hidayah and Abidin, 2018).

For expanding the applicability of the technique, tools for modeling technical equipment for LLE is required. And with the current standards for sustainability and resource management, processes with less use of material and time are required. ReDrop has been developed for decades to solve this need. The ReDrop program has been developed for more than two decades at AVT-Thermal Process Engineering of RWTH Aachen University and later continued at CEET, TU Graz, and PEPs at the university of Liège (Henschke, 2004). The approach used in ReDrop brings several benefits in terms of knowledge, because the experience-based design and optimizations is replaced by knowledge-based design and optimization.

This thesis takes place because of the need of drop-based experiments required to feed the program, and therefore, being able to model LLE columns, including those with reactions occurring in the surface of the drops. A Single-drop cell placed in the university of Liège must be validated to continue with the experimentation regarding reactive extraction. Which will be used to model columns for the purpose of extracting valuable metals from acid solutions coming from the leaching of electronic waste.

Based on the need of validating the single-drop cell, the study of drop-base mass transfer and some of the related phenomena are required, to understand the results after the experimentation. The standard systems recommended for this scenario and use in this thesis are, water, acetone, and n-butyl acetate.

2 Literature review

2.1 Liquid-Liquid Extraction

Liquid-Liquid Extraction (LLE) also known as Solvent Extraction (SX) is a process for separating components of a liquid (the feed) by contact with a second liquid phase (the solvent). The process is based on the differences that exist between the physicochemical properties of both phases with regards to the component to be extracted. Among these physicochemical properties are polarity, hydrophobicity/hydrophilic character, density, and solubility (Green and Perry, 2008)

In a more precise way, the transfer of components from one phase to the other is driven by a deviation from thermodynamic equilibrium, and the equilibrium state depends on the nature of the interactions between the feed components and the solvent phase. The potential for separating the feed components is determined by differences in these interactions.

The LLE process produces a solvent-rich stream called the extract, which contains the desired portion of the feed, and an extracted-feed stream called raffinate as shown in Fig. 2-1. Usually, a commercial process includes two or more auxiliary operations to perform the conditioning of the feed, the further purification of the resulting phases if needed, or the isolation of the desired product.

LLE is used in a wide variety of operations across all industries, it is used to recover, isolate, purify, clean desired components in industries like hydrometallurgy, nuclear fuel, petrochemicals, coal and wood-derived chemicals, complex organics such as pharmaceuticals and agricultural chemicals, wastewater treatment, food processing and the recovery of biomolecules from fermentation broth. (Green and Perry, 2008)

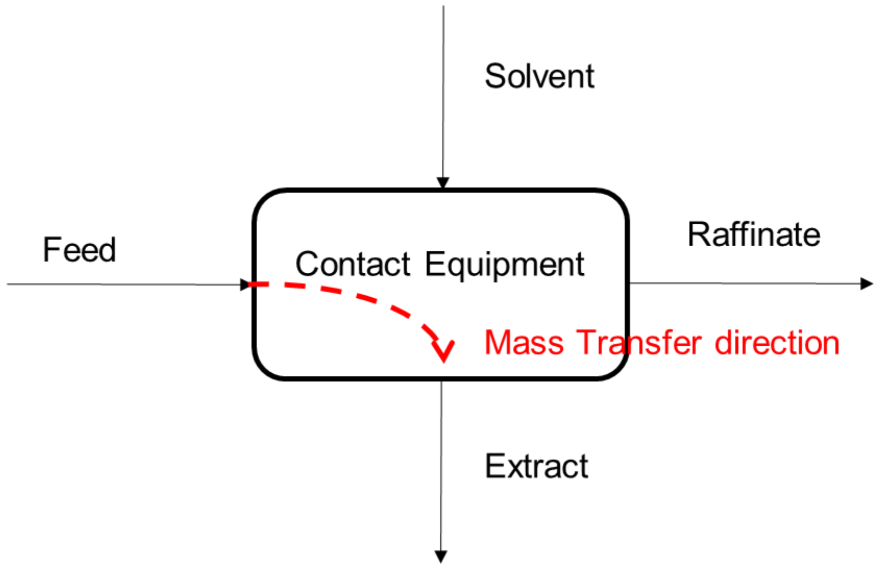


Fig. 2-1:Illustration of simplified LLE and direction of mas transfer of desired component.

2.2 LLE in Hydrometallurgy

As mentioned before in section 2.1, LLE is a versatile technology with several fields of application including hydrometallurgy. Hydrometallurgy is the extraction and refining of metals using solutions in liquid media, often involving aqueous solutions as the first step (leaching). In general hydrometallurgy uses processes that leach the desired metal at relatively low temperatures (T < 300°C) in comparison with pyrometallurgy. The metal solution must then be refined, which involves the separation and purification of the desired metal, for later being able to produce it in solid phase as pure metal or as a valuable compound. In hydrometallurgy, the solvent used for refining the metal is a selective agent. This agent can target a specific metal or a specific family of metals and extracts them from the aqueous phase. Reactive extraction relies on the interactions between transfer components and a responsive extractant at the boundary between phases. Generally, four different types of reaction mechanisms are identified. (Bart, 1982)

- Extraction by cation exchange: Usually carried out using organic acids such as carboxylic acids, sulfonic acid, and phosphoric acids. Protons are extracted by the anion formed in the acidic head of the organic compound, As the reaction liberates cations (H+) in the solution, a decrease of the pH is observed along with the increase of the extraction degree. The complex formed is neutral and stays in the organic phase thanks to its organic tales, thus being extracted by the solvent (Tavlarides, Bae and Lee, 1987). A specific example of this kind of process is the extraction of zinc with di(2-ethylhexyl) phosphoric acid (D2EHPA.)

- Extraction by anion exchange: The extractants used are usually basic organic extractants. They can easily form a salt when in contact with the aqueous acid solution (which is normally the form of the leachate). Commercially available extractants are based on amines and quaternary ammonium halides, its usefulness as extractant is essentially dependant on the metal’s ion ability to form anionic species in the aqueous phase (Tavlarides, Bae and Lee, 1987). Some of those examples of anion exchange are presented briefly in (Sole, Mooiman and Hardwick, 2018), where zinc is extracted from nickel electrolytes, uranium extracted by anionic resins or by carbonate-based reactions.

- Extraction by solvation: This extraction is based on the action of the solvating extractants on the metal’s ions solvated in water. Briefly, the solvating agent replaces the water around the metal ion as solvating agent, therefore, increasing the solubility of the metal in the organic phase and achieving the extraction. Solvating extractants are organic reagents that have only donor groups that do not contain dissociating protons.Therefore, they are neutral extractants. (Tavlarides, Bae and Lee, 1987)

- Extraction by chelation: Chelation is the process in which two molecules of the chelant compound form a complex with the metal ion by interactions between its multiple bonding sites (polydentate) and the ion. The bonding sites usually are donor sites, that stabilizes the ion in its interior. Some examples of chelating agents are the oximes and crown ethers as see in Fig. 2-2.

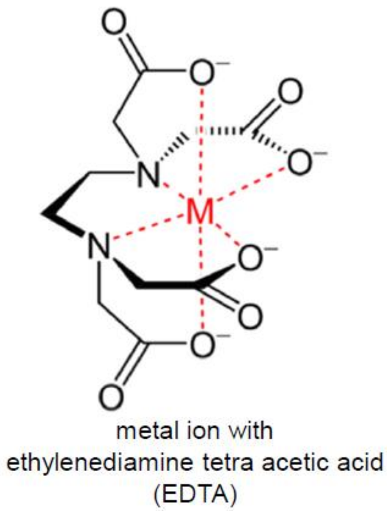


Fig. 2-2: Chelation reaction example

2.3 Types of equipment for LLE

The variety of commercial equipment options is large and includes stirred tanks and decanters, specialized mixer-settlers, a wide variety of agitated and non-agitated extraction columns or towers and various types of centrifuges.

All types of extractors in counter current, can be represented by stages as shown in Fig. 2-3. In this schematic the feed enters the first stage and gets in contact with the extract coming from the next stage (Y2). The raffinate exiting the stage (X1) has been depleted of solute, while the extract has been loaded with it. In the opposite side of the column the solvent enters the column with ideally no solute and gets in contact with the raffinate of the stage r-1, in which most of the solute has been depleted. The resulting extract goes up until it reaches the feed stage.

In this section the most common types of extraction equipment will be discussed to understand the challenges when dimensioning them, but also, to understand the underlying phenomena that had to be considered for the modelling.

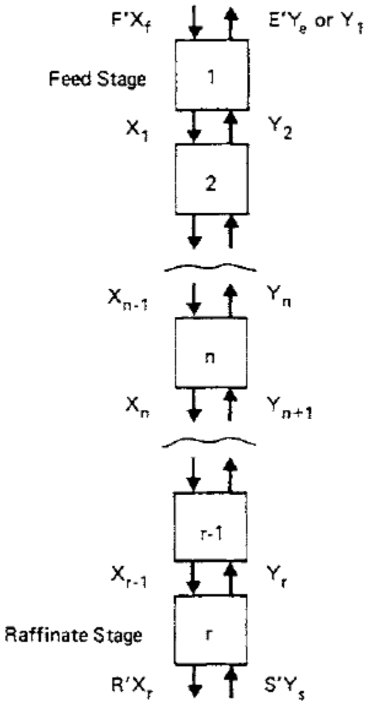


Fig. 2-3: Counter current extraction. (Green and Perry, 2008)

2.3.1 Mixer-settlers

The firs type of equipment is the combination of mixer-settlers, which are widely used in the hydrometallurgical industry as well as in multistep batchwise production of specialty chemicals including pharmaceuticals and agricultural chemicals. This type of equipment is the most basic, being based on the equilibrium extraction.

In general, each mixer-settler is a stage of the process as can be seen in Fig. 2-4, depending on its type, batchwise or continuous feed. In case of batchwise extraction the same vessel used for mixing often is used for settling. This type of operation brings a great flexibility to the process and isolation from other batches as is normally required in the pharmaceutical industry.

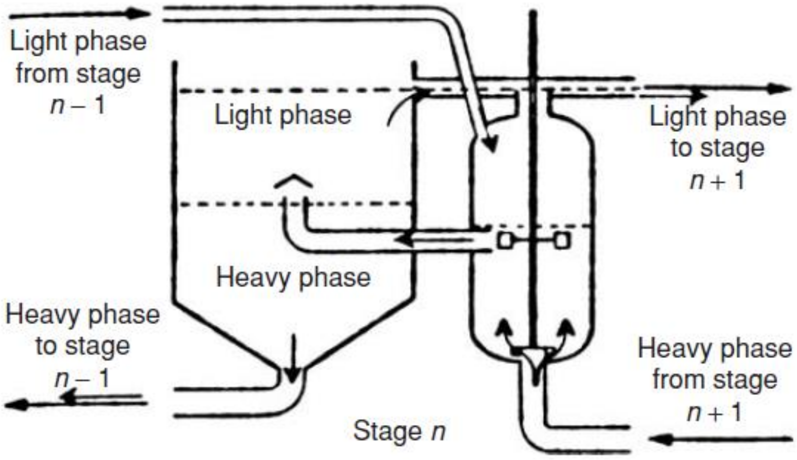


Fig. 2-4: Mixer-Setler representation. (Green and Perry, 2008)

2.3.2 Static extraction columns

Static extractors include spray-type, packed, and sieve tray columns. (Green and Perry, 2008). They are called static, because only liquids are in movement during operation. This type of equipment offers advantages such as availability in large diameters for high production rates, simple operation with no moving parts and associated seals, and a relatively small footprint compared to mixer-settler equipment. The primary disadvantage coming from static extraction columns is the low mass-transfer efficiency compared to that of mechanically agitated extractors. This usually limits applications to low viscosities media (less than 5cP), low to moderate interfacial tensions media (0.003 to 0.02 N/m) and no more than three to five equilibrium stages.

Spray column is the least efficient static extractor in terms of mass-transfer performance, due to considerable back mixing (axial mixing) effects. It finds use in processing feed that would easily foul other equipment. Packed and sieve tray columns improve mass-transfer performance by limiting back mixing.

2.3.2.1 Spray columns

It is one of the oldest and simplest types of equipment used for putting in contact two liquid phases in counter current flow. It normally consists of an empty vertical vessel with a distributor located at one end. The distributor is used to disperse one of the liquids into drops. These drops then rise or fall against the flow of continuous phase, being collected at the other end of the column after coalescing and forming a layer of phase that is withdrawn, as can be seen in Fig. 2-5.

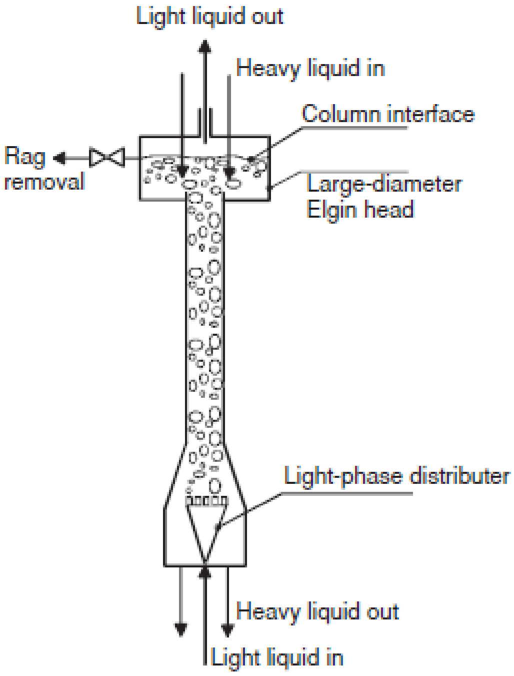


Fig. 2-5: Spray column diagram. (Green and Perry, 2008)

In spray columns, (Wongpat, 2010) the axial mixing is relatively higher than in other columns, leading to the reduction of the driving force along the axis of the column which leads to the decrease of the extraction efficiency. Consequently, this type of column is used for low number of equilibrium stages processes, for example washing, neutralizing, and direct heat-transfer. (Green and Perry, 2008)Spray columns are used when a high load of solids is present in the phases since there are no surfaces in which the solids can get sedimented.

2.3.2.2 Packed columns

Packed columns have a similar geometry to spray columns. The column has packing, which is a solid media placed inside the column to promote the dispersion of the drops, increase the contact time, and create favourable conditions for coalescence. Packing's main use is to decrease the axial mixing and therefore improve extraction efficiency.

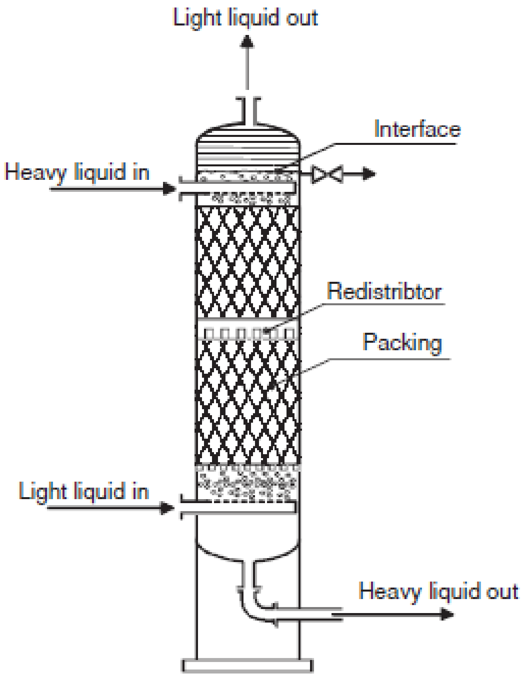


Fig. 2-6: Packed column diagram. (Green and Perry, 2008)

The packing referred to in Fig. 2-6 can be random (as in Fig. 2-7) or structured (as in Fig. 2-8), for each type of packing there are several manufacturers and types of packings. In general, the material selected for the packing should be stable at process conditions and should preferably be wetted by the continuous phase to avoid issues with dispersed phase.

Fig. 2-7: Examples of Random packing types.(Maćkowiak, 2010)

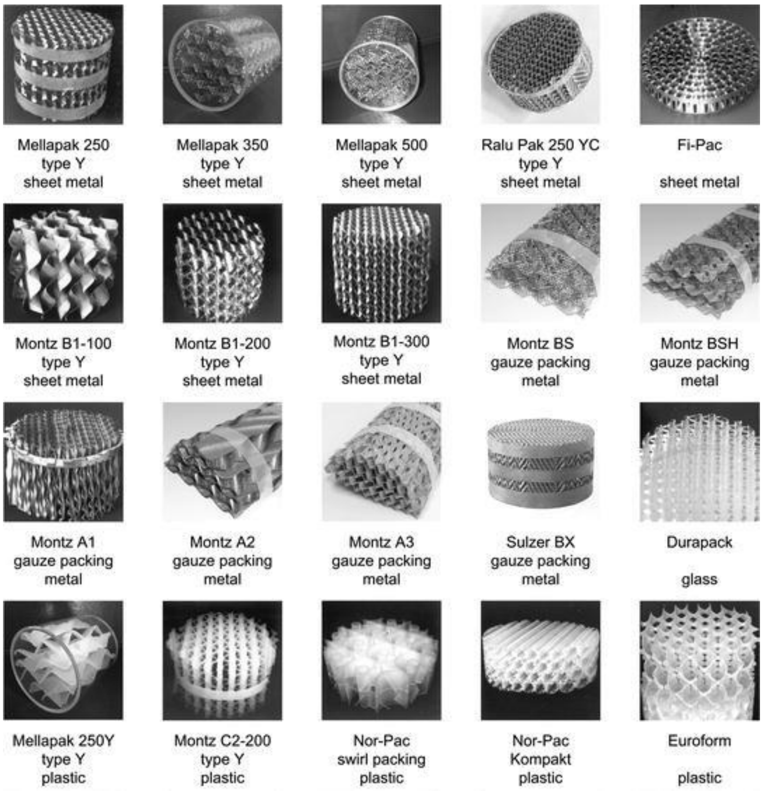


Fig. 2-8: Example of structured packing types.(Maćkowiak, 2010)

2.3.2.3 Sieve tray columns

Sieve tray columns, also called sieve plate or perforated plate columns, are in essence the same as spray columns but with internal trays which have several perforations, and a downcomer which allows the phase with the lowest flow.

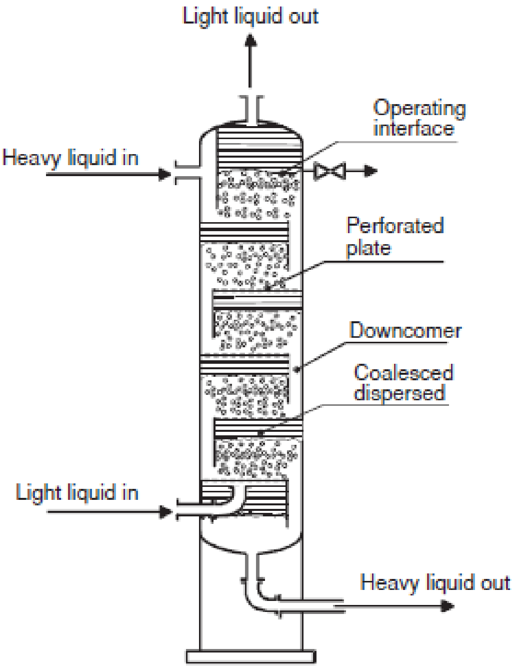


Fig. 2-9: Sieve tray column diagram. (Green and Perry, 2008)

In Fig. 2-9 is represented a column in which the light phase is dispersed by the tray's perforations. The continuous phase flows horizontally across each tray and passes to the tray beneath through the downcomer. (Green and Perry, 2008) The trays virtually eliminate (or greatly reduce) the axial mixing or back mixing of continuous phase and allows a repeated coalescence and redispersion into droplets of the dispersed phase that enhance the mass-transfer rates. In general, the overall efficiency of a sieve tray is low, on the order of 12 to 30%. Higher efficiencies can be achieved in systems with low to moderate interfacial tension. It is usually more common to disperse the phase with the highest volumetric flow, in order to promote the dispersion and therefore increase the interfacial area for mass-transfer.

2.3.3 Agitated extraction columns

As described in section 2.3.2, static extraction columns are used in applications with fluids having low to moderate interfacial tension, due to restrictions in mass-transfer. When fluids with a moderate to high interfacial tension are used, (Green and Perry, 2008) the mass-transfer efficiency can be improved by mechanically agitating the liquid-liquid dispersion within the column to control in a better way the drop size population. The most common types include various rotary-impeller columns, reciprocating-plate column, and rotating-disc contactor (RDC).

2.3.3.1 Scheibel extraction column

In its third iteration, the Scheibel extraction column consists of a vessel (as all the previous columns), with a central shaft to which several impellers are attached, surrounded by stationary baffles to direct the flow of droplets discharged from the impeller tips, as shown in Fig. 2-10: Scheibel column extractor (third iteration). .

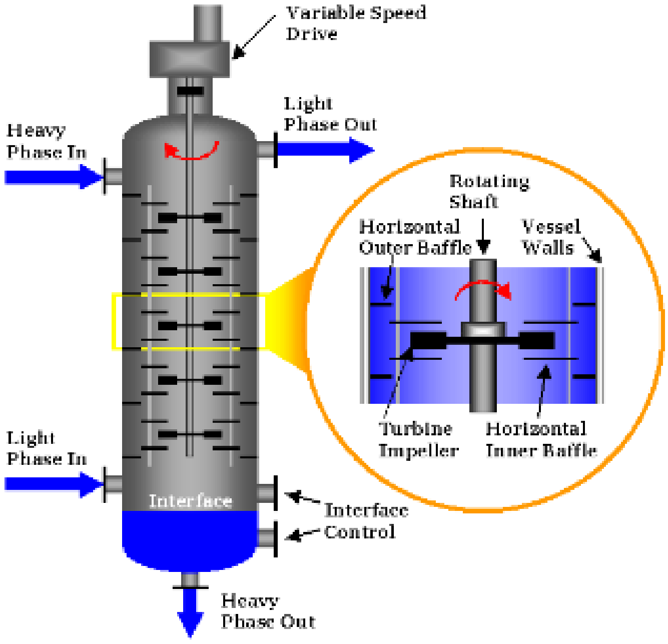


Fig. 2-10: Scheibel column extractor (third iteration). (Koch modular process systems, 2023)

Scheibel columns are well-suited for handling systems with high interfacial tension, because they can be designed with a large number of stages (Koch modular process systems, 2023) (each impeller-baffle is a stage). On the other hand, they are not well-suited for mixtures that tend to emulsify easily, due to the high shear rate generated by the impeller. Owing to its characteristics, the Scheibel column has proved to be one of the more efficient extractors in terms of height of theoretical stage. This makes it ideal for applications in which the total heigh of the equipment is restricted.

2.3.3.2 Kühni column

Kühni columns, like Scheibel columns, use impellers as mixing elements on a central shaft. (Green and Perry, 2008) Perforated partitions or stator plates extend over the vessel to separate the extraction stages and reduce the axial mixing between stages.

Fig. 2-11: Kühni column internals. (Sulzer, 2018)

The effect of the separation of the internals has been studied widely, It was found that as the fractional free-flow area between compartments increases, the throughput increases, but at the expense of increased axial mixing. According to (Sulzer, 2018), the previously mentioned behaviour allows to compensate stage by stage the changing conditions of any system, which translate to a constant high column performance.

Some of its advantages include the previously mentioned flexibility in terms of operation, the capacity to have more than 30 theoretical stages in one single vessel, and the wide range of viscosities that it can handle as well as interfacial tension higher than 0.002 N/m.

2.3.3.3 Reciprocating plate columns

The use of reciprocating plates represents another approach when agitating a dispersion within an extraction column (Green and Perry, 2008). Thanks to a better distribution of shear forces over the cross section, this design results in a more uniform drop size distribution. This characteristic allows the use of systems with moderate interfacial tension and with a high tendency to emulsify. Another advantage of this design is its capacity to handle slurries of solids, containing as much as 30% solids by weight.

There are several examples and variations of this design, the differences generally involve changes in the plate open area, plate spacing, inclusion or omission of static baffles or downcomers, and in general the disposition of specific geometrical parameters. For the purpose of this document, the Karr reciprocating-plate column shown in Fig. 2-12 will be described as a representative of this type of design.

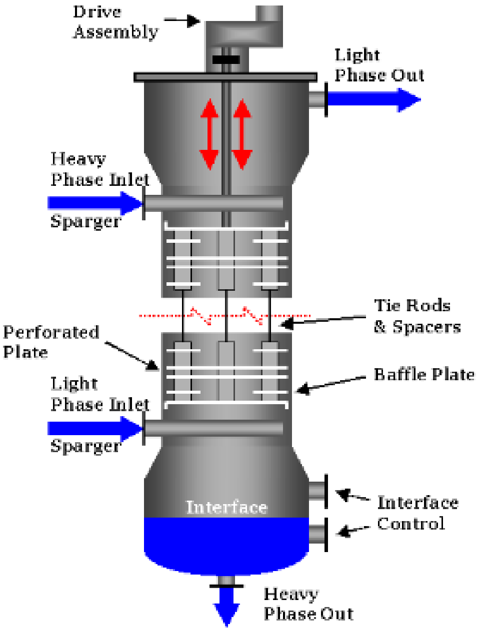


Fig. 2-12: Karr reciprocating-plate column representation. (Koch modular process systems, 2023)

The Karr reciprocating-plate column (Koch modular process systems, 2023) uses dual-flow plates with 50% to 60% open area and has no downcomers. Because of the high open area, they can be operated with relatively high throughput compared to other agitated columns' designs. As shown in Fig. 2-12, the plates are mounted on a central shaft that moves up and down through a stroke length of around 5 cm. For diameters greater than 0.3 m, doughnut-shaped baffle plates may be added every 5 lates, typically within the plate stack to minimize axial mixing.

Since the plates can be constructed in non-metallic materials, this type of column is well suited to handle corrosive media. Similarly to Kühni columns, the distances between plates can be adjusted according to changes in physical properties inside the column. This can improve the drop size population towards more uniform distribution.

2.3.3.4 Rotary disc contactors (RDC)

The RDC can be described as a vessel with sections defined by annular baffles along the length of the column, to which rotating discs attached to a shaft are in the middle of the sections. The rotating disc is usually smooth and flat and oversees providing the agitation within the stage. Its diameter is less than the opening of the annular baffles, as can be seen in Fig. 2-13.

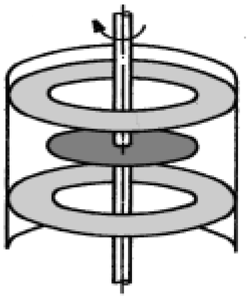


Fig. 2-13: RDC internals representation. (Pfennig, 2022)

The RDC design has been widely used, as its construction is relatively simple. It is available in large diameters for high production rates and low energy consumption. On the other hand the relatively open arrangement leads to some axial mixing, and therefore to a mass-transfer performance decay in comparison with previous designs

(2.3.3.2, 2.3.3.3). Nevertheless, this design is suitable for systems with moderate viscosities, up to about 100 cP, as well as fouling systems.

2.3.3.5 Pulsed-liquid columns

This type of equipment is an iteration of static columns, seen in sections 2.3.2.2 and 2.3.2.3. A rapid reciprocating motion of relatively short amplitude is applied to the liquid content to improve the extraction rates. However, a consequence of improving mass-transfer by pulsation is the reduction of the throughput.

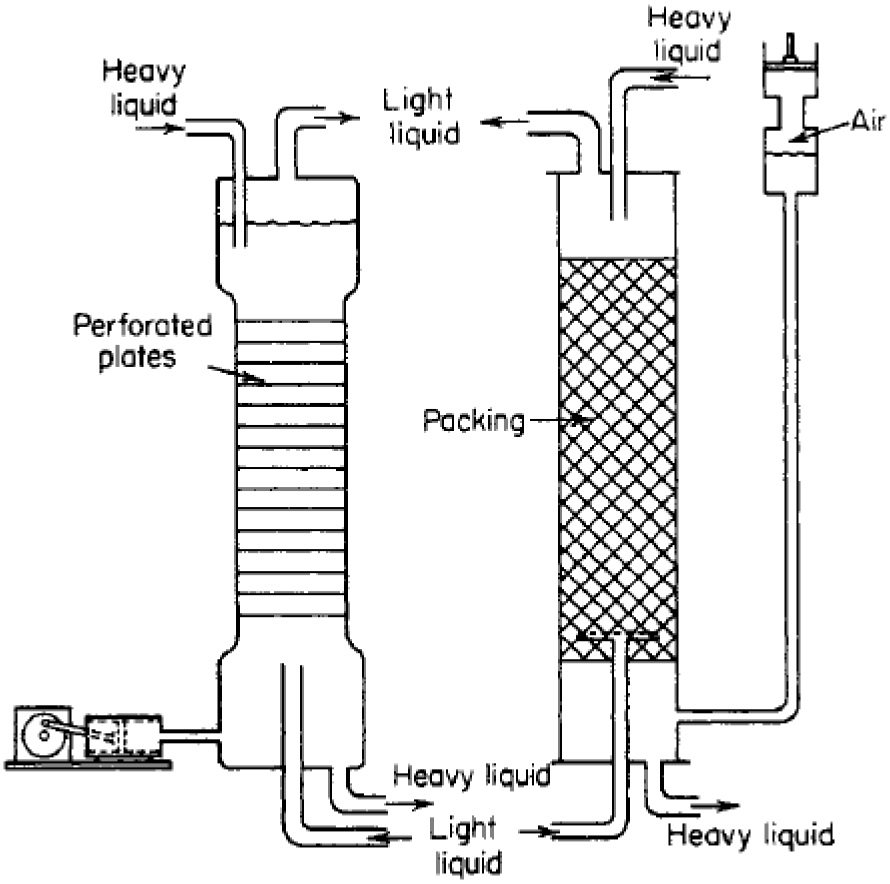


Fig. 2-14: Pulsed-liquid columns. Sieve tray column with pump-type pulse generator (right) and packed column with air pulser (left). (Green and Perry, 2008)

The main advantage of this type of design over designs with rotating internals, is that it provides a sealed agitated extraction column, which is an important feature when processing highly corrosive or dangerous radioactive liquids. (Green and Perry, 2008). Its operation is similar to that of reciprocating-plate extractors, but more energy is required to move the column volume.

2.4 Challenges in dimensioning and design

One of the major objectives of engineering, and specifically of chemical engineering, is to design processes to satisfy a need. After understanding the need, the designer will be constrained by many factors, which will narrow down the number of possible designs as shown in Fig. 2-15. In this section, the design of LLE columns will be briefly studied, with the objective of understanding the different needs and constraints that are involved.

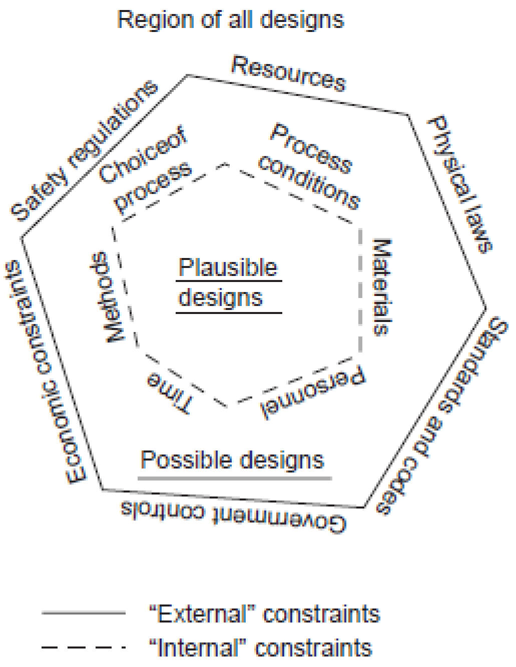


Fig. 2-15: Design constrain. (Towler and Sinnott, 2008)

As seen in previous sections (2.1 and 2.2) LLE is a widely used technique, although its use is not as extensive as e.g., distillation, even though it possesses several advantages, such as energy requirement. (Garthe, 2006) This is mainly due to the large number of parameters (constraints) that influence the fluid dynamics and mass-transfer behaviour in extractions columns as shown in Fig. 2-16. Addressing all constraints is a laborious task, which requires considerable data-processing and -calculation capacity, to correctly design the required equipment. For that reason, the dimensioning of such columns has been considered challenging.

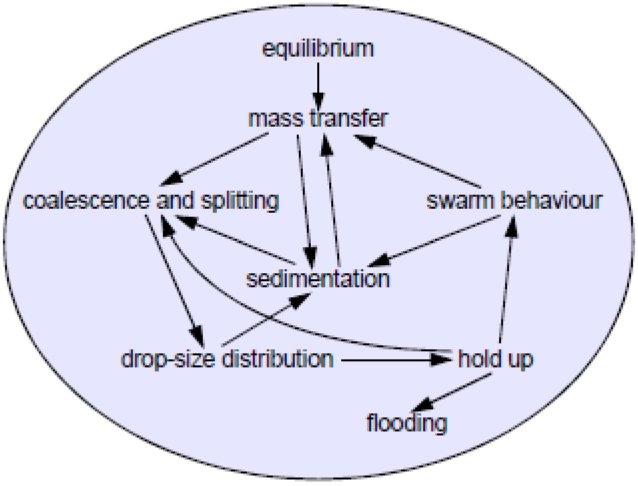


Fig. 2-16: Some of the interactions taking place in LLE columns. (Pfennig, 2023)

According to (Green and Perry, 2008), successful approaches to designing an extraction process begin with an appreciation of the fundamentals of phase equilibrium, mass-transfer principles, and fluid dynamics behaviour. However, the current standard of knowledge requires the designers to perform preliminary tests, to identify for example, which solvent is the more suitable for the specific application, understand the interactions in a precise way and to identify the principles for scaling up.

Usually, the way to approach the preliminary tests consist in building mini-plant or pilot plant experiments. Based on the results of these experiments, models are developed to predict the performance of the pilot plant, and consequently, models to predict the full-scale equipment which are then conducted to scale-up methods.

In many cases, the mass-transfer and fluid dynamic resistances change with increasing the scale of operation. therefore, accurately scaling-up the data is also needed. The required know-how often comes from experience operating commercial equipment of various sizes, or from running pilot-scale equipment of sufficient size to develop and validate the correlations for scaling-up. (Green and Perry, 2008)

All the experience required, the equipment needed to gain the experience and the liquids used in the experimentation, come with an associated high cost as well as considerable amounts of time.

Currently, there exists a heightened level of interest in exploring the path that is founded on the behaviour of individual droplets, fundamental in counter-current LLE columns. As shown in section 2.3, the phenomena that appeared in all types of equipment, is the mass-transfer with single drops as main facilitator. The basic phenomena typically studied during experiments with single drops are the breakage mechanisms, drop velocities, and most importantly, the mass-transfer rates. (Garthe, 2006). Moreover, according to (Pfennig, 2022), for reactive extraction it is crucial to understand the individual drop behaviour since it is the only way to describe the reaction kinetics properly.

Experiments with single drops are performed in laboratory scale columns, which typically have reduced dimensions, as is the case of the SDC used in this thesis, or several other devices used by different researchers as is the case of (Garthe, 2006), which used columns with diameter of 80 mm and height of 1 m. Therefore, the volumes of liquids required are very low in comparison with pilot plant experiments. Additionally, this experimental trend improves the time required, which leads to an enormous reduction in associated costs for the final product.

Modelling approaches for the description of an extraction column are available, some of those are based on equilibrium stages, as it is the HTU-NTU method (height of transfer unit – number of transfer units), or modelling based on drop behaviour with a mean drop diameter. These stage-based models and calculations using the HTU-NTU concept can only describe the behaviour of extraction columns to a certain extent. This is because they do not consider the complexity of interactions between different phenomena occurring within the columns as shown in Fig. 2-16. (Pfennig, 2023)

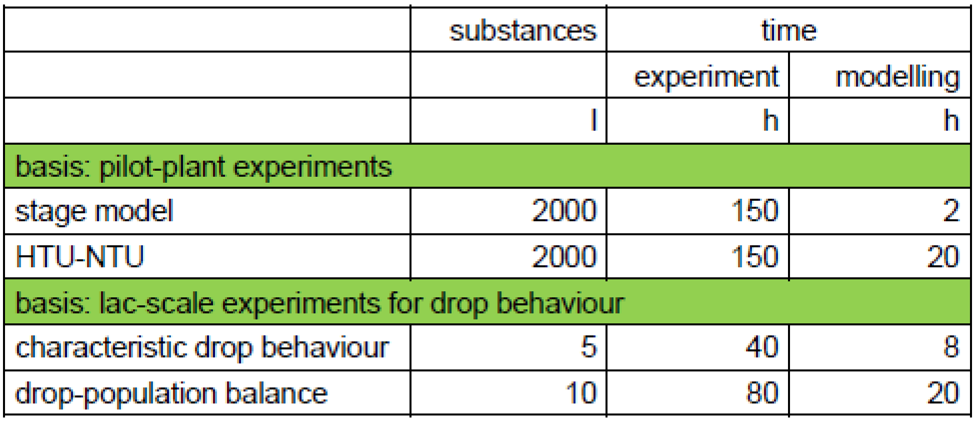
For accurate design simulations of extraction columns, several different phenomena need to be considered, such as the changes in drop-size distribution across the length of the vessel which is caused by drop-coalescence, breakage as well as convection. Sedimentation and its effect on mass transfer and vice versa, also must be considered. In terms of fluid dynamics, the operational limits must be determined, as is the case for flooding point, axial dispersion, and hold-up. (Garthe, 2006)

2.5 ReDrop and the Single-Drop Cell

As described in previous section 2.4, to properly describe and therefore model an extraction column, all the complex interplay between the different phenomena taking place inside them must be considered. One way to do so, is using ReDrop (Representative Drops), which consists on assembling a drop-population model that considers all acting phenomena over the drops and follow them during their entire lifetime in the extraction column. The ReDrop algorithm leads to a transient simulation of the behaviour of the column until steady state is reached. It is a powerful tool for modelling extraction columns, as it requires only a few minutes of simulation to reach steady state. (De Foy and Pfennig, 2023)

Small impurities in LLE may influence the drop behaviour in terms of sedimentation, mass transfer and coalescence significantly (Schulz *et al.*, 2021b), the models describing these phenomena are set with specific parameters that are fitted to the experimental data from single-drop experiments with the original liquid-liquid system. (Pfennig, 2023).

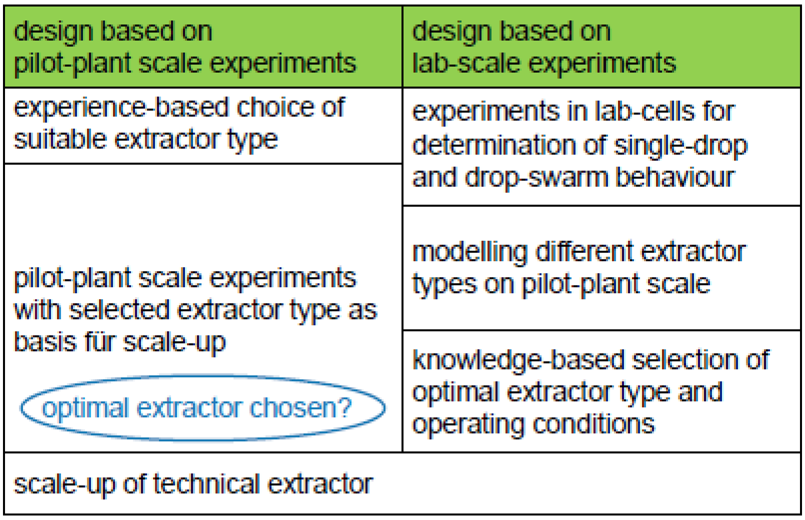
To use the program, the model parameters must be known for the specific material system under study. Laboratory-scale experiments are therefore performed to evaluate the parameters. These experiments are standardized and require only a few liters of both phases. This is a considerable advantage over the conventional design method based on pilot-plant experiments, which require a large amount of solution and a long experimentation time as show in Fig. 2-17.



	substances	time	
		experiment	modelling
	l	h	h
basis: pilot-plant experiments			
stage model	2000	150	2
HTU-NTU	2000	150	20
basis: lac-scale experiments for drop behaviour			
characteristic drop behaviour	5	40	8
drop-population balance	10	80	20

Fig. 2-17: Potential time, material, and cost savings of Drop-based approach (Pfennig, 2023)

The ReDrop program has been developed for more than two decades at AVT-Thermal Process Engineering of RWTH Aachen University and later continued at CEET, TU Graz, and PEPs at the university of Liège (Henschke, 2004). As shown in Fig. 2-18, the approach used in ReDrop brings several benefits in terms of knowledge, because the experience-based design and optimizations is replaced by knowledge-based design and optimization.



design based on pilot-plant scale experiments	design based on lab-scale experiments
experience-based choice of suitable extractor type	experiments in lab-cells for determination of single-drop and drop-swarm behaviour
pilot-plant scale experiments with selected extractor type as basis für scale-up optimal extractor chosen?	modelling different extractor types on pilot-plant scale
	knowledge-based selection of optimal extractor type and operating conditions
scale-up of technical extractor	

Fig. 2-18: Comparison of design methods using pilot-plant experiments and lab-scale individual-drop experiments (Pfennig, 2023).

ReDrop also has the advantage of allowing any type of column to be designed based solely on generic single-drop experiments at the laboratory scale. Different configurations can therefore be studied numerically in order to choose the optimal column type for the desired application. (De Foy and Pfennig, 2023)

This thesis takes place because of the need of drop-based experiments required to feed the program, and therefore, being able to model LLE columns, including those with reactions occurring in the surface of the drops. A Single-drop cell placed in the university of Liège must be validated to continue with the experimentation regarding reactive extraction. Which will be used to model columns for the purpose of extracting valuable metals from acid solutions coming from the leaching of electronic waste.

Based on the need of validating the single-drop cell, the study of drop-base mass transfer and some of the related phenomena are required, to understand the results after the experimentation. The standard systems recommended for this scenario and use in this thesis are, water, acetone, and n-butyl acetate.

2.6 Drop-base mass transfer kinetics

In this section a short review of the mass transfer phenomena of single drops will be presented. All mathematical models are extensively studied in the reference literature, and will not be repeated in this document.

2.6.1 Sedimentation

As mentioned in section 2.4, and across section 2.3, all extraction columns perform through the drops that are generated inside. Because these drops never have the same diameter, a distribution of drop diameters is always assumed. In order to understand the mass transfer in single droplets, it is required first to understand the hydrodynamic behaviour at various drop diameters. It has been demonstrated (Henschke and Pfennig, 1999) that sedimentation velocity and mass transfer linked to each other.

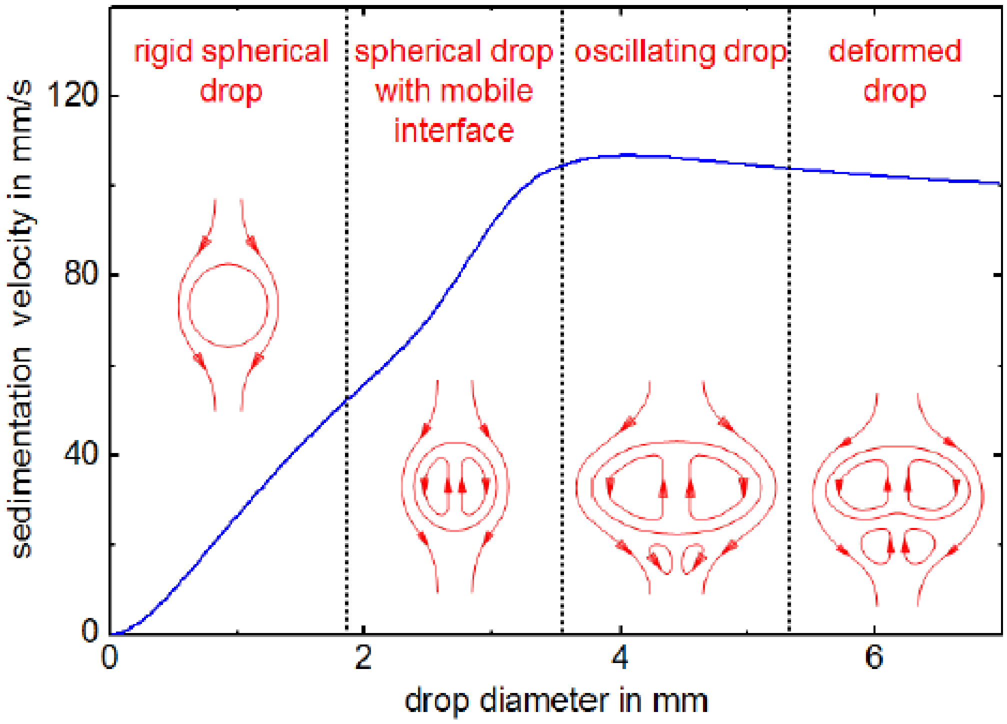


Fig. 2-19: Sedimentation velocity as function of drop diameter (Henschke, 2004)**.**

Fig. 2-19 shows the four different zones described by the drop sedimentation theory, which is based on the terminal velocity a drop reaches in an infinitely extended continuum. The first section is rigid spherical drops, in which the small droplets behave like rigid spheres and present no internal circulation. As the drop diameter increases, shear forces at the interface increase and induce internal circulation. This section is called spherical droplets with mobile interface. The inner circulation reduces drag resistance, generating an increase in sedimentation velocity. As the diameter of the drops increases, shear forces cause oscillations, and drops start changing shape, which then increases drag resistance and a reduction in sedimentation velocity. As the drop falls through the surrounding medium, the shear forces acting upon it gradually increase. This causes the drop to lose its once perfectly spherical shape, resulting in an increase in drag. Ultimately, this drag causes the drop's sedimentation velocity to decrease.

2.6.2 Mass Transfer

Mass transfer description and quantification is still a field in which enough space for investigation is still available. In the case of LLE, it is required to analyse the phenomena occurring in between two liquid phases. Thus, the double resistance theory depicted in Fig. 2-20 (Treybal, 1980), was used as a reference.

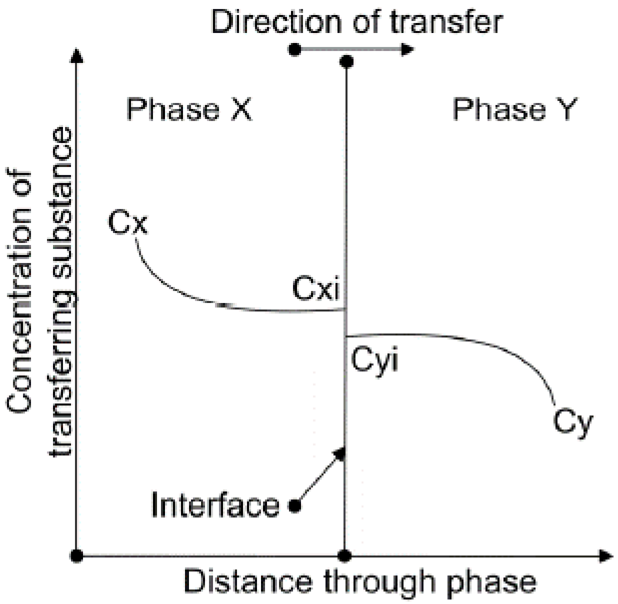


Fig. 2-20: Concentration profiles at the interphase during mass transfer, based on the double resistance theory.

The mass transfer is characterized by diffusion processes as well as convective mechanisms in the interior and the external adjacent regions of the drops. The transfer rates are controlled by the mass transfer resistance in both phases, while resistance in the interface is assumed to be zero. According to Fick's law, the mass transfer flux across an interface can be describe with the expressions

$$J = k_x \left(C_x - C_{xi}\right) \quad , \tag{2-1}$$

$$J = k_y \left(C_{yi} - C_y\right) \quad . \tag{2-2}$$

Where J is the flux of transfer component through the interface and k is the individual mass transfer coefficient. cx, cxi, cy, cyi are represented in Fig. 2-20, and are the different concentrations across the liquids and their interface. It is virtually impossible to know the concentration in the interface, therefore, Fick's law needs to be rewritten in terms of equilibrium concentration,

$$J = K_{\mathrm{c}} \left(C_x - C_x^{*}\right) \quad . \tag{2-3}$$

$$J = K_c\left(C_y^* - C_y\right) \quad . \qquad (2\text{-}4)$$

Kc is the overall mass transfer coefficient and c* is the equilibrium concentration of transfer component. Kc has a direct relation with the individual mass transfer coefficients and is represented by the following expressions.

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{1}{mk_d} \quad . \qquad (2\text{-}5)$$

$$\frac{1}{K_d} = \frac{m}{k_c} + \frac{1}{k_d} \quad . \qquad (2\text{-}6)$$

Where m is the slope of the red lines represented in Fig. 2-21, which is an approximation based on interpolation of the equilibrium curve and the driving force. Consequently, Kc is the sum of the resistance of both phases.

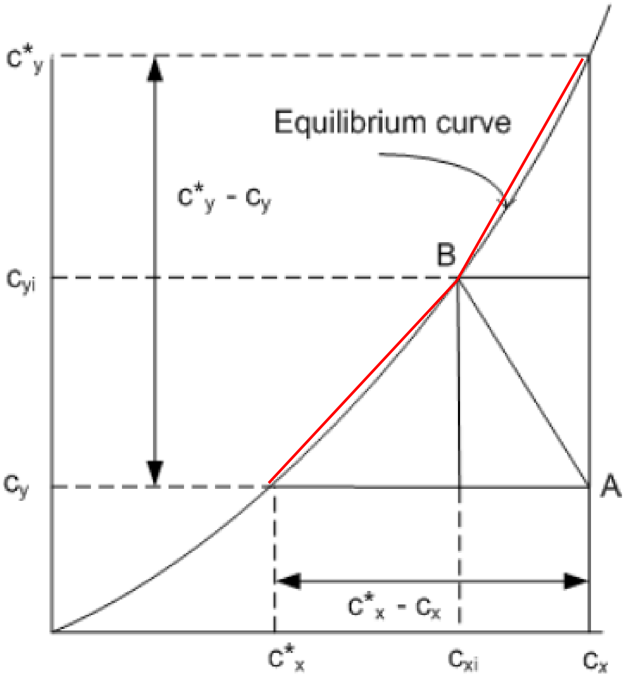


Fig. 2-21: Concentration driving force at drop interface. Modified from (Wongpat, 2010), based on (Treybal, 1980)

Until now, we have discussed mass transfer calculations based on the double resistance theory. However, Newman introduced the concept of single drops in 1931, which we need to explore further.

2.6.3Mass-transfer coefficient in single drops

Newman (1931) solved the continuity equation for a spherical drop without internal circulation and no resistance in the continuous phase,

$$\frac{y(r,t)-y^*}{y_0-y^*}=-\frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\frac{\sin(n\pi r)}{R}\exp\left(-(n\pi)^2 Fo_d\right) \quad . \tag{2-7}$$

and integrated it over the radius of the drop and obtained the time dependent average concentration profile (Kopriwa *et al.*, 2012)

$$\frac{y(t)-y^*}{y_0-y^*}=-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-(n\pi)^2 Fo_d\right) \quad . \tag{2-8}$$

With

$$\mathrm{Fo_d}=\frac{D_\mathrm{d}t}{R^2} \quad . \tag{2-9}$$

Where Dd is the molecular diffusion coefficient of the transfer component in the dispersed phase, t the residence time and d the drop diameter. The variables y0 and y* represent the initial concentration and equilibrium concentration inside the drop respectively.

The variable y(r,t) represents the concentration inside the drop as function of the radial position and time, that is why a second equation integrated over the whole volume of the drop is also presented. In that second equation the concentration is only dependent on time, which is exactly what is possible to find in the single-drop cell experiments mentioned in section 2.5. The left side of the equations XX is called “dimensionless concentration”, which has a value of 1 when no mass transfer has occurred, and 0 when equilibriums has been reached.

The equations XX present a particular challenge, its convergence for short times and evaluation time. Thus, in order to compute them faster an approximate solution was presented by Mersmann (1986).

$$\frac{y(t)-y^*}{y_0-y^*}=1-\frac{6}{\sqrt{\pi}}\sqrt{Fo_d}+2.996Fo_d \quad for\ Fo_d<0.1584 \quad . \tag{2-10}$$

$$\frac{y(t)-y^*}{y_0-y^*}=\frac{6}{\pi^2}\exp\left(-\pi^2 Fo_d\right) \quad for\ Fo_d \geq 0.1584 \quad . \qquad (2\text{-}11)$$

After this, Kronig and Brink (Kronig and Brink, 1951) proposed an analytical extension of Newmann's equation to drops with internal circulation. It was assumed that the effects of circulation were comparable to those of diffusion and that the current line in the drop area at high velocity was also similar to the laminar circulation (Adinata, 2011). With it, they derived a factor to use an effective diffusion coefficient, which enhanced the original diffusion coefficient 2.7 times. Handlos and Baron (1957) proposed a model based on a special type of turbulent internal circulation, which was in the form of random radial motions, presumably originated from drop vibrations, superimposed upon internal streamlines (toroidal internal circulation). This led to a mass transfer coefficient of:

$$k_\mathrm{d}=\frac{0.00375 v_\infty}{\left(1+\frac{\eta_\mathrm{d}}{\eta_\mathrm{c}}\right)} \quad . \qquad (2\text{-}12)$$

This model has been criticized by many authors (Henschke and Pfennig, 1999; Kopriwa et al., 2012), due to the elimination of the direct relationship of the mass-transfer coefficient to the molecular diffusion. However, some research groups have pointed out that the application of this model results in a better correspondence with experimental data than other models (Garthe, 2006).

(Henschke and Pfennig, 1999) brought a different approach, in which an enhancement factor was proposed, but based on experimental data, therefore fitted, and refined for every system. The parameter called Instability constant (C_{IP}) accounts for interfacial phenomena, also called Marangoni effects, produced by interfacial-tension gradients along the drop surface. The larger the diameter of the drop, the greater the interface area, the greater interfacial-tension gradients. They proved that these phenomena could increase mass transfer coefficients up to three times, as shown in Fig. 2-22.

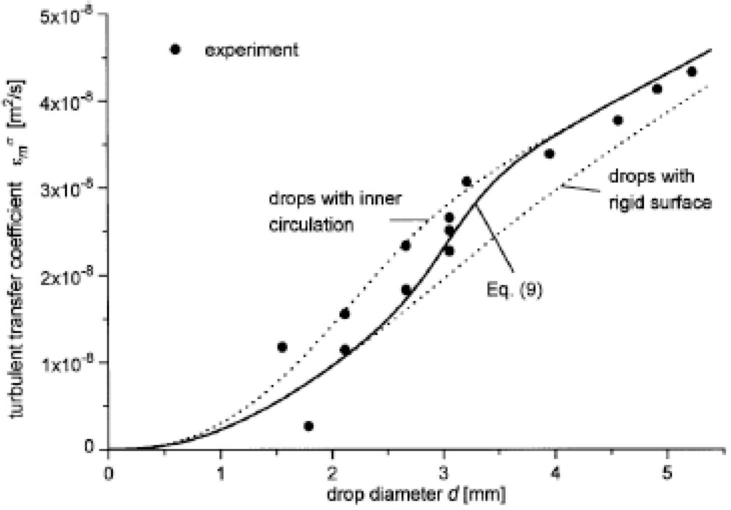


Fig. 2-22: Dependence of the turbulent-transfer coefficient on drop diameter. (Henschke and Pfennig, 1999)

$$D_{\mathrm{eff}} = D_{\mathrm{d}} \frac{v_\infty d}{C_{\mathrm{IP}}\left(1+\frac{\eta_{\mathrm{d}}}{\eta_{\mathrm{c}}}\right)} \quad . \tag{2-13}$$

Or as originally establish by them:

$$\varepsilon_m^\sigma = \frac{v_\infty d}{C_{\mathrm{IP}}\left(1+\frac{\eta_{\mathrm{d}}}{\eta_{\mathrm{c}}}\right)} \quad . \tag{2-14}$$

2.6.4 Sedimentation and mass-transfer interaction

When comparing the sedimentation velocity of drops with different diameter and with and without mass transfer, it is observed that those drops having mass transfer, experience a considerable reduction in sedimentation velocity as shown in Fig. 2-23.

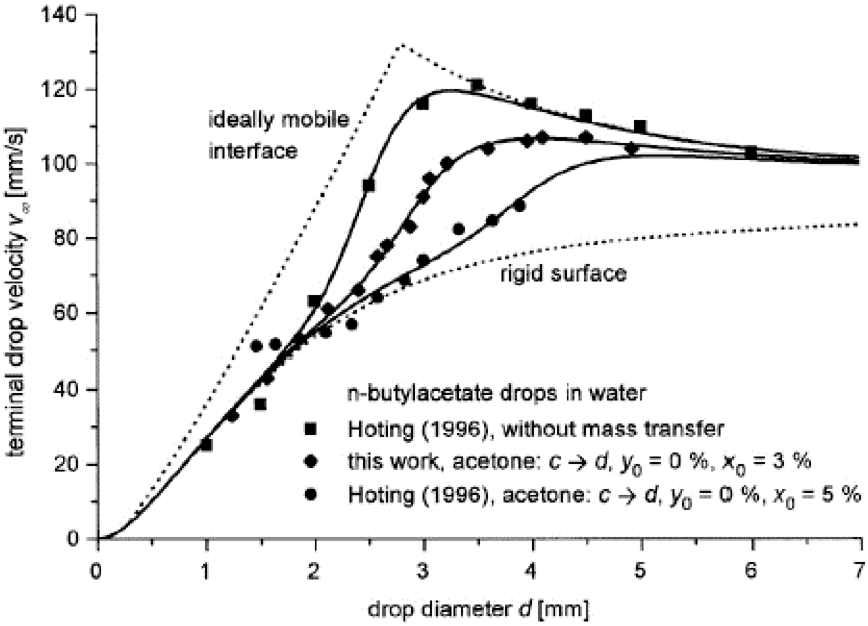


Fig. 2-23: Influence of mass transfer on the sedimentation of water (c), n-butyl acetate (d), acetone (c to d) (Henschke and Pfennig, 1999).

For Fig. 2-23. (Henschke and Pfennig, 1999) used various models to draw the lines and smoothed the transitions from one model to the other. Also, the measurement with no mass transfer corresponded to large drops almost at the limiting case of an ideally mobile interface with complete laminar internal circulation. It is observed how the increase of mass transfer reduces the sedimentation velocity down to the limiting case or rigid interface with no internal circulation, and have the greatest effect in the diameter range of 2.5 mm to 4 mm.

As was analysed by these models, the behaviour can have two causes, one is that the interface indeed becomes rigid due to the mass transfer; second, the mass-transfer-induced turbulence inside the drop leads to a stochastic and irregular movement of the interface, as a result of which the drop slows.

3 Objectives of the work

3.1 General

Validate the mass transfer measuring cell of the Chemical Engineering Laboratory of the University of Liège, using the recommended standard system from the European Federation of Chemical Engineering consisting of water, acetone, and n-butyl acetate.

3.2 Specific Objectives

To develop a user manual for the single-drop cell equipment set-up (mass transfer measuring cell) to standardize the operation, maintenance, storage, and troubleshooting, therefore, facilitate the future work with it for the reactive extraction experiments.

4 Materials and Methods

In this work, liquid-liquid mass-transfer experiments with a standard test system were performed, the test system consisted of water, acetone, and n-butyl acetate, in which the acetone is transferred from the continuous (aqueous) phase to the dispersed (organic) phase. The continuous phase consisted of a solution with a concentration of 3 to 5 % in mass of acetone in water previously saturated with n-butyl acetate. The dispersed phase consisted of n-butyl acetate saturated with water with no acetone.

The experiments were performed in a mass-transfer measuring cell which will be described in detail further in this chapter. The organic phase obtained after the mass-transfer experiments was then analysed via UV-Visible spectrophotometry after the construction of a calibration curve.

All measurements were mass-based, to avoid the effect of temperature in the density of the liquids.

4.1 Material System

Since the main objective of this work was to validate the single-drop cell equipment for further experimentation, the standard system recommended by the European Federation of Chemical Engineering was used: water, acetone, n-butyl acetate. Deionized water (DI) was used as the continuous phase, acetone (analytical grade) and n-butyl acetate (Analytical grade) were solute and dispersed phase, respectively. Dispersed and continuous phases were saturated with each other at room temperature to avoid the effect of diffusion in between them and therefore, the effect in the mass transfer of acetone. The direction of mass transfer was from continuous to dispersed phase.

4.1.1 Continuous phase

As mentioned in section 4, the continuous phase contains DI water and acetone, the water was previously saturated with n-butyl acetate to avoid the interference on the mass transfer of the acetone. The saturation procedure consisted of contacting for 12h at least DI water and n-butyl acetate. The amount of n-butyl acetate was determined after the solubility in water at 20°C, temperature at which the experiment took place.

Its solubility in water at 20°C is 7 g/L (National Center for Biotechnology Information, 2023).

Before preparation of the solution, the excess of n-butyl acetate was separated in a glass decanter, then transferred to the dispersed phase bottle. With this, it was verified no excess disperse phase would be present in the continuous phase.

3 L of solution were prepared for the experiments, this due to the capacity of the single-drop cell, first, a 3 L beaker was weighted, then according to the percentage desired it was calculated the amount of acetone to add, for 3% it was 90 g, assuming a water density of 1 g/L. The previously saturated water was then added to the beaker until 2900 g + beaker mass was obtained, and then the acetone was added and stirred for 2 minutes with a magnetic stirrer.

The solution was introduced into the single-drop cell immediately after the conclusion of the stirring period, with the aim of minimizing potential losses from evaporation and preventing any spillage over the equipment.

4.1.2 Dispersed phase

The process for preparing the disperse phase was similar to that for the continuous phase, nevertheless, the amount of DI water added to the organic phase was not determined so precisely, but it was added until a layer of water was formed in the bottom of the bottle, then agitated and lastly stored for 12 hours.

After the settling time of 12 hours a separation process took place in the same way described for the continuous phase, a glass decanter was used, the excess water was added to the continuous phase bottle, minimizing wasting of chemicals.

4.2 Experimental Set-Up

This section describes all the equipment used to perform the experiments of mass transfer, as well as the general methodology followed to perform an experiment, moreover, a manual detailing each part of the system, operation, maintenance, and troubleshooting was created, and is one of the main annexes of this thesis. Therefore, for more details please refer to it.

4.2.1 Single-Drop Cell (SDC)

The single-drop cell is an equipment that allows the determination of mass transfer rates as function of drop diameter, solute concentration, and contact time of the drop with the continuous phase (Henschke and Pfennig, 1999) which was first developed for this purpose by Schröter et al. in 1998.

The SDC is built only with glass, PTFE, and stainless steel, which brings excellent properties against corrosion, and does not interfere with any reaction due to degradation of the materials. The main characteristic of the SDC body is its conical shape that allows the drop to levitate due to the counter current flow of continuous phase, and in which sieve trays can be placed to determine the effect on the mass transfer.

The working principle of the SDC is the difference in density of the continuous and dispersed phase, as well as their solubility/miscibility between each other, which must create a two-phase system. As described before, the dispersed phase is an organic solvent which is lighter than water (the main component of the continuous phase) and therefore drops of dispersed phase are generated in the bottom of the cell by a nozzle with the aid of a computer-controlled dosing system, and due to the difference in density it rises at a certain velocity, then, thanks to the action of a pump, the continuous phase counter current flow matches the velocity of the generated drop stabilizing it in the conical section of the SDC as shown in Fig. 4-1.

The drop is kept in that position during the desired time, then the pump is turned off and the drop ascends to the sampling cone, through which the drop is withdrawn with the dosing system mentioned in section 4.2.1. This procedure must be repeated until the desired amount of organic sample has been recovered to be analysed. That is why the whole procedure is controlled by a custom-built program that controls the different components.

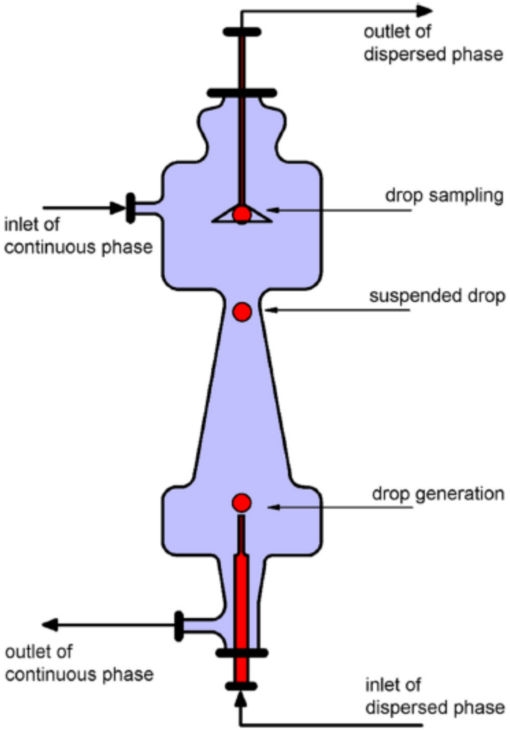


Fig. 4-1: Single-drop cell diagram (Pfennig, 2023)

The SDC was built as a double walled equipment to allow temperature control with a heat transfer fluid, that in this case is DI Water, it is also equipped with a thermistor to measure the temperature in the SDC with an accuracy of 0.1 °C.

4.2.2 Auxiliar equipment

The rest of the system is composed of a settling cell that serves as reservoir for the continuous phase, a gear pump, a rotameter, an overflow vessel, a heat exchanger, a dosing system composed of an automated Hamilton precision syringe drive (PSD) equipped with two syringes and a set of nozzles of different diameters, a heating system, a cooling system and finally a computerized control system. All these components are shortly described in this section, for more detail, please refer to the SDC manual.

4.2.2.1 Settling cell, rotameter, overflow vessel, and heat exchanger

The settling cell, rotameter, overflow vessel, and heat exchanger are components also constructed in glass and PTFE mainly and serve as safety and conditioning components for the continuous phase. The total available volume of these components plus the SDC (and piping) is 3L. The settling cell is a double walled vessel in which most of the volume of continuous phase is kept, the heating system is connected to this heat exchange circuit together with the double wall of the SDC. As it names describes, settling experiments can be performed in this cell, nonetheless, not in parallel with the SDC in operation.

The rotameter measures the volumetric flow of continuous phase thanks to its graduation and floating body made of PTFE. It directly receives the flow from the pump, is then connected to the heat exchanger which is a glass shell and tube (coil type) heat exchanger mainly for cooling purposes. These two components are connected at the top with the overflow vessel, a safety component that allows to retire air trapped in the system, as well as receive overflow due to an excess in initial volume or overpressure.

4.2.2.2 Gear pump, heating, and cooling systems

The pump used in SDC is a Verder Gear V0108, it has a maximum capacity of 70 L/h at 5 bars of pressure. It can handle noncorrosive lubricating or non-lubricating liquids. The gear pump is a rotary displacement pump in which two gears engage with each other, the transfer of fluid is caused by counter rotation of two gears in a gear chamber. A specific feature of the pump that is relevant is the magnetic coupling, which is hermetically sealed. There is not a rotating shaft end, which can cause leakage by wear of lip seal rings or shaft. The pump head is statically sealed with O-rings. This configuration brings several benefits, specially related to contact in between liquids and the environment, it also adds safety to the experiments because the magnetic coupling has a limit of torque from which there is no more torque available and the coupling stops working.

The main heating system is a Lauda Thermostat type NBD317 with two controlling boxes, one for the pump and one for the heating system. The cooling system used is a VWR signature, circulating bath 1157P model, which has a 13L capacity and has a range from 200 °C to -30 °C. The use of the heating system was mainly for cleaning purposes and to keep the temperature constant. The cooling system was used more often, due to the added heat by the recirculating pump. It helped adjusting and maintaining the system’s temperature in between 20.1 to 20.8 °C

4.2.2.3 Hamilton precision syringe drive (PSD)

The dosing system that creates and withdraws the drops is a custom-built set of Hamilton PSDs as shown in Fig. 4-2, made of two PSDs, one per syringe and per action (create and withdraw) to the dispersed phase. For this thesis, it was used an airtight 5 mL syringe per PSD. This system allowed the accurate control and repeatability of the dosing as well as withdrawal of the dispersed phase, a crucial requirement for mass transfer experiments.

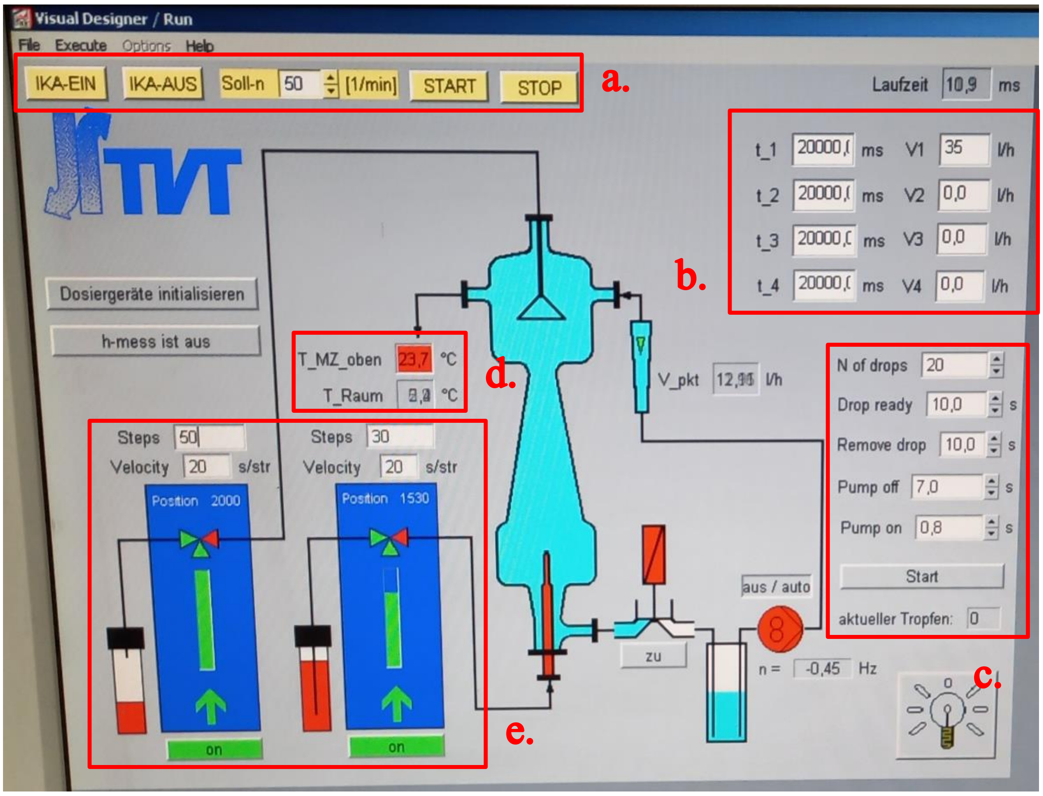
As mentioned above, a set of nozzles is present, the nozzles have different opening tip diameters, which as a rule of thumb, correspond to half of the desire diameter of the drops generated. Indicating that for a diameter of 3.22 mm or 3.06 mm a nozzle of 1.5 mm is required. The nozzle can be installed before filling the SDC with continuous phase or after, but it requires to be prefilled with dispersed phase to avoid any contamination of the dispersed phase due to continuous phase intrusions into the nozzle.

Fig. 4-2: Hamilton precision syringe drive. (Hamilton Company, 2013)

4.2.2.4 Control system interface

As mentioned before, the control system is a custom-built program and interface, created in Visual Designer 4.0 from Intelligent Instrumentation Company. The following descriptions are based on Fig. 4-3. **a.** is the menu developed for the attachable accessories as it could be a shaft for agitation.

The next section, **b.** is used to set different speeds of counter current flow at different times, the time is in milliseconds and the speed is in L/h of the program. It is very useful when stabilizing drops in certain region of the cone or when it is necessary to change the position of the drop in relation to a sieve tray previously installed. In this thesis it was mainly used for stabilization of the drop in the upper part of the cone. If there is only one speed and time defined, the program will use that value for the duration of the experiment and no changes in speed will take place.



Soll-n 50 [1/min]

Laufzeit 10,9 ms

t_1 20000,(ms V1 35 l/h

t_2 20000,(ms V2 0,0 l/h

t_3 20000,(ms V3 0,0 l/h

t_4 20000,(ms V4 0,0 l/h

T_MZ_oben 23,7 °C

T_Raum 2,2 °C

V_pkt 12,95 l/h

N of drops 20

Drop ready 10,0 s

Remove drop 10,0 s

Pump off 7,0 s

Pump on 0,8 s

aktueller Tropfen: 0

n = -0,45 Hz

Steps 50

Velocity 20 s/str

Position 2000

Steps 30

Velocity 20 s/str

Position 1530

Fig. 4-3: Control system interface.

Section c. is where the parameters of repetition are placed, as it is the number of drops generated in continuous, the moment in which the pump is started after the drop is generated, the moment of turning off the pump, the suction time (which must match with the desired contact time) and the time in which the next drop can be started. It is recommended to let at least half a second to generate the next drop. In section c. is also possible to know how many drops have been generated.

The following section (d.) is where it’s possible to monitor the temperature values inside the SDC, it turns red when the temperature is above 20.9 °C but can be modified for the desired temperature range. It can also be monitored the room temperature.

The last section (e.) is where the dosing system is controlled, as shown in the figure, the left pictogram is connected to the funnel for the withdrawn of drops, and the right one is connected to the nozzle, which generates the drops. In that section is possible to set the steps and the speed at which the syringes will be actuated, in terms of seconds/stroke. The higher the number the slower the stroke. Parameters in all sections but d., can be changed at will during the experimentation, meaning that adjustments can be done to modify the operation if necessary.

It can be seen the pump and a valve that is in red colour, those buttons are mainly created to operate in manual mode the system, which is done for the initializing of an experiment from the filling of the SDC. All this information is detailed in the manual of the entire system.

4.2.3 Performing the experiment

The first step to initiate an experiment is to decide which nozzle diameter will be used, as a rule of thumb it should be half of the drop's desired diameter; the drop diameter is then, the first parameter to be set. As shown in section 2.6, the diameter of the drop changes its behavior, and for mass transfer experiments it is required a spherical drop with mobile interface, which means, diameters in between 1.5 mm and 4 mm are required. The selected diameters were 3.06 mm and 3.22 mm due to the availability of experimental results for the recommended material system with the same diameters. Therefore, a nozzle of 1.5 mm was used for the entire set of experiments.

The second step is to determine the volume of dispersed phase that will be injected trough the nozzle by the syringe and its actuator, according to (Leeheng, 2014) the equations that connects these two parameters are:

$$V_\mathrm{d} = \frac{V_\mathrm{s} S}{2000} \quad . \tag{4-1}$$

Where V_d is the drop volume, V_s is the syringe volume and S is the number of steps required to generate the drop volume. And then, assuming the drop is perfectly spherical, its volume is related to is diameter.

$$V_\mathrm{d} = \frac{\pi D^3}{6} \quad , \tag{4-2}$$

After equating the previous equations and solving for S, it is obtained the direct relation in between the steps and the drop's diameter.

$$S = \frac{1000 \pi D^3}{3 V_\mathrm{s}} \quad . \tag{4-3}$$

After computing the available parameters as diameter and volume of the syringes, six (6) and seven (7) steps were determined to be set to generate drops of 3.06 mm and 3.22 mm respectively.

The speed at which the dispersed phase should be injected was determined by trial and error, it must comply with the following criteria:

a. Drop detachment in one single stroke.

b. No secondary droplets are generated.

c. No dispersed phase remains attached to the tip of the nozzle, or it will be wetted and will continue to be until cleaned with acid.

The geometry of the nozzle also affects the drop generation, so it is required that the tip is completely flat and with no nicks at all. The injection speed is substance specific according to its viscosity and system temperature.

At this point is where temperature control is required at its best, it is necessary to adequate the temperature to the desire value, for this thesis it was in 20.0°C, nevertheless it fluctuated in between 19.8 °C and 20.7 °C in a time span of 10 hours, so changes were not sharp and more gradual and therefore corrected on time.

Once all parameters were set, the programming of the experiment was done, aiming to obtain 3 mL of sample at least. To make sure the sample is representative, the first milliliter was completely discarded, then 3 mL were generated and taken apart as first sample, two more samples of 3 mL were generated per contact time, making it in total at least 9 mL of sample in three different vessels.

For the equilibrium concentration, the sampling cone was filled with dispersed phase dosed trough the nozzle without the action of the pump, so the dispersed phase ascended freely until completion of the cone’s volume. Once it was full, a flow velocity of 20 L/h was set to maintain a constant temperature for the 2 hours required to reach equilibrium. This sample was withdrawn completely as equilibrium.

Three samples of continuous phase were taken for each contact time, the first one at the beginning to know the starting concentration. The second sample once the three samples of dispersed phase were taken and the final one after the equilibrium experiment, this to ensure a stable concentration of solute during the entire experiment.

4.3 Analytical Method

As analytical method to determine the concentration of acetone in both continuous and dispersed phase, UV-VIS Spectrophotometry was chosen, due to its reliability, accuracy, repeatability, and speed at which is carried each measurement. The equipment used was a Genesys 150 from ThermoFisher Scientific, in Scanning mode in between 200 to 350 nm wavelength with intervals of 1 nm and slow speed.

It was required the construction of two calibration curves, one for continuous and one for dispersed phase, a blank with air was established for all measurements, and each measurement was repeated three times. The average of the measurements for each sample was used for the evaluation method.

4.3.1 Calibration curves

The calibration curves were constructed by measuring a set of samples with known concentration, the preparation of this samples consisted in measuring a predetermined mass of acetone and dilute it with DI water for the continuous phase and with n-butyl acetate for the dispersed phase. The best range of detection is below 1.5 delta A (absorbance) and because of it, each one of the samples had to be diluted by a factor of 10.

The calibration curves were obtained as shown in Fig. 4-4. The calculation of sample concentration was done by means of the regressed equation of the interpolation between the curve points. The equations are given as follows:

$$y = -5\times10^{-5}x^{2} + 0.0047x \quad , \tag{4-4}$$

With , R^2 = 0.9998 (organic phase)

$$y = 7\times10^{-5}x^{2} + 0.0032x \quad . \tag{4-5}$$

And R^2 = 1 (aqueous phase)

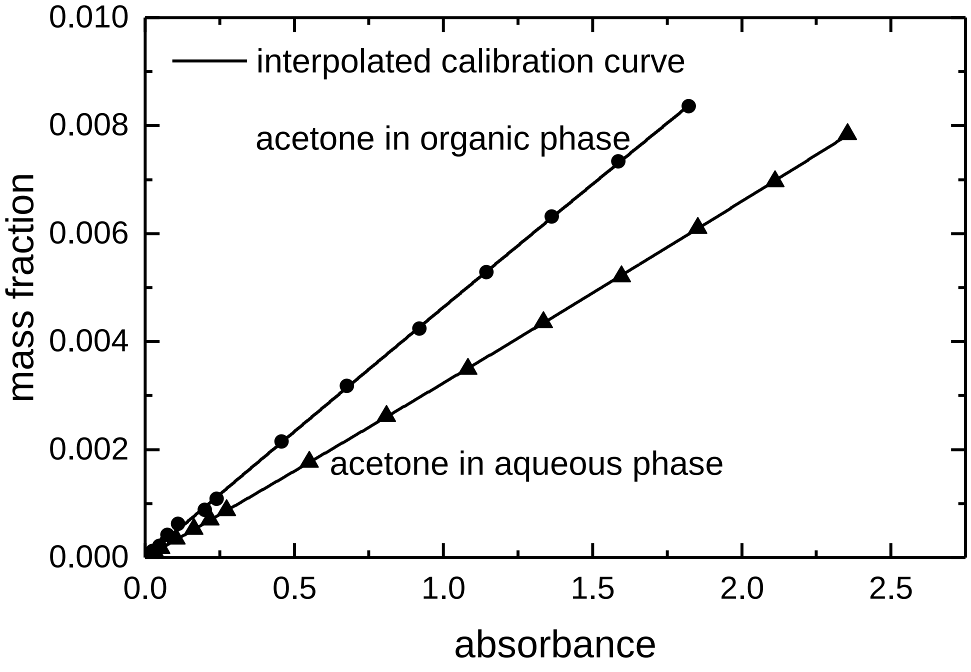


Fig. 4-4: Calibration curves of acetone for continuous and dispersed phase.

4.3.2 Dilution and storage of the samples

The dilution consisted in measuring the weight of 1 mL of sample and dilute it to obtain 10 mL, meaning 9 mL of DI water or n-butyl acetate were added depending on the sample, the total mass was obtained, and the dilution factor was determined by mass. This dilution factor was later used for the calculations of concentration according to the calibration curves. The samples were analysed maximum the next morning after being withdrawn from the SDC.

4.4 Evaluation method

The evaluation method is based on the principle of driving force, in this case is related to the equilibrium concentration that can be reached in the dispersed phase. The equilibrium concentration (y^*) was studied for various periods of time, finding that at 2 hours (7200 s) it was possible to make sure an equilibrium existed.

In general, the driving force of any natural phenomena is based on the difference of the magnitudes of the parameter to be measured at the beginning (or a desired time) of the phenomena and the end or equilibrium state of the phenomena. In this case it is the concentration of the transfer component in the dispersed phase, which is then compared to the equilibrium concentration.

$$y^{+} = \frac{y(t) - y^{*}}{y_0 - y^{*}} \quad . \tag{4-6}$$

As we can see in the previous equation, the dimensionless concentration (y^+) is defined in terms of the initial, equilibrium and a specific time concentration. All these parameters are controlled or measured in the experiment, which then makes possible its evaluation. The general phenomena that will occur is that the closer to the equilibrium, the lower the mass transfer, therefore at short contact times the dimensionless concentration will have a greater difference in between points, in comparison with long contact times, in which from point to point the difference will be smaller, all this, due to the decrease in the driving force.

The dimensionless concentration has been modelled for years, having several models available in the literature, as can be seen in section 2.6.3.

5 Results and discussion

In accordance with the objectives of this thesis and based on the experimental performance it is possible to present two types of results and discussions. The first one will be related to the operability of the SDC, including some challenges observed and therefore their corresponding possible solutions.

The second part will focus on the validation of the SDC and its performance in relation to other experimental data sets gathered through the literature review, as well as to the models that form the basis of the ReDrop program.

5.1 SDC Operability

Based on the necessity of having a completely functional and reliable SDC, for conducting future experiments related to reactive extraction, an operational manual for the SDC has been created and is included in the appendix of this document. Various existing operating procedures were studied and analyzed, similar to the one provided in the corresponding appendixes of (Thonus, 2022).

It should be noted that a majority of the key components of the equipment are custom built, which generates the need for a deeper understanding and therefore, an increase in time dedicated to the mechanical aspects of the system. A steep learning curve was needed, thus a deep analysis of all the sections of the SDC was performed as can be appreciated in section 4.2 and the corresponding section of the appendix.

Based on the experimental understanding of the operation principles of the SDC, the optimal conditions for its performance have been determined. This conditions involve the installation of an updated cooling systems to maintain a consistent temperature, positioning the equipment in a laboratory area less affected by the environmental factors, ensuring the highest levels of safety, and compiling various other recommendations within the manual.

Regarding operability and with the risk of sound obvious, significant attention must be directed towards the sampling cone (also called funnel or collection cone). As depicted in Fig. 5-1, a teflon tip is placed on the inlet of the sampling cone capillary, serving two primary purposes. First: facilitate the coalescence of dispersed phase upon reaching the tip. Second: it act as a level indicator for the right amount of dispersed phase that has to be kept to avoid contamination with continuous phase.

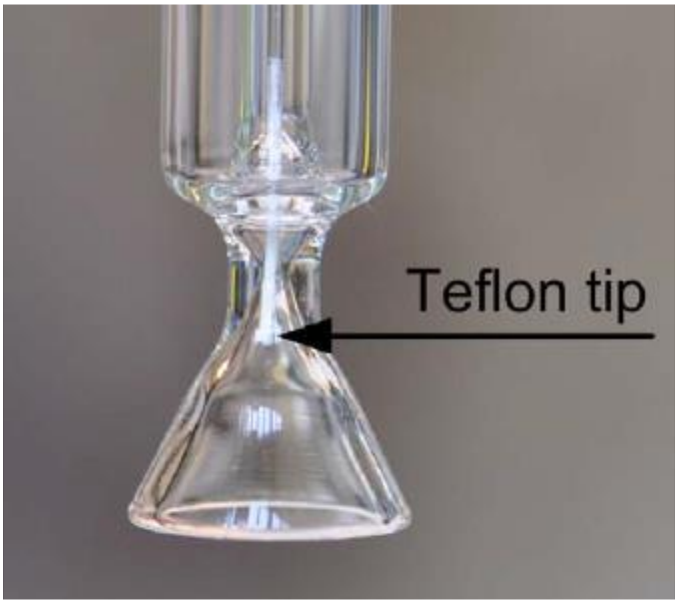


Fig. 5-1: Teflon tip placed in the inlet section of the glass capillary on the sampling cone.

The sampling cone presents two main challenges. The first one is its opening (aproximately 20 mm), which permits drops to ascend, without being collected by it, and therefore a fast corrective action must be taken by the operator to avoid contamination with continuous phase. The reaction time before the withdrawal is in the order of 1.8 s, which often proves insufficient. It is noteworthy that maintaining a certain level of dispersed phase within the sampling cone is crucial, approximately equivalent to the volume of a single drop reaching the midpoint of the teflon tip.

Usually, losing one drop and have a slow response is not a problem, however, losing two consecutive drops and having a slow response could potentially lead to the termination of the experiment. This is where the second challenge emerges: the necessity of maintaining a level of dispersed phase outside the capillary to retain the continuous phase.

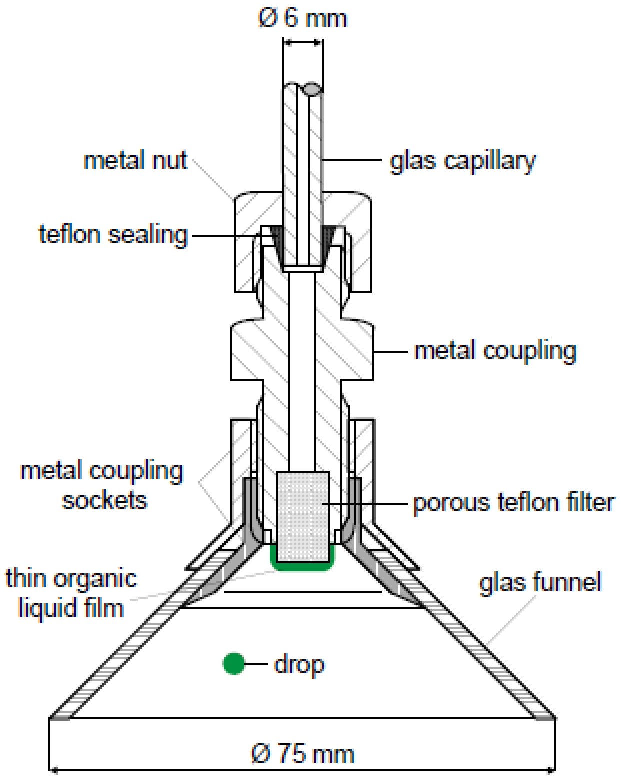


Fig. 5-2: Diagram of the sampling cone (funnel) used by Garthe (2006).

According to Garthe (2006), the material used for the metal couplings is stainless steel, which tends to be wetted by water rather than by an organic compound. In contrast, teflon is preferably wetted by organic substances, rendering it the preferred material for the system used in this document.

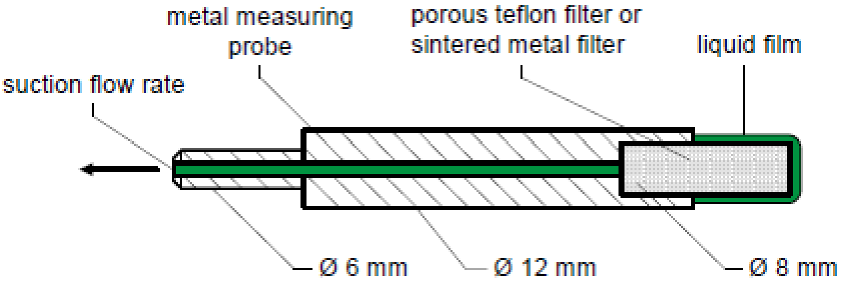


Fig. 5-3: Sampling probe dimensions and materials possibility, used by Garthe (2006).

To address the two challenges encountered with the current sampling cone, it is advisable to employ a configuration similar to the one utilized by Garthe(2006), as illustrated in Fig. 5-2 and Fig. 5-3, However, a modification is recommended in terms of the cone's diameter, reducing it from 75 mm to a maximum of 35 mm to align with the SDC body diameter of 40 mm. With this proposed alteration, the occurrences of drops bypassing the sampling cone will be significantly reduced. Furthermore, this change will virtually eliminate the necessity of maintaining a volume of dispersed phase in contact with the continuous phase

5.2 Validation of the SDC

To validate the SDC, several experiments were performed, as outlined in section 4.2. Two drop diameters were used (3.06 mm and 3.22 mm) and contact times of 5, 8, 10, 12, 14 and 16 seconds were established., The outcomes of these experiments are illustrated in Fig. 5-4. The experimental results have been superimposed onto Henschke's model to demonstrate the mass transfer behaviour, particularly focusing on the rate at which mass transfer diminishes.

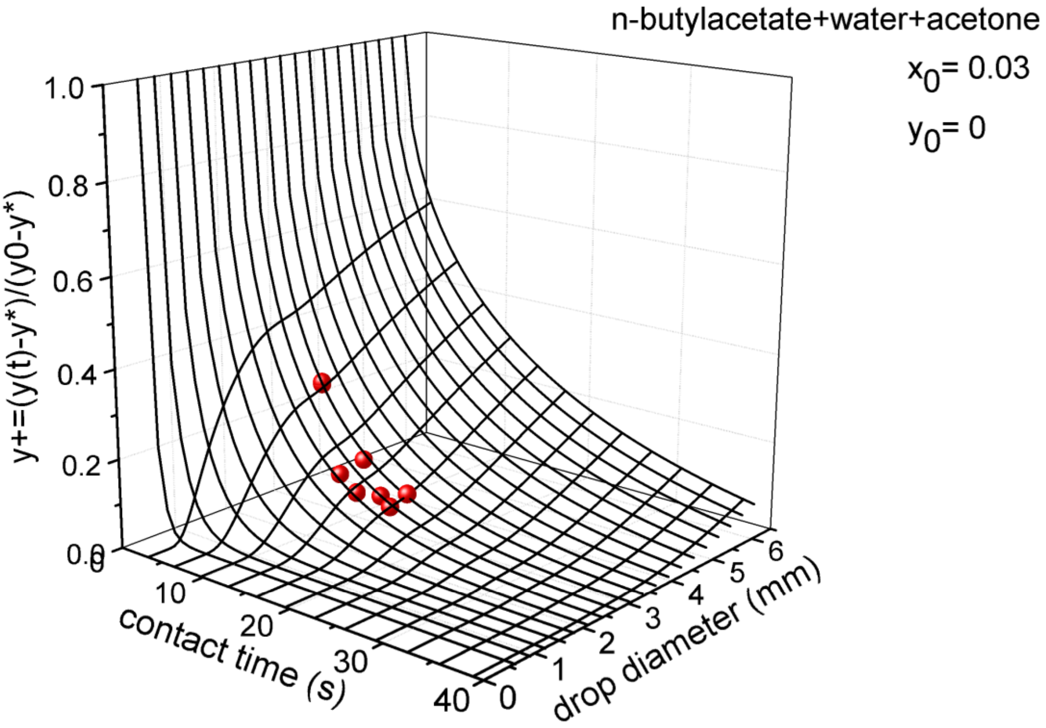


Fig. 5-4: Dimensionless concentration for n-butyl acetate, water, acetone system with two drop diameters and various contact times

Henschke’s model has been used by several authors to model their experimental results, the usual way is to present them as shown in Fig. 5-4 when no comparison is yet established. For the case of Neuendorf, his results are presented as shown in Fig. 5-5.

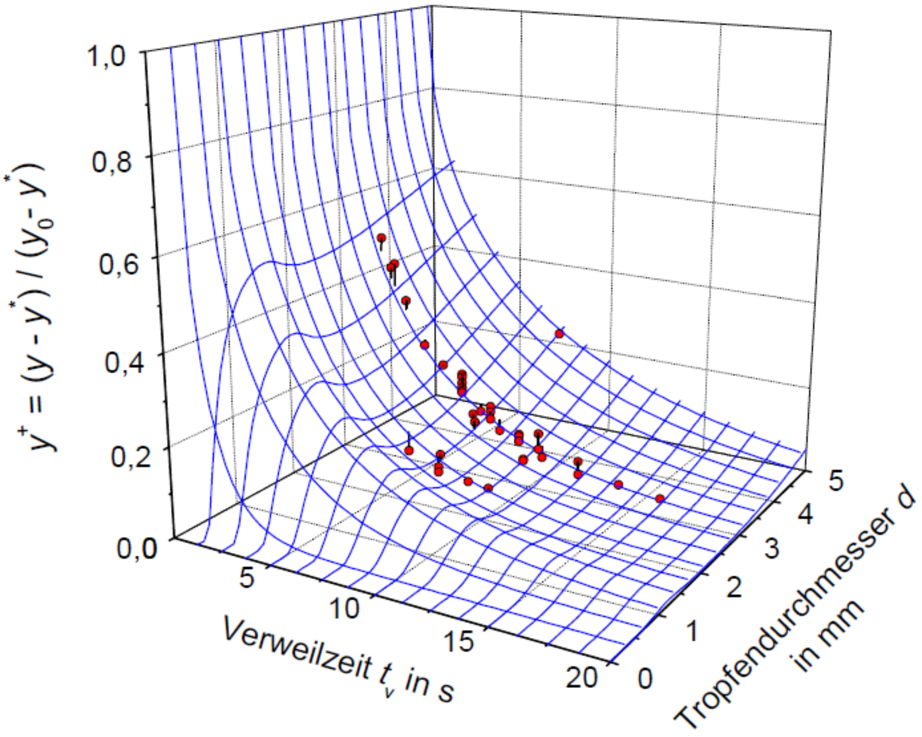


Fig. 5-5: Mass transfer values for the material system n-butyl acetate (d) + water (c) + Acetone (c to d) without internals, x_0: 0.05, y_0: 0 (Neuendorf, 2005)

However, this presentation of data only let us compare the experimental set in between themselves. It means, according to Fig. 5-5 it is possible to say that most of Neuendorf’s experimental points agree with the model for contact times greater than 5 s.

In Fig. 5-6 it is intriguing to observe the significant disparity between the models proposed by Newman and Kronig-Brink in comparison to the experimental results. The rationale behind the continual refinement of these models over the years becomes evident, aimed at reducing errors. Conversely, it's worth noting the remarkable correlation displayed by the Handlos and Baron model with the experimental data, even though it has faced criticism for not accounting for the diffusion coefficient of the substances.

In Neuendorf’s work (2005), a series of experiments were also conducted involving various contact times and drop diameters, as shown in Fig. 5-5. The experiments using drop diameters of 3.22 mm were utilized for comparison purposes, potentially allowing for the validation of the experimental data obtained in this study. As shown in Fig. 5-6, both sets of experimental data align up to a contact time of 16 seconds (excluded), at which point their behavior becomes closer to both Henschke's model and the experimental data.

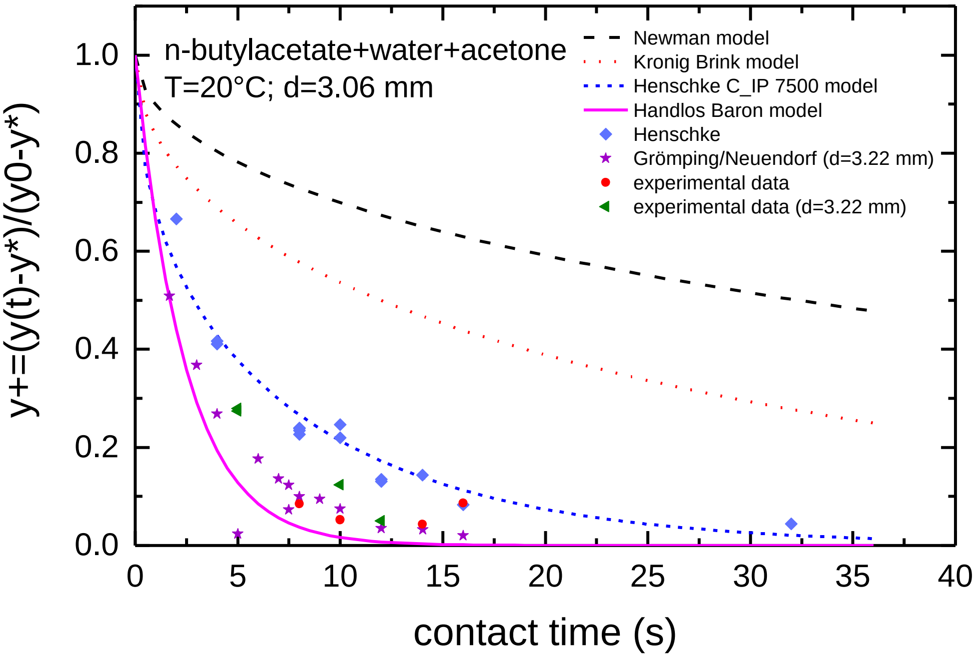


Fig. 5-6: Comparison of experimental points from various authors (Henschke and Pfennig, 1999; Neuendorf, 2005) against various models (Newman, 1931; Kronig and Brink, 1951; Handlos and Baron, 1957; Henschke, 2004)

A substantial discrepancy is observed between the data obtained from both Neuendorf's study and this document, concerning Henschke's model and data. This inconsistency could potentially stem from the fact that the same SDC was employed in Neuendorf's work as in this thesis. As a result, the operational challenges previously outlined (section 5.1) might have been identical between the two studies. The retention of a volume of dispersed phase within the sampling cone could plausibly contribute to the apparent accelerated mass transfer observed in both sets of experiments. Despite the relatively modest exchange area, diffusion-driven mass transfer could occur, misleadingly enhancing the recorded mass transfer rates

Conversely, this deviation could be attributed to the utilization of outdated parameter sets for the Henschke model. Despite its widespread adoption and recognition in literature as a reliable model, as illustrated by (Schulz *et al.*, 2021a), it is conceivable that the model's parameters have evolved over time, potentially leading to disparities in the results

It is observed that the experimental points obtained in this thesis for a drop diameter of 3.22 mm, have a divergence in comparison with the data obtained by Neuendorf for the same drop diameter. This divergence can potentially be explained by the dissimilarity in continuous phase concentrations between the two sets of experiments. Neuendorf's experiments were conducted under a continuous phase concentration of 5% mass of acetone, while the experiments in this thesis maintained an average concentration of 3%. Interestingly, when the percentage difference is calculated in between the data, an average of 46% is obtained. This suggests that Neuendorf's experiments exhibited a mass transfer rate approximately 46% faster than those in this thesis. This phenomenon was anticipated by Henschke and Pfennig (Henschke and Pfennig, 1999) when considering changes in boundary conditions for future column modeling, and later confirmed by (Kalvoda, 2016).

It is noteworthy that the experimental points performed in this document with a drop diameter of 3.06 mm, demonstrate a better correlation with Neuendorf's experimental data. This alignment can be attributed to the findings of (Kalvoda, 2016), wherein she explores changes in boundary conditions through mass transfer experiments in a column with a concentration profile. She examined that drops with smaller diameters exhibit faster mass transfer due to an enhanced mass transfer coefficient. Consequently, drops with a 3.06 mm diameter in a continuous phase with 3% acetone exhibit similar mass transfer rates to drops with a 3.22 mm diameter in a continuous phase with 5% acetone.

The experimental points with a contact time of 16 seconds from Henschke and this document have considerable agreement. However, when examining data collected with shorter contact times, it could be deemed coincidental. Nevertheless, an alternative perspective can shed light on this.

In (Schulz *et al.*, 2021a) the concept of conjugated problem is discussed, indicating a region in the mass transfer process where both continuous and dispersed phase resistance are relevant. This phenomenon often occurs after an extended duration, as illustrated in Fig. 5-7.

To provide further clarity, it is important to consider that the anomalous behavior observed in the points following a contact time of 16 seconds might potentially be associated with the conjugated problem.

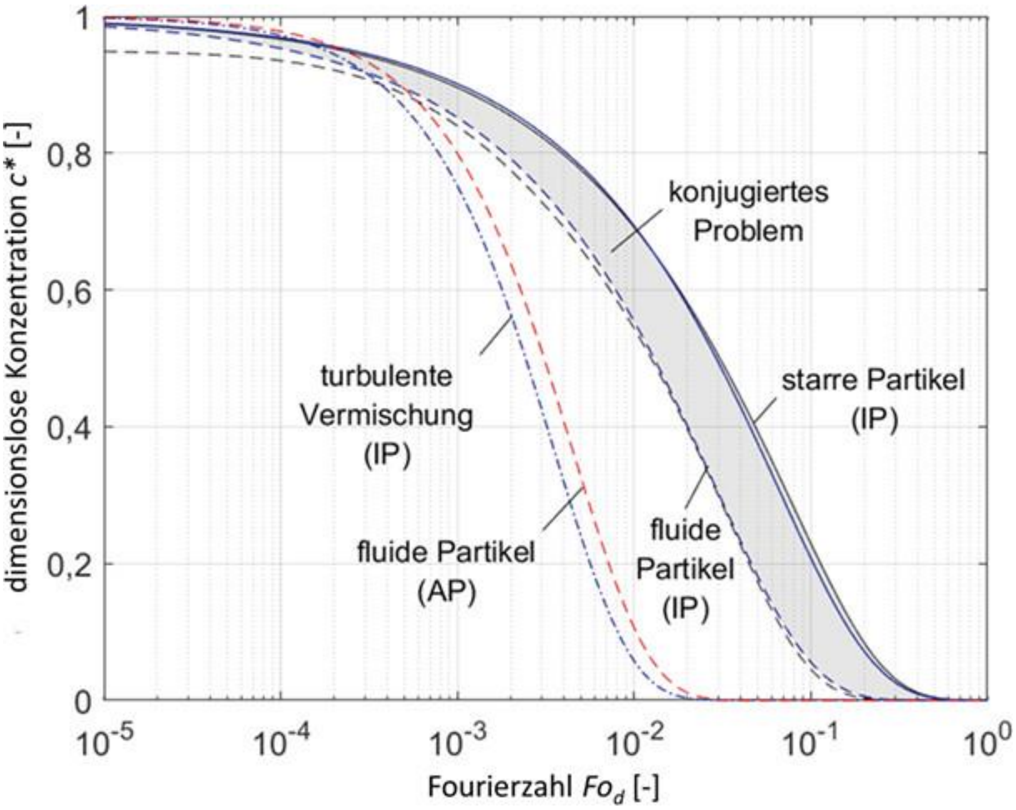


Fig. 5-7: Time course of the concentration in a dimensionless representation for a drop with a diameter of 2 mm, calculation of the inner problem (IP) under different conditions as well as the outer problem (AP) for the material system toluene/acetone/water with D Ad = 2.78 · 10 −9 m 2 s −1 and D Ac = 1.15 10 −9 m 2 s −1 after (Misek, Berger and Schröter, 1985), taken from (Schulz *et al.*, 2021a)

After a meticulous examination of the data and theoretical considerations, it becomes evident that the SDC has yielded favorable outcomes, thus rendering it suitable for subsequent testing and experimentation.

6 Conclusions

6.1 Operability Challenges and Solutions for the SDC

The reliable operation of the single-drop cell is a key aspect for the execution of future reactive extraction experiments. To achieve this, an operational manual was meticulously written to ensure the consistent and reliable performance of the SDC. The intricate nature of the custom-built components necessitated a comprehensive understanding of the mechanical aspects, demanding a substantial investment of approximately 100 hours. Thorough analyzes were conducted for each section of the SDC, yielding intricate insights expounded upon in Section 4.2 and the corresponding appendix. The depth of documentation presented in this work significantly surpasses the level of detail typically encountered in existing literature. Significantly, recommendations based on the experimental understanding of SDC's operation conditions were established. These recommendations encompass the implementation of an enhanced cooling system for temperature stability, strategic placement within the laboratory environment to mitigate external influences, and the enhancement of safety measures. These directives are meticulously compiled within the operational manual.

6.2 Comparative Validation of the Single-Drop Cell

The validation process of the SDC encompassed a comprehensive series of experiments involving varying drop diameters and contact times. Through meticulous comparisons with established models, such as Henschke's model, and other experimental datasets, notably Neuendorf's, intricate dynamics of mass transfer were elucidated. Notably, Neuendorf's data exhibited strong alignment with the model for contact times higher than 5 seconds. The disparities observed between the models and the experimental data prompted an exhaustive exploration of potential factors contributing to the discrepancies. A significant observation emerged regarding the divergence in continuous phase concentrations between Neuendorf's data and the present experimental dataset. This disparity yielded distinct mass transfer rates, with Neuendorf's experiments showcasing a 46% faster rate, a phenomenon attributed to evolving boundary conditions, as forecasted by Henschke and Pfennig. Furthermore, a compelling correlation surfaced between drop diameters and mass transfer rates, with smaller drops exhibiting improved mass transfer coefficients. This observation aligns with the findings of Kalvoda, who identified enhanced mass transfer rates for smaller drop diameters due to the influence of the mass transfer coefficient. Consequently, the experimental validation highlights the single-drop cell's viability for conducting further experimentation in the realm of reactive extraction

6.3 Implications of Sampling Cone Design on Mass Transfer

The pivotal role of the sampling cone within the experimental setup was emphasized, shedding light on the challenges tied to its design, primarily its diameter. The diameter measuring approximately 20 mm generated an operational concern, allowing drops to ascend without being captured. To counter this issue, corrective measures were taken to avert contamination of the dispersed phase. Notably, the reaction time was insufficient at approximately 1.8 seconds, necessitating improvements. Further analysis underscored the necessity of maintaining a specific volume of dispersed phase within the sampling cone to mitigate the risk of contamination and ensure accurate results. Considering these challenges, a proposed modification to the sampling cone’s design was presented, drawing inspiration from previous work by Garthe. This redesigned configuration, characterized by a reduced cone diameter of up to 35 mm to align with the SDC's body diameter, is anticipated to significantly enhance drop capture rates. This modification, in turn, is expected to eliminate the necessity of maintaining a volume of dispersed phase.

6.4 Considerations for Model-Experimental Discrepancies

A crucial aspect of this study revolved around the evaluation of model-experimental discrepancies, particularly in relation to Henschke's. The divergence observed between the models and the experimental data incited a thorough examination of potential underlying causes. One plausible explanation under consideration was the potential influence of outdated model parameters, a hypothesis substantiated by the model's extensive citation in literature. Additionally, operational challenges encountered during experiments, which might have been shared with prior studies like Neuendorf's, were suggested as an additional conceivable element contributing to the observed deviations. This underscores the importance of meticulous control over operational conditions and transparency in sharing operational experiences to enhance the reproducibility and comparability of results.

6.5 Towards Comprehensive Understanding and Future Experimentation

This analysis significantly contributes to the comprehensive understanding of the operability and validation aspects of the single-drop cell's. The operational challenges and corresponding solutions elucidated here offer a valuable resource for researchers seeking to employ the SDC in future experiments. The validation exercises, complete with meticulous comparisons against existing models and experimental datasets, have provided valuable insights into the complex dynamics of mass transfer. These insights not only enhance the understanding of the SDC's capabilities but also pave the way for future explorations in the realm of reactive extraction. The profound implications of sampling cone design on performance underscore the criticality of ongoing enhancements in experimental setups. In sum, this work constitutes a significant advancement in the field, providing researchers with a comprehensive toolkit to harness the potential of the single-drop cell and contribute to the progress of studies in reactive extraction.

7 Annexes

8 References

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