Single-Drop Experiments for Challenging Conditions as Basis for Extraction-Column Simulations

José Manuel AYESTERÁN JEREZ[1], Florian BUCHBENDER[1], Murat KALEM[2],
Eva KALVODA[3], and Andreas PFENNIG[4],*

[1]AVT - Thermal Process Engineering, RWTH Aachen University, Wüllnerstr. 5, 52062, Aachen, Germany; [2]Covestro Deutschland AG, Distillation & Phase Separation, 51365 Leverkusen, Germany; [3]TU Graz, Institute of Chemical Engineering and Environmental Technology, Inffeldgasse 25/C/II, 8010 Graz, Austria; [4]University of Liège, Department of Chemical Engineering - Product, Environment, and Processes (PEPs), Quartier Agora, Allée du Six Août, 11, 4000 Liège, Belgium

Different single-drop cells are presented, which allow a very detailed evaluation of sedimentation and mass transfer for a variety of systems. This includes a cell, in which a concentration profile in the continuous phase can be imposed similar to that encountered in real extraction columns. In the cell for investigating stirred extraction columns, a method was implemented to select those drops for analysis, which did not break when passing through the stirred compartments. This allows attributing each mass-transfer result exactly to a defined drop size. Finally, reactive systems have been investigated and the results compared with a Lewis-type mass-transfer cell. It turns out that with these dedicated equipment, which can be integrated into the identical basic experimental rig, a wide variety of experiments are possible, which lead to detailed understanding of the underlying basic drop processes.

1. Introduction

Conventionally, extraction columns are designed based on pilot-plant experiments. This requires a relatively large amount of substance of at least several 100 liters for each phase. The scale-up from a pilot-plant experiment is only possible, if the type of column internals is identical in the technical and pilot-plant equipment. As a consequence, first experience-based column-type selection is required before the pilot-plant experiments can be performed. If it is later realized that the choice of column type was not optimal, significant additional effort is required. Thus a more versatile design method for extraction-column design has been developed in recent years, which is based on drop-based column simulation. This method allows prediction of column performance based on lab-scale experiments with a small amount of original material system. The results of the single-drop experiments are utilized to fit model parameters of corresponding models describing sedimentation, mass transfer, as well as coalescence and splitting, which are then used in the extraction-column simulation. This simulation method has been implemented previously as indicated in Figure 1 based on a Monte-Carlo approach to solve the population balances by regarding a suitably large ensemble of individual drops as they pass through the column [1,2]. The accuracy obtained with such a simulation is typically better than 10%. The consistency of the drop-based approach becomes obvious from its ability to even predict the limit of operability of the extraction column by flooding with a corresponding accuracy. The drop-based approach has also proven to be accurate for challenging systems like ionic liquids and industrial systems [3,4]. To increase the accuracy of the simulation, quality and scope of the drop models need to be extended.

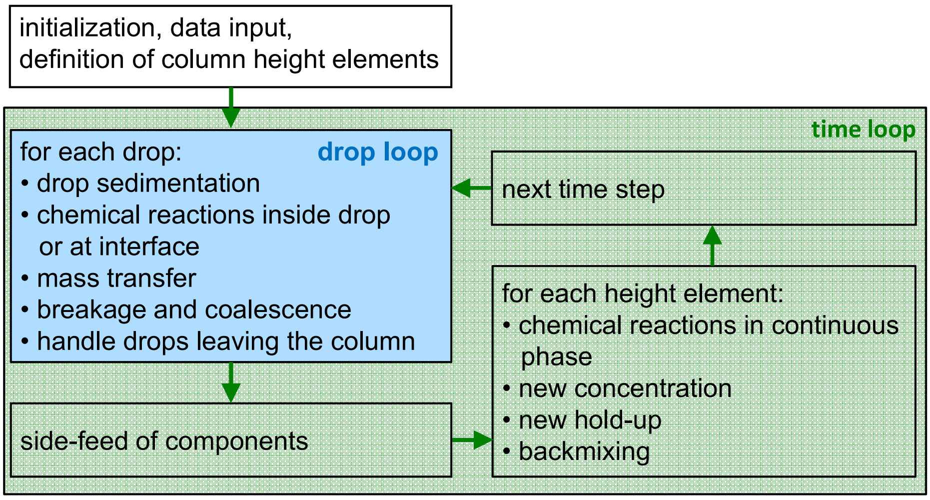

Figure 1. Principal sketch of the ReDrop algorithm.

2. Experimental

The goal of a series of studies was to challenge and extend existing drop models. For example, in typical mass-transfer cells a drop is rising in a tube filled with a continuous phase of given composition and collected after a certain rising height. Alternatively the drop is levitated in a conical cell by a counter-current flow of continuous phase [5]. In both cases the continuous phase has a constant concentration. On the other hand, in extraction columns this is not observed, since the drops instead encounter a continuous phase with a pronounced concentration profile along the column through which the sedimenting droplets pass. Also, it has been found in several studies that sedimentation velocity and mass transfer are strongly linked [6]. Thus it is actually desirable on the one hand to be able to impose a concentration profile in the continuous phase through which the drops are passing and on the other hand facilitate simultaneously measuring mass transfer and sedimentation velocity in detail. Thus a corresponding single-drop cell has been designed as shown schematically in Figure 2. In this cell layers with four different concentrations can be generated, which remain stable for extended periods of time, if the proper order with respect to density is regarded. The drops for the mass-transfer and sedimentation measurement are then produced with a computer-driven syringe and a nozzle of defined inner diameter. If the syringe and nozzle parameters are chosen appropriately, individual drops of very reproducible volume can be generated. At the top of the cell the drops are collected with a drop-collection funnel, which is again connected to a computer-driven syringe. The change in concentration between the produced and collected drops allows quantifying the mass-transfer rate. At the same time the rising drops are recorded with a video camera, which later allows detailed evaluation of sedimentation velocity. The results show that as found previously mass transfer and sedimentation velocity are linked [7,8]. The stronger mass transfer takes place, the slower the drops sediment, which can be explained by mass-transfer induced instabilities at the interface [9,10]. On the other hand it has been shown that mass transfer can be modelled by a shell model, where an effective diffusion coefficient similar to the previous approach can be used but needs modification to obtain exact description of the experimental data [5].

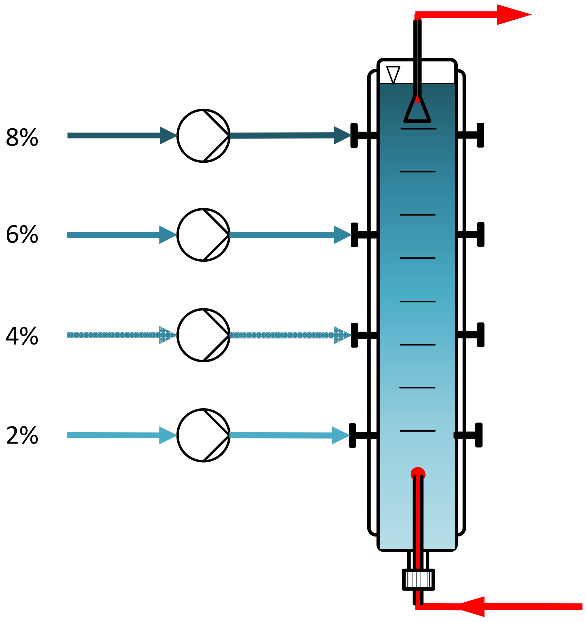

Figure 2. Mass-transfer and sedimentation cell for single-drop experiments with concentration profile

Also the influence of internals on mass transfer needs to be properly depicted by corresponding models in accurate column simulations. This requires corresponding single-drop cells for validating the models. While such cells have already been proposed for sieve trays and packings [5,11], the challenges for rotating internals are especially demanding, because chances are high that a drop will break by interaction with the stirrer or the shear region in its vicinity. To nevertheless be able to attribute an experimental datum to drops of defined diameter, a single-drop cell has been designed, which allows selecting individual drops for the measurement after they passed the internals as shown in Figure 3. In this cell a glass sphere with a conical hole is introduced, which is manually operated. If a drop did not break on its path through the cell, the larger opening of the glass sphere is oriented downward so that the drop is selected and passed into the drop-collection funnel, from where it is again withdrawn with a computer-driven syringe. In case a drop has split into several daughter drops, the opening of the glass sphere is oriented vertically, which guides the daughter drops such that they pass past the drop-collection funnel. Evaluating mass transfer in drops of defined diameter obtained with this mechanism, it turns out that while packings have essentially no influence, mass transfer is slightly enhanced by the stirring.

For modelling sedimentation in columns with rotating internals, the residence times below and above the stirring element as well as in the stirring-element zone together with the corresponding transfer probabilities between these zones have to be characterized experimentally and corresponding models derived [12]. This allows drop-based modelling, where the behavior of the individual drops is described with a stochastic model accounting for the transfer probabilities between the different regions of the stirred compartment. This model can depict also the residence-time distribution for the drops, where some drops are caught within the compartment for some time, while others pass relatively quickly and move on to the next compartment above. The modelling approach in principle also allows drops from the compartment above to be passed on in downward direction with a certain small probability.

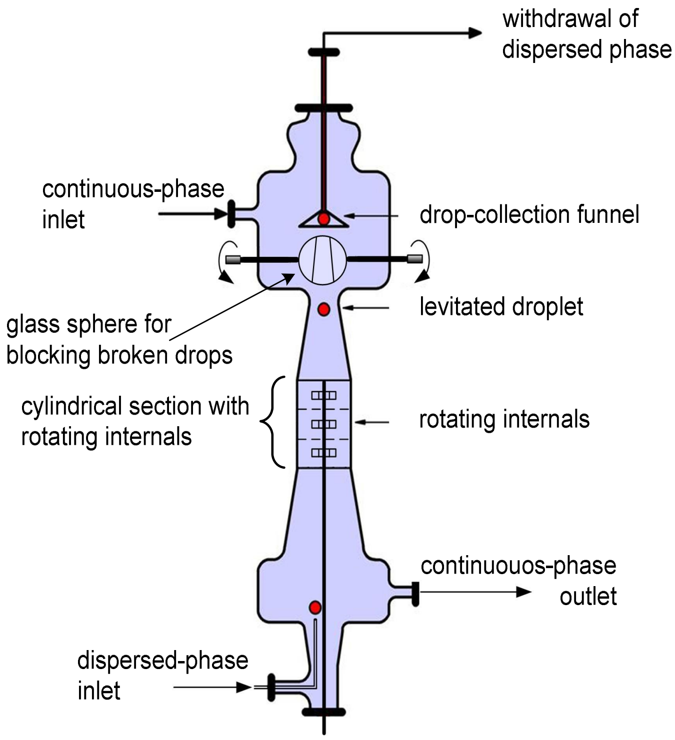

Figure 3. Mass-transfer and sedimentation cell for single-drop experiments with rotating internals

Reaction kinetics may occur on top of the mass transfer induced by Nernst distribution. This needs to be described by corresponding approaches including reaction kinetics [13,14]. If suitable models have been found, the results for drops should compare well with those obtained with a defined flat interface, e.g. for experiments performed in a Lewis-type cell [15]. It turns out that the local reaction kinetics together with the diffusive resistance need to be taken into account to obtain an appropriate description of mass transfer. Nevertheless, in the simulation of an extraction column it is possible to describe mass transfer with an effective diffusion coefficient, which takes the influence of the reactive extractant into account [14].

3. Results and Discussion

Exemplarily here the results obtained with a concentration gradient in the cell shown in Figure 2 are shown in Figure 4. The experiments were performed with the EFCE standard test system for solvent extraction water (c) + n-butyl acetate (d) and acetone as mass-transfer component. The experiments have been performed at room temperature, which varied slightly around 20°C, where for the evaluation, the exact temperatures have been measured and the physical properties used as interpolated for that temperature. The concentration profile in the continuous phase has been varied in [8] for several characteristic cases, where in Figure 4 the results for an essentially constant slope is shown. As indicated above, the simulation of mass transfer was realized with a shell model, where the mass transfer has been described with the model proposed by Henschke [5], which has been slightly modified for the effective diffusion coefficient of the dispersed phase [8]:

$$D_{d,eff} = D_{phys} + \frac{v_\infty}{C_{prof}\left(1 + \frac{\eta_d}{\eta_c}\right)}$$

where D_{phys} is the physical Fickian diffusion coefficient of acetone in the dispersed phase, v_∞ is the sedimentation velocity of the drop as determined by independent measurements and correlated with the Henschke model as described e.g. in [6], and the η are the viscosities of the dispersed and continuous phase as indicated by the index. C_{prof} is an adjustable system-specific parameter, which has been determined to be 1785000m^{-1}. It has been shown previously that the majority of the mass-transfer resistance is located inside the drop.

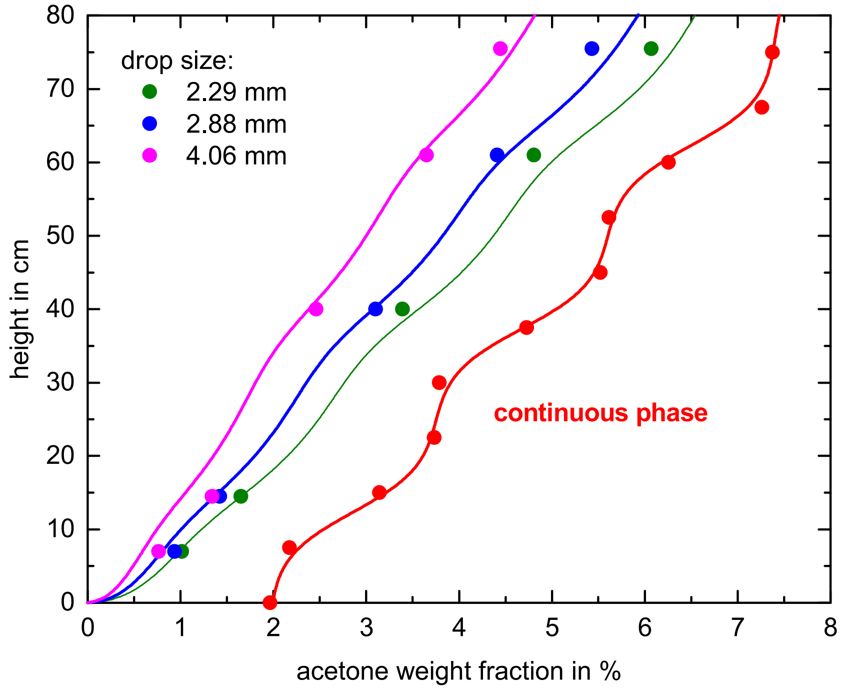

Figure 4. Mass-transfer results obtained with a concentration gradient in the laboratory cell shown in Figure 2 at room temperature for the system water (c) + n-butyl acetate (d) and acetone as mass-transfer component [8]. Model results for the drops are shown as lines.

The investigations also show that the concentration jump, which the drop encounters as it is first contacted with the continuous phase, determines, if interfacial turbulences set in, which lead to an enhancement of mass transfer by a factor of 1.5 in effective diffusion coefficient throughout essentially the entire residence time at least in the laboratory cell shown. In the case shown in Figure 3, the

Marangoni number at the interface divided by the drop diameter lies above the limit for the onset of such turbulences, which has been found to be $2.3 \times 10^{-8} m^{-1}$[8].

Overall, based on these suitably designed single-drop cells and dedicated experiments it thus turns out that conventional models need significant enhancement in order to properly describe the effects addressed, which are encountered in extraction columns under realistic conditions. The structure of such models as well as the model parameters are obtained from experiments in the measuring cells described. Besides deriving improved detailed models, the insights gained can also be used directly to optimize extraction-column performance. Thus, a proposal for reducing the volume of stirred columns without significant effect on drop residence times has been derived and experimentally validated. This optimized stirred compartment is based on the insight that the residence time of drops below the stirrer is short and that this volume can thus be deleted with only little effect on separation performance. This leads to a stirrer position, which not vertically centered in the compartment but closer to its lower stator [12].

References

1) M. Kalem, F. Buchbender, A. Pfennig. *Chem. Eng. Res. Des.,* **89**(1), 1-9 (2011).
2) A. Pfennig, T. Pilhofer, J. Schröter, in R. Goedecke, Fluid-Verfahrenstechnik, Wiley-VCH, Weinheim, 907-992 (2006).
3) F. Buchbender, F. Onink, W. Meindersma, A. de Haan, A. Pfennig, *Chem. Eng. Sci.*, **82**, 167-176 (2012).
4) F. Buchbender, M. Schmidt, T. Steinmetz, A. Pfennig, *Chem. Ing. Techn.*, **84**, 540-546 (2012).
5) M. Henschke, A. Pfennig, *AIChE J.*, **48**(2), 227-234 (2002).
6) M. Kalem, M.Y. Altunok, A. Pfennig, *AIChE J.*, **56**(1), 160-167 (2010).
7) E. Cvetkovic, A. Pfennig, Proceedings of the 7th International Berlin Workshop on Transport Phenomena with Moving Boundaries and More, 30th-31st October, Berlin, Germany (2014)
8) E. Kalvoda, Ph.D. thesis, TU Graz, https://diglib.tugraz.at/download.php?id=5891c8d717f30&location=browse, (2016).
9) A. Pfennig, *Chem. Eng. Sci.*, **55**(22), 5333-5339 (2000).
10) R. Schott, A. Pfennig, *Mol. Phys.*, **102**(4), 331-339 (2004).
11) H.-J. Bart, D. Garthe, T. Grömping, A. Pfennig, S Schmidt, J. Stichlmair, *Chem. Ing. Techn*. **78**(5), 543-547 (2006).
12) F. Buchbender, A. Fischer, A. Pfennig, *Chem. Eng. Sci.,* **104**, 701-716 (2013).
13) M.Y. Altunok, M. Kalem, A. Pfennig, *AIChE J.*, **58**(5), 1346-1355 (2012).
14) M. Kalem, Einzeltropfenbasierte Simulation von pulsierten Siebbodenkolonnen für die Reaktivextraktion, Shaker Verlag, Aachen, 2015.
15) E. Bertakis, M. Kalem, A. Pfennig, *Chem. Eng. Sci.*, **63**(19), 4881-4887 (2008).