

Solvent Extraction Design for Highly Viscous Systems

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The change from fossil-based feedstock to bio-based raw materials will lead to changes in the molecular structure of reagents used in the chemical industry. Bio-based raw materials are richer in oxygen, leading to intermediates and products rich in oxygen as well. This will lead to lower vapor pressure and higher viscosity of the systems. Thus liquid-based separations like solvent extraction will increase in importance. Also separation-process design needs to be adapted to properly account for higher viscosities. With drop-based simulation, extraction-column performance can be predicted to better than 10% accuracy, being time and resources saving compared to pilot-plant experiments. In previous work, appropriate models describing all drop phenomena like sedimentation and mass transfer were combined in a simulation tool, called ReDrop (REpresentative DROPs). The models implemented in ReDrop have been largely validated for low-viscous systems. In order to extend the capabilities of ReDrop and describe the entire viscosity range, models have to be tested for a variety of different material system with single-drop lab-scale experiments. In this work mass transfer has been evaluated with single-drop experiments for two systems with different viscosity. The first one is the standard EFCE system composed by water + acetone + butyl acetate. Results were compared with the mass-transfer evaluation for the aqueous two-phase system with higher viscosity composed by water and PEG + albumine + water and phosphate. The results show that the transport of a component between two immiscible phases is strongly influenced by the viscosity of both phases as well as the molecular size of the transferred component. The single-drop results are the basis for validation and extending the applicability of existing models to higher viscosity, which are then introduced into ReDrop.

1. Introduction

The oxygen content in bio-based feedstock is higher as compared to fossil starting material. Thus, intermediates and products of the future chemical industry will be rich in oxygen as well. Polar interactions and hydrogen bonding will be present in mixtures. This in turn will lead to lower vapor pressures and higher viscosity of the systems. Process design has to account for these changes throughout the entire production process, starting from raw-material supply ending at purification and separation steps. The aim of this work is to study some relevant aspects related to liquid-liquid extraction, in order to optimize extraction-column design with a focus on highly viscous systems. The knowledge in the area of solvent extraction in highly viscous systems, as e.g. applied for separation of pharmaceuticals from fermentation broth or extraction of biomaterials from a complex oxygen-containing matrix, is limited.

Thus an investigation on extraction-column behavior for viscous systems is required.

With drop-based lab-scale experiments and simulation, extraction-column performance can be predicted to better than 10% accuracy, being time and resources saving compared to pilot-plant experiments [1]. This is possible, because only a limited number of elementary processes, namely sedimentation, coalescence and splitting, mass transfer, as well as the interactions among the droplets and with the column internals influence the behavior of individual drops of the dispersed phase in the column. In previous work, appropriate models describing these effects were combined in a simulation tool, called ReDrop (REpresentative DROPs). The main idea of ReDrop is to follow the behavior of a sufficiently large number of individual drops along their paths through the column and to solve the population balance accounting for the interconnected phenomena mentioned [1-2]. The appropriate lab-cell measurements are used to derive the corresponding models describing the individual drop behavior with respect to the above-mentioned basic phenomena. The ReDrop simulations have been validated for a variety of systems, mostly standard test systems [3], which have been defined by the EFCE in the past [4], but also for technical systems [1, 7, 8], for which the results of the ReDrop simulations were compared with those of pilot-plant scale experiments. The predictions agreed to better than 10% with the experimental data available. The strength of this drop-based approach is apparent from its ability to even predict the limits of operating the extraction column, namely the flooding point, with similar accuracy. The models implemented in ReDrop have been largely validated for low-viscous systems with viscosities of around 1 mPas [3] and for systems with viscosities of the order of 100 mPas [5]. Since the model parameters even for describing drop sedimentation greatly differ for the different viscosity regimes, the intermediate range has to be investigated to obtain a complete picture. This will result in models and simulation tools capable of describing the entire viscosity range of interest.

2. Experimental

2.1 Material system

Sedimentation velocity and mass transfer of a single drop of dispersed phase rising in the continuous phase has been studied with a sedimentation vessel coupled with a single-drop cell, described in the next section, where a conical glass tube is used to levitate the drop by a counter flow of continuous phase [6].

Before investigating high-viscous systems with the single-drop cell, the equipment for mass transfer measurement, which had been transferred to Liège from TU Graz, Austria, has been validated by analyzing mass transfer and sedimentation behavior of an EFCE standard test system for solvent extraction with low viscosity composed by water, acetone and butyl acetate. The direction of mass transfer has been chosen to be from continuous to dispersed phase. The water has been saturated with butyl acetate, then 5%wt. of acetone were added to the continuous phase. The dispersed phase is composed by *n*-butyl acetate saturated with water.

As an example for viscous systems single-drop behavior previous results obtained for aqueous two-phase systems (ATPS) with a system of phosphate and PEG (polyethylene glycol) are included in this evaluation as well. The investigated system was composed of PEG 2000 at a weight fraction of 13.5 wt% and a phosphate buffer at 8 wt%. The pH of the system was set to 9 by using a mixture of di-

potassium hydrogen phosphate and sodium dihydrogen phosphate at a temperature of 25°C. The physical properties of the system are given in Table 1. Mass-transfer component was the protein albumin with a molecular mass of 65 kDa, which was chosen as a representative for valuable bio-molecules. Mass transfer was from salt-rich continuous phase to PEG-rich droplet phase.

The single-drop results are the basis for validation and extending the applicability of existing models which are introduced in ReDrop. Suitable material systems for solvent extraction with high viscosity are chosen based on the standard test systems proposed by the EFCE [4]. For the first investigations, the aqueous phase is chosen as continuous phase, where the viscosity is increased by adding a suitable polymer like PEG. The dispersed-phase viscosity is increased by dissolving suitable compounds such as paraffin oil in an organic solvent immiscible with water, like e.g. *n*-butyl acetate. Diffusion of the transfer component is influenced by the mass-transfer resistance induced by continuous and dispersed-phase viscosity. Single-drop measurements in viscous systems will allow to understand how viscosity influences the parameters of the model. In previous work [5] the parameters have been fitted for the system composed of water + PEG as continuous phase and toluene + paraffin as dispersed phase. Viscosity of the continuous phase was varied between 80 and 100 mPas and viscosity of the dispersed phase was increased to 64 mPas by adding paraffin oil. Further investigations are thus focusing on the intermediate range of viscosity between 1 mPas and 100 mPas.

Table 1. Physical properties of the investigated ATPS.

phase	density kg/m ³	viscosity mPas	interfacial tension mN/m
continuous	1195.9	2.145	
dispersed	1088.0	9.250	

2.2 Single-Drop Experiments

Sedimentation velocity of single drops has been evaluated in a cylindrical vessel maintained at a temperature of 20°C. The vessel has an inner radius of 4 cm and his height is 40 cm. It can be filled with up to 2010 ml of continuous phase. Inside this vessel, a drop of known volume is produced with the help of a computer driven syringe, which can inject a defined volume of dispersed phase at a defined velocity via a glass nozzle. The glass nozzle is installed in the vessel and connected to the syringe by a PEEK hose of suitable diameter. By finding the right amount of dispersed phase to inject and the right velocity to correctly produce one single drop, individual drops with the drop diameter of interest can be generated. Each drop detaches from the glass nozzle tip and its path is recorded with a video camera. Knowing the numbers of frames, and consequently the time, needed for the drop to rise in the continuous phase through a defined distance, sedimentation velocity can be easily determined.

Single-drop mass-transfer investigations have been carried out in the cell shown in Figure 1. The glass cell has a conical section in the mass-transfer zone. The maximum inner diameter of the cell is 5 cm, and the distance between the drop production point and the collection funnel is 15 cm. All parts of the device consist solely of glass, teflon and stainless steel in order to minimize the influence of contaminants. The cell is maintained at 20°C. The drop is again produced by a computer-driven syringe

and a glass nozzle, with which the right volume of liquid required to produce one drop with chosen diameter is injected. The drop then rises until it reaches the conical part, in which a counter-flow of continuous phase is induced by a pump. It will rise until its sedimentation velocity matches the counter flow of continuous phase, which allows to realize different contact times between the two phases. After the chosen contact time, the counter flow of continuous phase is switched off, the drop can continue its path along the cell, and is collected in a glass funnel. The glass funnel is connected to another syringe which withdraws the exact amount of liquid corresponding to the volume of the drop. After a sufficient number of drops has been withdrawn, typically between 300 and 600 depending on the volume, the sample of dispersed phase can be analyzed. The concentration of transferred component in the drop is determined using UV-Vis spectroscopy, which allows to calculate the dimensionless driving concentration difference of acetone in *n*-butyl acetate drops as a function of the contact time. The dimensionless driving concentration difference is defined as:

$$y^+ = \frac{y(t) - y^*}{y_0 - y^*} \quad (1)$$

where $y(t)$ is the concentration of transferred component in the drop at the residence time t , y^* is the equilibrium concentration of transferred component in the drop and y_0 is the initial concentration of transferred component in the dispersed phase. The dimensionless driving concentration difference is 1 when no mass transfer has occurred and 0 when mass transfer is finished and the concentration of transferred component in the dispersed phase has reached his equilibrium value.

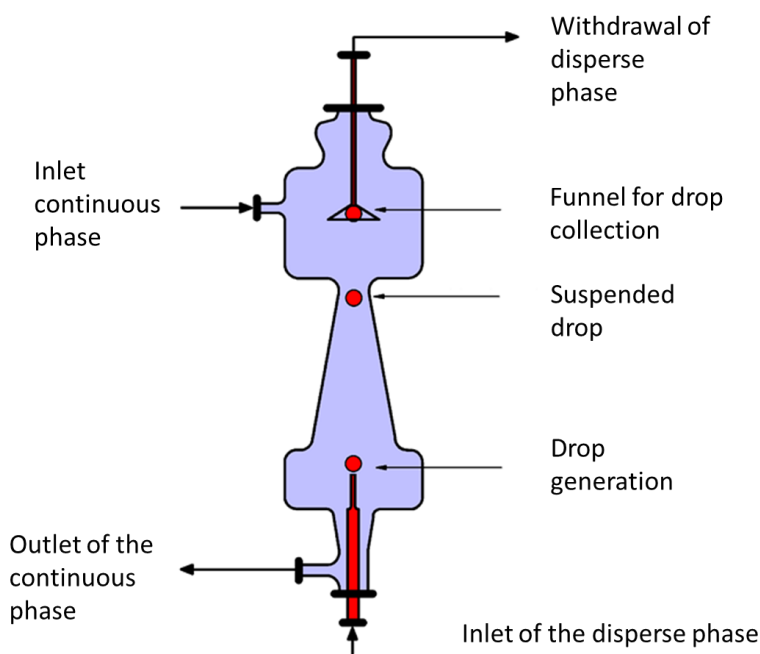


Figure 1. Single-drop cell for single-drop based mass-transfer measurements [6].

3. Results and Discussion

Sedimentation velocity of a single drop as function of its diameter shows typically the behavior

presented in Figure 2. In this work three different drop diameters have been investigated for the system water + acetone + butyl acetate. Figure 2 compares the obtained values for sedimentation velocity with previous results. It is apparent that the new data match almost exactly with the previous data. Drops of *n*-butyl acetate in water behave like rigid spheres for the smallest drop diameter. The larger drops investigated behave as drops with internal circulation, showing a mobile interface. This result shows that the cell is properly working after its transfer to Liège and the methods applied have been validated at the same time.

Mass-transfer results for the standard system water + acetone + butyl acetate are reported and compared with previous data, [6,9], in Figure 3. y^+ decreases from 1, when no mass transfer has occurred and the drop starts with its initial concentration, to 0, when mass transfer ceases. As expected, the dimensionless concentration difference decreases with contact time. The results in Figure 3 show as expected that for drops with smaller diameter faster mass transfer results. This shows that also the mass-transfer cell has been validated and the proper procedures have been established at the University of Liège. As a basis for the future viscous system investigations, previous results related to the aqueous two phase system described above are presented. The results are shown in Figure 4 with the dimensionless driving concentration difference over the residence time of the drops and the drop diameter. The results show, that mass transfer is significantly slower than in the system water + butyl acetate + acetone shown in Figure 3. Reasons for this drastically reduced mass transfer are the higher viscosity of the dispersed phase as well as the size of the mass-transfer component, which is several orders of magnitude larger compared to the acetone in the organic-aqueous system.

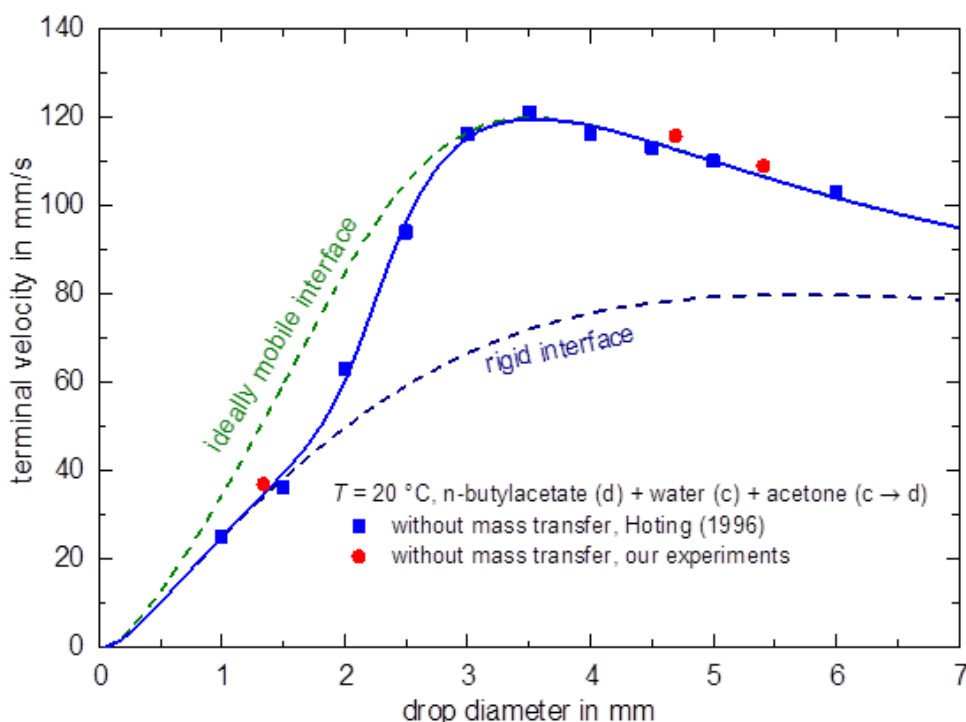


Figure 2. Sedimentation velocity of *n*-butyl-acetate drops in water as a function of the drop diameter.

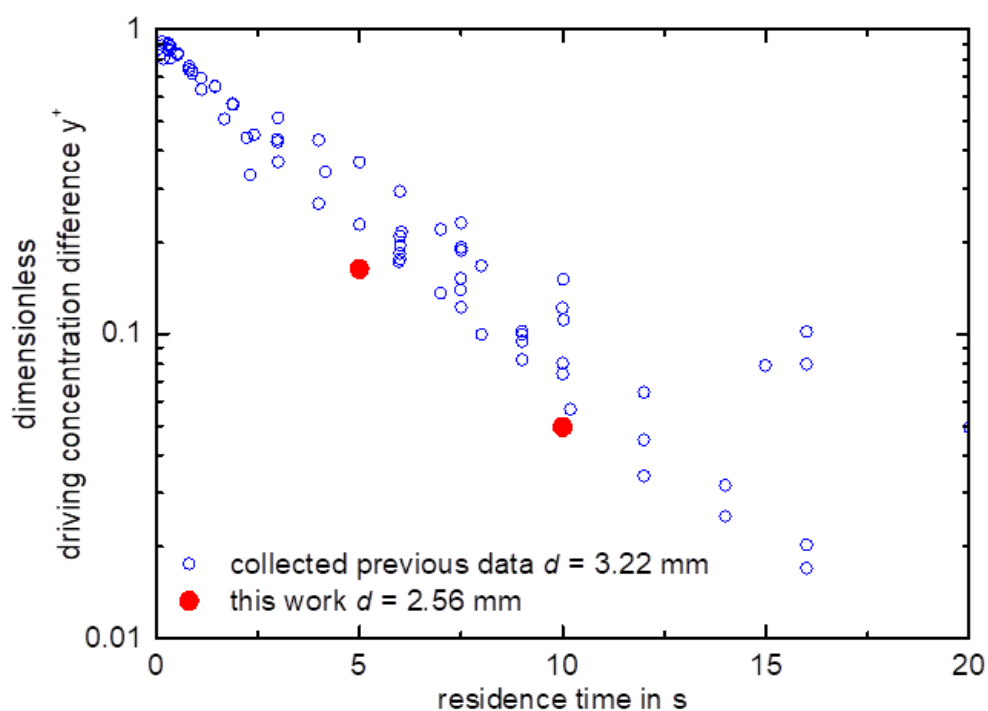


Figure 3. Dimensionless driving concentration difference as a function of residence time.

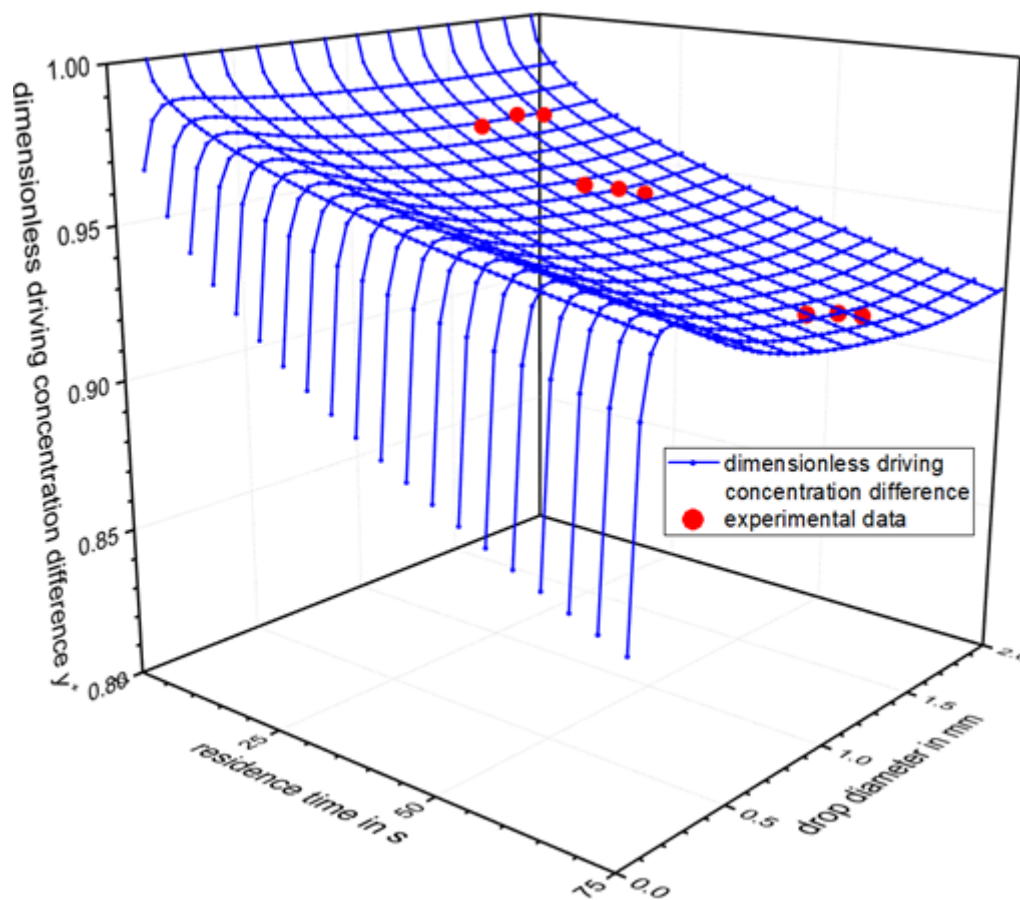


Figure 4. y^+ as a function of residence time and drop diameter for the aqueous two-phase system.

In the future work, sedimentation and mass transfer will be investigated by changing the properties of the material system, in order to adapt the models to system with increased viscosity in both phases. The influence of the molecular size of the transferred component will be taken also into account as well, since the investigation on ATPS showed that mass transfer is significantly slowed down for large transfer molecules.

4. Conclusion

The validation of the lab-scale equipment to quantify single-drop behavior with the standard test system shows good agreement with previous data. Sedimentation velocity of single drops of *n*-butyl acetate in water without mass transfer agrees with previous data, where small drops behave like a rigid sphere, while with increasing drop diameter sedimentation velocity reaches that of deformed drops with ideally-mobile interface. Mass transfer has been evaluated for three different drop diameters and for different residence times. Results are in good agreement with previous results as well. For an aqueous two-phase system it has been shown that mass transfer is significantly slower than that in low-viscous systems. Thus the basis has been established for investigating systems with increased viscosity in the future. First results are presented at the ISEC2017, Myazaki, Japan.

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