

Using a Raman sensor for the investigation into the mass transfer in compressed multi-phase flows in micro channels

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ABSTRACT

For an appropriate design and for the optimization of extraction processes, the mass transfer between different phases is essential. In order to quantify the mass transfer, composition data of the participating phases are required as a function of time which are yet challenging or even impossible to determine. This is in particular the case for a pressurized liquid/liquid system consisting of CO₂ bubbles dispersed in a water/organic solvent bulk phase inside a conventional extraction vessel, where a parallel mass transfer of solvent into the CO₂ bubbles and of CO₂ into the bulk phase occurs.

The use of microfluidics for an optical *in situ* investigation into multi-phase systems at elevated pressure conditions however, provides new opportunities.

A transfer of the above mentioned system to a transparent, pressure resistant micro capillary system (MCS), leads to a segmented periodic flow pattern of alternating CO₂ bubbles and organic/water plugs and additionally transfers the temporal to spatial domain comparable to the residence time in the system. A transparent MCS allows the fast and precise control of conditions, fast analysis and short optical path lengths of light through the capillary which permits optical access to the interior of the single phases. Due to this optical access a Raman sensor could be used to measure the molar composition of the bubble or the plug phase at different positions in the MCS and thus the temporal evolution of the composition of the phases. The quantification is possible, as the Raman signal is species specific and its signal intensity is a function of the molar density of the species in the mixture. A phase-specific optical measurement setup with a high temporal resolution is introduced and applied to a droplet-based system at ambient pressure conditions. It guarantees to only probe the composition of either the droplet or the plug phase which is necessary due to the high flow velocities inside the MCS.

INTRODUCTION

The determination of mass transfer coefficients in multi-phase systems in contact with supercritical CO₂ using conventional methods is challenging and time consuming due to the intrinsic high-pressure conditions. Yet, the determination of mass transfer parameters requires fast screening of the dynamics of concentration with a high spatial and temporal resolution

that can be provided –if the systems under investigation are accessible with light– using optical measurement techniques. This optical access is usually blocked by multiple phase boundaries in multi-phase systems. To circumvent the optical restriction, transparent microfluidic systems (MFS) are applied which permit an optical access due to a short optical path length of the light through the capillary and allow to clearly resolve the systems' interior [1-3]. Besides the optical access, MFS in general allow fast analyses and precise control of process conditions at a low throughput of substances.

Recently, the determination of the dissolution rate, the solubility and the diffusion of gaseous CO₂ into organic solvents in MFS has been demonstrated at ambient pressure using shadowgraphy [4-9], making use of the reduction of the volume of phase (a) that is dissolved in phase (b). In a segmented flow of alternating CO₂ bubbles and organic solvent plugs, the reduction of the volume of the CO₂ bubbles was related to the dissolution rate of gaseous CO₂ into the liquid solvent as a function of the residence time t , assuming that the solubility of water in CO₂ is negligible. This assumption does not hold for processes, taking place at elevated pressure conditions and is explicitly wrong for miscible systems as organic solvents and pressurized CO₂. Consequently, the mass transfer takes place in parallel and the alteration of the volume of neither the compressed gas phase nor the liquid phase can straight forward be assigned to one of the two transfer paths alone.

In 2013, we presented an extension of the above mentioned shadowgraphic evaluation strategy of the mass transfer applied to a special case, where an emulsion system of organic solvent droplets dispersed in a water phase was in contact with pressurized CO₂ [2]. In this study, the mass transfer could be quantified -only for one instance in time- using the refractive index of the emulsion droplets as an indicator for the composition inside the droplets and correlate this to the volume of the CO₂ phase.

For a general interpretation of the mass transfer in microfluidic multi-phase systems at ambient and elevated pressure conditions, a measurement technique is required which can quantify the species concentration inside the different phases with a very high temporal resolution, as the periodicity of the alternating phases in MFS can be in the kHz range.

In this contribution we present a phase-specific Raman measuring setup that is triggered to the periodic phase change in the flow. This technique will be described exemplarily using a model system at atmospheric pressure, where Acetone (Ac) is transported between two almost immiscible compounds water (W) and ethyl acetate (Ea), as Ac is miscible in Ea and W. This technique is identically applicable to elevated pressure conditions using supercritical CO₂ and first experiments are currently run in our labs. The first results will be presented on a poster at this conference.

MATERIALS AND METHODS

Two mixtures were previously produced and separately fed to the MFS using two syringe pumps. Mixture (a) which later forms the organic phase (OP) consists of 50/50vol% of Ac and Ea and mixture (b) which later forms the water phase (WP) consist of water, saturated with Ea.

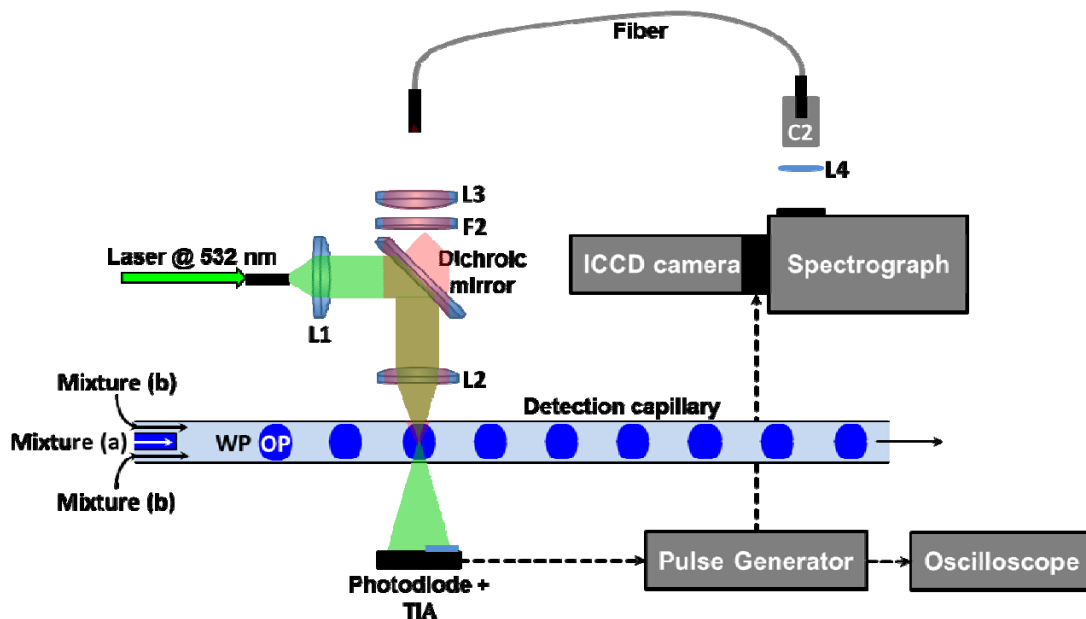


Figure 1: Schematic of the experimental micro capillary and optical setup; OP: Organic phase; WP: Water phase; L1,4: Convex lens; L2,3: Achromatic convex lenses; F2: Long pass filter (535 nm).

Mixture (a) and mixture (b) are introduced to the detection micro capillary using two, concentrically arranged capillaries. During a short period, the two fluids mix and latterly split into two phases, forming a segmented flow of alternating organic droplets and water plugs. During the residence time (phase contact time) inside the measuring capillary, Ac will travel from the OP into the WP. Depending on the flow rate of the pumps, the droplet frequency can range from several Hz up to kHz. The quantification of the Ac concentration inside the OP and WP at a specific measuring position (corresponding to a residence time) was performed using a triggered Raman setup as sketched in Figure 1.

A continuous wave laser at 532 nm was focused into a fiber, guided to the mobile optical system, subsequently collimated (L1) and focused into the capillary. The red-shifted Raman signals, generated in the focal volume, are back scattered, imaged onto a fiber and guided to the detection system. The dichroic mirror, with a high reflectance for wavelengths shorter than 540 nm and a high transmittance for wavelengths longer than 540 nm, and the long pass filter (F2) suppress the elastically scattered light. The signals are spectrally dispersed in a spectrograph and detected on the CCD chip of an intensified camera. A similar setup with the application of a not-intensified CCD detector is frequently used for macroscopic systems in our labs [10, 11] and will be presented in detail in an oral contribution of our group by Julian J. Schuster.

The acquisition and quantification of the species concentration only in one phase is based on three requirements for the detection strategy.

- a) The acquisition has to be phase specific (online distinguish between WP and OP).
- b) The acquisition time has to be short enough to guarantee that after the initiation of the acquisition, the WP plug is not replaced by the OP droplet.
- c) The Raman signal intensities have to be calibrated to extract the species concentration from the intensity ratios.

The realization of requirement a) and b) were fulfilled by using the triggering scheme, sketched in Figure 2.

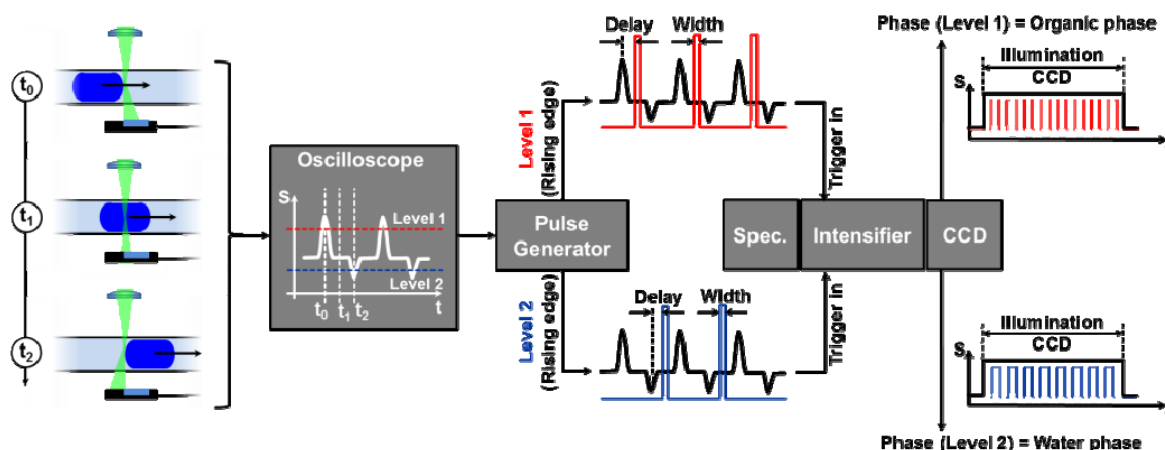


Figure 2: Scheme of the triggering setup using the transmitted and refracted laser beam as master signal to distinguish between the different phases; t: time; Spec.: spectrometer.

Requirement (a, phase specificity) was realized by installing a photo detector below the capillary acting as a trigger input for a pulse generator which itself triggers (initiates) the spectra acquisition. As illustrated in Figure 2 (left side), the photo detector is placed in a way that the laser beam diverging from the focal spot is reflected from the phase boundaries (discontinuous change in refractive index) either onto (t_0) the photo detector for “arriving” OP droplets or away from (t_2) the photo detector for “leaving” OP droplets (arriving WP plugs). The resulting signal sequence of the photo detector is visualized on the oscilloscope as it is sketched in Figure 2 and is transmitted as trigger-in signal to the pulse generator. Two different voltage levels were set in the setup of the pulse generator to online distinguish from the voltage-signals' rising edge between the OP (level 1) and the WP (level 2) and consequently allow the initiation of the spectra acquisition for either the OP or the WP. Using this master signal for only triggering the CCD detector and shutter (minimum acquisition time of 18 ms), the spectral analysis would be just possible for very slow flows with a droplet frequency of only some Hz and at the same time with a very low signal to noise ratio due to the very short illumination time.

Requirement (b) was realized by using an intensifier as an electrical gate between the spectrograph and the CCD detector which allows exposure times of ns and thus makes the spectral analysis of fast flows (periodicity of kHz) possible. The intensifier is synchronized to the segmented flow (master signal from the photo detector) and the exposure time of the CCD detector can be shifted using the pulse width and delay from the pulse generator as illustrated in Figure 2. For this setup, the CCD detector can have acquisition times of several seconds (large signal to noise ratio) and will only acquire the Raman signals of one specific phase (depending on level 1 or 2) but as an accumulation of hundreds of droplets or plugs.

The acquired Raman intensities have to be calibrated to extract the molar concentration of one species out of these ternary mixtures (Requirement c).

RESULTS

As the whole measuring setup is mobile compared to the immobile MFS, the species concentration can be monitored for both phases at different positions downstream to the mixing nozzle. With the known and adjusted flow rates, the species concentration can now be

plotted as a function of the residence/contact time of the droplets and plugs, as it is illustrated exemplarily in Figure 3. The flow rates of both mixtures (a, WP) and (b, OP) were set to $50 \mu\text{l}\cdot\text{min}^{-1}$. The spectra were acquired consecutively for the OP and the WP at one measuring position with a delay between the trigger and the intensifier activation of 40 ms and a gating time of the intensifier of 40 ms for a fixed acquisition time of the CCD detector of 3 seconds.

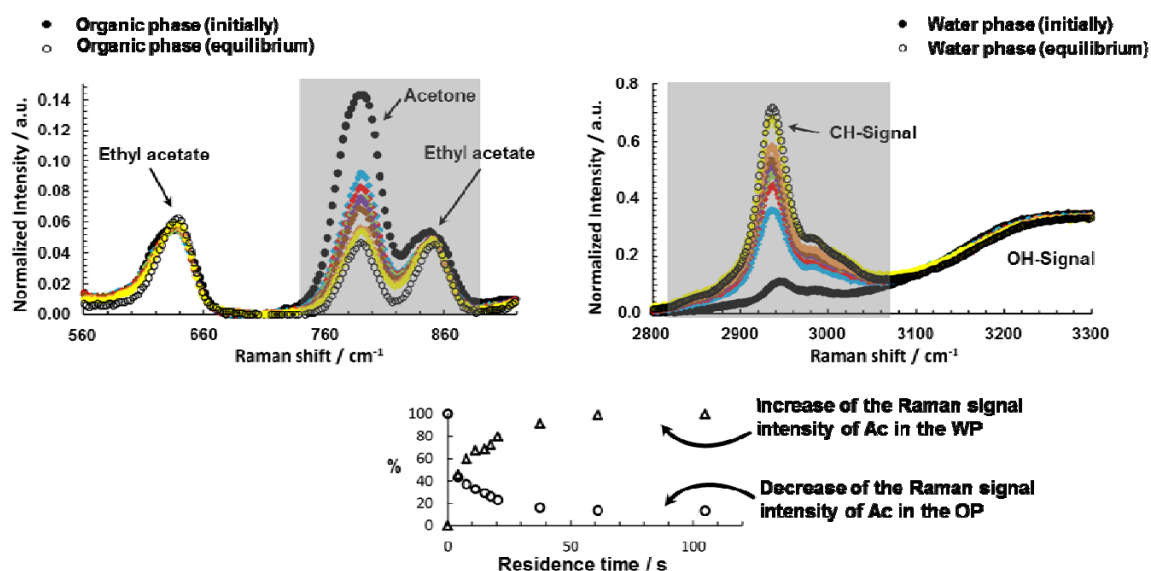


Figure 3: Decreasing Ac Raman signal in the OP -spectra normalized to the Raman intensity of an isolated Ea peak ($600 - 670 \text{ cm}^{-1}$)- and increasing Ac Raman signal in the WP - spectra normalized to the Raman intensity of the OH-vibration ($3100 - 3650 \text{ cm}^{-1}$) for different distances to the mixing nozzle and its evolutions as a function of the residence time.

An adaption of the exemplary system of two liquids at ambient pressure to two phase systems at elevated pressure with supercritical CO_2 is currently done in our labs and some first results will be presented at this conference.

CONCLUSION

In this contribution a phase-specific Raman measuring setup was introduced which allows the characterization of the composition of the phases of multi-phase systems in MFS. This technique was described exemplarily using a model system at atmospheric pressure but is identically applicable to elevated pressure or supercritical conditions. Measurements of the composition of phases as a function of time allows the characterization of mass transfer processes and makes the determination of mass transfer coefficients possible what will help to design and optimize extraction processes at elevated pressure conditions. First experiments are currently run in our labs. The first results concerning pressurized CO_2 will be presented on a poster at this conference in May.

ACKNOWLEDGEMENT

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