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Evaluation of static micromixers for flow-through extraction by emulsification

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Abstract

With increasing spread of microreaction technology an evaluation of microfluidic tools has become an important aspect. By using an extraction process of iodine from water to *n*-hexane in an emulsion, the usability of seven different micromixers was tested under same conditions. Extraction efficiency was defined and the dependence on flow rate, phase ratio and the behaviour of the generated emulsion after leaving the micromixer, passing the outlet tube, were observed. This method even provides the possibility to distinguish the micromixers in view of their extraction capability. The comparison among each other and with a simple T-junction shows significant differences in extraction behaviour, which can be interpreted as differences in emulsification behaviour.

Keywords: Emulsification; Static micromixer; Microextraction; Flow-through process

1. Introduction

Extraction and other phase transfer processes play an important role in chemical technology. In classical devices, emulsification is used in liquid/liquid phase transfer processes. In microreaction technology either emulsification [1–3] or laminar flow in microcontactors [4] can be applied.

In most cases, the phases must be separated after the phase transfer processes. Therefore, the application of emulsifier is avoided in order to improve the phase separation. In consequence, such emulsions are stable only for a limited time. Under reduced shear stress, the emulsified liquid droplets fuse quickly. The efficiency of formation of emulsion and the size distribution are important for the efficiency of the whole extraction process under these conditions.

In this work, the suitability of different micromixers for flow-through emulsification and liquid/liquid extraction is studied. Former studies has shown qualitative differences of mixing behaviour between different micromixers [1,2,5,6]. It was also known from previous investigations, that static micromixers can be applied advantageously for the generation of emulsions [3]. Therefore, multilamination mixers [3,5,6] as well as split and recombine mixers [7] can be used. The efficiency of emulsification is dependent on the properties of both immiscible liquids, the kind of lamination and the volume flow rate. In the following, the process of continuous extraction by emulsification with different static micromixers is described and the behaviour of different mixers is quantified by the characterization of the efficiency of extraction.

2. Experimental

As test process, the extraction of iodine from an aqueous solution into *n*-hexane was used. The Nernst coefficient of the distribution equilibrium of iodine in these both liquids at ambient temperature (22 °C) was measured at 19.86 ppm-mass.

The process of microflow-through emulsification and extraction was realized by an experimental arrangement with two syringe pumps connected with both inlet channels of the micromixers (see Fig. 1). Syringes of 10 mL volume were used. After emulsification, the process liquid was collected in a plastic tube for phase separation. This occurred simply by sedimentation. The tube connections, made of PTFE and PEEK with an inner diameter of 0.5 mm, between the micromixer and the separation tube possessed a length between 0.17 m and 1 m. The distribution of iodine between both phases was characterized by UV–vis spectral photometry (Specord 200, Analytik Jena).

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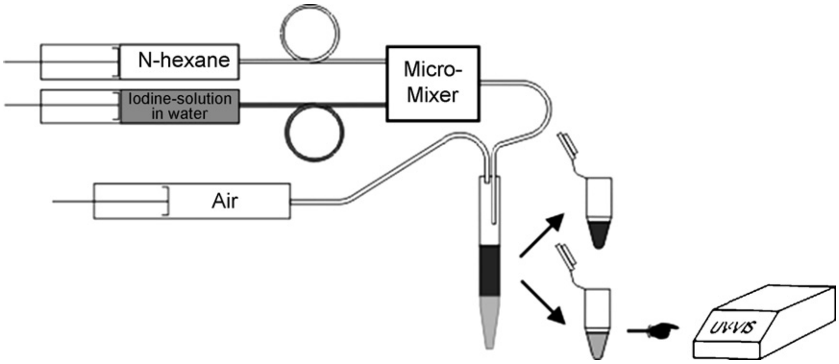

Fig. 1. Experimental setup with two syringe pumps, loading the tested micromixer. A smaller syringe filled with air was used to empty the plastic tube manually under controlled conditions.

The separation was done in a plastic tube with an open tip at the lower end. During collecting the emulsion and separation, the liquids were prevented to leak due to surface tension and depression in the tube. The heavier phase was guided in a cup for analyzing in the UV–vis spectrometer by using the air-filled syringe.

The spectral absorption characteristic of iodine is strongly influenced by solvents. In aqueous solutions, iodine has three absorption maxima at 290 nm, 356 nm and 455 nm. Solved in *n*-hexane, the number of absorption maxima is reduced to one at 527 nm. For determining the concentrations of iodine by absorption in both phases, the wavelength of 455 nm and 527 nm had been used. The calibration comprehends the range from 7.5 ppm-mass to 320 ppm-mass with a correlation factor of 0.998.

The emulsification and extraction behaviour of six different micromixing devices were studied:

(A) Multilamination mixer-type “Interdigital”:
  - Mikroglas Chemtech GmbH [8].
  - Material: Futuran® Glas.
  - Connection: 1/4 in. screw with ferrules.
  - This mixer consists of two times 30 channels, in which the two educts are routed. Each of this channel is 70 μm deep and 150 μm wide. The channels discharged in a broad exit channel alternating.

(B) Multi nozzle mixer-type SR:
  - Little Things Factory GmbH [7].
  - Material: Borosilikat Glas B33® (Schott™).
  - Connection: M5 screw.
  - The one fluid guiding channel of this mixer consist of 18 several dead end channel segments, which have as only exit five small nozzles. These nozzles are arranged serial and orthogonally to the channel segment to achieve additional a length retardation of the five partial fluids. The dimension of the channel is 800 μm versus 350–450 μm.

(C) Shear force mixer-type X:
  - Little Things Factory GmbH [9].
  - Material: Borosilikat Glas B33® (Schott™).
  - Connection: M5 screw.
  - The mixer geometry leads to a separation of the main flow into three to six smaller flows. The flows are rejoined in a cross junction by cross flow. The channel is 250 μm broad and 250–300 μm deep.

(D) Bar mixer-type ST:
  - Little Things Factory GmbH [9].
  - Material: Borosilikat Glas B33® (Schott™).
  - Connection: M5 screw.
  - The mixer is a one channel mixer with bars inside. These bars are arranged in a 45° angle to the flow direction and a 90° angle among there next neighbours. The channel dimensions are 1100 μm versus 1100 μm. The dimension of the bars is around 250–500 μm.

(E) Split and recombine mixer-type “Statmix-6”:
  - IPHT Jena [10].
  - Material: Glas/Silicon.
  - Connection: 10/32 in. flange.
  - The main flow, consisting of two fluid layers, of this one channel mixer is split of into two partial flows. After splitting, the arrangement of the flows is revolved to 90° parallel to the flow direction and rejoined perpendicular to the splitting direction. The main channel contains eight of these mixing steps for doubling the number of fluid layers.

(F) Tube-T-junction:
  - Upchurch Scientific.
  - Material: PEEK.
  - Connection: 1/4 in. screw with ferrules.
  - The inner diameter is 500 μm.

(G) Edged channel mixer (LTCC):
  - ZMN Ilmenau (centre of micro- and nanotechnologies) [11].
  - Material: LTCC.
  - Connection: 10/32 in. flange.
  - *L*ow *T*emperature *C*o-fired *C*eramic (LTCC) is a well-known material, which is used in microelectronics. The mixing channel is a sharped wiggly line channel with 90° edges. The dimension is 500 μm versus 500 μm.

The process efficiency was classified by the concentration of residual iodine in the aqueous solution after phase separation. The behaviour of all static mixers was investigated at 15–17 different flow rates in a range between 10 mL/h and 2450 mL/h.

3. Results and discussion

The efficiency of extraction is influenced by the quality of emulsification and by extraction time. In absence of emulsifier, the extraction time is mainly determined by existence of the highly dispersed state, that means the action of shear forces on the liquid and furthermore, by the residence time inside the mixing devices. Two limiting cases can be distinguished. At very low flow rates, the shear stress is low, so in consequence, the efficiency of emulsification will be low too. But a transport-controlled extraction needs long time, so if the flow rates are low, the time is sufficient for the time need of diffusion through the whole diameter of capillaries, microchannels or drops. In result the extraction yield can become very high, if the residence time is long enough. The second limiting case at the opposite is given at very high flow rates. In this case, the shear forces are high so the emulsification is intensively caused by the better drop splitting. In consequence short diffusion lengths in the different phases are generated by smaller drop diameter. In succession the domination of diffusion time became subordinated and the extraction yield is mainly determined by the shear force. At very high flow rates, the droplet size is not further reduced. So, the emulsification efficiency would move to a certain limit value.

The residual iodine concentration in water depends on the phase ratio. The influence of phase ratio on the final distribution of iodine was studied in experiments using the split and recombine mixer Statmix-6 (IPHT). The concentration of iodine in the aqueous solution at the outlet shows an increase with increasing ratio of water to hexane flow rate. The distribution of iodine between the aqueous phase and the hexane phase was nearly identically with the theoretical value at volume ratios of water to hexane smaller than 0.6 and at a flow rate of 60 mL/h (see Fig. 2). Faster increasing residual iodine concentrations in water were found at higher volume phase ratios indicating a decrease in the extraction efficiency. The result, using the Statmix-6 mixer is nearly the same like the best reachable residual concentration of the Nernst distribution. This was created due to a vortex mixer for cups. At phase ratios higher then 0.6 the result of the micromixer became worse than the optimum Nernst distribution.

The experimentally observed extraction efficiency does not only depend on the inlet volume flow ratio but also on the absolute flow rate. In all cases, we observe a very low residual iodine concentration in the aqueous phase at lowest flow rates. But, the residual iodine concentration increased with increasing flow rate in the lower flow rate range, particular in case of the simple T-junction emulsification (see Fig. 3, top curve). The residual iodine concentration remains high over a comparatively broad flow rate range (about 400 mL/h and 1500 mL/h) in the experiments with the T-junction. In this flow rate range the extraction efficiency is low. A certain decrease of residual iodine was found at high flow rates (above 1500 mL/h). It is to assume that the increase in residual iodine at low flow rates is caused by reduction of residence time at increasing flow rates, whereas the improvement of extraction at higher flow rates is due to the improvement of the emulsification.

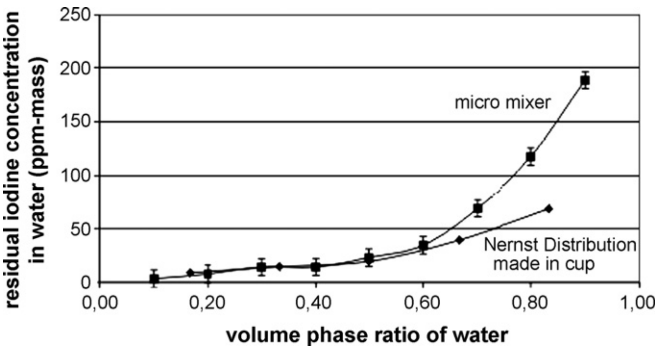

Fig. 2. Dependence of the residual iodine concentration in water on the volume phase ratio of water and n-hexane.

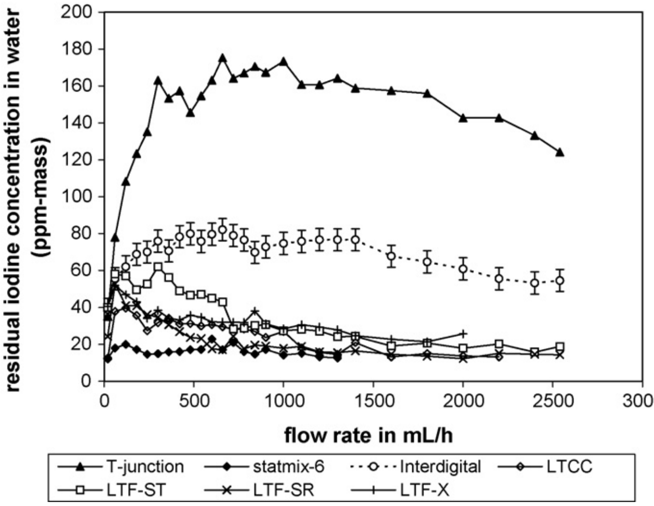

Fig. 3. Residual iodine concentration in dependence on the flow rate for different mixers.

In contrast to this, the result of the Statmix-6 (see Fig. 3 lowest curve) show much lower residual iodine and an independence on the flow rate over the whole investigated flow rate range. This behaviour can be interpreted by a high emulsification efficiency over the whole flow rate range.

A comparison between different micromixers and the T-junction is given by the extraction efficiency η over a larger flow rate range. The extraction efficiency is defined by

$$\eta = \frac{c_0 - c_{\text{res}}(j)}{c_0} \tag{1}$$

The values of η for a flow rate range between 10 mL/h and 2540 mL/h are given in Fig. 4. The diagram shows that all micromixers possess significantly better extraction behaviour than the simple T-junction, but they are distinguished considerably in their efficiency and flow rate dependence. The multilamination mixer shows a saturation value of extraction efficiency of about 0.75. This value is better than the value of the simple T-junction (about 0.55), but much lower than the values for the nozzle mixer and the split and recombine mixer with saturation values about 90 and 95%. In addition, the multilamination mixer shows a significant flow rate dependence at lower flow rates. This suggests an unsatisfied emulsification at lower

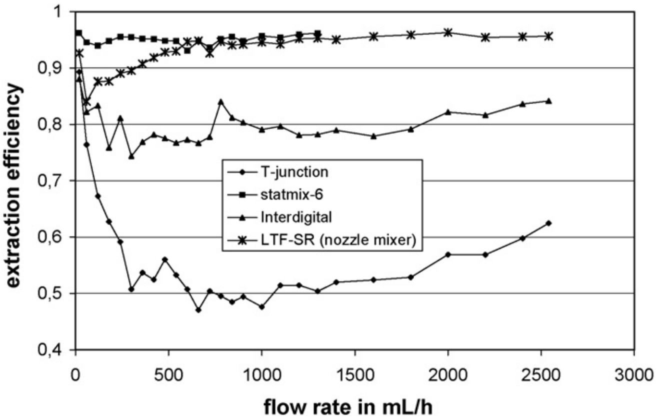

Fig. 4. Extraction efficiency in dependence on the flow rate of four selected mixers.

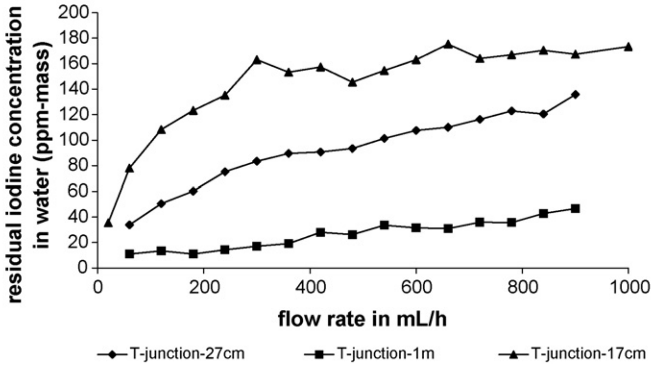

Fig. 5. Influence of the outlet tube length, acting as resident time variable on the residual iodine concentration.

flow rates and an additional residence time effect. In the case of nozzle mixer this effect is observable only for the lowest flow rate.

The influence of processes inside the connecting tube between the fluid outlet ports of the mixers and the tube for phase separation was studied in order to evaluate the role of diffusive transport and phase transfer processes after passage of mixers. It was found, that in case of lower emulsification efficiency (T-junction) the tube length is important for the obtained extraction yield. The concentration of residual iodine in water was drastically reduced by a longer outlet tube (see Fig. 5). The decrease of the residual concentration of iodine using longer outlet tubes indicates a continuous extraction during the flow through of the emulsion. So the emulsion is soonest separated in the 5 mL tube and not even in the outlet tube.

4. Conclusions

The investigation shows, that micromixers can be used for flow-through liquid/liquid extraction processes easily by using emulsification without surfactant. Furthermore, the extraction result can be used for the classification of microfluidic devices. Differences in extraction results and its dependence on flow rate can be interpreted as the influence of emulsification and residence time. So, this extraction process can be used for evaluation of micromixers. It was shown, that a multilamination mixer is more efficient than a simple T-junction, whereas a nozzle-type mixer (LTF) and a split and recombine mixer (Statmix-6, IPHT) shows the best results for emulsification and thus for extraction. It has further been shown, that the residence time plays an important role in case of less efficient emulsification. Larger internal volumes cause a bigger residence time and therefore a better extraction yield.

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