

Micro-Scale Liquid-Liquid Separation in a Plate-Type Coalescer

E. Kolehmainen,^a I. Turunen,^a

^a*Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, FIN-53851 Lappeenranta, Finland*

Abstract

The plate-type coalescer was constructed and tested for the continuous separation of immiscible liquids in micro-scale. Two plates formed the main structure of the coalescer. A flat and rectangular channel was situated between the plates. The material options for the plates were PTFE, stainless steel and glass which formed the contact surfaces for the fluids in the device. The liquid-liquid dispersion generated by the standard slit interdigital micromixer was fed in the coalescer where the coalescing of the droplets occurred. The coalescer had two outlets, one for the aqueous phase and the other for the organic phase enabling the continuous separation and withdrawal of separated phases. The performance of the coalescer was evaluated with respect to the channel height, flow rate, residence time and plate configuration. It was observed that in suitable conditions, the plate-type coalescer offered the efficient phase separation continuously under stable operation. The separation method utilizes the interaction between the fluids and channel surface. The flat channel, 100 μm or 200 μm , enabled the fluid-surface interaction. By using PTFE and stainless steel materials as channel surfaces and the total flow rate less than 180 ml/h, the stable operation and complete separation of aqueous and organic phases were possible. 180 ml/h corresponds superficial velocity of 3.3 cm/s in 100 μm height channel and 1.7 cm/s in 200 μm height channel. The phase separation in the coalescer took place considerably faster than conventionally in a decantation container.

Keywords: microprocess, liquid-liquid separation, extraction, coalescer

1. Introduction

Microprocess technology represents process intensification at its extreme eliminating the extra heat and mass transfer limitations in chemical processing. Several applications of microreactors have been presented for chemical reactions [1], but still microprocesses for separation purposes are rare. In micro-scale extraction processes, it is relatively easy to create dispersion by using micromixers, but separation of immiscible liquids may be a challenge.

Mass transport phenomena govern the efficiency of extraction process. Therefore, large interfacial area is desirable. The characteristics of generating liquid-liquid dispersion by a micromixer have been demonstrated by Haverkamp et al. [2].

Benz et al. [3] investigated the extraction performance by using a micromixer and settler set-up. They reported efficient mass transport in the micro-scale extraction process. Other extraction processes in micro-scale have been reviewed by Wojcik and Marr [4].

In the intensification of extraction processes, the efficient separation of liquid phases is an important objective. Wengeler et al. [5] presented a micro hydrocyclone for liquid-liquid separation. The separation method utilized difference in the densities of two phases. Okubo et al. [6] demonstrated successfully the performance of a simple microchannel device for coalescing of dispersed droplets. The coalescing method is based on the difference in wetting properties of surface materials. Aqueous and organic liquids have different contact angles on different surfaces. This feature leads to velocity difference between liquid phases in the coalescer and liquid droplets start to coalesce. In their equipment, the channel heights were only 5 μm and 12 μm and contact times were fraction of second, less than 0.12 s.

The process development of microprocesses is usually assumed to perform by number-up principle. This can mean large number of parallel processing units. In order to minimize manufacturing costs, it is desirable to keep the structure of the repeatable single unit as simple as possible. Therefore, a plate-type coalescer is an interesting option for liquid-liquid separation.

Clogging is an evident risk in microprocesses. In order to increase to feasibility of the microprocess, it is recommended to take under consideration what is the reasonable smallest dimension for the unit. A goal in this study was to construct the coalescer which enables reliable continuous phase separation and where channel dimensions are larger and contact times longer than in the device presented by Okubo et al. [6]. By using larger dimensions, the aim is to decrease pressure drops and the risk of clogging. In this study, the efficiency of the plate-type coalescers was tested for the continuous separation of immiscible liquid streams. The aim is also to use such a device later in the connection of an extraction process. The performance of the devices was studied by means of droplet size information and phase separation efficiency measurements.

2. Experimental study

2.1 Experimental set-up

The coalescing of the liquid droplets took place in a plate-type coalescer. The coalescer consisted of two plates. A rectangular flat channel was machined on the surface of the other plate and the channel was situated between the plates. The dimensions of the channel in the coalescer were as follows: width 15 mm, length 200 mm, height 100 μm and 200 μm . The used materials were stainless steel, PTFE and glass. The diaphragm pumps were used to feed the fluids through the micromixer into the coalescer. The liquid-liquid dispersion was generated in the standard slit interdigital micromixer manufactured by IMM. The width of the interdigitally configured channels in the micromixer was 40 μm . The coalescer contained two outlets, one for aqueous phase and the other for organic phase. The structure of the coalescer is rather simple, therefore manufacturing costs of such a device are not high. The schematic drawing and the photograph of the experimental system are depicted in Figure 1.

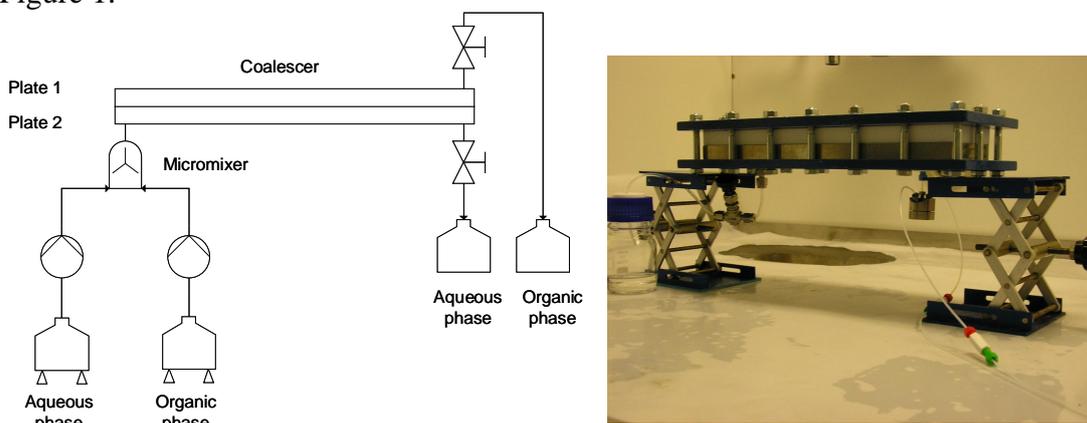


Figure 1. The schematic drawing of the experimental set-up and the photograph of the coalescer.

2.2 Experimental procedure and material properties

Experiments were conducted at temperature of 295 K. The used streams were water as aqueous phase and Shellsol D60 with tris(2-ethylhexyl)phosphate (TEHP) as organic phase. Tris(2-ethylhexyl)phosphate can be used as a solvent in liquid-liquid extractant or separation agent of metals. Tris(2-ethylhexyl)phosphate was added into Shellsol to form 10 weight-%, 30 weight-% and 50 weight-% organic solution. The summary of the liquid streams are presented in Table 1.

Table 1. The composition of the streams used in the experiments.

Aqueous phase	Organic phase
Water	Shellsol + 10 weight-% tris(2-ethylhexyl)phosphate
Water	Shellsol + 30 weight-% tris(2-ethylhexyl)phosphate
Water	Shellsol + 50 weight-% tris(2-ethylhexyl)phosphate

In the experiments, aqueous and organic phases were fed through the standard slit interdigital micromixer to form dispersion. After the micromixer, the dispersion was introduced immediately into the coalescer where coalescence of liquid droplets took place. Separated phases were then withdrawn continuously from the outlets. Two different channel heights, 100 μm and 200 μm , could be used by changing the plates.

Droplet size measurements were carried out by using a light microscope with an image processing software. Average droplet diameters and droplet size distributions were derived from analyzed data.

Contact angles were determined by means of the sessile drop method. A container was filled with Shellsol and TEHP solution. The solid surface was placed horizontally in the container under the fluid level. After that, a water droplet was injected on the solid surface. The angle between the baseline of the droplet and the tangent on the boundary of the fluids was measured optically. The definition of the contact angle is illustrated in Figure 2.

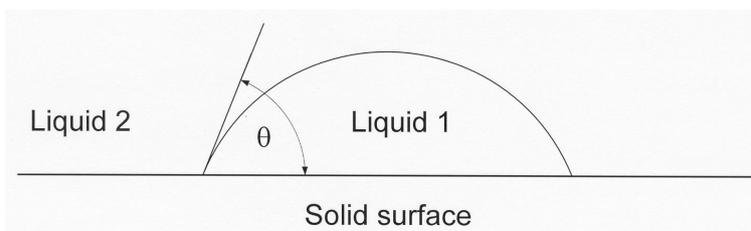


Figure 2. The definition of the contact angle θ . The system consists of two liquids and a solid surface.

Surface tensions and interfacial surface tensions for the fluids were measured by the DuNouy ring method and a tensiometer. In the method, certain force was needed to pull a horizontal ring from the liquid surface and the needed force was converted to the value of surface tension [7]. The interfacial tensions were measured for the interphase of water and Shellsol with TEHP. The measured properties are presented in Table 2.

Table 2. Surface tensions and interfacial tensions of the fluids at temperature of 295 K.

Fluid	Surface tension (mN/m)
Water	72
Shellsol + 10 weight-% tris(2-ethylhexyl)phosphate	26
Shellsol + 30 weight-% tris(2-ethylhexyl)phosphate	28
Shellsol + 50 weight-% tris(2-ethylhexyl)phosphate	29
Shellsol	26
tris(2-ethylhexyl)phosphate	30
<i>Interfacial tensions (mN/m) between water and Shellsol with tris(2-ethylhexyl)phosphate</i>	
Water/Shellsol + 10 weight-% tris(2-ethylhexyl)phosphate	42
Water/Shellsol + 30 weight-% tris(2-ethylhexyl)phosphate	47
Water/Shellsol + 50 weight-% tris(2-ethylhexyl)phosphate	46

3. Results and discussion

3.1 Droplet sizes

Droplet sizes and size distributions are important information when studying the performance of the coalescer. Droplet diameters in the feed streams before the coalescer were studied as a function of the total flow rate and fluid composition. The volumetric flow ratio of the aqueous phase to the organic phase was 1:1. It was observed that average droplet diameter decreased when the total flow rate was increased and also the content of the organic phase had an effect on the average droplet diameter. The higher was the TEHP content in the Shellsol-solvent the smaller was the average droplet diameter mainly. The dependence of droplet diameter on the total flow rate at different organic phase contents is presented in Figure 3.

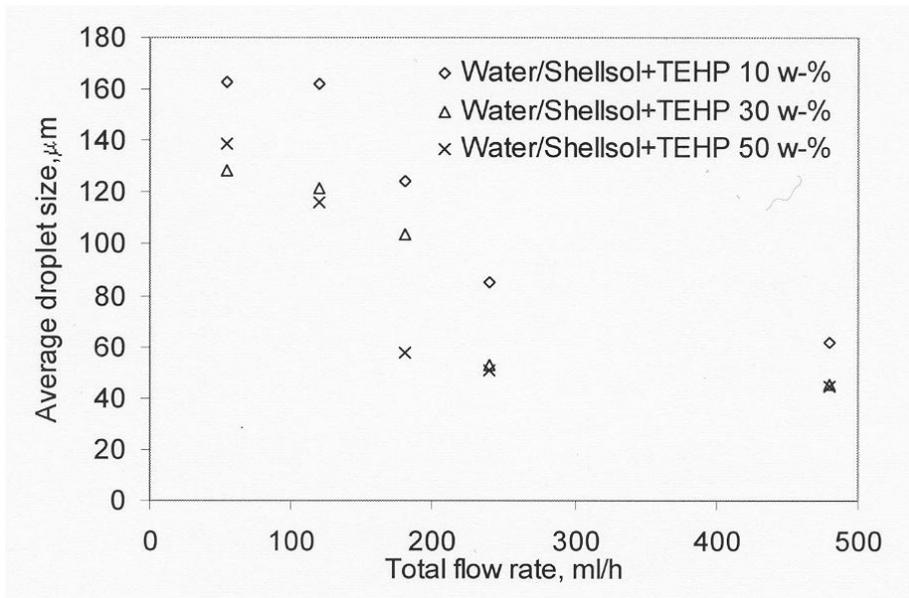


Figure 3. Average droplet diameters before the coalescer as a function of the total flow rates at different compositions of the organic phase. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

From the droplet diameter data, volumetric base cumulative droplet size distributions were derived. The cumulative droplet size distributions were calculated for each TEHP contents in Shellsol and the distributions are presented in Figures 4, 5 and 6. Also, from the distributions can be seen that droplet diameter decreases when flow rate is increased.

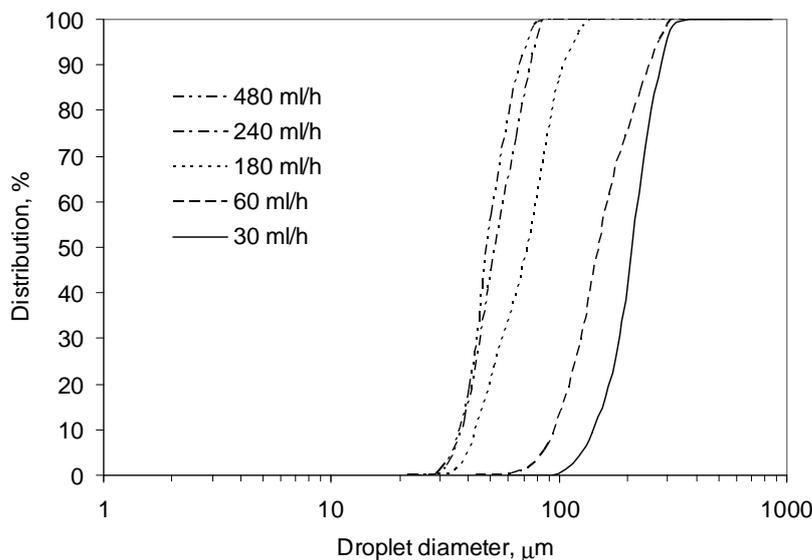


Figure 4. The volumetric cumulative droplet size distributions before the coalescer. The feed streams were water and Shellsol with 50 w-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

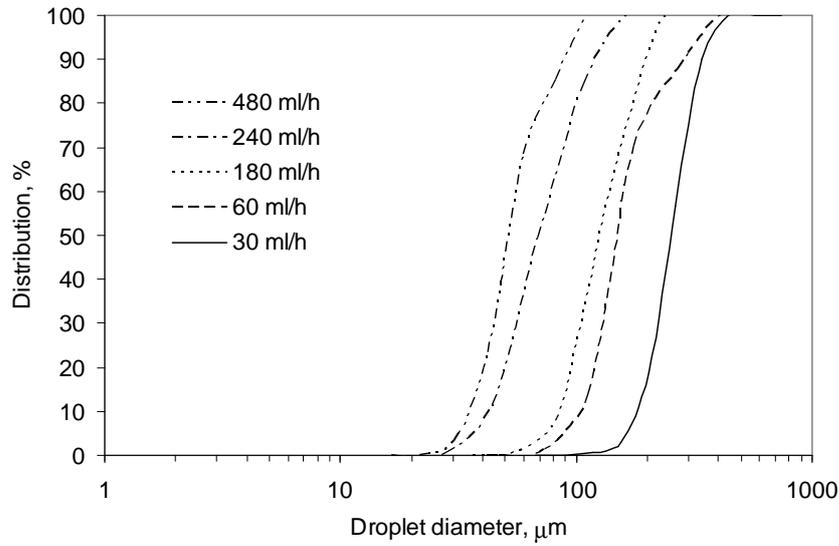


Figure 5. The volumetric cumulative droplet size distributions before the coalescer. The feed streams were water and Shellsol with 30 w-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

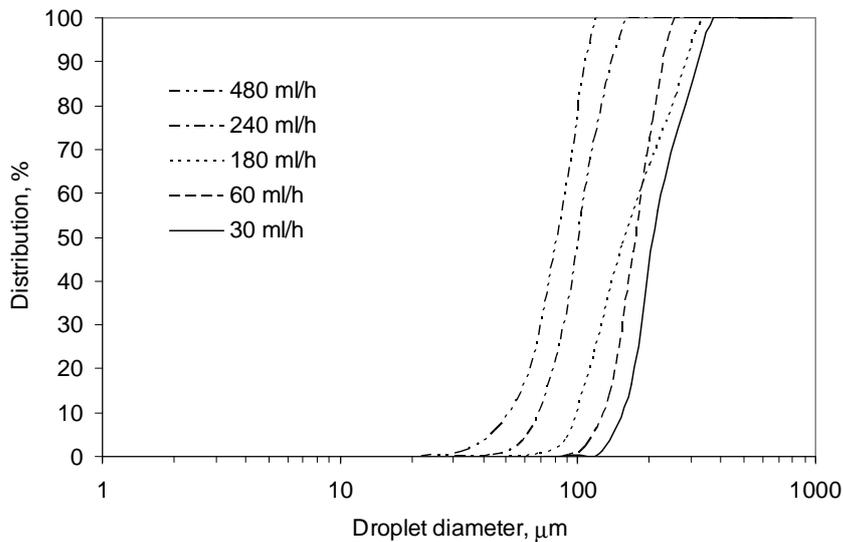


Figure 6. The volumetric cumulative droplet size distributions before the coalescer. The feed streams were water and Shellsol with 10 w-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

3.2 Contact angles

The contact angles were measured in order to illustrate the interaction between fluids and a solid surface. The contact angles correlate the ability of a fluid to wet the surface and spread on it. PTFE is highly hydrophobic surface and water can not wet the surface. Stainless steel and glass are more hydrophilic materials than PTFE and spreading of water is observable on these surfaces. The contact angles are presented in Table 3.

Table 3. The contact angles of water in Shellsol with TEHP on the solid surface.

Solid surface	Contact angle (°)
PTFE	160
Stainless steel	102
Glass	87

3.3 Efficiency of phase separation

Results showed that high separation efficiencies could be achieved in the plate-type coalescer. Separation efficiency is defined on the basis of the mass fractions of the component in the inlet and the outlet by Equation (1).

$$E = 100\% \frac{x_{i,INLET} - x_{i,OUTLET}}{x_{i,INLET}} \quad (1)$$

where $x_{i,INLET}$ and $x_{i,OUTLET}$ denote the mass fractions of the component in the inlet and the outlet of the coalescer, respectively. Water was the aqueous component and Shellsol with TEHP was the organic component. The volumetric flow ratio of the aqueous phase to the organic phase was 1:1. The highest flow rate used in the experiments was 480 ml/h corresponding superficial velocity of 8.9 cm/s in 100 μm height channel and 4.4 cm/s in 200 μm height channel. Separation efficiency was studied with respect to surface material of the plates, channel height, fluid composition, average fluid velocity and residence time. The results showed that complete separation could be achieved when the total flow rate was less than 180 ml/h. 180 ml/h corresponds superficial velocity of 3.3 cm/s in 100 μm height channel and 1.7 cm/s in 200 μm height channel. Figures 7, 8 and 9 show results from the experiments with stainless steel and PTFE plates.

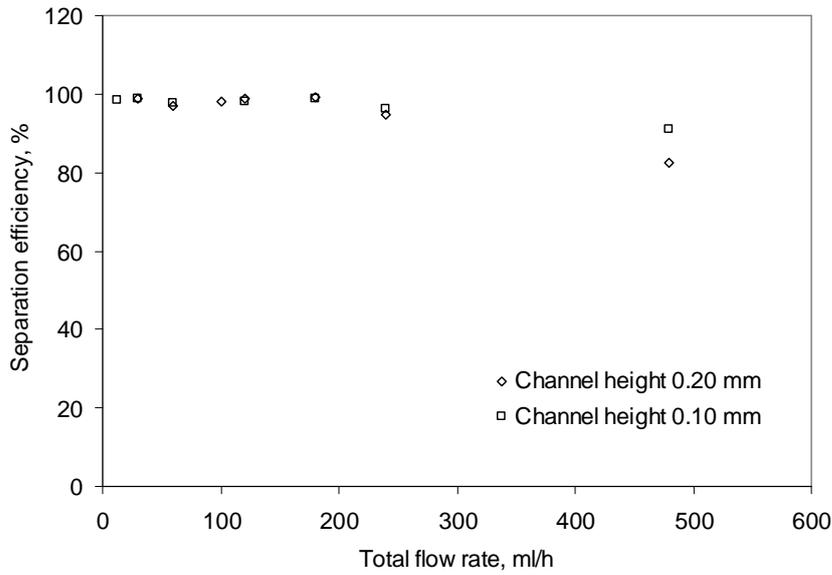


Figure 7. The separation efficiency as a function of the total flow rate at different channel heights. The plate materials were stainless steel and PTFE. The feed streams were water and Shellsol with 10 w-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

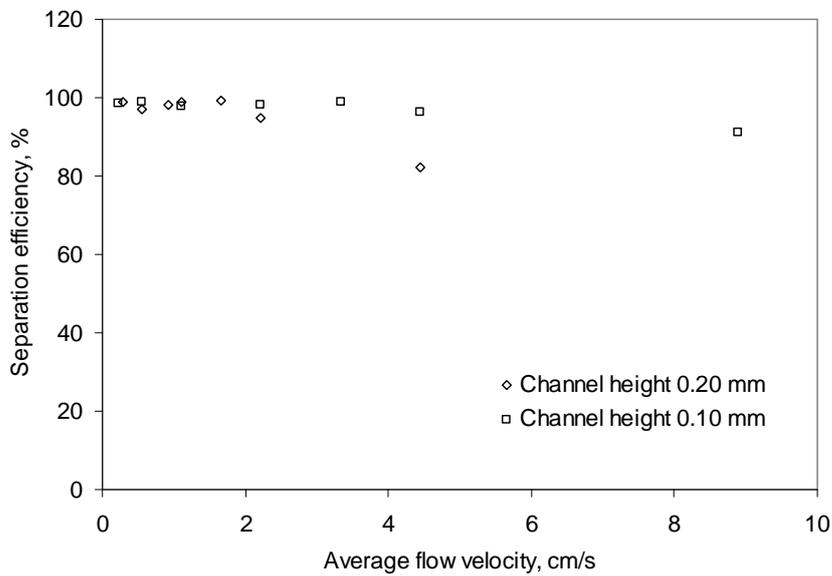


Figure 8. The separation efficiency as a function of the average flow velocity at different channel heights. The plate materials were stainless steel and PTFE. The feed streams were water and Shellsol with 10 w-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

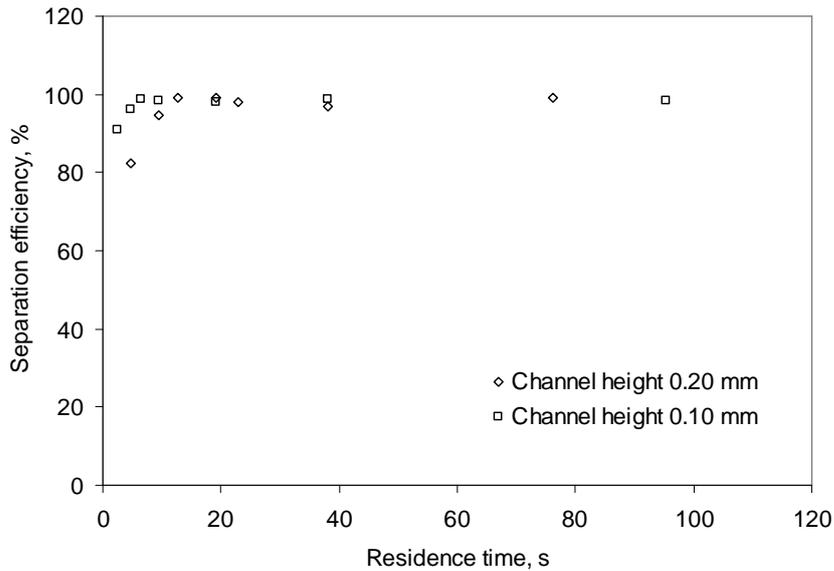


Figure 9. The separation efficiency as a function of the residence time at different channel heights. The plate materials were stainless steel and PTFE. The feed streams were water and Shellsol with 10 w-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

The complete separation could be achieved in the experiments where droplet diameters were larger in the inlet than the channel height of the coalescer. When the total flow rate was less than 100 ml/h, the average droplet diameter was then larger than 100 μm . In these cases, the coalescer with 100 μm channel height enabled the complete separation of phases. The dispersed droplets have the forced contact to the channel surface when the channel height is smaller than droplets. This feature enables the formation of velocity difference between the droplets in the channel and further promotes the phase separation essentially. The mechanism for droplet coalescence by means of the wall contact was described thoroughly by Okubo et al [6]. In addition, the results showed that complete phase separation could be achieved also in the cases where droplet diameters were smaller than channel height of the coalescer. Considering the cumulative droplet size distributions in Figures 4, 5 and 6, it can be noticed that the inlet contained smaller droplets than 200 μm , but still the separation efficiency was very high when the channel height was 200 μm and the total flow rate was less than 180 ml/h (superficial velocity 3.3 cm/s in 100 μm height channel and 1.7 cm/s in 200 μm height channel). The situation was similar also when 100 μm channel height was used and the inlet stream contained smaller droplets than 100 μm . This indicated that the dispersed droplets first collide with each other without forced contact to the channel surface and then coalesce into larger droplets. The larger and coalesced droplets have then the forced contact to the channel surface which causes the velocity difference between the droplets. In the channel, the smallest droplets reach the larger droplets which move slower due to forced surface contact. After reaching the larger droplets, smaller droplets coalesce into them. The aqueous phase tend to spread on the more hydrophilic surface whereas organic droplets spread on the

hydrophobic surface. The boundary between liquid phases formed and they separated into two layers in the coalescer before outlets. Both phases could be withdrawn from the coalescer via their own outlets continuously in steady-state.

The difference between channel heights 100 μm and 200 μm became observable when the separation efficiency was investigated as functions of the average flow velocity and the residence time of the liquid-liquid mixture in the coalescer. By short residence times and higher average flow velocities, the coalescer with 100 μm channel resulted in more efficient separation than the coalescer with 200 μm channel as illustrated in Figures 8 and 9. The content of the organic phase, thus the concentration of TEHP in Shellsol, had not significant influence on the separation efficiency.

The effect of the plate materials was also investigated. The configuration with PTFE-stainless steel resulted in the highest separation efficiency under steady-state operation. In the PTFE-stainless steel device, more hydrophilic stainless steel surface exists and water is able to wet it more easily. The behaviour of the PTFE-glass configuration was similar to PTFE-stainless steel system. Even if glass is more hydrophilic material than stainless steel, as presented in Table 3, no clear differences were observed in the operation between PTFE-stainless steel and PTFE-glass configurations. PTFE-PTFE configuration could not provide continuous steady-state phase separation. At the beginning of the device, some of the droplets were able to coalesce with each other, but later in the device the further coalescing was incomplete due to the poor wetting of PTFE surface with water. Water can neither wet the PTFE channel surface nor spread on it easily. The stable boundary between liquid phases was not able to form. Therefore, phase separation remained inefficient under steady-state operation with PTFE-PTFE plates. The horizontal plate arrangement was used in most of the experiments. Besides, experiments were carried out by installing the plates in the vertical position. The results did not show significant difference in separation efficiencies between horizontal and vertical positions. Thus, gravity effect can be neglected in this system.

It was also observed when flow rate exceeded the value 180 ml/h, turbidity started to exist in aqueous phase outlet of the coalescer. The turbidity was a consequence of the small organic droplets in the aqueous phase. For the droplets in the aqueous outlet, the droplet size measurements revealed that the average droplet diameter varied between 30 μm ...60 μm . The largest droplets and some of the smallest were able to coalesce and be separated while rest of the smallest droplets remained dispersed in the aqueous phase causing the turbidity.

In order to evaluate the performance of the plate-type coalescer, phase separation tests were also carried out by decantation in a container. The liquid-liquid dispersion produced by the micromixer was introduced into the container and let to separate freely by decantation. The average droplet diameter at the beginning of the decantation was 60 μm ...120 μm . The time required for the phase separation and disappearance of turbidity by decantation was measured. As can be seen from Table

4, the required time for phase separation by decantation is more than 30 min. The plate-type coalescer was able to decrease the separation time remarkably having residence time for complete separation even less than 20 s.

Table 4. Decantation times for the phase separation in the container.

Composition of the dispersion	Decantation time (min)
Water/Shellsol + 10 weight-% tris(2-ethylhexyl)phosphate	>30
Water/Shellsol + 30 weight-% tris(2-ethylhexyl)phosphate	>30
Water/Shellsol + 50 weight-% tris(2-ethylhexyl)phosphate	>40

3.4 Discussion on scale-up

The structure of the plate-type coalescer is rather simple. This is a clear benefit if scale-up is considered. In microprocess technology, the process development should be usually performed by number-up concept. This means repetition of the miniaturized processing units. However, this approach is very challenging because some new problems appear such as fluid distribution problems. If number-up concept is considered, economical issues have to be taken into account carefully. If the structure of a single process unit is complicated, then the manufacturing costs will also be high. This results in increased investment and installation costs on the plant level. Therefore, it is essential to explore simple and/or efficient structures for microstructured units in order to make microprocesses a feasible option in chemical engineering. In this study, a simple device for liquid-liquid separation was presented. The channel dimensions of the coalescer were on reasonable level, no clogging was observed during the experimental work. By using the flat rectangular channel shape, the high increase in number of channels can likely be avoided during scale-up and number-up instead of using e.g. square channels. In addition, fewer numbers of the channels in microstructured device decreases manufacturing costs and facilitates the achievement of uniform flow distribution between the channels. The structure of the presented device is not complicated and therefore the manufacturing of such a device is not expensive.

4. Conclusions

The applicability of a plate-type coalescer as a micro-scale liquid-liquid separator was tested in this study. The coalescer consisted of two parallel plates which were the contact surfaces for the immiscible fluids. Between the plates, a rectangular and flat channel was manufactured. The height of the channel was either 100 μm or 200 μm , the width and length were 15 mm and 200 mm, respectively. The plate materials were PTFE, stainless steel and glass. The results showed that the simple coalescer could perform the complete phase separation when suitable conditions and plate configuration were chosen. The highest separation efficiency with stable operation was achieved by using PTFE-stainless steel plates. Reducing of the channel height from 200 μm to 100 μm had a favourable effect on separation efficiency at higher flow rates. However, the coalescers were able to coalesce the droplets whose diameter before the coalescer was less than the channel height. This behaviour was an indication that the small droplets first collide with each other to form larger droplets and then the enlarged droplets have the interaction with the surfaces of the coalescer. The interaction between fluids and the surfaces of the coalescer promotes the liquid-liquid separation further. The liquid-liquid separation occurred considerably faster in the plate-type coalescer than in a decantation container. The results enable the intensification of the liquid-liquid separation process. The development of simple and cheap, but still efficient devices for microprocess technology is fundamental because in scale-up of such technology the parallelization can not be likely avoided. If the manufacturing and installation costs of a repeatable unit in scale-up, or in number-up, can be kept on the reasonable level, microstructured processes will be feasible also economically.

Nomenclature

E	Separation efficiency (%)
x_i	Mass fraction of a component (-)

Greek symbols

θ	Contact angle ($^\circ$)
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Subscripts

i	component i
INLET	inlet stream
OUTLET	outlet stream

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References

- [1] V. Hessel, S. Hardt, H. Löwe, *Chemical Micro Process Engineering, Fundamentals, Modelling and Reactions*, Wiley-VCH, Weinheim, 2004.
- [2] V. Haverkamp, W. Ehrfeld, K. Gebauer, V. Hessel, H. Löwe, T. Richter, C. Wille, The potential of micromixers for contacting disperse liquid phases, *Fresenius J. Anal. Chem.*, 364(1999) 617-624.
- [3] K. Benz, K.-P. Jäckel, K.-J. Regenauer, J. Schiewe, K. Drese, W. Ehrfeld, V. Hessel, H. Löwe, Utilization of micromixers for extraction processes, *Chem. Eng. Technol.*, 24(2001) 11-17.
- [4] A. Wojcik, R. Marr, Mikroverfahrenstechnische Prinzipien in der Flüssig/Flüssig-Extraktion, *Chem. Ing. Tech.*, 77(2005) 653-668.
- [5] R. Wengeler, H. Nirschl, F. Herbstritt, W. Ehrfeld, Studies on a micro hydrocyclone for liquid-liquid separation, *Filtration*, 6(1) (2006) 21-26.
- [6] Y. Okubo, M. Toma, H. Ueda, T. Maki, K. Mae, Microchannel devices for the coalescence of dispersed droplets produced for use in rapid extraction processes, *Chem. Eng. J.*, 101(2004) 39-48.
- [7] D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth-Heinemann Ltd, Oxford, 3rd edn., 1991.