

Optimization of liquid-liquid extraction and multiphase flow in microstructured reactors

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Abstract

Industrial scale liquid-liquid extraction is carried out in mixer-settler units or extraction columns. As a result of large size of industrial extractors, mixing performance is not very effective and as a consequence extraction efficiency decreases. From miniaturization of the mixing space towards channels in the range of some microns a significant improvement in overall extraction efficiency is expected. Mass transfer inside microchannels is limited in most cases to diffusion because of the laminar flow pattern. Due to diffusion distances in microchannels in the range of 0.5 and 1000 microns mass transfer can be kept at optimum conditions. In course of this project the systems n-hexane/acetone/water was investigated. Extraction efficiency was determined for different operating conditions by varying the process parameters flow rate, temperature and phase ratio. The mixing step was carried out in different microreactors, which differ in their mixing principle, material and total flow rate. The aqueous phase and the solvent phase were fed to the microreactors co-currently. Phase separation was carried out in a gravity mini settler. Extraction efficiency of the micromixers was determined by recording both, overall mass transfer as well as mass transfer in the settler. By application of microreactors using a so called "splitting and recombination" mixing principle, overall extraction efficiency between 80 and 99 % was achievable.

1 Introduction

Liquid-liquid extraction is a common separation process taking advantage of the different solubility of solutes (product component or impurity) between carrier phase (feed) and a solvent phase which is immiscible with the carrier phase. The solute is expected to dissolve more readily and becomes more concentrated in the solvent phase. Any liquid-liquid separation process consists of at least one mixing step and a separation step. The mixing step provides intensive phase contact between feed and solvent in order to obtain a maximum of mass transfer. After mixing, the solvent (extract phase) has to be separated from the raffinate phase in a phase separator (settler).

Industrial scale liquid-liquid extraction is carried out in co-current, cross-current or counter-current mode in mixer-settler units or different types of extraction columns. As a result of large size of industrial extractors, mixing and as a consequence extraction efficiencies are of limited performance. From miniaturization of the mixing space towards channels in the range of some microns a significant improvement in overall extraction efficiency is expected.

Two different modes of micromixing immiscible liquids can be applied. The first mode follows the dispersive mixing principle, which is characterized by formation of droplets of the dispersed phase in the continuous phase. The dispersive type of micromixers tends to form emulsions. In this case micromixing has two main benefits for the mixing step in extraction processes. Both effects are caused by a very small drop size. Smaller drops increase the surface area and as a consequence mass transfer. Smaller drops shorten diffusion distances additionally.

The second mode is characterized by a non-dispersive principle. In latter application the both phases form a film inside the microchannel. Laminar flow of the liquid layers is a boundary for non-dispersive mixing. In the ongoing research program a T-type micromixer from mikroglass chemtech GmbH was investigated. The mixer consists of 20 parallel microchannels with a rectangular cross-section of 700 μm x 200 μm . At maximum total flow rate of 20 ml/min the Reynolds-number Re according to *equation 1* of less than 2.38 was calculated.

$$Re = \frac{w \cdot l}{\nu} = 2.38 \quad (1)$$

Re [-]	Reynolds-number
w [m/s]	velocity
l [m]	characteristic length
ν [m ² /s]	kinematic viscosity

Accordingly mass transfer in microchannels is limited to diffusion.

Following the general definition of mass transfer (*equation 2*), the flux increases with increasing mass transfer coefficient. Mass transfer coefficient is by definition calculated from the diffusion coefficient D and the boundary layer thickness δ as shown in *equation 3*.

$$\dot{N} = k \cdot A \cdot \Delta c \quad (2)$$

\dot{N} [mol/s]	flux
k [m/s]	mass transfer coefficient

$A [m^2]$ *Interfacial area*
 $\Delta c [mol/m^3]$ *concentration difference*

$$k = \frac{D}{\delta} \quad (3)$$

$D [m^2/s]$ *Diffusion coefficient*
 $\delta [m]$ *boundary layer thickness*

In microchannels the boundary layer thickness and therefore the diffusion distance is very small. Due to diffusion distances in microchannels in the range of approximately 0.5 and 1000 microns mass transfer can be kept at optimum conditions [1]. These considerations are valid for micromixers, which are characterized by the mixing principle of alternating multilamination of fluid layers. The mass transfer area will increase by increasing the number of channels.

As demonstrated with the system toluene/water/acetone [2] residence time in the order of milliseconds suffices the necessity to reach thermodynamic equilibrium. Backmixing does not affect microextraction negatively.

2 Experimental Methods and Analyses

2.1 Chemicals

Low level impurities already can have noticeable effects on both mass transfer and equilibrium. N-hexane and acetone of p.a. quality were bought from Fluka. Distilled water was prepared on site. All chemicals were used without any further purification.

2.2 Apparatus and procedure

In this project mass transfer of acetone from n-hexane into water was investigated. Extraction efficiency was determined for different operating conditions by varying the process parameters flow rate, temperature and phase ratio of feed and solvent. The mixing step of the extraction process was carried out in different micromixers and microreactors respectively to compare different mixing principles. The aqueous phase and n-hexane were fed into the microreactor/micromixer co-currently. Extraction efficiency of the micromixers was determined by recording both, overall mass transfer as well as mass transfer in the settler. To determine the effect of pump pulsation different pumps were tested. Phase separation was carried out in a cylindrical gravity settler made of glass. *Table 1* shows a summary of the mass transfer tests with different microreactors and pumps. *Table 2* summarizes the type of microreactors and the technical specification [1], [3], [4].

Extraction	Pumps	Parameter	Microreactor					
			SIMM V2	CPMM R840	CPMM R1200	StarLam	mgt Design T-Mixer	mgt Triangular
n-hexane/acetone/water	HNP	Flow Rate	v	v	v	v	v	v
		Phase Ratio	v	v	v	v	v	v
		Temperature					v	
	Ismatec	Flow Rate	v				v	v
		Phase Ratio	v				v	v
		Temperature					v	

Table 1: Microextraction tests

Microdevice	V_{max} [ml/min]	Internal microstructure	Manufacturer
mgt Design T-Mixer	20	700 μ m x 200 μ m	mikroglas chemtec GmbH
mgt Triangular	17	50 μ m x 150 μ m (channel dimensions of fluid feed)	mikroglas chemtec GmbH
SIMM V2	33	Inlay silver/copper 40 μ m x 300 μ m	IMM GmbH
CPMM R840	1000	840 μ m x 840 μ m (mixer inlet cross section; 8 mixing stages)	IMM GmbH
CPMM R1200	1660	1200 μ m x 1200 μ m (mixer inlet cross section; 8 mixing stages)	IMM GmbH
StarLam	5000	50 μ m	IMM GmbH

Table 2: List of the microreactors plus specification

The extraction experiments were carried out in an apparatus arrangement according to *Figure 1*. Between pump (P1) and microreactor the feed stream is directed over a sensor-block (Bürkert), which is used to measure temperature and pressure with an accuracy of ± 0.1 K and ± 0.01 MPa respectively. A pressure control valve and a check valve are integrated in the sensor block. A second line of the same setup is installed to feed the solvent (distilled water) into the microreactor. Inside the microreactor the immiscible liquids are mixed. After passing a temperature sensor and a control valve the mixed phase is discharged into a gravity settler. The whole microreactor is equipped with a temperature control loop. Constant temperature of several feed liquids in the storage tanks and the gravity settler is provided by further temperature control loops.

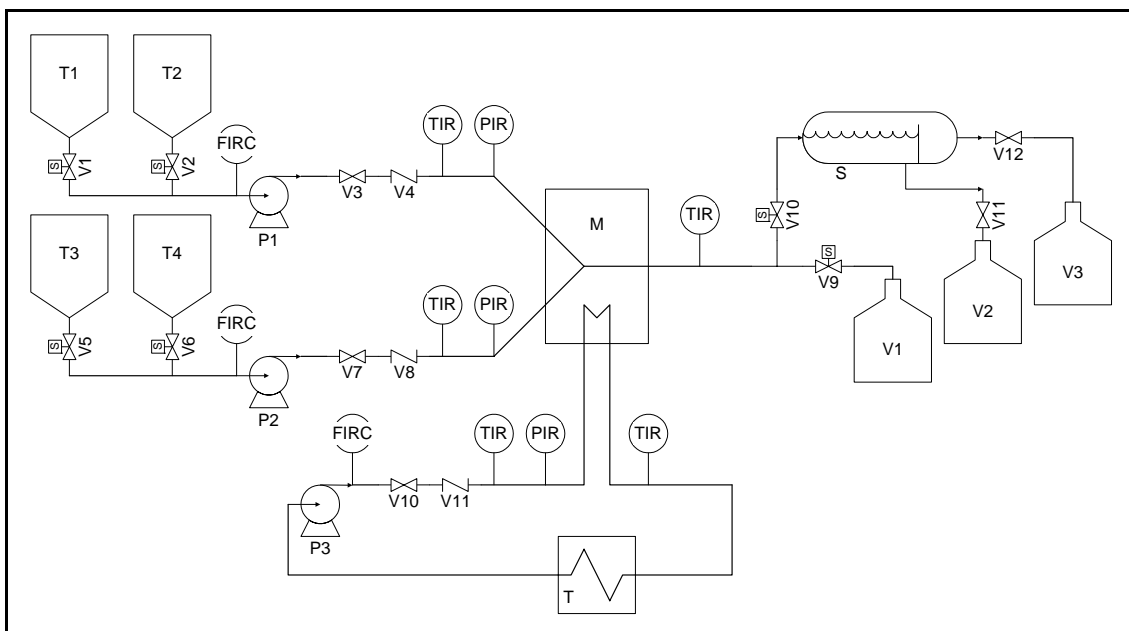


Figure 1: Experimental setup of the microplant: (T1) Feed storage tank, (T3) Solvent storage tank, (T3, T4) Purge tanks, (P1) Feed pump, (P2) Solvent pump, (P3) Heat carrier pump, (T) Cryostat, (M) Microreactor, (S) Settler, (V1) Waste vessel,

(V2) Raffinate vessel, (V3) Extract vessel, (V1, V2, V5, V6, V9, V10) Solenoid valves, (V3, V7, V10) Pressure control valves, (V4, V8, V11) Check valves, (V11, V12) Valves

Two pumps of different operating principle the piston pump Ismatec, Type Reglo-CPF digital and the toothed wheel pump HNP, Type mZR 4605, and therefore different pulsation rate, was tested. The piston pumps were used for providing low total flow rate of the liquids of 4 to 24 g/min. At high flow rate of 24 to 380 g/min gear pumps were used.

The mass flow rate of the hexane feed and the aqueous solvent were recorded continuously. For this purpose each storage tank was placed on a balance (Kern) with integrated RS-232c interface. The recorded mass data were processed in the control software LabView7, National Instruments.

2.3 Analysis

The acetone concentration of the feed, the extract phase and the raffinate phase was determined with density probe (Anton Paar, type DMA45) under temperature control of the sample. The temperature of the samples was kept constant at 293.15 K. Different portions of acetone were dissolved in n-hexane and water respectively to provide mixtures for calibration of the density probe in a concentration range of 0 to 5 Vol-%.

3 Results and Discussion

Extraction of acetone from n-hexane into the solvent water in microreactors according to the specification of *Table 2* was investigated in three series of experiments. In the first series the total flow rate was varied, in the second series the phase ratio of feed and solvent was varied and the temperature was varied in the third series.

From experimental results the mass balance was calculated. The composition of the extract phase and the raffinate phase was then compared with the operation diagram based on McCabe Thiele projection. Finally the extraction efficiency was calculated from the ratio of the experimentally obtained process data and the theoretical equilibrium composition data according to *equation 4*.

$$Eff = \frac{c_E}{c_{E, equ}} \cdot 100 \quad (4)$$

Eff [%]	Extraction efficiency
c_E [-]	Concentration of acetone in the extract phase
$c_{E, equ}$ [-]	Concentration of acetone in the extract phase at equilibrium

To determine the contribution of the settler to the overall extraction efficiency the experiments were repeated in the same experimental setup except the microreactor which was substituted with a T-type mixer.

Comparison of the microreactors was based on grouping the range of the total flow rate. For low total flow rate of 4 to 24 g/min the *SIMM V2 (Slit Interdigital Micro Mixer Version 2)*, *mgt Design T-Mixer (Mikroglastechnik Microreactor Design T-Mixer)* and *mgt Triangular (Mikroglastechnik Triangular Interdigital Micro Mixer)* microreactors were compared, and for higher total flow rate of 24 to 380 g/min the *CPMM R840 (Caterpillar Split-Recombine Micro Mixer R840)*, *CPMM R1200 (Caterpillar Split-Recombine Micro Mixer R1200)* and *StarLam (Star Laminator)* microreactors were compared.

3.1 Extraction at a constant phase ratio and increasing total flow rate

In the first series of experiments, the influence of the total flow rate on extraction efficiency was investigated. All experiments were carried out at constant temperature of 293 K.

3.1.1 Total flow rate of 4 to 24 g/min

The total flow rate in this series of experiments was increased from 4 to 24 g/min, while the phase ratio of hexane feed and aqueous solvent was held constant at 1. *Table 3* shows the flow conditions of the experiments.

Feed [g/min]	Solvent [g/min]	Total flow rate [g/min]
2	2	4
4	4	8
6	6	12
8	8	16
10	10	20
12	12	24

Table 3: Flow conditions of the experiments for total flow rate of 4 to 24 g/min

The results of the overall extraction efficiency at low total flow rate are shown in *Figure 2*. The *SIMM V2* microreactor has an average efficiency of 73 % over the whole range of flow rate. The results obtained in experiments with the *mgt Design T-Mixer* indicate a slight decrease of efficiency from 70 to 55% with increasing total flow rate, whereas only a relative low efficiency between 53 and 48% was recorded from experiments with the *mgt Triangular* microreactor.

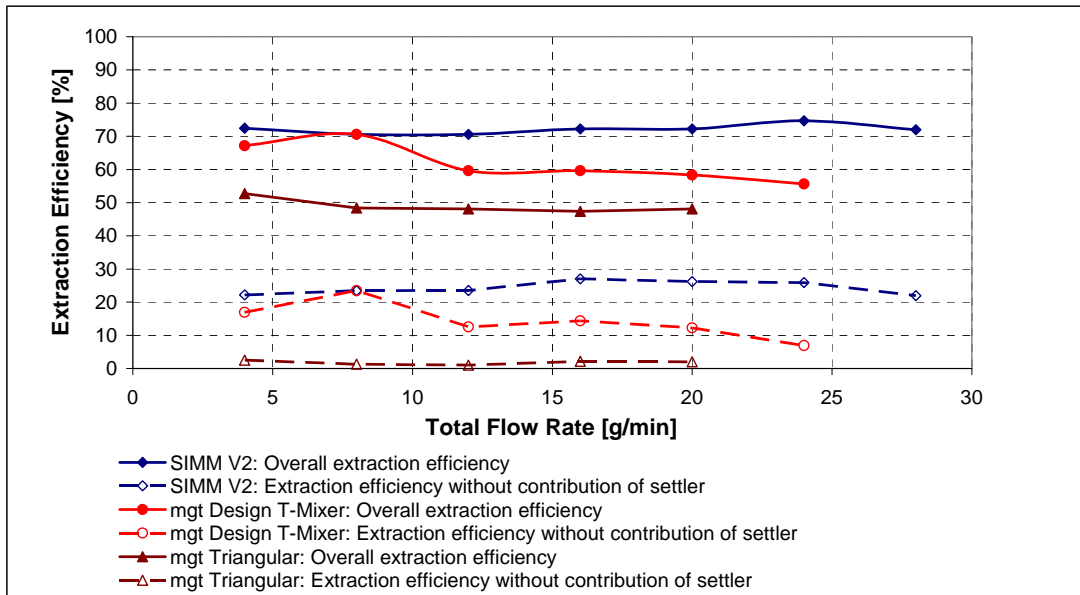


Figure 2: Total flow rate dependence of the overall extraction efficiency and extraction efficiency without contribution of the settler (broken lines) at constant phase ratio of feed and solvent of 1 for the *SIMM V2*, *mgt Design T-Mixer* and *mgt Triangular* microreactor; T=293 K

3.1.2 Total flow rate of 24 to 380 g/min

At high total flow rate of 24 to 380 g/min and constant phase ratio of feed and solvent of 1, the test program shown in *Table 4* was worked out.

Feed [g/min]	Solvent [g/min]	Total flow rate [g/min]
12	12	24
16	16	32
32	32	64
64	64	128
128	128	256
190	190	380

Table 4: Flow conditions of the experiments at a total flow rate of 24 to 380 g/min

As shown in *Figure 3*, the investigated microreactors performed very well. Extraction efficiency of 80 to >99% was observed. The performance of the *CPMM R840* reactor enabled extraction efficiency close to equilibrium at a total flow rate of 150 g/min. Extraction efficiency obtained with the *CPMM R1200* microreactor was comparably high for elevated flow rate of 250 g/min. The *StarLam* microreactor performed constantly well on a very high level of 90% over the whole flow rate.

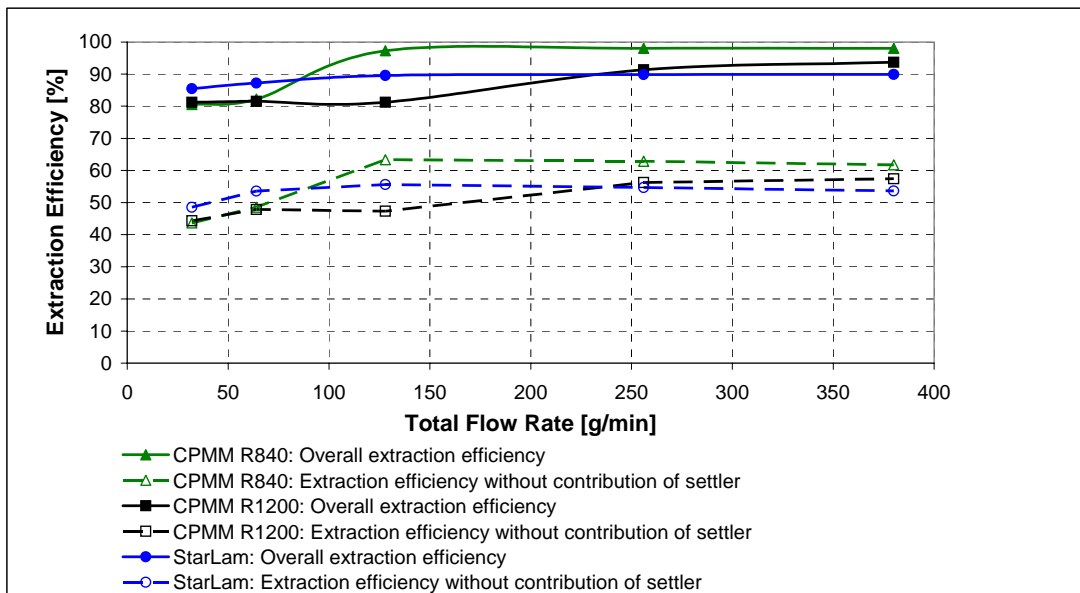


Figure 3: Total flow rate dependence of the overall extraction efficiency and the extraction efficiency without contribution of the settler (broken lines) respectively at constant phase ratio of feed and solvent of 1 for the *CPMM R840*, *CPMM R1200* and *StarLam* microreactor; $T=293\text{ K}$

3.1.3 Contribution of the settler

For consideration of the contribution of the settler all experiments were repeated in the same experimental setup except the microreactors. Instead of microreactors a conventional T-type mixer was installed.

The dotted lines in *Figure 2* and *Figure 3* show the extraction efficiency without contribution of the settler. Comparison of the results for low total flow rate, shown in *Figure 2*, with the results obtained for high total flow rate, recorded in *Figure 3*, shows an unexpected effect of the performance of equipment.

3.2 Extraction at a constant total flow rate and varying phase ratio

The effect of the phase ratio of feed and solvent on the overall extraction efficiency was determined in the second series of experiments. All experiments were carried out at a constant temperature of 293 K.

3.2.1 Low total flow rate

The efficiency dependence on the phase ratio was analyzed at a constant total flow rate of 22 g/min. The investigated range of operation is summarized in *Table 5*.

Feed [g/min]	Solvent [g/min]	Total flow rate [g/min]
2	20	22
4	18	22
6	16	22
8	14	22
10	12	22
12	10	22
14	8	22
16	6	22
18	4	22
20	2	22

Table 5: Flow conditions for the series of experiments at a constant total flow rate of 22 g/min

As shown in *Figure 4*, the same tendency for both microreactors was observed. After an increase at low phase ratio extraction efficiency passed a maximum to finally drop again when exceeding the optimum range of the phase ratio.

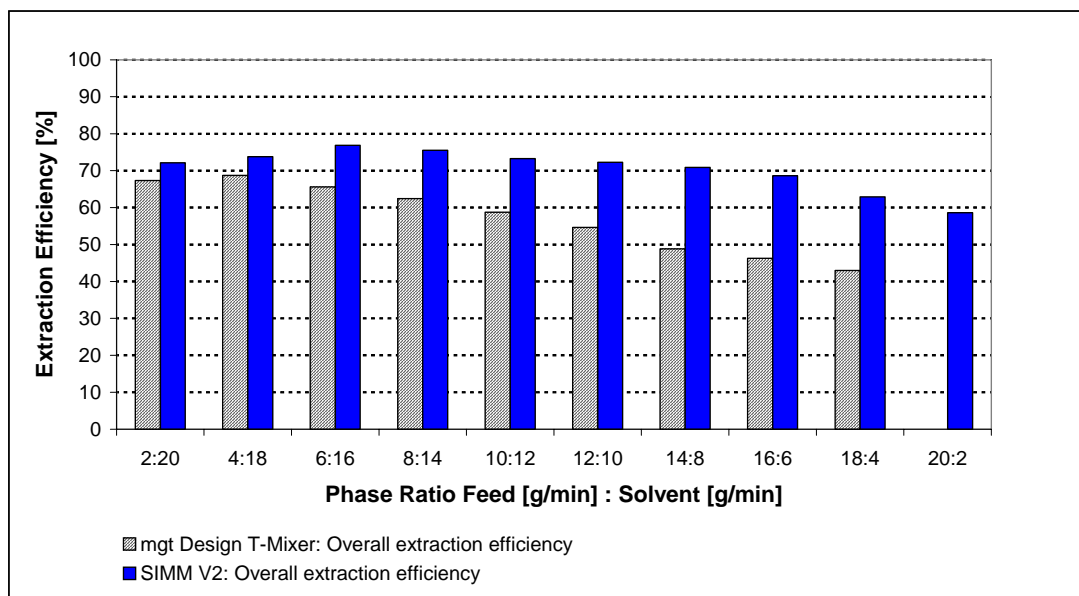


Figure 4: Dependence of the overall extraction efficiency for varying phase ratio of feed and solvent at a constant total flow rate of 22 g/min for the *SIMM V2* and *mgt Design T.Mixer* microreactor; T=293 K

3.2.2 High total flow rate

The range of operation investigated is listed in *Table 6*.

Feed [g/min]	Solvent [g/min]	Total flow rate [g/min]
20	160	180
40	140	180
60	120	180
80	100	180
100	80	180
120	60	180
140	40	180
160	20	180

Table 6: Flow conditions for the series of experiments at a constant total flow rate of 180 g/min

Efficiency dependence on phase ratio is again similar for all microreactors. As shown in *Figure 5* extraction efficiency again passes a maximum.

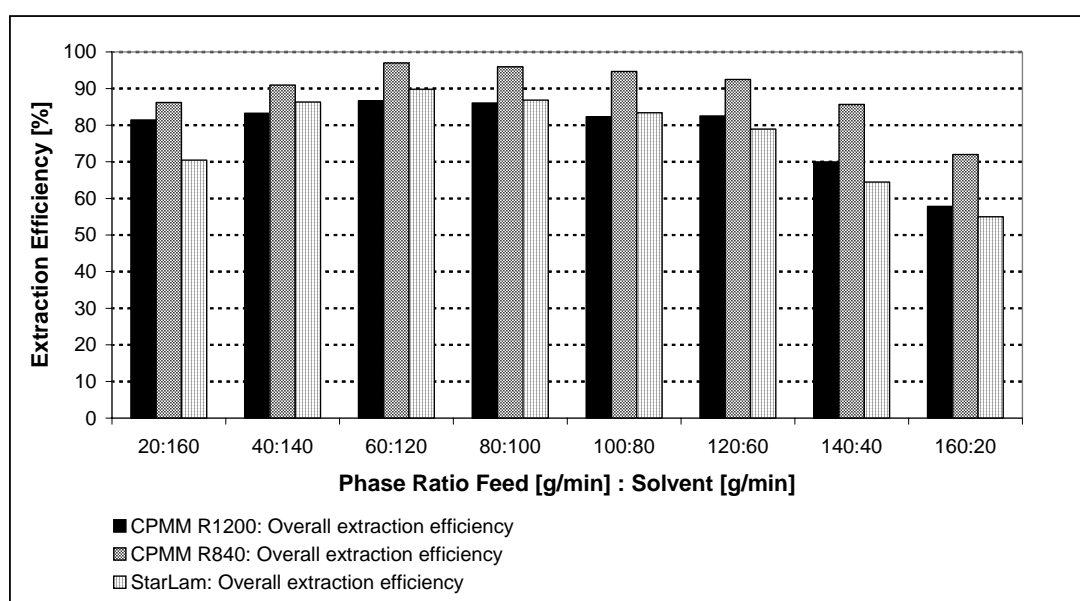


Figure 5: Dependence of the overall extraction efficiency for varying phase ratio of feed and solvent at a constant total flow rate of 180 g/min for the *CPMM R840*, *CPMM R1200* and *StarLam* microreactor; $T=293$ K

3.3 Effect of the temperature

Because of the high vapor pressure of hexane and acetone temperature of operation was limited to operation below $T = 300$ K. The results do not permit any correlation with the type of microreactor. Temperature dependence of operation efficiency will have to be investigated with a different test system.

4 Summary

The best results were obtained with the *CPMM* and *StarLam* micromixer with a net extraction efficiency of 60%. Pressure drop was 1.5 bar at the highest flow rate (380 g/min) by using the *CPMM*, whereas only 0.5 bar pressure drop was recorded from investigation of the *StarLam* microreactor. It can be concluded from the results of investigation that the mixing principle of these microreactors performs best in liquid-liquid extraction applications.

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