A Ceramic Microfiltration Tube Membrane Dispersion Extractor

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Although the phase-free membrane extraction process has shown many advantages over the traditional extraction, the process is still at the experimental stage. On the other hand, in a new extractor a microfiltration membrane is used as a dispersion medium. The mass-transfer performance of the new extractor was tested with 30% TBP (in kerosene)–nitric acid–H_2O as an experimental system. The overall mass-transfer coefficient and the equipment efficiency were calculated with the concentrations of the inlet and outlet. The extractor was designed and constructed with two special inner elements for improving the performance further. The effects of the transmembrane pressure, the continuous-phase flow rate, and the geometric parameters of the inner elements on the mass-transfer performance, as well as on the flux of the dispersion phase, are discussed. The experimental results showed that very higher efficiency was reached. The inner elements could improve the mass-transfer performance greatly by changing the two-phase contact status. The results suggested that the mass-transfer process could be completed quickly while the drop size was in the range of micrometers. In addition, the flux of the dispersed phase was mainly influenced by the transmembrane pressure, not by the equipment structures, inner elements, and the continuous-phase flow rate. The new extractor can be operated with very higher efficiency and higher flux, and the efficiency can be predicted with a cubic polynomial. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 382–387, 2004
Keywords: extractor, microfiltration tube membrane, micromixing, mass transfer

Introduction

Liquid–liquid extraction is one of the most important unit operations in chemical technology. Searching for highly effective extractors is an appealing job for many researchers in this field. The phase-free extraction process—membrane extraction as a good example—has shown some advantages over the traditional extraction process. In the process microporous membranes are used as the barriers to separate the two phases (Yang et al., 1986; Prasad et al., 1990). On another front, another new kind of membrane extractor with a microfiltration membrane as dispersion medium was proposed, and very high performance was reached in our work (Sun et al., 2000; Chen et al., 2002).

The new membrane extractor is mainly based on the development of the micromixing and microchannel reactors, especially the techniques of the microporous membrane emulsification and microchannel mixing emulsification. Actually, in the process of membrane emulsification, one phase is dispersed into another phase, with the microfiltration membrane as the dispersion medium. Up to now many researchers, such as Kawashima et al. (1991), Nakashima et al. (1991), Omi et al. (1994), Katoh et al. (1996), Schroder et al. (1998), and Luo et al. (2000), have published their results. The mechanisms of the membrane emulsification, as well as the effect of the operational conditions, have been studied with different kinds of microporous membranes and working systems. One of the most important conclusions drawn from their work is that the uniformly sized liquid

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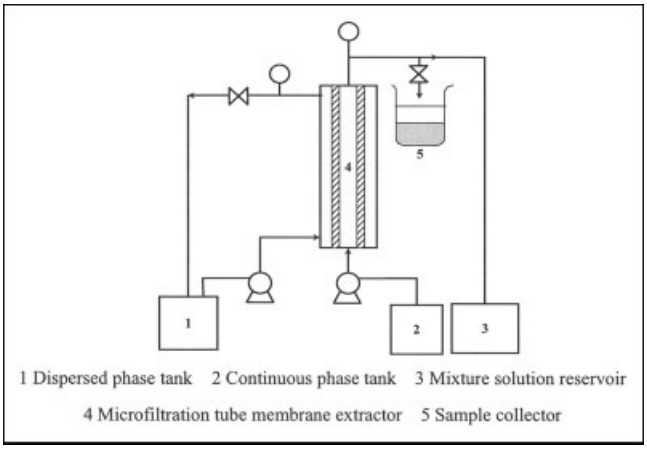

Figure 1. The experimental setup.

droplets with a diameter in the micrometer range, which results in lower energy cost.

As is well known, in numerous conventional extractors, including mixer settler cascades, sieve plate-, packed-, pulsed- and rotating disk extraction columns, the size of the droplets produced is in the 0.1-mm to 3-mm range. Therefore, the mass-transfer area, also called the specific surface area, is small, and the mass-transfer coefficient is slightly low. It is well known that the smaller the drop size of the disperse phase is, the larger the specific surface area that can be provided. Furthermore the smaller droplets result in a shorter diffusion distance inside the droplets, and a higher mass-transfer coefficient can be achieved. If we calculate the individual mass-transfer coefficients of the continuous and dispersed phases with $Sh_c = 2$ and $Sh_d = 6.58$, respectively, we can get that the individual mass-transfer coefficients will increase greatly with a decrease in the size of the droplets. Thus, good dispersion technology is the premise for improving efficiency. Benz et al. (2001) utilized a microchannel mixer in extraction. They found that much higher efficiency was reached when the droplets were in the 20–60-μm range. But the processing technique for making microchannel mixers seems very difficult and expensive. Therefore it is a very inviting task to find a much easier way to apply the micromixing process to a mass-transfer

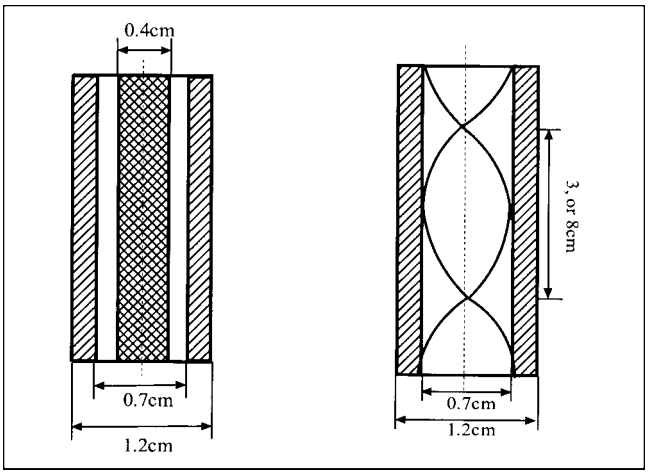

Figure 2. Structure of inner elements.

Table 1. Physical Properties of the Working System

	Density (kg/m^3)	Viscosity (mpa · s)	Interfacial Tension (mN/s)
Aqueous phase	998.0	1.05	9.95
Organic phase	835.0	2.09	

process. In this work, a new extractor with a microfiltration tube membrane as a dispersion medium is designed, and its mass-transfer performance is tested with a working system. In order to reach an optimal micromixing level, some inner elements are designed. The geometric parameters of the extractor and the inner elements are investigated, and the influence of the phase flow rate and transmembrane pressure on the mass transfer are also studied.

Experimental Apparatus and Analytical Method

The apparatus used in this study is shown in Figure 1. One hydrophilic α-Al_2O_3 tube membranes with the length of 19.3 cm were used, which were kindly provided by the Membrane Center of Chemical Engineering University of Nanjing. The structures of the tube membrane were 1.2 cm OD, 0.7 cm ID, and 0.8-μm pore diameter.

In order to improve the mixing of the two phases in the extractor, two kinds of inner elements were designed and used in the membrane extractor. One was a concentric column to make the unmixed region smaller; the other one was the helical column to enhance two-phase mixing. They were made of stainless steel. The structure of the elements is shown in Figure 2.

30% TBP (in kerosene)–nitric acid–H_2O was chosen as an experimental system. The physical properties are list in Table 1. In the micromixing process, the oil phase passed through the membrane and dispersed in the water phase. Nitric acid was transferred from the oil phase to the aqueous phase. The concentration of the two phases at the inlet and the outlet was measured using the titration method. In this work, the stage efficiency of Murphee E and the flux F_d of the dispersed phase passing through the membrane were taken as the compared parameters.

Results and Discussion

Phase-separation phenomenon in the micromixing process

In most textbooks, it is usually stated that the dispersed-phase droplet size is in contradiction with the phase separation,

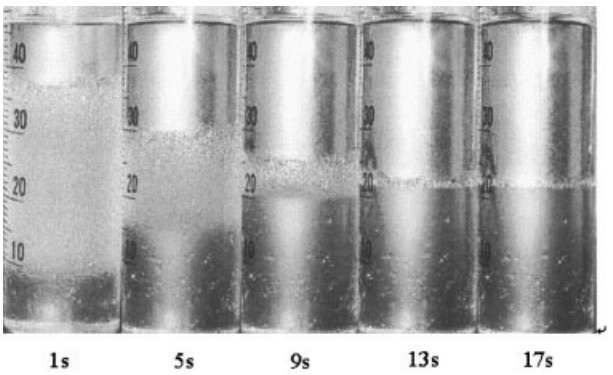

Figure 3. Pictures of phase separation process.

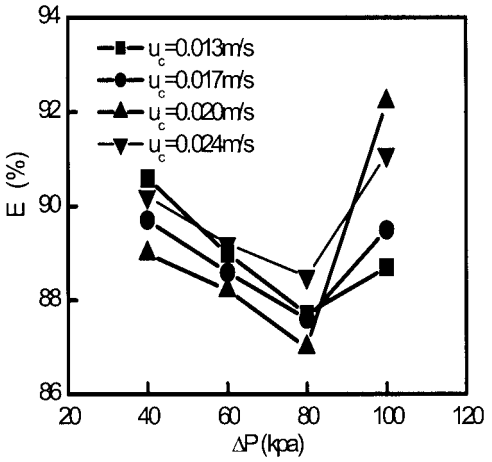

Figure 4. Influence of u_c and ΔP on E.

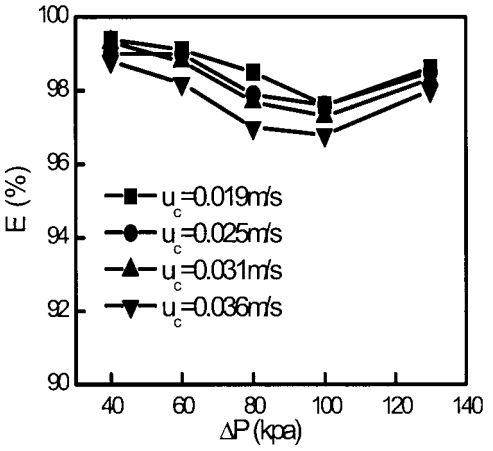

Figure 6. Influence of u_c and ΔP on E in extractor with concentric column.

namely, the smaller the drop size, the harder the phase separation will be. Actually, in a micromixing process with a microporous membrane as the dispersion medium, the drop size is in the micrometer range (Benz et al., 2001; Chen et al., 2002; Schroder et al., 1998), so it is important to know if the phase separation is fast enough for an extraction application. In order to watch the phase-separation phenomenon of a micromixing system, we collected a mixture sample under the conditions of the continuous-phase flow rate $u_c = 0.02$ m/s and the transmembrane pressure $\Delta P = 60$ kPa, and took some pictures of the process. The results are shown in Figure 3.

In our experiment, we found that the speed of the phase separation in a micromixing process was unexpectedly fast. For the system with a phase ratio of about 1/3, the phase separation was completely finished in 13 s. It is therefore a helpful result of applying the micromixing process to the liquid extraction.

Effects of continuous-phase flow rate u_c and transmembrane pressure ΔP

Figures 4 and 5 show the effects of continuous-phase flow rate and the transmembrane pressure on the efficiency and the dispersed phase flux for the extractor without any inner elements, respectively.

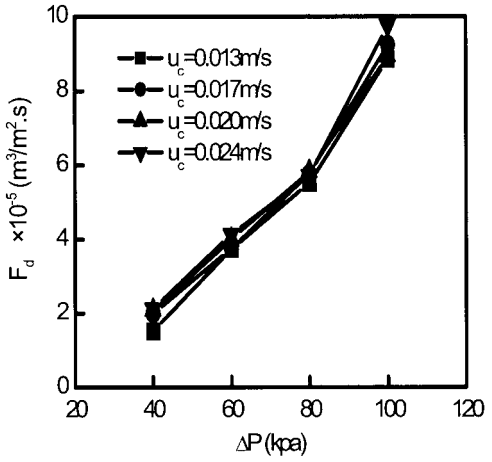

Figure 5. Influence of u_c and ΔP on F_d.

In general, the efficiency in a normal extraction process increases with the decrease in the two-phase volume ratio, and with the increase of residence time when the two phases are very well mixed. In the micromixing extraction process, it was found that at a certain continuous-phase flow rate, the extraction efficiency decreased slightly first with an increase of the transmembrane pressure, then increased. The most likely reason is that at low transmembrane pressure, the flux of the dispersed phase is low, and the two-phase ratio is low, too. The total transferred solute is lower to reach higher extraction efficiency. So the two-phase flow characteristic is not greatly influenced by the mass-transfer performance. With the transmembrane pressure increasing, the phase ratio is increased, and the total transferred solute is also increased. So the influence of the two-phase mixing condition on the mass-transfer performance will become serious. Two-phase mixing is not in very good condition with just an increase in the transmembrane pressure. Therefore, the efficiency was decreased. However, if the transmembrane pressure increases further, the two-phase mixing is improved—making it a positive factor in improving the extraction efficiency—then the efficiency increases. This agrees with the relationship that was found by Benz and co-

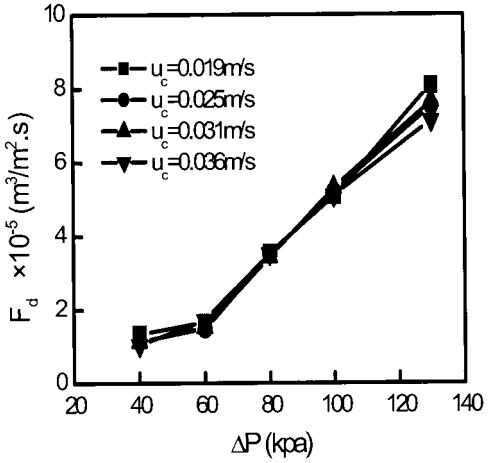

Figure 7. Influence of u_c and ΔP on F_d in extractor with concentric column.

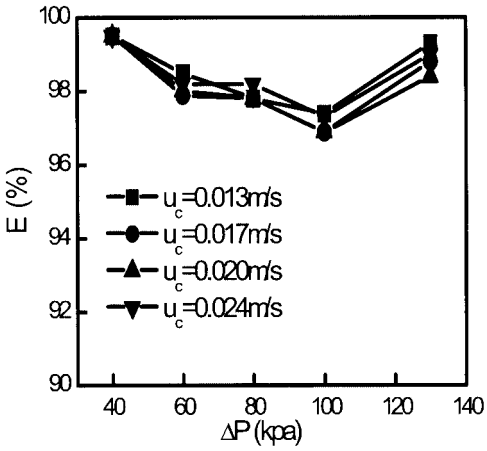

Figure 8. Influence of u_c and ΔP on E in extractor $H = 8$ cm.

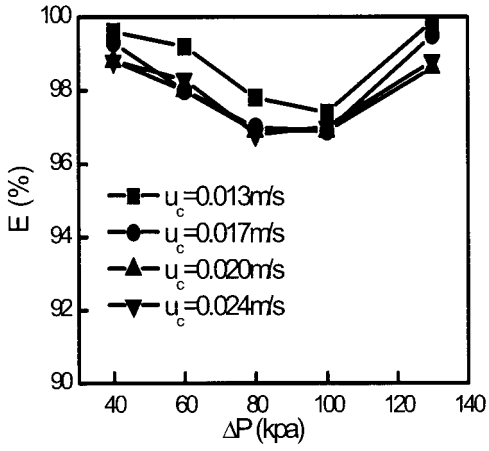

Figure 10. Influence of u_c and ΔP on E in extractor H = 3 cm.

workers (2001) in their experiment. A similar relationship between the extraction efficiency and the continuous phase flow rate at a certain transmembrane pressure can also be seen in Figure 4. All the values of the efficiency in the extractor without inner elements are lower than 92%, which means that either the mass-transfer rate is not fast enough or the two phases are not mixed very well. According to the principles of mass transfer, we know that if the drop size is about several micrometers, the mass-transfer coefficient will be high enough to rapidly reach an equilibrium state between the two phases. It is therefore certain that it is not a question of the mass-transfer coefficient, and so must be a problem of the two-phase mixing. It can be thought that the two phases meet near the surface of the membrane, and mass transfer happens mainly in this region. If the inner diameter of the tube membrane is slightly bigger, the inside of the tube can be separated into mixing and unmixing zones. The larger the ratio of the mixing zone to the unmixing zone, the greater the extraction efficiency. Therefore, it can be concluded that there is an unmixing zone in the extractor without inner elements. In order to improve the mixing ability of the two phases, in the following experiments, some special inner elements were installed in the tube membrane to change the two-phase flow characteristics.

Figure 5 shows us that the flux of the dispersed phase was mainly affected by the transmembrane pressure, and that the continuous-phase flow rate has almost no influence on the flux. This is because the membrane resistance for the dispersed phase is much higher than the pressure drop in the tube side.

Influence of inner elements on extractor performance

Figures 6 and 7 show the results in a 4-mm-diam extractor with a concentric column as its inner element. In the extractor with the concentric column, the curves of the efficiency and the flux of the dispersed phase are similar to those obtained in the extractor without any inner elements. But it can be seen that the efficiency with the element input is improved greatly at the same experimental conditions, that is, almost one theory stage can be reached after the two phases pass through the extractor. The results affirm our assumption in the previous section very well. Apparently, in the micromixing process, the mass-transfer performance is mainly controlled by the two-phase mixing status. Meanwhile the inside space was decreased by the inner

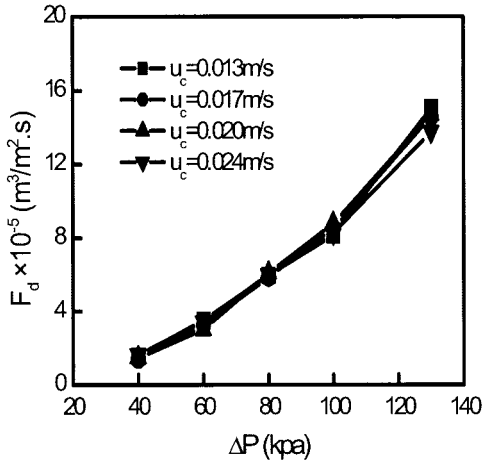

Figure 9. Influence of u_c and ΔP on F_d in extractor $H = 8$ cm.

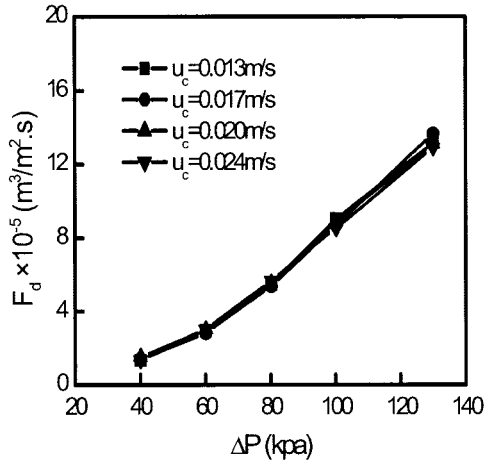

Figure 11. Influence of u_c and ΔP on F_d in extractor H = 3 cm.

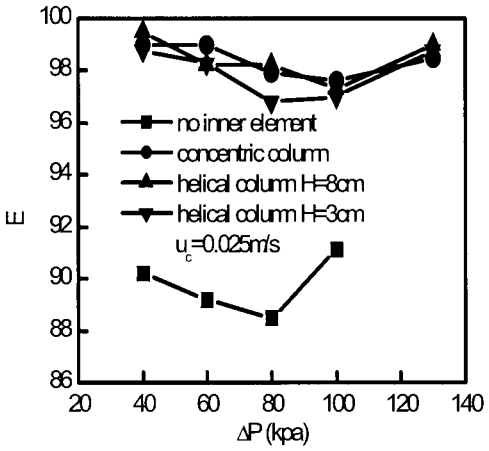

Figure 12. Comparison of efficiency for different inner element.

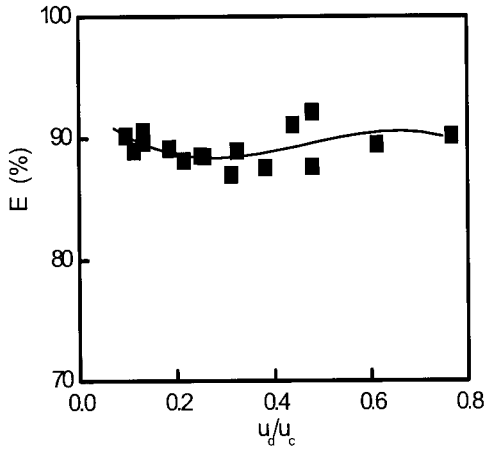

Figure 14. Influence of the phase ratio of u_d/u_c on E without any inner elements.

element input. The possible reason is that the actual average transmembrane pressure was decreased as inner elements were used, although the measurable drop was the same. Because the dispersed-phase flux was actually influenced by the average transmembrane pressure along the tube, so it was decreased.

There are other ways to improve the contact of the two phases besides changing the tube's interior space. According to the structure of some commercial static mixers, the helical columns with different spiral pitch were suggested for the inner elements in this work. Figures 8 and 9 are the results in the extractor for a helical column with a spiral pitch $H = 8$ cm, while Figures 10 and 11 show the extraction performance in the extractor with a helical column with a spiral pitch $H = 3$ cm.

The experimental results obtained in the extractor with the helical column as the inner element proved that the two-phase contact and the mass-transfer performance were greatly enhanced. In this extractor one of the theory could also be reached. But in the experiment, the spiral pitch affected the extractor performance slightly, and the flux of the dispersed phase was also decreased slightly, due to the increase in the pressure drop in the tube side. Because the cross-section area of the tube stayed nearly the same as that of the empty tube, the flux of the dispersed phase was not decreased as much as when the concentric column was the inner element.

Figures 12 and 13 show the comparison of the mass-transfer performance and the flux of the dispersed phase in the extractor with different inner elements. It can be seen that when the inner element was installed in the extractor, the mass-transfer performance was greatly enhanced under the similar experimental conditions. But the flux of the dispersed phase was decreased with the addition of the inner elements. In particular, when the concentric column was the inner element, the decrease in the flux was much greater than that for the other two inner elements. When we compare the two types of inner element, we conclude that the performance of the helical column is better than that of the concentric column. Therefore, the helical column is the preferred choice for the inner element. Because the spiral pitch has no apparent influence on extractor performance, the spiral pitch of the helical column can be in the range of 3 cm to 8 cm.

Figures 14 and 15 show the influence of the phase ratio of the organic phase over the aqueous phase on the extraction efficiency. Figure 14 contains the results of the extractor without any inner elements, and Figure 15 depicts those of the

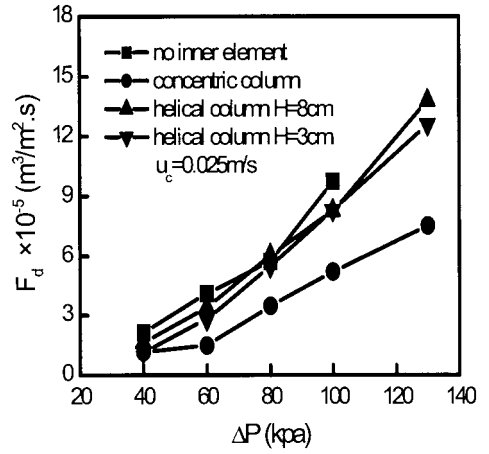

Figure 13. Comparison of flux of dispersed phase for different inner element.

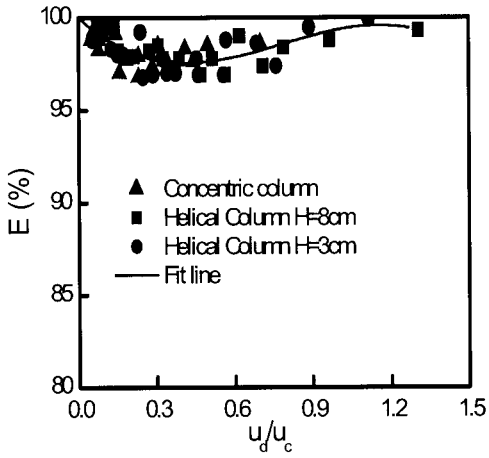

Figure 15. Influence of the phase ratio of u_d/u_c on E having inner elements.

extractor with the inner elements. It can be seen in the two figures that the efficiency decreases as the phase ratio increases up to a minimum value, then grown up with the phase ratio. The experimental points in Figure 14 can be evaluated with a cubic polynomial very well, and also the same for the data in Figure 15. The result is similar to that obtained in a microchannel mixer (Benz et al., 2001). For extractors without any inner elements and with an inner element, the efficiency can be calculated by the following equations, respectively:

$$E = 93.4 - 42.53\left(\frac{u_d}{u_c}\right) + 109.89\left(\frac{u_d}{u_c}\right)^2 - 78.61\left(\frac{u_d}{u_c}\right)^3$$

(for no inner element)

$$E = 100 - 13.82\left(\frac{u_d}{u_c}\right) + 22.85\left(\frac{u_d}{u_c}\right)^2 - 9.69\left(\frac{u_d}{u_c}\right)^3$$

(for inner elements).

Conclusions

In an extractor with a microporous membrane as the dispersion medium, the size of the droplet is in the micrometer range which means it is a micromixing process in which a very large specific surface area and a big mass-transfer coefficient can be offered. In this work, we investigated the phase separation for the micromixing process. We found that the speed of the phase separation was unexpectedly fast, so this micromixing process is a better way of enhancing liquid extraction. The experimental results show that a much greater efficiency can be reached. The flux of the dispersed phase is increased by an increase in the transmembrane pressure. The continuous-phase flow rate has almost no effect on the flux of the dispersed phase. By installing some interior elements in the extractor, the mass-transfer performance can be greatly enhanced. Almost one stage of the theory can be achieved. The results mean that in a micromixing process the two-phase flow state, for example, the two-phase contact state, is a key factor that affects the mass-transfer performance. If the two phases are mixed ideally, the efficiency will be as much as 100%. The efficiency can be predicted for the micromixing extractor with a cubic polynomial. Compared to microchannel mixers, this new extractor is very easy to make.

Acknowledgment

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Notation

E = stage efficiency of Murphee
F_d = flux of the dispersed phase passing through the membrane
H = spiral pitch of the helical column
u_c = flow rate of the continuous phase
u_d = flow rate of the dispersed phase
ΔP = transmembrane pressure

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