

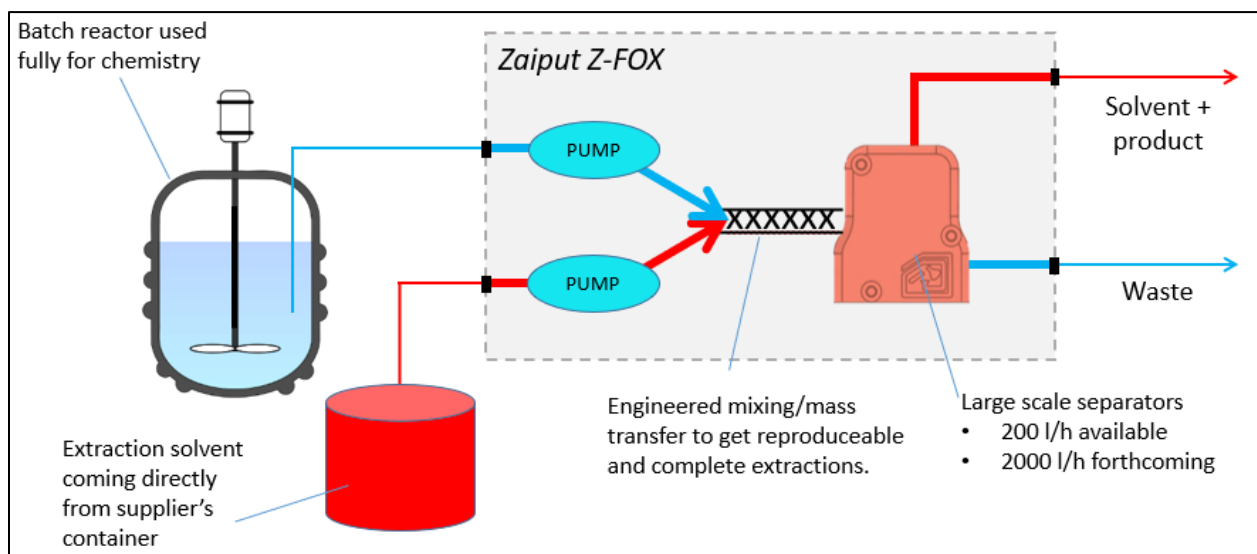
# Analysis and design of Mass Transfer for Continuous Liquid-liquid extraction with Static Mixers: a practical approach.

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## Introduction

Liquid-liquid extraction (LLE) is an extremely popular chemical processing technique used to purify compounds of interest partly due to its large capacity at low energy requirements. LLE consists of two primary steps – mass transfer and phase separation, which, when effectively coupled, provide a “theoretical stage” of extraction. In traditional extraction techniques, two phases are extensively mixed through overhead mixers in a batch vessel before gravitational forces cause the two phases to settle out. This methodology provides inherent disadvantages, from more obvious drawbacks like the time it takes to mix the two phases and allow them to settle, to more subtle inefficiencies like conducting extractions in reactor vessels which reduces a plant’s productivity by the extractive ratio. A change in extraction paradigm is needed to improve this antiquated method of LLE.

Zaiput Flow Technologies has taken the first step in this effort by developing a continuous liquid-liquid separator. This scalable, membrane driven separator allows for the instantaneous separation of biphasic systems and can even separate emulsified systems due to its lack of reliance on gravity as a driving force of separation. This separator can be hooked up to a batch vessel after mixing to reduce settling times, allowing for a degree of plant efficiency improvement. Further advantage can be gained, however, if the mixing between phases can also be brought in to flow. This not only eliminates the waiting time for mixing, but also opens up capacity in the upstream reactor since there is no longer dead space in the reactor left for the extractive solvent – allowing for reactor output improvements of 2x or more. Unfortunately, there is not a well-defined predictive model for determining the mixing type and length for this inline mass transfer.



**Figure 1.** Future extraction setup leveraging full reactor capacity and inline extraction.

In this paper we attempt to simplify and model mixing and mass transfer phenomena using static mixers in a tube to roughly estimate the time required to reach chemical equilibrium in a given liquid-liquid extraction process. To the best of our knowledge, there has been little or no effort in analyzing mass transfer over time during a continuous liquid-liquid extraction process such as this one.

In order to estimate the equilibrium times, we simplify our mass transfer problem as a diffusion one. In the next sections, we explain our approach on how we modelled diffusion of a solute in two immiscible phases, and how we estimated the effective diffusivity constant for the liquid-liquid extraction process, as well as the characteristic diffusion length given by the mean droplet radius. In the end, we then present our model results with some experimental validation.

### **Mass transfer Approach**

In liquid-liquid extraction, mass transfer is driven by a difference in chemical potential in towards a more stable condition with lower free energy (chemical equilibrium). The presence of two immiscible phases introduces mass transfer limitations from a thermodynamic standpoint compared to a natural diffusion mass transfer process with only one phase. Mass transfer will happen until equilibrium is reached rather than when the concentration gradient is zero. Although convection also plays a role, diffusion of solutes in liquids is still the most important principle even in liquid-liquid extraction. Therefore, in our model, we treat the liquid-liquid extraction process as a regular molecular diffusion in liquids with its governing conservation of mass equations and diffusivity as the proportionality constant (see next section for more details). This requires an estimation of the effective diffusion constant for our given liquid-liquid extraction process, which is explained later on in this paper.

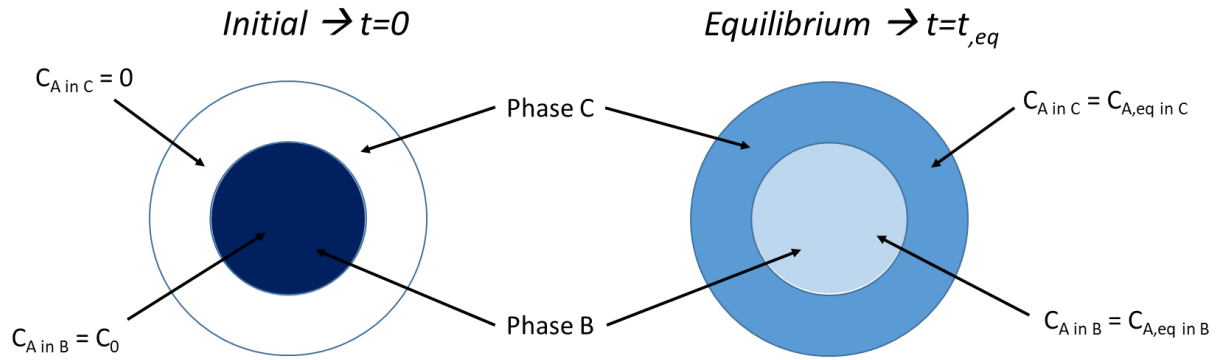
Static mixers are implemented to carry out many different mixing operations and their main principles are well documented (Grace, 1971; Mutsakis, 1986; Cybulski, 1986; Myers, 1997; Thakur, 2003). Static mixers can be very helpful in continuous liquid-liquid extraction processes as well because they allow the two phases involved to be brought into intimate contact with a high degree of turbulence in order to obtain high mass-transfer rates. Although there has been plenty of work, both experimentally and theoretically, on the characterization and effects of implementing static mixers in terms of degree of mixing or particle size distribution (Middleman, 1974; Chen, 1978; Haas, 1987; Berkman, 1988; Streiff, 1997; Legrand, 2001; Theron, 2011) there has been little or no effort in analyzing mass transfer while using static mixers (Streiff, 1977). Furthermore, to the best of our knowledge, no one has studied static mixers from an extraction perspective. This is most likely due to the lack of theoretical studies, complexity in experimental work, multiplicity of factors that may play a role, and scarcity of continuous equipment capable of carrying out liquid-liquid extraction in a tube.

In our liquid-liquid extraction setup, the static mixer causes droplet breakup of the two immiscible phases. For our purposes, this can be seen as an increase in mass transfer due to faster diffusion because of a reduced length scale and increased interfacial area. If we model the original feed phase after mixing as a system of droplets containing the solute, the smaller the droplet the less time it would take for the solute to diffuse out and leave that droplet and be extracted by the adjacent phase. In transient diffusion problems, the diffusion time is indeed directly proportional to the square of the characteristic length, which for our case, if we simplify the droplets to be of spherical shape, would be the radius of the droplet. Because of their strong impact on diffusion time to reach equilibrium, droplet size obtained after the static mixer were therefore investigated and presented later in this paper.

In conclusion, our idea was to model the complex mass transfer problem in continuous liquid-liquid extraction processes by assuming a transient diffusion problem happening inside a droplet. This applies whether the solute is “entering” the droplet (droplet is the extraction solvent) or “leaving” it (the droplet is the raffinate phase). Details on the model are presented in the next section.

### Mass Transfer Model

In our setup, the continuous and dispersed phase are travelling together inside a tube. As mentioned earlier, we modelled our mass transfer phenomena as a transient diffusion problem happening inside of a sphere, therefore using spherical coordinates. The idea behind this is to simplify the droplet of the dispersed phase as sphere particles surrounded by the continuous phase, as depicted in Figure 2. The model is valid whether the solute is originally in the dispersed phase (as in Figure 2) or in the continuous phase since the mathematical problem is the same in both cases.



**Figure 2.** Representation of the spherical mass transfer model for the concentration of solute A (intensity of blue color represents concentration) in the two phases initially and at equilibrium. Phase B is the dispersed phase, while phase C is the continuous phase. In this case, the solute A is originally in phase B.

The complete conservation of mass equation in terms of concentration of a species  $i$  in spherical coordinates is the following (Deen, 2011):

$$\frac{\partial C_i}{\partial t} + v_r \frac{\partial C_i}{\partial r} + \frac{v_\theta}{r} \frac{\partial C_i}{\partial \theta} + \frac{v_\varphi}{r \sin \theta} \frac{\partial C_i}{\partial \varphi} = D_i \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_i}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C_i}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 C_i}{\partial \varphi^2} \right] + R_{Vi} \quad \text{Eq. 1}$$

In our system, the presence of two immiscible phases B and C leads to a coupled system of two equations, one for the concentration of the solute A in the continuous phase C and one in the dispersed phase B, which both need to be solved simultaneously. This is because the concentration of the solute in the continuous phase depends on the dispersed phase, and vice versa. However, to simplify the mathematical problem, we can decouple the system and solve Eq. 1 only for the concentration profile of the solute A inside the inner sphere (phase B) in the model. The effect of the continuous phase C can be included in this case by switching the diffusivity constant  $D_{AB}$  to an effective diffusivity  $D_{ABC}$  (see next section for explanation). For our purposes, this effective diffusivity can be treated similar to an overall mass transfer coefficient for our liquid-liquid extraction process. The role of the phase ratio between the two phases

has an impact on the effective diffusivity of the system (see next section for more details) but does not change the mathematical solution to Eq. 1 when considering the concentration of A inside the sphere because there is no radial dependence outside the dispersed phase.

Furthermore, by assuming that the dispersed phase and the continuous phase after the static mixer are travelling at roughly the same speed and there are no substantial disruption phenomena happening inside the sphere of liquid, it is possible to neglect the convection terms of Equation 1. Furthermore, by making the fair assumption of symmetry and homogeneity in the small spherical droplet, only diffusion in the radial direction can be considered, therefore dropping the two angular diffusion terms. The reaction term can also be dropped due to this being an extraction process in which the amount of molecules of solute does not change during this step because there are no chemical reactions. This is also valid for acid-base extractions because, although the solute might react and change into its conjugate, the total number of molecules between original solute and conjugate is unchanged. The final assumption, required to solve the partial differential equation analytically by providing one more boundary condition, is to consider the concentration of the solute in the two phases to be already in equilibrium at the interface right from the beginning. This is a reasonable assumption since mass transfer of the solute A from phase B to phase C starts in the static mixer during the droplet breakup process. All of these considerations lead to the following simplified equation:

$$\frac{\partial C_A}{\partial t} = D_{ABC} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_i}{\partial r} \right) \right] \quad \text{Eq. 2}$$

where  $D_{ABC}$  is the effective diffusivity of the LLE system described in details in the next section. By making the substitution  $U=C_A r$  (common substitution done in many spherical coordinates problems), the problem can be rewritten as:

$$\frac{\partial U}{\partial t} = D_{ABC} \left[ \frac{\partial^2 U}{\partial r^2} \right] \quad \text{Eq. 3}$$

with the following boundary conditions:

$$U = 0 \quad \text{at} \quad r = 0 \quad \text{at any } t > 0 \quad \text{Eq. 4}$$

$$U = rC_{A0} \quad \text{at} \quad t = 0 \quad \text{at } 0 < r < R \quad \text{Eq. 5}$$

$$U = RC_{A,eq} \quad \text{at} \quad r = R \quad \text{at any } t > 0 \quad \text{Eq. 6}$$

where  $C_{A,eq}$  and  $C_{A0}$  are the equilibrium and the initial concentration, respectively, of the solute in the dispersed phase, while  $R$  is the radius of the spherical droplet of the dispersed phase. The initial concentration is uniform throughout the sphere (Eq. 5), except at the interphase where it is assumed to be already in equilibrium (Eq. 6).

The solution of this problem leads to the following dimensionless concentration profile (Williams and Crank, 1975):

$$Z(r, t) = \frac{C_A - C_{A0}}{C_{A,eq} - C_{A0}} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{R} \exp(-D_{ABC} n^2 \pi^2 t / R^2) \quad \text{Eq. 7}$$

thus, the equilibrium time can be estimated by extrapolating the time required to make  $Z$  approximately equal to 1.

## Effective Diffusivity Estimation

While the diffusivity of a diluted gas mixture (as long as it is at low pressure) can be derived using the kinetic theory of gases, this theory does not hold for liquids since only gases can be assumed to be spherical particles that are completely elastic upon collision with each other. Since such derivation does not apply for liquids, and no other theory for diffusion in liquids is yet well established, only semi-empirical equations have been used to estimate diffusivities of solutes in liquids (Geankoplis, 2003).

The only theoretical derivation that predicts diffusivity of a solute (A) in a liquid (B) accurately is for very large solutes only, and it was obtained starting from the Stokes-Einstein equation and making few assumptions, leading to the following (Geankoplis, 2003):

$$D_{AB} = \frac{9.96 \cdot T \cdot 10^{-16}}{\mu \cdot V_A^{1/3}} \quad \text{Eq. 8}$$

where  $D_{AB}$  is diffusivity in  $\text{m}^2/\text{s}$  of solute A in liquid B,  $\mu$  is dynamic viscosity of the solution in Pa.s,  $T$  is temperature in K, and  $V_A$  is the solute molar volume at its normal boiling point in  $\text{m}^3/\text{kg mol}$ . This equation is not accurate for smaller solutes that have a molecular weight of less than 1000 g/mol or a molar volume less than  $0.5 \text{ m}^3/\text{kg mol}$ .

One of the most accurate and robust semi-empirical equation is the Wilke-Chang correlation:

$$D_{AB} = \frac{1.173 \cdot T \cdot 10^{-16} \cdot (\theta \cdot M_B)^{0.5}}{\mu_B \cdot V_A^{0.6}} \quad \text{Eq. 9}$$

where  $M_B$  is the molecular weight and  $\theta$  is an “association parameter”, which is 2.6 for water and 1.0 for a typical organic solvent (Geankoplis, 2003).

Since the Wilke-Chang correlation predicts diffusivities quite accurately for most cases around room temperature, it is therefore our default equation to estimate the diffusivity for the system involved in the liquid-liquid extraction process, unless the solutes are very large molecules or high temperatures, in which we would use Equation 8.

It is important to mention that the diffusivity constant is pairwise in a multi-species system, so if we consider molecular diffusion in liquid-liquid extraction, there are two diffusivity constants that play a role: the diffusivity of the solute in the original feed phase ( $D_{AB}$ ) and the diffusivity of the solute in the extracting phase ( $D_{AC}$ ). The latter is also important because the rate of diffusion of the solute in the extracting phase also plays a role in how fast the solute leaves the original feed phase. In fact, if the solute diffuses very slowly in the extracting phase close to the interface between the two phases because of a low diffusivity in the extracting phase, the concentration gradient (which drives diffusion in a regular mass transfer process) at the interface would take more time to reach the same level it would if the diffusivity was higher, therefore slowing the entire mass transfer process down. In other words, if the extracted solute takes more time to “leave” the area close to the interface and diffuse in the bulk extracting phase, the solute gradient concentration at the interface which drives mass transfer is less sharp/efficient, leading to an increase in time required for more solute to leave the original phase, therefore requiring more time to achieve chemical equilibrium.

In sophisticated diffusion problems such as this one, the regular molecular diffusivity is usually substituted by a dispersion coefficient or effective diffusivity, in which factors such as turbulence, dispersion, and tortuosity are included to accurately determine the effective diffusivity for such system. Although it would

be very complicated to model in our case, it is clear that both diffusivities contribute to the overall effective diffusivity associated with a given extraction system. For our practical purposes and simplifications during the estimation of the time required to achieve equilibrium in a liquid-liquid extraction process, we defined the effective diffusivity ( $D_{ABC}$ ) of the extraction system to be a linear combination of the two estimated diffusivities ( $D_{AB}$  and  $D_{AC}$ ), meaning that the effective diffusivity lies somewhere between the two. A good first prediction would be to use the weighted average diffusivity based on the two phase flowrates in the system. In the case of a 1:1 flowrate ratio between the phases, the estimated effective diffusivity ( $D_{ABC}$ ) would then be simply the average of the two estimated diffusivities ( $D_{AB}$  and  $D_{AC}$ ). It is important to mention that a weighted average diffusivity is a reasonable and fair estimation for mass transfer sizing purposes, although it might not be the most accurate estimation method for certain systems.

With those simplifications and by neglecting other phenomena such as dispersion and tortuosity, it is thus possible to approximately estimate the effective diffusivity in liquid-liquid extraction in an easy way. Later on in this paper, we provide a simple tool to estimate the effective diffusivity value for any liquid-liquid extraction system.

### Static Mixer Particle Size estimation

In our studies, we decided to focus our attention on the Kenics static mixer which is very popular and the most investigated mixer for liquid-liquid emulsification (Middleman, 1974; Chen 1978; Haas 1987; Berkman, 1988; Yamamoto, 2007;).

The mean particle size in Kenics static mixers, usually defined as the mean Sauter Diameter ( $D_{32}$ ) which is the ratio of volume and surface area, can be predicted using available semi-empirical correlations which the majority have been based on Kolmogoroff's theory of turbulence (Hinze 1955, 1959). One of the limitations of those correlations is the fact that this theory does not apply well with static mixers because it assumes a flow field that should be both homogenous and isotropic. However, starting from this theory and taking into consideration the Reynolds and Weber numbers, Middleman (1974) proposed a correlation to estimate the Sauter mean diameter of a droplet in a Kenics mixer. After him, different authors have proposed similar correlations, and those are reported in Table 1 (see Author's article for more details and variables explanation).

**Table 1.** Correlations for the prediction of droplet mean diameter ( $D_{32}$ ) resulting from emulsification in Kenics static mixers with their range of applicability in terms of Reynolds and Weber number. The tube diameter range used in their experiments is also included.

Authors	Correlation	We	Re	D (cm)
Middleman (1974)	$\frac{D_{32}}{D} = KWe^{-0.6}Re^{0.1}$	~5-300	~ $10^3$ - $10^4$	~1.22-2.54
Chen and Libby (1978)	$\frac{D_{32}}{D} = 1.14We^{-0.75} \left(\frac{\mu_d}{\mu_c}\right)^{0.18}$	NA	NA	NA
Haas (1987)	$\frac{D_{32}}{D} = 1.2We^{-0.65}Re^{-0.2} \left(\frac{\mu_d}{\mu_c}\right)^{0.5}$	5-236	184-8090	0.335-0.794
Berkman and Calabrese (1988)	$\frac{D_{32}}{D} = 0.49We^{-0.6} \left(1 + 1.38Vi \left(\frac{D_{32}}{D}\right)^{0.33}\right)^{0.6}$	144-665	>12000	1.91

## Model Results

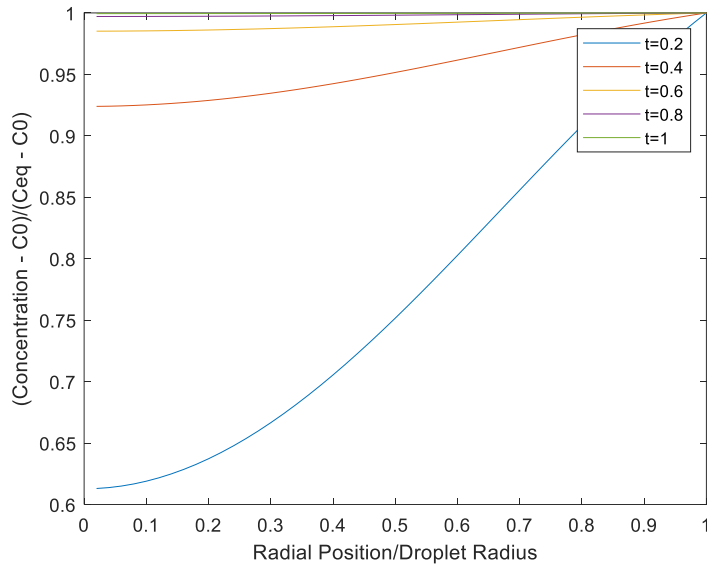
In this study, we investigated the liquid-liquid extraction of acetone from water using toluene with a 1:1 volume ratio between the two phases. The diffusivity of acetone in water at 25 °C was estimated using Eq. 2 to be  $1.28 \times 10^{-9} \text{ m}^2/\text{s}$ , while the diffusivity in toluene was  $2.86 \times 10^{-9} \text{ m}^2/\text{s}$ . Therefore, the effective diffusivity of this LLE system was taken as  $2.07 \times 10^{-9} \text{ m}^2/\text{s}$  (average of the two due to 1:1 volume ratio). In our study, we used the correlation developed by Haas (1987) in Table 1 to predict the mean Sauter diameter of our droplets in order to have an idea on the mean radius, which is considered to be our characteristic diffusion length in our mass transfer model. The reason we picked this correlation was because our range of Weber and Reynolds number, as well as tube diameter lies the best within its range of applicability compared to the other correlations (Table 1). Droplet size mean diameters were predicted for two different tube diameters of interest (1/8" and 3/8") at different flowrates (from 20 ml/min to 3000 ml/min), and the results are shown in Table 2. Water was considered to be the continuous phase, while toluene was the dispersed phase as suggested by Ribeiro (2006) and others. Predicted droplet diameters inside the range of applicability of the correlation falls within the range obtained by Haas (1987) in his experiments (40-640  $\mu\text{m}$ ).

**Table 2.** Predicted mean droplet size diameter using Kenics static mixer in two different tubes at different flowrates using the correlation developed by Haas (1987). N.A. stands for "not applicable" and it was used if either Re or We were outside the range of applicability of the correlation (Table 1).

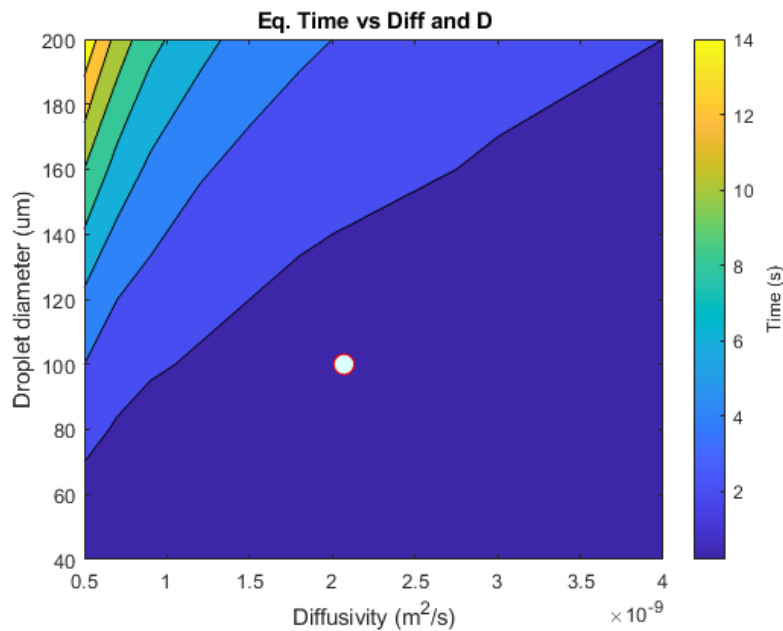
Flowrate (ml/min)	Tube Inside Diameter (inches)	Re	We	$D_{32}$ ( $\mu\text{m}$ )	Notes
20	1/8"	150	0.1	3845	NA
40	1/8"	300	0.6	1359	NA
80	1/8"	600	2.4	481	NA
120	1/8"	899	5.3	262	
150	1/8"	1124	8.3	187	
200	1/8"	1499	14.8	122	
300	3/8"	749	1.2	2107	NA
500	3/8"	1249	3.4	979	NA
1000	3/8"	2498	13.7	346	
1500	3/8"	3747	30.8	188	
2000	3/8"	4996	54.7	122	
2500	3/8"	6246	85.5	88	
3000	3/8"	7495	123.2	67	

Concentration profiles inside the spherical droplet and equilibrium time were obtained for this system by applying our mathematical model described earlier, using the effective diffusivity and varying droplet size diameter. Equilibrium time was calculated based on the time required to have a concentration above 99.9% of the equilibrium concentration at every radial position throughout the sphere. For example, for a 100  $\mu\text{m}$  droplet, it roughly takes 1 second to achieve equilibrium throughout the sphere as shown in Figure 3.

The effect of droplet size and diffusivity was obtained by solving the concentration profiles with different conditions within a reasonable droplet size and diffusivity range of values (less than 200  $\mu\text{m}$  droplets are typical when using static mixers, and diffusivity in liquids is usually between  $0.5 \times 10^{-9}$  and  $4 \times 10^{-9}$ ). As it was done earlier, the equilibrium time was calculated based on the time required to achieve a uniform concentration above 99.9% of the equilibrium concentration at any radial position within the droplet. These results are shown in Figure 4.



**Figure 3.** Dimensionless concentration profiles as a function of dimensionless radius inside a 100  $\mu\text{m}$  sphere after different time intervals. Equilibrium is reached when the value of  $Z$  ( $x$ -axis) is above 0.999 at any radial position.



**Figure 4.** Estimated equilibrium time as a function of effective diffusivity and droplet size diameter in a continuous LLE process. The white dot corresponds to the studied system (acetone-water-toluene) with a droplet diameter of 100  $\mu\text{m}$ , leading to an equilibrium time of 1.0 sec.



With our model, it is thus possible to rapidly approximate the time required to achieve equilibrium in any continuous liquid-liquid extraction process happening in a tube. This provides a quick approximation when setting up a continuous liquid-liquid extraction process by giving an estimate of the tube length required to achieve equilibrium at a given flowrate and tube diameter for any solvent system. For example, in our studied system, times and tube length requirement at the investigated flowrates are reported in Table 3 (only for the cases in which the correlation was applicable).

**Table 3.** Equilibrium times and tube length requirement for a water-acetone-toluene extraction system using Kenics static mixers at different flowrates for two different tubes.

Flowrate (ml/min)	Tube Inside Diameter (inches)	$D_{32}$ ( $\mu\text{m}$ )	Model Eq. Time (s)	Tube Length Required (cm)
120	1/8"	262	6.4	162
150	1/8"	187	3.4	107
200	1/8"	122	1.4	59
1000	3/8"	346	11.2	262
1500	3/8"	188	3.4	119
2000	3/8"	122	1.4	65
2500	3/8"	88	0.8	47
3000	3/8"	67	0.6	42

### Experimental Validation

In our experimental setup, we used a 1:40 and 1:10 acetone/water solution by volume and toluene as our extracting solvent. The two solutions were pumped at the same flowrate and merged into a single tube containing Kenics static mixer followed by an empty tube. At the end of the tube, the aqueous and the organic phases were separated using a Zaiput membrane based separator. A sample from both phases was collected at the outlets of the separator and analyzed using HPLC. The goal of this experimental study was to find out the residence time required to achieve equilibrium before separation. Multiple trials were performed by varying the length of the empty tube (residence time) as well as the flowrate of the two phases. The HPLC collected samples were used to calculate the partition coefficient of acetone in the two phases, and this was compared to the equilibrium partition coefficient ( $K_{D,EQ} = 0.65$  when 1:40 acetone-water ratio and 0.70 when 1:10 ratio) which was obtained by a traditional batch experiment (manually mixed the system by strong shaking in a vial and allowed time to settle by gravity, then HPLC on both layers).

The results of these experiments are shown in Table 4 (ID: 3/8") and in Table 5 (ID: 1/8"), and the comparison between experimental and model prediction is summarized in Table 6.

**Table 4.** Summary of the experiments performed with the acetone-water-toluene LLE system, using 3/8" ID tubing with 32" of Kenics static mixer followed by empty tubing.

<b>Water/Acetone Ratio</b>	<b>Water/Acetone Flowrate (ml/min)</b>	<b>Toluene Flowrate (ml/min)</b>	<b>Tube Length (cm)</b>	<b>Residence Time (s)</b>	<b>KD (O/A)</b>
40:1	250	250	180	12.8	0.6
40:1	500	500	180	7.7	0.63

**Table 5.** Summary of the experiments performed with the acetone-water-toluene LLE system, using 1/8" ID tubing with 12" of Kenics static mixer followed by empty tubing.

<b>Water/Acetone Ratio</b>	<b>Water/Acetone Flowrate (ml/min)</b>	<b>Toluene Flowrate (ml/min)</b>	<b>Tube Length (cm)</b>	<b>Residence Time (s)</b>	<b>KD (O/A)</b>
40:1	20	20	30	3.6	0.59
40:1	80	80	30	0.9	0.65
40:1	20	20	150	17.8	0.65
40:1	80	80	150	4.5	0.65
40:1	50	50	30	1.4	0.64
10:1	20	20	30	3.6	0.63
10:1	40	40	30	1.8	0.66
10:1	60	60	30	1.2	0.65
10:1	80	80	30	0.9	0.54
10:1	100	100	30	0.7	0.55
10:1	20	20	100	11.9	0.65
10:1	40	40	100	5.9	0.70
10:1	70	70	100	3.4	0.70
10:1	80	80	100	3	0.68
10:1	100	100	100	2.4	0.67

**Table 6.** Comparison of model predicted to experimental equilibrium time for water-acetone-toluene L-L extraction in a tube (ID: 1/8" until 200 ml/min, 3/8" above 200 ml/min) using Kenics static mixers. N.A. stands for "not applicable" and it was used if either Re or We were outside the range of applicability of the correlation (Table 1).

Flowrate (ml/min)	Model Eq. Time (s)	Experimental Eq. Time (s)
40	NA	17.8
80	NA	5.9
120	6.4	4
150	3.4	~1-3.4
200	1.4	~1-3
500	NA	> 13
1000	11.2	~8-9
1500	3.4	NA
2000	1.4	NA
2500	0.8	NA
3000	0.6	NA

### Recommendations and tube length selection charts

The goal of this section is to use engineering judgment combined with the findings from this study to come up with easy to consult charts for the selection of the length of tubing required to successfully carry out any continuous LLE using our proposed equipment system.

A typical unit of Kenics static mixer usually consists of 10 to 12 elements. Although Middleman (1974) shows that a unit of 10 elements of Kenics static mixer is sufficient to reach the terminal mean droplet size distribution, Haas (1987) and Berkman (1988) used in their experiments units of 21 and 24 elements, respectively, because they suggest higher viscosities require more time to reach such distribution. A longer static mixer portion would increase the chances of reaching terminal droplet size distribution, increase mixing and contact of the two phases, even for very challenging or viscous systems, as well as slowing down the coalescence rate in the empty tubing portion. When considering mass transfer during the LLE process, coalescence after the mixer strongly reduces mass transfer because droplet size has a quadratic effect on equilibrium time. This leads to the proposition for alternating static mixers units and empty tubing to allow less time for coalescence due to repetitive mixing, thus allowing the system to be closer to the terminal droplet size distribution throughout the tubing which enhances mass transfer (smaller droplets). It is for all these reasons that we suggest using multiple units of Kenics static mixer for LLE application, especially at low diameters.

For flowrates up to 200 ml/min, we recommend using our 2' tubing unit of 1/8" or 5/32" ID tubing (OD: 1/4"). The tubing unit contains roughly 4-5" of Kenics static mixers (StamixCo: 4 units of HT-40-3.18-12-' [PP or HT-40-3.18-12-AC, or 3 units of HT-40-3.75-10-PTFE) followed by roughly 19-20" of empty tubing before entering into the membrane based separator (Zaiput SEP-200). For more challenging extractions,

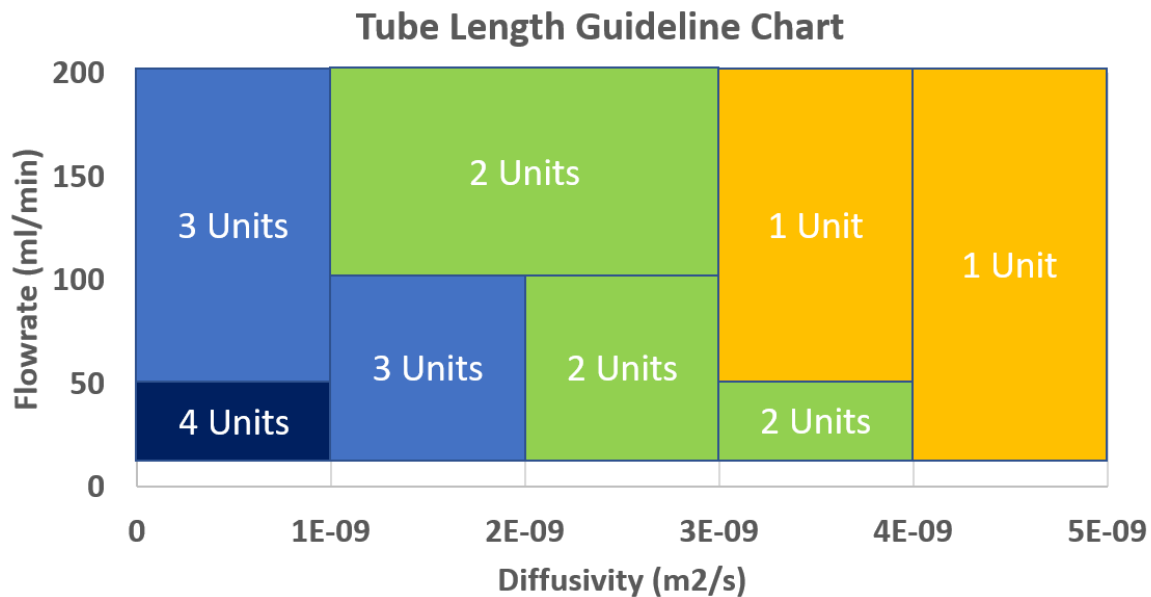
especially when the effective diffusivity is low, we recommend using multiple units of this tubing in order to achieve equilibrium (see Figure 5 for recommended number of tubing units).

Above 200 ml/min until 3000 ml/min, we recommend using our 3' tubing unit of 3/8" ID tubing (OD: 1/2"). The tubing unit contains roughly 8" of Kenics static mixers (StamixCo: 1 unit of HT-40-9.47-24-PP or HT-40-9.47-24-AC, or HT-40-9.30-20-PTFE) followed by roughly 28" of empty tubing before entering into the membrane based separator (Zaiput SEP-3000). As it was for flowrates below 200 ml/min, we recommend using multiple units of this tubing in order to achieve equilibrium (see Figure 6 for recommended number of tubing units).

With those recommendations, the following charts (Figure 3-8) represents easy to consult tools for an approximation of the length of 1/8" ID, 5/32" or 3/8" ID tubing required to achieve equilibrium for any LLE system given effective diffusivity (see estimation section if needed) and flowrate (Figure 5 - 6).

When developing those charts, a safety factor was added to the length required in order to increase the approximation's robustness, making it more likely to be applicable to a large number of systems. It is important to mention that the below charts represent a great guideline for sizing a continuous liquid-liquid extraction system such as the one we propose. However, tubing length could be adjusted after experimentation with the suggested length in order to lower the dead volume (if equilibrium is reached with the suggested length) or to improve extraction (if residence time was not enough to reach equilibrium).

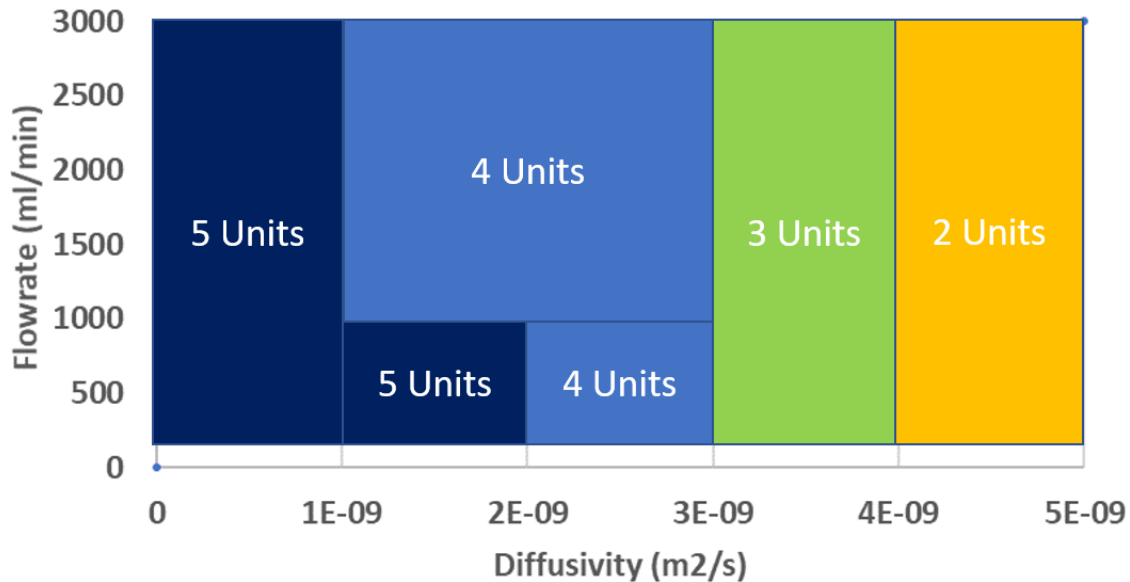
**1 Unit = 2' of tubing (ID=1/8" or 5/32") containing ~4-5" of Kenics Static Mixer**



**Figure 5.** Approximate tubing length (ID=1/8" or 5/32") required to achieve equilibrium, depending on flowrate (20-200 ml/min) and effective diffusivity ( $D_{ABC}$ ) range, using Zaiput SEP-200. (If needed, consult the following diffusivity estimator section to obtain effective diffusivity).

1 Unit = 3' of tubing (ID=3/8") containing ~8" of Kenics Static Mixer

### Tube Length Guideline Chart

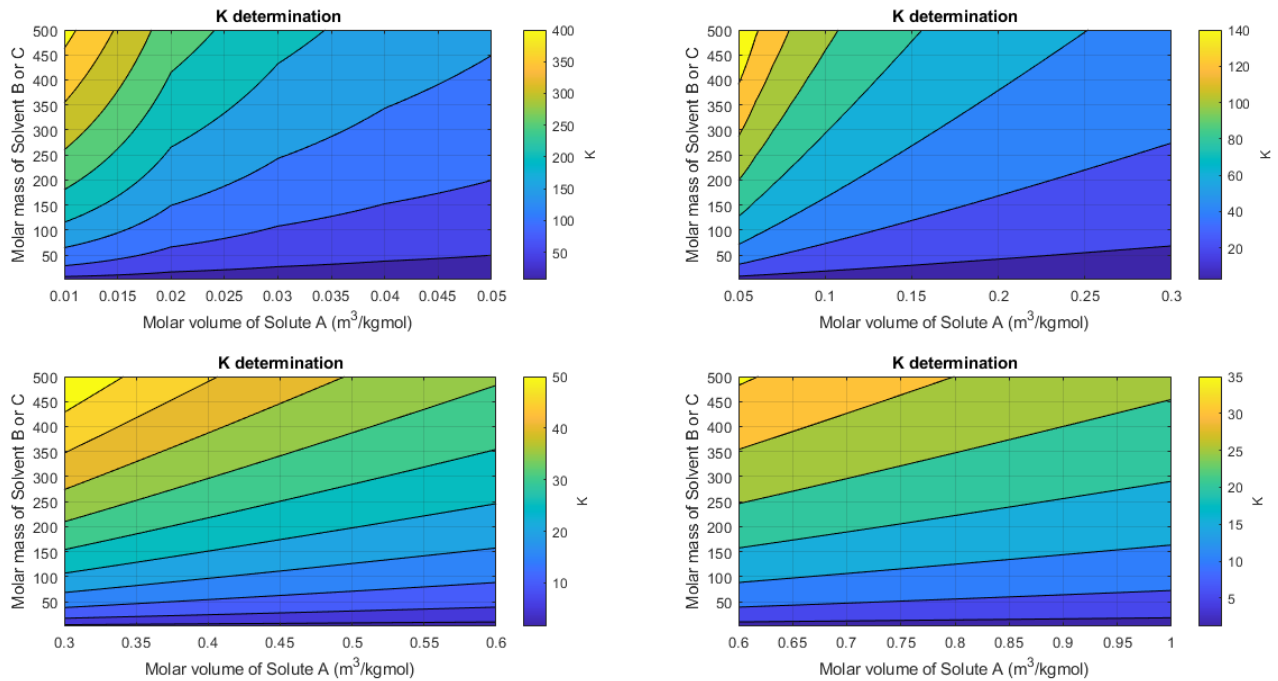


**Figure 6.** Approximate tubing length (ID=3/8") required to achieve equilibrium, depending on flowrate (200-3000 ml/min) and effective diffusivity ( $D_{ABC}$ ) range, using Zaiput SEP-3000. (If needed, consult diffusivity estimation section to obtain effective diffusivity).

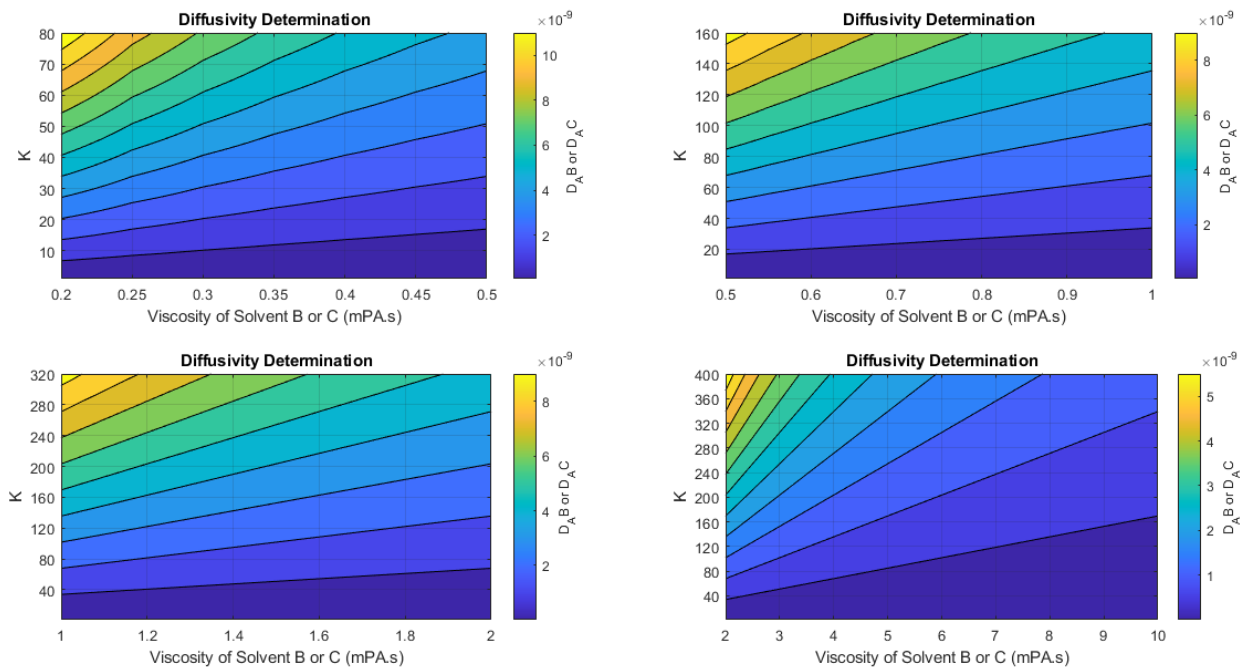
### Effective Diffusivity Estimator

The goal of this section is to guide in the estimate of the effective diffusivity for any liquid-liquid extraction system by providing easy to consult charts. As a reminder, the effective diffusivity ( $D_{ABC}$ ) is the weighted average (based on flowrate ratio) of the diffusivity of the solute in solvent B ( $D_{AB}$ ) and the one in solvent C ( $D_{AC}$ ), therefore both need to be estimated first. To start, we can estimate the role of the molar mass of the solvent B (or C) and the molar volume of the solute A by extracting two values of K (dimensionless variable) from Figure 7: one using the molar mass of solvent B and one using the one for solvent C. Once K values are known, they can be used with the viscosity of the corresponding solvent (B or C) to extract the two values of  $D_{AB}$  and  $D_{AC}$  from Figure 8. If the value of K is outside the chart (Figure 8) for a given viscosity, that means the diffusivity is very high above  $5 \cdot 10^{-9} \text{ m}^2/\text{s}$ . Also, it is important to keep in mind that if the extraction does not happen at room temperature (298 K), the two values of diffusivities should be adjusted by multiplying them by the ratio of the actual temperature (in Kelvin) and room temperature (298 K). Furthermore, if the solvent is water, the approximated diffusivity for the solute in water should be multiplied by 2.6.

At this stage, after adjusting for temperature and for water, the only thing left is to calculate the effective diffusivity ( $D_{ABC}$ ) by computing the weighted average (based on flowrate ratio) of the approximated values of  $D_{AB}$  and  $D_{AC}$ .



**Figure 7.** Approximation of the value of  $K$  as a function of the molar mass of the solvent B or C and the molar volume of the solute A. Molar volume is the ratio between molar mass and density.



**Figure 8.** Approximation of the value of the diffusivity as a function of the previous obtained  $K$  value and the viscosity for Solvent B or C. The system effective diffusivity can be obtained by the weighted average of the two extracted values of diffusivity ( $D_{AB}$  and  $D_{AC}$ ).

## Further Considerations and Conclusions

The ability to accurately model mass transfer for in-line mixing solves one of the key barriers to the accurate design of continuous extractive systems. With these models in place, which led to the development of easy to use consultation charts for sizing mass transfer in order to reach equilibrium, and the before mentioned continuous membrane separators from Zaiput Flow Technologies, continuous extractive platforms, which have several advantages compared to more traditional approaches, can be easily constructed.

In this work, we have shown that this model is not only a powerful tool, but it is also easily scalable across a range of flow rates and tubing diameters, and applicable to nearly all extractive systems. Future work can be done to further validate our model and apply the theory at even larger flow rates.

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