Thin Layer Extraction—A Novel Liquid–Liquid Extraction Method

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The overall task of a liquid–liquid extraction process consists of selectively transferring solutes from a donor solution to a recipient solution through a liquid extractant, with the purpose of purifying the donor solution and/or recovering a valuable solute. Thin layer extraction (TLX) is a novel method to carry out this task, using specialized equipment and temporal modes of operation. In TLX, a minute amount of an extractant that is firmly attached as thin layer to a solid substrate is intimately and frequently brought into contact alternately with the donor and recipient solutions. TLX incorporates the complete extraction/stripping scheme into one single device. Following presentation of the underlying concepts, the structural, design, and operational aspects are discussed. TLX is applicable on a wide range of scales and can be easily scaled up to production floor size or down to the microscale. It has inherent operational, safety, and environmental qualities.
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Introduction

The separation of components in a liquid solution is one of the backbones of the chemical industry. It is a major consumer of energy and is often associated with causing or preventing pollution. One of the more energy-efficient methods of separation is liquid–liquid extraction. Unfortunately, the application of liquid–liquid extraction requires that a solvent mixture be tailored to each specific case and the design and operation of liquid–liquid extraction plants are somewhat more complicated than that in more general but energy-intensive methods such as distillation. Simplifying the practice of liquid–liquid extraction can be the key to its more widespread application.

Liquid–liquid extraction addresses the recovery or the purification of a desired dissolved substance through the selective transfer of dissolved species from one liquid solution to another. This transfer is done through an intermediary substance, an extractant, which is usually diluted by a diluent, together forming a solvent that is insoluble in the liquid solutions. The process involves an extraction step in which the donor solution is brought into contact with the solvent at conditions that favor the selective transfer of the desired species from the donor solution to the extractant, and a stripping step in which the recipient solution is brought into contact with the same solvent at conditions that favor the transfer of the desired species from the extractant to the recipient solution. In cases where there is a limited amount transferred in a single contact instance, the effect is multiplied by carrying out each of the extraction and stripping steps in countercurrent trains of contacting stages (Figure 1).

Each of the extraction and stripping steps entails, at each contacting instance, two operations: first, intimate contact between the phases for mass transfer and then coalescence and phase separation. In conventional liquid–liquid extraction, with the solution and the solvent flowing in bulk, dispersion of one phase in the other is the mode of attaining enough transfer area for mass transfer, therefore, requiring recoalescence of droplets to permit phase separation. This generates a contradiction in what concerns the desirable

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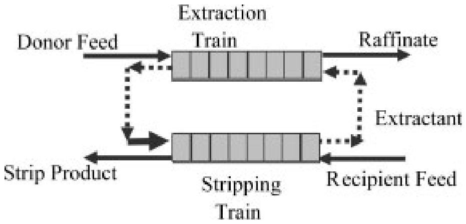

Figure 1. Typical liquid–liquid extraction scheme.

degree of mixing when dispersing one phase into the other: intense mixing promotes mass transfer, but makes the phase separation more difficult. The conventional approach also engenders bulky equipment and a significant inventory of solvents.

Initially, liquid–liquid extraction was carried only in Mixer-Settler trains. Over the years, more intensive processes have been refined that reduce plant size and solvent inventory to some extent, notably extraction columns, centrifugal extractors, and more. Thin layer extraction (TLX) intensifies extraction one notch further by eliminating the conflict between mass transfer and phase separation while also optimizing mass transfer. The plot is not entirely new. In her comprehensive monograph,[1] Blumberg stated, "when two liquids flow as thin films in contact without dispersion, coalescence has no place in the system." Later on, Kim[2] proposed using a particulate polymeric adsorbent instead of a liquid solvent that would be easier to separate after mixing. Particulate polymeric adsorbents are indeed widely used in the context of ion exchange, in which the solutions essentially alternate in flowing through a bed of reactive resin beads. This approach, while avoiding the conflict of phase dispersion and separation, has its limitations because in it, mass transfer depends on the diffusion of the adsorbed species into and out of the pores in the resin beads, a slow process. That, combined with the non-negligible pressure drop through the dense bed, limits the velocity of the solutions through the bed and leads to long cycles of operation, which, in turn, requires large beds of resin, in proportion to the amount of solute in the feed solution. An early attempt[3] to improve on Kim's approach by coating the polymer particles with a thin layer of an extractant failed to provide a practical method because it missed important facets of the problem.

Liquid–liquid extraction stands out between all other separation methods in its low-energy consumption, its moderate operating conditions that make it fit to process sensitive materials and its potential selectivity. In Blumberg's monograph,[1] it is also regretted that a method with such positive attributes has not yet been generalized to the point of penetrating a wider range of applications in the chemical industry. This failing can be traced to the relative simplicity of the competition, such as membranes at one end and distillation at the other, which mostly do not require an intermediary but rely instead on a substantial energy input. Trends that discredit energy-intensive methods will act to the benefit of reliable frugal alternatives. The TLX method simplifies liquid extraction and facilitates the choice of an extractant, thereby improving its prospects to play a greater role in laboratory and in industry.

In spite of the somewhat similar name, TLX should not be confused with thin layer chromatography (TLC). TLX is a continuous separation method, using a liquid extractant in the plant or the laboratory, whereas TLC is a batch chromatographic laboratory analysis tool, using a gel or a solid adsorbent.

In the following, it will be assumed, for the sake of simplicity, that the extractant is organic, and the solutions are aqueous.

The thin layer extraction concept

In thin layer extraction (TLX), the solvent is replaced by a solid substrate supporting a thin layer of a liquid extractant. The substrate consists of a thin hydrophobic microporous material that will imbibe and retain strongly an oily extractant. A thin film of the donor or recipient solution flows past, or briefly rests close to, the extractant layer. Thus, two thin layers, oily and aqueous, are in intimate contact (Figure 2). The layers will typically be 20–100 μm thick.

This constitutes ideal conditions for mass transfer between the solution and the extractant, because it maximizes the contact surface and minimizes the length of the diffusion path of the solutes in and between the solution and the extractant. With the extractant layer firmly attached to the microporous substrate, separation of the phases is trivialized. This leaves mass transfer rate as the sole consideration determining the process time span.

The capacity of a layer of extractant to contain an amount of solute is proportional to its thickness. Then how shall one obtain a meaningful amount of mass transfer? By integrating the extraction and stripping steps into a single location and by switching frequently between modes of extraction and stripping. This makes it possible to process significant volumes of solutions of any concentration while using a relatively minute amount of extractant.

In conventional extraction plants, the active extractant substance is seldom used in a pure form, but is almost always combined with diluents and modifier because of economic and phase separation considerations. In TLX, it will be possible and economical if so desired to use the extractant in a pure or concentrated form. The many constraints, governing the choice of a solvent system in liquid–liquid extraction, are thus reduced to those related to the extractant itself, namely, reversible reactivity and selectivity.

Finally, in conventional liquid–liquid extraction, solvent entrainment often necessitates further purification of the product solutions and/or constitutes a loss of costly materials. In TLX, with the extractant firmly attached to the solid substrate, contamination of the solutions by the extractant is practically eliminated.

The TLX technology

The TLX technology is intended to exploit the TLX concept in complete extraction and stripping schemes by means

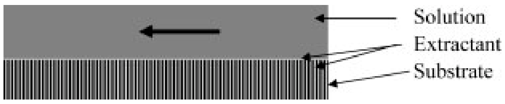

Figure 2. Enlarged view of the contact zone in TLX.

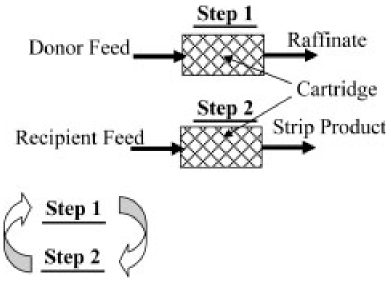

Figure 3. Conceptual TLX cell.

of devices and temporal modes of operation that rely on a proper choice of materials, structures, and timing.

The TLX cell

The core of every TLX process is the TLX cell that consists of a cartridge, a flow arrangement, and a timed program of operation. The TLX cell is the equivalent of a stage in classical equilibrium separation processes, except that the equilibration here relates to an entire cycle of extraction and stripping operation. In a TLX cell (Figure 3), the cartridge is brought into contact consecutively with one or more donor and recipient solutions and generates products whose compositions are at, or close to, equilibrium with the extractant in the respective extraction or stripping steps. Each TLX cell constitutes a microcosm of the entire extraction/stripping process.

The cartridge

The cartridge is an open-cell macroporous matrix made of a solid thin hydrophobic microporous substrate. The cartridge is characterized by being porous at two widely different scales: (a) the microporosity of the substrate is designed to hold firmly the extractant onto the substrate, (b) the macroporosity of the cartridge relates to the space between the substrate walls. It is designed to permit access of the solutions to the substrate-supported extractant layer.

Every cartridge may be imbibed with a liquid extractant of our choice. The extractant will be anyone of the common extractants used in the industry, depending on the specific separation task, with a preference for those that are potent and characterized by a low solubility in water, for example, amines with a long hydrocarbon chain. The extractant is then firmly attached to the substrate, as shown in Figure 2.

Cartridges are classified by the thickness of the supported extractant layer and the substrate layout in the cartridge. The thickness of the extractant layer is related to the nature of the substrate material while the layout in the cartridge may be sparse or dense.

Dense cartridges are designed to be operated with the macropores full with the solutions, at least part of the time. Dense cartridges have thus a predefined fixed ratio β of the extractant to the solution.

Sparse cartridges are designed to provide easy and uniform access of a sprayed solution to the surface of the substrate-supported extractant. The thickness of the solution film in a sparse cartridge is controllable by the amount of solution sprayed within a spraying cycle.

Cartridges are intended to be manufactured in standard types, sizes, and properties.

The Flow arrangement

The flow arrangement provides for the donor and the recipient solutions to alternate frequently and periodically in being brought into contact with the TLX cartridge. This may be achieved by rotating the cartridge through regions where it is brought in contact with the respective donor or recipient solutions or by letting the donor and recipient streams reciprocate in contacting a standing-still cartridge.

Operation Program

The cyclic program of operation determines when and for how long each of the participating solutions is brought into contact with the cartridge. The cycle of operation includes necessarily a time for feeding the solutions and a time for discharging the solutions, which may or may not coincide. In addition, a cycle of operation may include a waiting time for extending the contact of the phases or other maintenance functions. The average throughput of a TLX plant will then almost always differ from the instantaneous rate at which the solutions are fed to the cartridge. Everything considered, the cycle period will be generally short, a matter of seconds. The recommended contact time as a function of the substrate type and phase ratio is part of the cartridge specification.

The multistage TLX process structure

Like in any other extraction process, when a single contacting stage fails to provide the desired extent of solute transfer between the donor solution and the recipient solution, one resorts to countercurrent multistage processing. However, the structure of a multistage countercurrent TLX plant differs from that of the familiar extraction and back extraction trains where an extractant-bearing solvent is circulated in a countercurrent direction to each of the donor and the recipient solutions as shown in Figure 1. It also differs from that in ion-exchange fixed bed processing.

Because in TLX, each stage performs a single operation of the entire process. When we stack together several TLX stages to form a multistage TLX process, with the product of one stage serving as the feed to a next stage, we obtain a countercurrent flow arrangement in which the donor solution is flowing in one direction and the recipient solution is flowing in the opposite direction, while the extractant is conceptually “flowing” in a crosscurrent direction to both as shown in Figure 4. Note that a single TLX column will replace an entire multitrain conventional extraction plant.

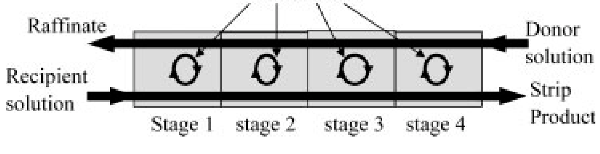

Figure 4. The multistage countercurrent TLX structure.

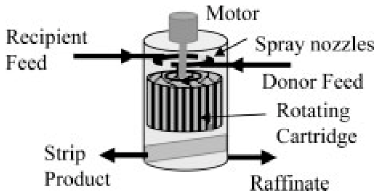

Figure 5. A rotary TLX cell.

Embodiment examples of TLX cells

We present, here, two particular equipment configurations of interest, out of several that have been tested successfully. For the sake of simplicity, all examples here refer to a process consisting of a single extraction step and a single stripping step.

Dense Cartridge Cells Embodiments. A dense cartridge cell is periodically flooded with the donor and the recipient solutions in alternating order. The filling and the emptying of the cell may be done with the help of pumping or by being pushed and replaced by some other fluid such as air or an inert gas or a liquid, which may be the processed solutions themselves. The timing may follow an immediacy pattern when the recipient solution displaces the donor solution and vice versa or may include idle time periods.

Sparse Cartridge Cell—The Rotary TLX Cell. The rotary TLX cell (RTLX) consists of a vertical cylindrical sparse cartridge that can be rotated on its vertical axis (Figure 5). The cartridge is divided into virtual sections. At any instant, one section of the cartridge is exposed to the donor solution, and the other section is exposed to the recipient solution. Rotation of the cartridge causes the sections to alternate in role. Two fixed sets of fine spraying nozzles are installed on top of the cartridge at fixed positions, one spraying the donor feed solution and the other spraying the recipient feed solution, each onto its respective section of the cartridge. Below the cartridge, there are two collecting pans, one collecting the raffinate and the other collecting the strip product.

The timed program of operation consists of (a) rapid switching of the sections position by rotation, (b) spraying time, during which both the donor feed and the recipient feed solutions are simultaneously sprayed onto their respective sections of the cartridge, (c) a wait time, (d) a shake time, during which the cartridge is gently shaken to reject any solutions that may cling onto the cartridge into the respective collecting pans. This timing cycle constitutes half a cycle of operation. When repeating the timing cycle, the section of the cartridge that was previously exposed to the donor solution will be exposed now to the recipient solution and vice versa. Two timing cycles constitute one process cycle. Process cycles are repeated indefinitely.

Multistage equipment embodiments

The Micro TLX Extractor (MTLX). MTLX is a dense cartridge multistage embodiment. It consists of an elongated tube filled with an elongated dense cartridge (Figure 6).

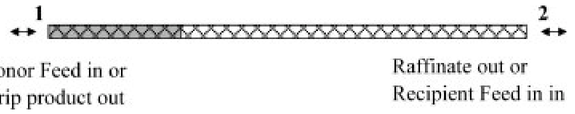

Figure 6. The micro-TLX extractor.

A fraction of the cartridge, close to end (1) of the tube is filled by pumping into it a batch of the donor solution. Then, this batch of solution is made to travel as a slug along the tube at a controlled velocity by injecting behind it air or an inert gas, until it is discharged at end (2) of the tube as a raffinate. Now a fraction of the cartridge, close to end (2) of the tube is filled by pumping into it a batch of recipient solution, and this batch of recipient solution is made to travel as a slug along the tube in a direction opposed to that previously traveled by the donor solution, at a controlled velocity by injecting behind it air or an inert gas, until it is discharged at end (1) of the tube as a strip product. This completes a cycle of operation that is repeated indefinitely. This maneuver results in each section of the cartridge being alternately flooded with the donor and the recipient solution as shown in Figure 4 except that the cycle will include time periods when some length of the cartridge will not be in contact with any of the solutions. Those idle intervals obviously sum up to a time overhead that reduces the average throughput when compared with the instantaneous pumping rate of each batch. Still, this mode of operation imparts the MTLX with an unrivalled simplicity and flexibility.

Simplicity—because the entire multitrain multistage plant consists of a simply operated single tube. Flexibility—because the same tube will serve as a multistage extractor for any desired number of stages, depending on the sizes of the batches of solution pumped in the extraction and the stripping steps which, by the way, need not be equal.

There is neither an upper nor a lower limit to the scale of a MTLX extractor. There may be an upper limit to the diameter of the containing tube that will maintain the integrity of the slugs of liquid along their travel path. When this is the case, a larger throughput is possible by operating several smaller tubes in parallel.

The MTLX is of particular interest at the lower end of the scale, for microextraction, in which it may consist of a single microporous capillary, hence its name. The MTLX promises to be an attractive, flexible, safe, and economical laboratory tool.

Multistage RTLX. Rotary TLX cells may be stacked to form a multistage countercurrent column.

Figure 7 depicts a three-stage column as an example. The operation of a RTLX column is the same as the operation of a single RTLX cell, with the cycles in all cells in the column synchronized.

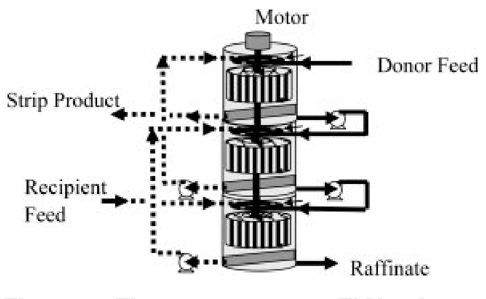

Figure 7. Three-stage rotary TLX column.

Multistage TLX performance analysis

Typical extraction objectives are to remove as much of the extracted species from the donor solution and to recover it in a concentrated form in the strip product. Measures of those objectives are

(a) The reduction ratio, R = (raffinate concentration)/(donor feed concentration) and

(b) The enrichment ratio, E = (strip product concentration)/(donor feed concentration).

Stressing any one of the two objectives may come at the expense of the other.

As we only wish to explore here the structural aspects of TLX, we shall assume that the solutions are dilute and study the case in which equilibrium between the phases is linear.

The design of a TLX column that is intended to process a concentrated solution, in which linear equilibrium may not be valid, will then follow a two-step procedure: first, using the linear model for a quick approximate evaluation of the number of stages necessary and the cartridge specification, followed by an accurate numerical simulation to fine tune the design.

Single-cell analysis

A component mass balance over a complete cycle gives

$$\begin{aligned} &F_d y_{df} + S x_s = F_d y_d + S x_e \\ &F_r y_{rf} + S x_e = F_r y_r + S x_s \\ &x_s = K_s y_r; \qquad x_e = K_e y_d \end{aligned} \tag{1}$$

Equation 1 may be rearranged to yield the products compositions for a single TLX cell.

Denoting $\varphi = \frac{F_r}{F_d}$; $\mu = \frac{K_e}{K_s}$; $\alpha = \frac{D_s}{D_e} = \frac{1}{\varphi\mu}$; where D_e is the extraction factor, $D_e = \frac{SK_e}{F_d}$, and D_s is the stripping factor, $D_s = \frac{SK_s}{F_r}$,

$$\begin{aligned} y_d &= \frac{[1+\alpha D_e] y_{df} + \varphi\alpha D_e y_{rf}}{1+(1+\alpha)D_e}, \\ y_r &= \frac{(D_e/\varphi) y_{df} + (1+D_e) y_{rf}}{1+(1+\alpha)D_e}, \end{aligned} \tag{2}$$

Evidently, $\varphi \leq 1$ or there would be no enrichment. Also, $\alpha < 1$ or equivalently $\mu > 1$ or there would be no extraction.

In the particular case of a solute-free recipient feed, or $y_{rf} = 0$, the single-stage reduction ratio R_1 and the enrichment ratio E_1 are

$$\begin{aligned} R_1 &= \frac{y_d}{y_{df}} = \frac{1+\alpha D_e}{1+(1+\alpha)D_e}; \\ E_1 &= \frac{y_r}{y_{df}} = \frac{(1-R_1)}{\varphi} = \frac{D_e}{[1+(1+\alpha)D_e]\varphi} \end{aligned} \tag{3}$$

Multistage TLX plant design

TLX Design Problem Formulation. Given a required plant donor solution throughput F'_{davg}, design objectives R and E, a given extractant and operating conditions (equivalent to specifying K_e and K_s).

Find the phase ratio, a corresponding number of TLX stages N and a strip solution flow rate that will satisfy the specifications R and E. On this basis, select a cartridge type and size that will satisfy the desired throughput F'_{davg}.

Multistage analysis

A structure similar to the one describing the multistage TLX has been studied by Rifai.[4] He provides a solution for the compositions in an N stage countercurrent extraction plus stripping plant with cross current circulation of the solvent, in the particular case when $y_{rf} = 0$. According to this solution, the raffinate composition for N stages and $y_{rf} = 0$ is

$$R(N) = \frac{y_{d1}}{y_{df}} = \frac{D_e - D_s}{D_e\left(\frac{D_e+1}{D_s+1}\right)^N - D_s}, \quad N > 1. \tag{4}$$

In terms of the parameters defined earlier, this translates into

$$R(N) = \frac{y_{d1}}{y_{df}} = \frac{(1-\alpha)}{\left(\frac{D_e+1}{\alpha D_e+1}\right)^N - \alpha}, \quad N > 1. \tag{5}$$

Following a simple mass balance, the enrichment ratio of the recipient product solution is given by

$$E(N) = \frac{(1-R)}{\varphi} = \frac{(D_e+1)^N - (\alpha D_e+1)^N}{[(D_e+1)^N - \alpha(\alpha D_e+1)^N]\varphi}, \quad N > 1. \tag{6}$$

Equation 5 can be reformulated to calculate the number of stages necessary to reach a specified reduction ratio R:

$$N = \frac{\log\left\{\frac{1-(1-R)\alpha}{R}\right\}}{\log\left\{\frac{D_e+1}{\alpha D_e+1}\right\}}. \tag{7}$$

An approximation to Eq. 5 may be useful for obtaining a quick estimate of the number of TLX stages necessary to achieve a desired reduction ratio R:

$$\begin{aligned} &\alpha < 1 \Rightarrow \left(\frac{D_e+1}{\alpha D_e+1}\right) > 1 \\ &\text{For sufficiently large } N, \left(\frac{D_e+1}{\alpha D_e+1}\right)^N \gg \alpha \\ &\text{Then, } \log(R) \approx \log(1-\alpha) - \left\{\log\left(\frac{D_e+1}{\alpha D_e+1}\right)\right\}N, \end{aligned} \tag{8}$$

which is a straight line in a plot of $\log(R)$ versus N with a slope of $-\log\left(\frac{D_e+1}{\alpha D_e+1}\right)$ (see Figure 8). For a high purity raffinate, the number of stages is readily obtained by plotting the straight line defined in Eq. 8.

We also find it useful to express N in Eq. 7 as a function of the reciprocal phase ratio $\frac{F_d}{S} = \frac{1}{\beta_d} = \frac{K_e}{D_e}$, which is a variable of physical significance representing the throughput rather than as a function of the abstract variables D_e and α:

$$N\left(\frac{F_d}{S}\right) = \frac{\log\left\{\frac{1-\alpha(1-R)}{R}\right\}}{\log\left\{\frac{K_e + \left(F_d/S\right)}{\alpha K_e + \left(F_d/S\right)}\right\}}. \tag{9}$$

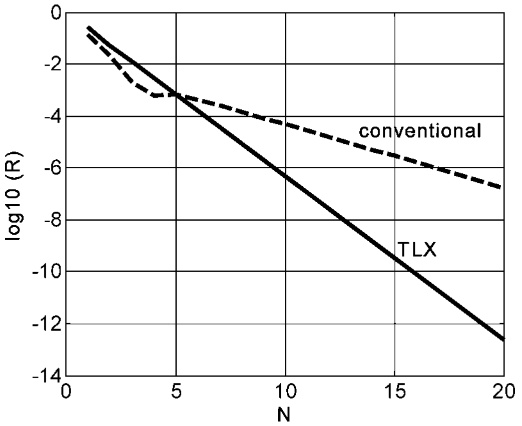

Figure 8. Typical plots of the reduction ratio versus N for α = 0.1, D_e = 5.69.

The phase ratio

The phase ratio is a parameter of central importance in TLX. The thickness of the extractant layer is determined by the supporting solid substrate, the thinner the better. The extractant layer will typically be 20–40 μm thick. On the basis of mass transfer considerations alone, we would prefer that the thickness of the solution film would also be as thin as possible, maintaining a high phase ratio, leading to more extraction, while also permitting an especially short contact time. On the other hand, a thin solution film also means a small throughput.

In the case of a dense cartridge, the phase ratio is a cartridge property. A denser cartridge engenders a higher phase ratio, making for more intensive contact at the cost of a smaller plant throughput. In the case of a sparse cartridge, the phase ratio is adjustable by means of the timing program.

Satisfactory results have been obtained with a donor solution layer thickness that was up to 10 times that of the extractant layer, but we need a more rational guide to our decisions. The suggested guide is to plot N versus $1/\beta$, following Eq. 9, for β up to 10. In case, there are more than one integer solutions for N in this range, we shall choose N on a cost-benefit basis, that is, by considering the incremental additional throughput we get when increasing N by one.

High purity raffinate

It is of interest to compare the reduction ratio R that is obtained in the TLX structure as shown in Figure 4 to that obtained in the conventional structure as shown in Figure 1 for the same conditions.

The performance of the conventional extraction-stripping scheme has been studied by Rifai.[5] A solution is offered for this system with a solute-free recipient feed:

$$\frac{R(D_e^{N+1}-1)-(D_e-1)}{(1-R)(D_e^{N-1})}=\frac{D_s^{M+1}-D_s^M}{D_s^M-1},$$

TLX is often constrained to have the same number of stages for extraction and stripping; thus, the comparison for $M = N$, which happens to be also according to Rifai[5] the optimum combination, yielding:

$$R_{\text{conventional}}=\frac{Q+(D_e-1)}{Q+(D_e^{N+1}+1)},\quad \text{where } Q=\frac{D_e^{2N-1}\alpha^N(\alpha D_e-1)}{(\alpha^N D_e^N-1)} \tag{10}$$

Figure 8 is a sample plot of log(R) versus N for TLX and for the conventional extraction scheme, for α = 0.1 and D_e = 5.69 (data relating to example 2 below).

Evidently, when a raffinate of extreme purity is desired, it is possible to obtain such with a significantly smaller number of TLX stages than would be required in the equivalent conventional scheme. This can be shown to be the case for a wide range of α and D_e.

The following two examples are intended to provide a feeling for the capabilities of TLX over a wide range of applications. The specific examples brought below have not been verified experimentally. They are in effect extrapolations of results obtained on a laboratory scale.

Design example 1

Task. Design a RTLX column that will process a relatively dilute donor feed solution according to the following specifications:

Throughput: 6 m^3/h (F'_{davg} = 1.67 kg/s)

Donor feed = citric acid solution at 10°C; recipient feed = water at 50°C; ρ_{soln} = 1000 kg/m^3.

Design objectives: 99% recovery and 500% enrichment (R = 0.01, E = 5).

Extractant: alamine 336, indicating K_e = 54 and K_s = 6. $\rho_{\text{extractant}}$ = 800 kg/m^3.

Design. Calculate: $\varphi = (1 - R)/E = 0.198$, ⇒ The strip solution rate should be 0.33 kg/s.

$\mu = K_e/K_s = 9$. Insert into Eq. 9, obtaining

$$N=\frac{1.6478}{\log\left\{\frac{\left(\frac{F_d}{S}\right)+54}{\left(\frac{F_d}{S}\right)+30.3}\right\}}, \tag{11}$$

Plot N as function of F_d/S over the range F_d/S = 1–10 (Figure 9).

There are, within the range explored, two integer values for N, N = 7 and N = 8 related respectively to F_d/S = 3 and F_d/S = 9. The actual throughput in each case can be evaluated by factoring in the additional contact time mandated by the thicker solution film. We shall then have to choose between two alternatives, each characterized by a number of stages and a throughput. Suppose this indicates a preference for N = 8 at the corresponding $1/\beta_d$ = 9 or β_d = 0.11 with a timing cycle period, T = 8 s. This will guide the choice of a cartridge and the cartridge extractant hold up:

$$S=\left(\frac{S}{F}\right)F'_{\text{davg}}T=1.47\text{ kg}.$$

Select a sparse cartridge whose specified extractant hold up is ≥ 1.5 kg and accepts an instantaneous spraying rate

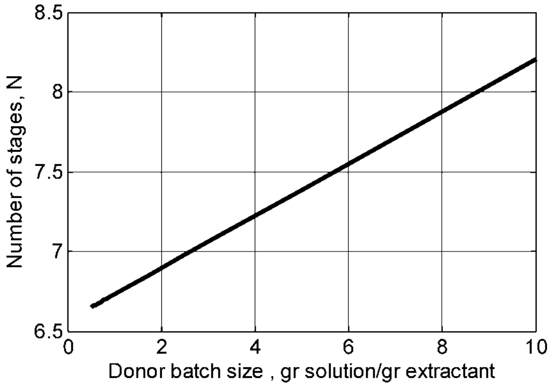

Figure 9. Number of stages necessary to satisfy the example specifications.

$F'_d \geq 1.67$ kg/s. The plant will use a total of $1.47N = 11.8$ kg extractant.

Design example 2

Task. It is desired to test in the laboratory the feasibility of purifying a solution by removing 99.999% of a dissolved impurity by extraction at 25°C and rejecting it into treated hot water at 60°C. The solution density is 1000 kg/m^3. The extractant density is 800 kg/m^3. Data about the equilibrium composition of the phases are not available.

The MTLX extractor at our disposal consists of a 0.5 m long, 0.6 mm ID × 1 mm OD single microporous capillary having a microporosity of 0.4.

The dense cartridge spec is 0.71 (m^3 extractant)/(m^3 solution).

Therefore, $\beta = 0.71 \times 0.8/1 = 0.569$ (kg extractant/kg solution).

The MTLX tube will contain 141 mg of solution and use 80 mg of extractant.

Procedure

Using MTLX for the generation of equilibrium data. With both the feed solution and the stripping water at 25°C:

(a) Soak the capillary with the extractant.

(b) Inject some donor feed solution through the capillary generously such as to wash it and load the extractant with the impurity up to equilibrium with the donor feed.

(c) Empty the capillary by air injection.

(d) Fill the capillary with a 141 mg batch of water at 25°C. Wait for 3–5 s and then empty the capillary by air injection, collecting the product for analysis.

(e) Fill the capillary with a 141-mg batch of donor feed solution at 25°C. Wait for 3–5 s and then empty the capillary by air injection, collecting the product for analysis.

Repeat steps (d) and (e) once or more to make sure that the limit cycle has been attained as evidenced by constancy of the analysis results.

(f) Now having measured y_{df}, y_d, y_r, and with β specified as a property of the cartridge and with $\varphi = 1$ and $\alpha = 1$ applying by definition to this experiment, use Eq. 3 to evaluate

$$K_e: \qquad K_e = \frac{D_e}{\beta} = \frac{(y_{df} - y_d)}{\beta(y_d - y_r)}.$$

(g) Repeat steps (d) to (f) with the feed and stripping solutions at 60°C to obtain K_s.

Using MTLX for the Generation of Design Parameters. Now knowing $D_e = \beta K_e$ and $D_s = \beta K_s$ and $\alpha = D_s/D_e$, use Eq. 7 to calculate N:

$$N = \frac{\log\left\{\frac{1-(1-R)\alpha}{R}\right\}}{\log\left\{\frac{D_e+1}{\alpha D_e+1}\right\}} = \frac{\log\left\{\frac{1-0.99999\alpha}{0.00001}\right\}}{\log\left\{\frac{D_e+1}{\alpha D_e+1}\right\}}.$$

For example, suppose we found in part A that $K_e = 10$ and $K_s = 1$, then inserting the values of α and D_e in the equation, we find $N = 7.87$, that is, we shall need $N = 8$ MTLX stages.

We are set now to implement the multistage test in the MTLX apparatus by

(a) Inject at end (1) of the tube a $141/N = 17.6$ mg batch of the donor feed solution at 25°C.

(b) Push the batch through the tube at a velocity of $v = 0.5/3N = 0.02$ m/s with air until it emerges at end (2) of the tube where it is collected as a raffinate for analysis.

(c) Inject at end (2) of the tube a $141/N = 17.6$ mg batch of the water at 60°C.

(d) Push the batch through the tube at a velocity of $v = 0.5/3N = 0.02$ m/s with air until it emerges at the end (1) of the tube where it is collected for analysis.

Repeat steps (a)–(d) one or more times to ensure constancy of the compositions.

Use the results to fine tune the design of a scaled up TLX plant.

Note, in Figure 8, that two conventional columns, 13 stages each would have been needed to obtain the specified $R = 0.00001$ when compared with a single eight-stage TLX column.

Strengths and Limitations of the TLX Process

Strengths

Efficient Use of the Extractant. TLX will operate with a pure extractant. The amount of extractant applied is minimal as every bit of it is fully accessible to contact the solutions. An opportunity is thus created to widen the exploitation of exotic extractants (e.g., ionic liquids), in applications perhaps deemed so far as prohibitive.

Safety and Health Profile Improved. TLX avoids solvents. Be it in a plant or in the laboratory, solvents represent a significant safety and health hazard. Explosion proof equipment mandated in extraction plants adds to their cost and even so, fires have been known to occur in extraction plants. The avoidance of flammable solvent inventories represents an inherent safety approach. Solvents are also known to unavoidably emanate as vapors to the atmosphere and drain into the ground and plant effluents, thereby representing a health liability to the operators and to the environment. Avoiding solvents altogether is certainly the safest approach.

Organic Entrainment Eliminated. Conventional extraction technology invariably includes a separation of the phases, which is never ideal, leaving some solvent entrained in the aqueous effluents of the plant. The plant effluents in a conventional extraction plant must therefore be further processed to remove this residual solvent, which may otherwise affect the product quality or leak to the environment. In TLX, there is no such entrainment.

Scale. TLX may be applied to liquid extraction at any scale, from the microscale to any larger scale. The modularity of the TLX cell makes for direct and reliable scale up or scale down of any process from the laboratory to any desired scale. Reducing the scale of an experiment in the laboratory also minimizes the consumption of chemicals in general, affecting safety, cost, and disposal problems.

Fit for Extreme Raffinate Purity. A relatively modest TLX column will provide extreme raffinate purities that would otherwise require a couple of much larger columns in the conventional scheme.

Low Pressure Drop. Pressure drop in TLX is low. This is critically important on the microscale.

Simplified Design and Operation. The choice of an extractant is guided by chemical considerations only. The design and scale up of TLX is free of the two-phase fluid dynamics considerations that plague conventional liquid–liquid extraction. The state of a TLX device will converge to a limit cycle within a few cycles indicating a short start up time.

This sums up into facilitated application of extraction.

Operating Cost. In the absence of mixing, the energy consumption in the operation of a TLX plant is even lower than that in a conventional extraction plant. It is probably the lowest of any separation plant.

Limitations

Generality. Even though the choice of an extractant is considerably less restricted in TLX than in conventional liquid–liquid extraction, the performance of TLX still depends on the selection of an extractant. This brings TLX to a generality standing in line with other separation methods that rely on a material separating agent such as adsorption or ion exchange but not quite as general as those using an energy separating agent such as distillation.

Suspended Solids. TLX is limited to the processing of clear or filtered solutions, because suspended solids or crud could possibly clog the relatively narrow passages. This will naturally exclude its application to some traditional liquid–liquid extraction applications such as in the mining industry, except perhaps where prefiltration would turn out to be economical.

Mutually Soluble Agents. The feed solutions should preferably be free of mutually soluble agents as those could gradually dilute and eventually remove the extractant from the cartridge, forcing an early recharge of the cartridge with a fresh batch of extractant.

Conclusion

TLX appears to be a promising alternative to many present day liquid–liquid extraction separations, be it in the laboratory or in the field. It also promises to facilitate the application of exotic extractants in separations and chemical reactions.

TLX may be classified as a “green” processing method as it conforms to inherent safety and inherent environment protection practice. Although those qualities are shared with ion exchange, TLX is clearly differentiated from ion exchange is that it will support flow rates that are much higher. Also, whereas an ion exchange process capacity is measured by the amount of solute retained thereby essentially limiting it to the processing of dilute feeds, TLX will process solutions of any concentration with almost equal ease.

Significantly, the exploration of TLX has thrust upon us the necessity to consider the extraction/stripping process as an entity, leading to the formulation of some relatively simple design rules. The modularity of the TLX technology permits direct translation of laboratory experience to a full-size industrial plant. The degrees of freedom in the design of a TLX plant are fewer than those in the design of a conventional LLX plant. The combination of simplicity and modularity may pave the way to widening the scope of extraction applications.

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Notation

t = contact time between the phases (s)
v = traveling velocity of solution slug in MTLX (m/s)
x = extractant composition at equilibrium (mass fraction)
y = solution composition (mass fraction)
D = extraction or stripping factor, dimensionless
E = enrichment ratio = (strip product concentration)/(donor feed concentration)
F = mass of a batch of solution (kg)
F' = instantaneous flow (or spraying) rate (Kg/s)
K = equilibrium distribution, mass fraction in extractant/mass fraction in solution
N = number of stages
R = reduction ratio = (raffinate concentration)/(donor feed concentration)
S = mass of the extractant (kg)
T = operation cycle period (s)
α = ratio D_s/D_e of stripping to extraction factors, dimensionless
β = phase ratio, kg extractant/kg donor solution
φ = ratio of stripping to extraction feed streams, dimensionless
μ = ratio of distribution constants in extraction/stripping, dimensionless
ρ = density, kg/m^3

Subscripts

d = donor
e = extraction
f = feed
r = recipient
s = stripping

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