Continuous extraction in a laboratory mixer-settler extractor

Introduction

Liquid-liquid extraction is an operation by which a solute species is removed from a solution by contact with an immiscible solvent. It is a mass transfer operation between two liquid phases. Each phase will have a different concentration with respect to the solvent. The phases can be allowed to separate and, if then mixed again, a further change in solute concentration occurs in each phase. This principle can be used for purifying liquid mixtures. Liquid-liquid extraction is used when the separation cannot be accomplished effectively by distillation, where the compounds in the solution have nearly the same boiling point or decomposition occurs upon heating. A common example is the recovery of minerals with solid-liquid extraction and subsequent separation of minerals from their mother liquor. The procedure is also widely used in pharmaceutical, food and petrochemical industries. In general, to process large amounts of samples/materials, or if the separation requires many theoretical steps, the mixer-settler is applicable.

Theoretical background

Definitions

The simplest extraction system comprises three components: the solute or the material to be extracted; the solvent, which must be completely immiscible with other liquid; and the diluent or non-solute portion of the feed mixture to be separated. It should be noted that a distinction must be made between the light and heavy phase, between the dispersed and continuous phase, and between the raffinate and extract phase. The solvent-rich phase leaving the extractor is termed the extract, while the solvent-lean (diluent-rich) phase is termed the raffinate. In an extraction, the solvent phase will always be the extracted phase; however, depending on the circumstances, the solvent can be either the heavy phase or the light phase and either the dispersed phase or the continuous phase. For a simple ternary system an equilibrium ratio (Nernst distribution coefficient) is defined as

\[ m = \frac{y}{x} \]  \hspace{1cm} (1)

Where \( y \) is the solute concentration in the extract phase,

\( x \) is the solute concentration in the raffinate phase.

The above-mentioned concentrations could be given either in molar fraction or in dimensions of (kg/m\(^3\)), (kg/kg) or (mol/m\(^3\)). The raffinate phase contains the material which is supposed to be extracted. The equilibrium ratio (distribution coefficient) depends on the temperature and composition. For practical purposes, the effect of pressure can be ignored as long as a liquid-liquid extraction unit is operated under moderate pressure. Reliable equilibrium data
are essential for analysis and design of an extraction. A large number of equilibrium data have been published in the literature. [1]

Another important feature of the operation is the ratio between the flow rates of the two immiscible liquids ($f$, phase ratio):

$$f = \frac{\dot{V}_E}{\dot{V}_R} \quad \text{or} \quad f = \frac{\dot{m}_E}{\dot{m}_R} \quad \text{or} \quad f = \frac{\dot{n}_E}{\dot{n}_R}$$

(2)

Where $\dot{V}$ is the volumetric flow rate,

$m$ is the mass flow,

$n$ is the molar flow;

indices $R$ and $E$ refer to the raffinate and extract phases, respectively.

The value of $f$ depends on the dimensions of the aforementioned flows, so care must be taken to use the same concentrations or flows in a given system.

**Countercurrent extraction calculations**

It is convenient to model the extraction process as a series of equilibrium stages (with $N$ denoting the number of equilibrium stages) even if the equipment operates in a differential mode (as in packed extraction columns). A theoretical or ideal stage is one where contact between the phases is sufficiently intimate and is maintained for a sufficient period of time for the distribution equilibrium to establish, bringing the raffinate and extract phases into equilibrium.

A countercurrent cascade allows a more complete removal of the solute than a concurrent extraction; furthermore, solvent is re-used so that less solvent is needed compared to a single stage extraction. A schematic diagram of a countercurrent multi-stage extraction is shown on Figure 1. ($E$ refers to extract, while $R$ refers to raffinate phase).

**Fig. 1: Schematic flow diagram of countercurrent cascade**

In the special case where the solvent and diluent are completely immiscible and the partition coefficient ($m$) is constant, an analytical equation can be used for the extraction calculations:

$$\frac{x_N - y_{N+1}/m}{x_0 - y_{N+1}/m} = \frac{E - 1}{E^{N+1} - 1}$$

(3)

where $E = f \cdot m$ is the extraction factor,
$y_{N+1}$ is the concentration of the material in the extraction solvent (in most cases a pure solvent is used, thus $y_{N+1} = 0$).

From equation (3) or from the diagram below (Fig. 2.) we can calculate the extraction loss ($x_N/x_0$), the extraction factor ($E$) or the number of equilibrium-states ($N$), if two of them are given.

Fig. 2.: Extraction loss diagram for a countercurrent extractor. $N$ is on the x axis, while $y$ axis shows the extraction loss in percentage.
If the solvent and diluent are completely immiscible, or their solubility does not change over the range of concentration of distributed substance, a McCabe–Thiele type analysis can be used for calculations. The same notation will be used as in the previous case. Raffinate rates and extract rates are constants throughout the apparatus. A solute flow balance for stages \( n \) through \( N \) is

\[
\dot{m}_R x_{n-1} + \dot{m}_E y_{N+1} = \dot{m}_R x_N + \dot{m}_E y_N
\]

(4)

Which may be rearranged to give:

\[
y_N = \frac{\dot{m}_R}{\dot{m}_E} (x_{n-1} - x_N) + y_{N+1}
\]

(5)

The latter is an equation of a straight line with a slope of \( \frac{\dot{m}_R}{\dot{m}_E} = \frac{1}{f} \). Since \( n \) represents any stage, the line (an operating line) can be drawn between the two points whose coordinates are \( (x_n, y_{n+1}) \) and \( (x_0, y_1) \). Figure 3 illustrates the graphical technique for counting off the number of equilibrium stages required. By reducing \( f \) (thus increasing the slope of the operating line), the concentration in the extract phase \( (y_j) \) increases, but more equilibrium steps are required for the separation. However, reducing \( f \) has a limit: when the operating line crosses the equilibrium line at composition \( x_0 \), the separation could only be carried out with an infinite number of equilibrium steps. In this case the phase ratio is called the minimal phase ratio and denoted by \( f_{\text{min}} \). When planning the procedure this must be strongly considered and a phase ratio far exceeding \( f_{\text{min}} \) must be chosen.

When the two phases are completely immiscible and the ratio between the flow rates changes only because solute is transferred from the raffinate phase to the extract phase, the same diagram and method can be used, with the criterion that we have to calculate with clean
solvents. In this case, the phase ratio $f$ is constant. The coordinate system must be defined differently from what was shown in figure 3, changing the axes so that

\[ Y = \frac{\text{solute}}{\text{solute-free solvent}} \text{ (kg solute/kg solvent)}, \]
\[ X = \frac{\text{solute}}{\text{solute-free diluent}} \text{ (kg solvent/kg of diluent)}. \]

The total flow rates of the two phases then become:

$E$: solute-free extract (usually pure solvent),
$R$: solute-free raffinate (usually pure diluent).

For partially miscible systems, ternary diagrams can be used for extraction calculations [2]. Systems with more than three components require computers to solve their model equations.

**Equipment**

Having decided on liquid-liquid extraction as the unit operation to reach a given separation, it is necessary to select suitable equipment for the task. The choices are: a mixer-settler, a series of mixer-settlers, some other contactor such as a column (which may be agitated or pulsed), or a centrifugal device.

Mixer-settler systems are relatively easy to operate, flexible and fairly simple to design, are free of backmixing, and the stage efficiencies are usually greater than 90%. They can handle difficult-to-disperse systems, such as those having high interfacial tension and/or large density differences between the phases. They can also cope with highly viscous liquids and solid-liquid slurries. The main disadvantages of mixer-settlers are the large ground area they occupy, the amount of piping required and the need for a solvent recovery plant. The equipment provided for small scale continuous tests consists of a series of small mixer-settlers, each vessel having a capacity of 225 dm$^3$. The apparatus design is of the cascading type and is made of glass. Each stage comprises a separate mixer and settler. The numbers of the stages are equal to the number of the equilibrium stages. The solvent and aqueous phases flow in a countercurrent manner from one stage to the next by gravity. Control of the interface level between the two phases can be achieved by adjustment of the height of the heavy phase outlet denoted by $H_N$ in figure 4. One stage of the mixer-settler apparatus is shown in Figure 4.
Geometric sizes of the extractor

Sizes of the mixing vessels
The emulsion formation in most of the cases takes place in a simple stirred vessel. Vessels with the following stirrers are suggested: turbine, disc-turbine or centrifugal stirrers. Furthermore, there are baffles in the tanks to provide more effective stirring. The commonly used geometric sizes are:

- The diameter of the stirrer: \( d_s = 0.33-0.4D \)
- Width of the stirrer balde: \( b = 0.05-0.1D \)
Width of baffle: \( w = 0.07 - 0.1D \)
Height of the liquid \( H = D \)
Stirrer distance from the bottom of the vessel: \( h = 0.33 - 0.5D \)

\( D \) is the diameter of the tank in meters.

Before moving to industrial scale application, the behavior of the liquid-liquid mixture in question must be investigated on laboratory scale devices to study the mass transfer. This is accomplished in batch experiments, as continuous systems are very costly due to their high material consumption. In a batch measurement, the two phases are layered on each other carefully. After this, the stirring is switched on and the chronometer is started. Samples are taken at certain times and, after sedimentation, the concentrations of the extractable materials are measured in both phases. The mass transfer can be defined with a first order kinetic, such as:

\[
1 - \eta_b = \frac{c - c^*}{c_0 - c^*} = e^{-kt}
\]  

(6)

Where \( \eta_b \) is the mass transfer efficiency in batch system,
- \( c \) is the concentration of the solute at time \( t \) (mol/dm\(^3\)),
- \( c_0 \) is the initial concentration (mol/dm\(^3\)),
- \( c^* \) is the concentration of equilibrium (mol/dm\(^3\)),
- \( k \) is the rate coefficient (1/s),
- \( t \) mixing time for a batch extraction (s).

The value of \( k \) rate coefficient can be determined by plotting \( \log(1-\eta_b) \) values versus time. Then this \( k \) value can be applied for the mixing vessels’ calculations in continuous experiments:

\[
1 - \eta_c = \frac{c - c^*}{c_0 - c^*} = \frac{1}{1 + \bar{t}k}
\]  

(7)

Where \( \eta_c \) is the mass transfer efficiency in the continuous mixing and \( \bar{t} \) is the average residence time (sec).

When working with molecules having low molar mass and viscosity, a residence time of 1–2 minutes should be enough to reach the equilibrium state. In more reactive processes (such as extraction of metals or gathering antibiotics produced by fermentation) longer residence times could be necessary and should be determined by measurements. The volume of the tank can be calculated from the feed flow and the residence time:

\[
V = \bar{t}(\dot{V}_{R0} + \dot{V}_{E(N+1)})
\]
The stirring rate is chosen with the following method. First, we mix the two phases in a laboratory vessel, with a volume of at least 10 dm$^3$. We set the stirring rate so that a homogenous phase is obtained in the vessel. The criteria of the scaling up is to have the same stirring power per volume of liquid both in the laboratory and in the industrial vessel. When stirring a liquid-liquid mixture, the mixing Reynolds number (Re$_m$) is high, thus the stirrer works in the turbulent region where the mixing Euler number is a constant. The power output of the stirrer depends upon the diameter and the stirring rate:

$$P = Eu * d_s^3 n^3 \rho \sim d_s^5 n^3$$

(9)

The volume of the stirred liquid is proportional to the cube of the stirrer diameter:

$$V = \frac{D^2 \pi H}{4} \sim d_s^3$$

(10)

In the equations $P$ is the power requirement of the stirrer (W),

$n$ is the stirring rate (1/sec),

$\rho$ is the density of the liquid emulsion (kg/m$^3$).

The stirring rate of the industrial stirrer is obtained from the criteria of equal power input per unit volume:

$$n_i = n_m \left(\frac{d_{xi}}{d_{sm}}\right)^{2/3}$$

(11)

Where $m$ index refers to the model experiment,

$i$ index refers to the industrial application.

**Geometric sizes of the settling pan**

The conventional settlers are cubical or vertical cylinder tanks. Emulsion breaking is not a precisely known phenomenon. In most cases, the key phenomenon is the aggregation of the droplets (coalescence), not sedimentation. Coalescence depends on the physicochemical properties, concentrations, and temperatures of the components. Thus, settlers must be designed based on the results of empirical experiments. Batch experiments offer an easy method to measure the sedimentation. The two liquids are measured into a vessel, and stirred at a high enough rate to create a homogeneous emulsion. Stirring is switched off after a few minutes, and the sedimentation time is measured. A sedimentation diagram can be drawn from the results (figure 5.), showing the height of the liquid versus measurement time.
The apparent sedimentation speed can be determined from the measurement, and from that the specific loading of the industrial equipment can be calculated (in dimensions of \([\text{m}^3/\text{m}^2\text{h}]\)):

\[
\frac{\dot{V}}{A} = \frac{H_d}{t_d}
\]  

(12)

Where \(\dot{V} = \dot{V}_{R_0} + \dot{V}_{E(N+1)}\) is the feed flow rate (\(\text{m}^3/\text{h}\)),

\(A\) is the surface of the settler (\(\text{m}^2\)),

\(H_d\) is the height of the liquid in the experiment in batch mode (\(\text{m}\)),

\(t_d\) is the sedimentation time.

The concentration dependence of the partition coefficient could be investigated also by sampling all of the vessels in a continuous measurement, separating the emulsions in separation funnel and measuring the concentrations in both phases.

**Measurement procedure**

The extractor

The two-stage extractor consists of 4 glass vessels with the same volume. The stirrers of the vessels could be controlled individually so a different stirring rate can be set in each vessel. The liquids are pumped into the vessels by a peristaltic pump; the volumetric flow rates are measured by a rotameter. The raffinate and extract streams flow into the collector vessels via a overflow tube and their quantity is determined by mass measurement. The level of the phase line (internal phase ratio) is set by changing the height of the heavy phase overflow pipe.

Extraction procedure – extraction of succinic acid from its aqueous solution with \(n\)-butanol

Fill the mixing and the settler units of the equipment with butanol-saturated water (lower phase) and with water-saturated butanol (upper phase). The volume ratio should be 1:1 in the vessels. During the entire measurement, the water level of the equipment must be checked and
adjusted when necessary. Before starting the extractor, the outlet pipes must be inserted into the collector vessels without touching the liquid inside. Start the stirring at 500 rpm.

The exact feed amount is given by the supervisor (0.8–1.2 dm³/hours suggested in general). When starting the feed, the rotameters should be checked and kept constant for the whole measurement by adjusting the peristaltic pumps. The volumetric flows corresponding to different settings of the peristaltic pumps are determined at the end of the measurement via calibration using the 3-way valves.

During the measurement the stirring (i.e. the emulsion formation), the water level and the feed must be supervised and the settings must be adjusted if necessary. During the start-up period, samples must be taken from the effluents and the concentration of succinic acid must be measured by titration.

\textit{Titration method}

20 ml of the sample is titrated with NaOH (the concentration of 0.1 mol/dm³) in the presence of phenolphthalein indicator. 10 ml of water should be added to the organic phase to promote the salt formation reaction. When the concentrations are constant in the effluents (about 40 minutes) the continuous measurement can be started.

\textit{Measurement procedure}

The plastic vessels must be weighed empty, and the solutions have to be collected in these vessels. After a half an hour the new (gross) weight and the acid content must be measured. Samples have to be taken from the settlers from both phases and their concentrations must be measured. After this, the feed must be stopped by switching off the pump and closing the rotameters. Stirrers also have to be switched off, the settler vessels must be emptied, butanol from stirrer vessel ‘A’ must be removed by rinsing with water. Samples must be taken from the initial solutions also, and their densities and succinic acid concentrations must be measured.

A conventional equilibrium extraction measurement must be done from the feed samples by using separation funnels. From this extraction measurement, the partition coefficient can be determined. (Measurements could be carried out at different concentrations of succinic acid by changing the quantity and the ratio of the phases).

\textit{Measurement data:}

<table>
<thead>
<tr>
<th>Water-saturated phase feed:</th>
<th>0.1 M NaOH (ml):</th>
<th>concentration:</th>
<th>density:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotameter:</td>
<td>volumetric flow:</td>
<td>density:</td>
<td></td>
</tr>
<tr>
<td>n-butanol-saturated phase feed:</td>
<td>0.1 M NaOH (ml):</td>
<td>concentration:</td>
<td>density:</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Start-up time measurement:</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
</tr>
<tr>
<td>(minutes)</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>0</td>
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<tr>
<td>10</td>
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<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>40</td>
</tr>
</tbody>
</table>

Steady state:
Measurement time:
Water collector vessel: tare: gross weight: raffinate: density:
0.1 M NaOH (ml): concentration:
Organic solvent collector vessel: tare: gross weight: raffinate: density:
0.1 M NaOH (ml): concentration:
Settler ‘A’: water-saturated phase: 0.1 M NaOH (ml): concentration:
Organic-saturated phase: 0.1 M NaOH (ml): concentration:
Settler ‘B’: water-saturated phase: 0.1 M NaOH (ml): concentration:
Organic-saturated phase: 0.1 M NaOH (ml): concentration:
Equilibrium measurement: water-saturated phase: 0.1 M NaOH (ml): concentration:
buthanol-saturated phase: 0.1 M NaOH (ml): concentration:

Additional information:

For the batch measurement a conical glass vessel is used having a volume of 10 dm$^3$. In the vessel, there are 4 baffles inserted. To check the level in the vessel, a measure scale is fixed to its outside wall. For stirring, a six-blade turbine stirrer is used.
The geometric sizes of the stirrer and the vessels must be written down. Measure 8 dm$^3$ solution into the 10 dm$^3$ vessels, the phase ratio will be given by the supervisor. The liquid level in the tank and the level of the phase boundary must also be written down.
Start the stirrer, and slowly start to increase the stirring rate until the liquid appears to be homogenous. Write down this value. Stirring has to be run for at least 5 minutes to reach a stable emulsion structure. Stop the stirring at certain times and read off the phase boundary of the clean phases (the upper phase is butanol, the lower is water). Sedimentation ends when the emulsion completely disappears.
Repeat the measurement by using 1.5 times higher stirring speed.

Measurement data should be collected in a table, for example:
Diameter of the tank: cm
Height of the tank: cm
Diameter of the stirrer: mm
Volume of the organic phase: dm$^3$
Volume of the aqueous phase: dm$^3$
Temperature of the liquid: °C
Liquid level in the tank: cm
Phase boundary level: cm
Distance of the stirrer from the top of the tank: cm
Stirring at: rpm

Sedimentation experiment

<table>
<thead>
<tr>
<th>time (s)</th>
<th>upper level (mm)</th>
<th>lower level (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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</table>

Evaluating the experimental results

Constructing a net material balance

\[
(\dot{V}_{R_0} \cdot \rho_{R_0} + \dot{V}_{E(N+1)} \cdot \rho_{E(N+1)}) \cdot \Delta t = m_{R_N} + m_{E_1}
\]  
(13)

\(\dot{V}_{R_0}\) is the volumetric flow rate of the water-saturated phase (cm³/min),
\(\rho_{R_0}\) is the density of the water-saturated phase (g/cm³),
\(\dot{V}_{E(N+1)}\) is the volumetric flow rate of the injected butanol-saturated phase (cm³/min),
\(\rho_{E(N+1)}\) is the density of the butanol-saturated phase (g/cm³),
\(\Delta t\) is the time (min),
\(m_{R_N}\) and \(m_{E_1}\) are the quantities of the raffinate and the extract flows (g).

The error of the net material balance (as a percentage of the feed) also has to be calculated.

Succinic acid component balance

\[
m_{R_0}x_0 = m_{E_1}y_1 + m_{R_N}x_N
\]  
(14)

Where \(x_0\) is the succinic acid concentration of the feed (g/g),
\(m_{R_0} = \dot{V}_{R_0}\rho_{R_0}\Delta t\) is the mass of the water-saturated feed in \(\Delta t\) time (g),
\(y_1\) is the succinic acid concentration in the extract (g/g),
\(x_N\) is the succinic acid concentration in the raffinate (g/g).

The error of the material balance (as a percentage of the feed) has to be calculated.

Investigation of the extraction stages:

Calculate the partition coefficient for each equilibrium stage.

Calculation of the retention time:
Calculate the average retention time of the phases ($\bar{t}$) in one stirring unit.
The volume of the stirring vessel is $V = 225 \, cm^3$.
The average retention time in one stirring vessel can be calculated as:

$$\bar{t} = \frac{V}{V_{R_0} + V_{E(N+1)}}$$

(15)

Apparent sedimentation speed:

$$u = \frac{H_d}{\bar{t}_d} \quad (m^3/m^2h)$$

(16)

Further calculations and graphs to hand in:
1. The start-up curve (changing of $y_1$ versus operating time).
2. Net material balance and the component balance of succinic acid and their errors.
3. The measured partition coefficient in certain units. Brief evaluation.
4. Residence time in the mixing vessel.
5. The minimal stirring revolution for a given phase ratio.
7. The apparent sedimentation speed from the known sedimentation time and the height of the liquid.

Recommended literature:


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