Extraction

*Liquid-liquid and aqueous two-phase extraction*

Henna Pauliina Ahokas, 657945
Johanna Kuronen, 477167
Yingfeng Wang, 661151
Espoo, 4.12.2017
# Table of contents

Abstract.............................................................................................................................................. 2
Background........................................................................................................................................ 2
Theory............................................................................................................................................... 3
   Principle........................................................................................................................................ 3
   Selection of solvent..................................................................................................................... 6
Importance / Case study .................................................................................................................... 6
   Importance.................................................................................................................................... 6
   Case study from bioprocess technology ...................................................................................... 7
Conclusions........................................................................................................................................ 8
References......................................................................................................................................... 10
Abstract

Extraction is a separation method based on isolating components based on their different solubilities on different solvents. Liquid-liquid extraction (LLE) is the most widely used type of extraction, and it consists of two liquid solvent phases. These are usually water or an aqueous phase and an organic solvent. Aqueous two-phase extraction (ATPE) is a unique type of liquid-liquid extraction, which consists of aqueous solutions of two polymers or a polymer and a salt. Liquid-liquid extraction is an important separation method in traditional industries such as hydrometallurgy and chemical processing, especially where distillation cannot be used. Aqueous two-phase extraction is used and researched especially in the biomolecule separation and purification because of its good features in for example protein recovery.

Background

When a compound or compounds need to be separated from a mixture to form a more distinct product, a separation process is needed. One of these processes is extraction, which is based on transferring components from one phase to another. It is based on the separable compound’s different solubility in different solvents. These solvents can mix with each other only to a limited extent so that they can be separated from each other. (Müller et. al. 2015) When the wanted compound has been extracted to the wanted solvent, the different phases are separated from each other and the compound-containing mixture goes through a separate process phase, for example distillation or stripping, to separate the compound from the solvent.

One of the most important types of extraction is liquid-liquid extraction (LLE), or solvent extraction. In LLE there are two liquid phases between which the compound transfer takes place. Usually one of the solvents is an aqueous mixture or water and the other is an organic liquid, for example dichloromethane or diethyl ether. (Galceran & Puignou 2006) LLE was initially utilized in the 1930’s in the petroleum industry. Since then, it has been used widely in different fields of industry including hydrometallurgical and pharmaceutical industries. (Law & Todd 2008)
Aqueous two-phase extraction (ATPE) is a form of liquid-liquid extraction, but it has unique features. In ATPE, the solvents can be aqueous solutions of two polymers or a polymer and a salt. (Goja et. al. 2013) Commonly used ATPE systems include polyethylene glycol (PEG) as the polymer and for example a phosphate as the salt phase. ATPE has been used since the 1960's and it's mainly used in biomolecule separation and purification, as it prevents for example protein denaturation better than the traditional liquid-liquid extraction. (Iqbal et. al. 2016; Chethana et. al. 2006; Goja et. al. 2013)

**Theory**

**Principle**

A liquid-liquid extraction is a technique for separating two immiscible liquids that are used to isolate components of a mixture based on a difference in their solubilities. In this technique, the idea is to separate a desired dissolved component from its solvent by transferring it to another solvent. The solvent in which the compound is transferred to is called the extract and the solvent, from which the component was transferred, is called raffinate. The transferring is caused by solvents' different solubilities and the larger the difference is, the greater is the extend to which the compound is extracted. (De Haan & Bosch 2013) However, according to Hendriks et. al. (2007) solubility can be changed by modifying the pH-value of the solvent. The adjustment of pH to the effective level will lead to higher selectivity. The right pH-value can be determined with the Henderson-Hasselbalch Plot. (Hendriks et. al. 2007) Down below in figure 1 is presented one example of the Henderson-Hasselbalch Plot. In this case recovery of amitriptyline is highest at pH-value higher than 9.
When the suitable solvents have been chosen and tested and the needed facilities are designed and built, the liquid-liquid extraction process starts with a loading the solvents into the column. Then solvents are agitated with a mixer to ensure that solvents are thoroughly dispersed. Other than mechanical stirring, pump circulation and air agitation can be used as well. Below is shown (fig 2) a schematic of a mechanical mixer. Also, extractors can be used to maximize the dispersion of one phase to another. However, emulsions may occur in over-agitating, especially with halogenated organic phases, not often with ethers. (De Haan & Bosch 2013)

After the agitation, the column has to be vent so that the pressure that has built up in the column, can be let out. After venting the column, mixed solvents need to rest and separate and then the heavier solvent is drained out of the column. If the solvent is partially miscible with the feed, a second separation process, usually distillation, is required to recover solvent from raffinate. Down below in figure 3 is presented the mechanism of liquid-liquid extraction.
Application of LLE should be considered over distillation in the following cases (De Haan & Bosch 2013):

- Dissolved or complexed inorganic components in organic or aqueous solutions
- Removal or recovery of components present in small concentrations
- When a high-boiling component is present in relatively small quantities in a waste steam
- Recovery of heat-sensitive materials and processing temperatures are needed
- Separation of a mixture according to chemical type rather than relative volatility
- Separation of close-melting or close-boiling liquids, when there is a solubility difference between solvents
- Mixtures that form azeotropes or exhibit low relative volatilities and distillation cannot be used.
There are also some ternary systems of LLE and they are often represented in a triangular diagram. In ternary systems, the solute is miscible with the carrier as well as the solvent. One of the disadvantages of LLE is that the necessity of a solvent increases the complexity and therefore costs of the process grows as well. (De Haan & Bosch 2013)

Selection of solvent

Solvents are usually chosen so, that the other phase is organic and the other one inorganic. Therefore, high polarity compounds tend to dissolve in inorganic, aqueous phase, whereas low polarity compounds solute in the organic phase. (De Haan & Bosch 2013)

Reactivity with the other chemicals involved and solubility are the most important qualities when selecting the solvent to use in liquid-liquid extraction. As well as density, interfacial tension, resistance to thermal degradation, boiling point, viscosity and toxicity of the chemical should be considered when selecting solvent for the application. Also cost of the chemical will determine whether it is economically wise to be used as a solvent. (Koch & Shivel 2015)

The partitioning coefficient, which is the ratio of concentrations of a solute that is distributed between two immiscible solvents at equilibrium, can be calculated from the equation (1) shown below.

\[
E = \frac{\text{amount of solute in extract phase}}{\text{amount of solute in raffinate phase}} = K \frac{\text{extract flow}}{\text{raffinate flow}}
\]  

(1)

Importance / Case study

Importance

From a hydrometallurgical perspective, solvent extraction is exclusively used in separation and purification of uranium and plutonium, zirconium and hafnium, separation of cobalt and nickel, separation and purification of rare earth elements etc., it's greatest advantage being its ability to selectively separate out even very similar metals. We obtain high purity single metal streams on 'stripping' out the metal value from the 'loaded' organic. Wherein we can precipitate or deposit the metal value.
Stripping is the opposite of extraction, transfer of mass from organic to aqueous phase. (Wikipedia 2017)

LLE is also widely used in the production of fine organic compounds, the processing of perfumes, the production of vegetable oils and biodiesel, and other industries. [not verified in body] It is among the most common initial separation techniques, though some difficulties result in extracting out closely related functional groups. (Wikipedia 2017)

Liquid-liquid extraction is an important separation technology for a wide range of applications in the chemical process industries (CPI). Unlike distillation, which is based on boiling point differences, extraction separates components based on their relative solubilities in two immiscible liquids. Extraction is typically chosen over distillation for separation applications that would not be cost-effective, or even possible, with distillation. (Koch & Shivel 2015)

Separation of single components from the multi-component mixture extraction of components present in the electrolytic solutions. Common industrial application of liquid-liquid extraction include in areas like bulk chemical industry, petroleum industry, fine chemical industry, pharmaceutical industry, biotech industry, food industry and hydrometallurgy. (SlideShare 2014)

Extraction processes are well suited to the petroleum industry because of the need to separate heat-sensitive liquid feeds according to chemical type (e.g. aliphatic, aromatic, naphthenic) rather than by molecular weight or vapor pressure. Other major applications include the purification of antibiotics and the recovery of vegetable oils from natural substrates. In metals processing the recovery of metals such as copper from acidic leach liquors and the refining of uranium, plutonium and other radioactive isotopes from spent fuel elements. Recently extraction is gaining increasing importance as a separation technique in biotechnology.

Case study from bioprocess technology

The main objective of the present work was to study the importance of modelling reaction and phase equilibria simultaneously with irreversible chemical reactions. Based on the mechanism presented in the literature, libraries consisting of irreversible reactions were constructed for the following cases: the hot water extraction of wood,
kraft liquor impregnation into wood, lignin oxidation in oxygen delignification conditions, and alkaline extraction of chlorine dioxide delignified pulp. (Kuitunen 2014)

OBC was further processed by partial depolymerisation of beta-glucan with acid- or enzyme-catalysed hydrolysis at relatively low water content using a twin-screw extruder as a bioreactor. The hydrolysed oat brans were extracted with hot water and centrifuged to obtain a water-soluble phase and an insoluble residue. (Sibakov 2014)

In order to provide valuable information for the process up-scaling, the features that affect the extraction (solvent and substrate properties, reaction conditions) and equipment requirements were studied profoundly. The studies progressed by examining the usability of the separated polymer fractions, by investigating the purity, reactivity and integrity of the polymers. (Roselli 2017)

The results revealed that the solvation selectivity towards hemicelluloses was governed by the molecule size of the carbohydrate polymers. Short hemicelluloses dissolve more readily in aqueous ionic liquids, while the cellulose fraction remains intact. Thus, the molar mass distribution (MMD) of the pulp is a decisive feature regarding the suitability of this pulp for the IONCELL-P process. A distinct difference in the size of hemicelluloses and cellulose allows for a more accurate tuning of the solvent-water mixture for the selective and efficient extraction of hemicelluloses. (Roselli 2017)

Conclusions

Liquid-liquid extraction is most beneficial in cases where complexed inorganic components are dissolved in aqueous solutions and transferable components are present in relatively small concentrations and quantities. LLE should also be considered in cases where recovery of heat-sensitive materials and processing are needed, the used mixtures form azeotropes and if separation of a mixture according to volatility is not an option, since solvents’ melting or boiling points are close to each other.

The common industrial application of Liquid-liquid extraction includes in the areas like Bulk chemical industry, Petroleum industry, Fine chemical industry and Hydrometallurgy etc. From a hydrometallurgical perspective, it's greatest advantage
being its ability to selectively separate out even very similar metals. There are also many case studies from bioprocess technology.
References


