Analytical model of mass transfer through supported liquid membranes

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Abstract

This report details the development and validation of a model for the simulation of supported liquid membrane processes, as applied to the extraction of lanthanides. Supported liquid membranes are systems where two phases, usually aqueous, are separated by a third phase, typically organic, which acts as a membrane, in order to separate solutes from one phase to the other. The model employs an analytical solution to the diffusion equation for the organic phase and linear approximations of the resistances to mass transfer in the aqueous phase boundary layers. The goal of this model is to underline the importance of taking these boundary layer resistances into account.
Sammanfattning

Detta arbete introducerar, deriverar och evaluerar en matematisk modell för simulering av vätskemembranprocesser, tillämpat på vätskeextraktion av lantanider. Immobiliserade vätskemembran betecknar system där två faser oftast vatten, separeras av en tredje organisk fas som agerar membran för att separera och transportera lösta komponenter från den ena vattenfasen till den andra. Modellen utnyttjar sig av en analytisk lösning till diffusionsekvationen för den organiska fasen och linjära approximationer för motstånden mot masstransport i de båda vattenfasernas gränsskikt. Målet med modellen är att understryka vikten av att inkludera dessa gränsskikt i beräkningarna.
## Nomenclature

### Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LM</td>
<td>Liquid Membrane</td>
</tr>
<tr>
<td>SLM</td>
<td>Supported Liquid Membrane</td>
</tr>
<tr>
<td>REE</td>
<td>Rare Earth Elements</td>
</tr>
<tr>
<td>FSSLM</td>
<td>Flat Sheet Supported Liquid Membrane</td>
</tr>
<tr>
<td>HFSLM</td>
<td>Hollow Fibre Supported Liquid Membrane</td>
</tr>
<tr>
<td>SX</td>
<td>Solvent Extraction</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene (teflon)</td>
</tr>
<tr>
<td>Per%</td>
<td>Percent pertraction</td>
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### Chemical Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M^{n+}$</td>
<td>n-valent metal ion</td>
</tr>
<tr>
<td>$MR_n$</td>
<td>Metal-extractant complex</td>
</tr>
<tr>
<td>RH</td>
<td>Acidic extractant species</td>
</tr>
<tr>
<td>$H^+$</td>
<td>Hydrogen ions</td>
</tr>
<tr>
<td>S</td>
<td>Arbitrary solute</td>
</tr>
<tr>
<td>R</td>
<td>Arbitrary carrier</td>
</tr>
<tr>
<td>X</td>
<td>Arbitrary counter-ion</td>
</tr>
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### Subscripts

<table>
<thead>
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<tbody>
<tr>
<td>$k$</td>
<td>Solute species</td>
</tr>
<tr>
<td>$B$</td>
<td>Bulk</td>
</tr>
<tr>
<td>$i$</td>
<td>Interphase</td>
</tr>
<tr>
<td>$eq$</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>$e$</td>
<td>Effective</td>
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### Superscripts

<table>
<thead>
<tr>
<th>Symbol</th>
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</tr>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Feed phase-membrane interphase</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Membrane-Stripping phase interphase</td>
</tr>
<tr>
<td>$f$</td>
<td>Feed side</td>
</tr>
<tr>
<td>$s$</td>
<td>Stripping side</td>
</tr>
<tr>
<td>$0$</td>
<td>Initial</td>
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</table>

### Roman Symbols

<table>
<thead>
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<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
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<tbody>
<tr>
<td>$N$</td>
<td>mol m$^{-2}$ s</td>
<td>Mass flux</td>
</tr>
<tr>
<td>$D$</td>
<td>m$^2$ s$^{-1}$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$C$</td>
<td>mol l$^{-1}$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$z$</td>
<td>m</td>
<td>One-dimensional distance through membrane</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$K$</td>
<td></td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>$h$</td>
<td>m s$^{-1}$</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>$V$</td>
<td>m$^3$</td>
<td>Volume</td>
</tr>
<tr>
<td>$A$</td>
<td>m$^2$</td>
<td>Area</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>Time</td>
</tr>
<tr>
<td>$P$</td>
<td>mol m$^{-3}$</td>
<td>Permeability Coefficient</td>
</tr>
<tr>
<td>$x$</td>
<td>[-]</td>
<td>Dimensionless concentration</td>
</tr>
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</table>

### Greek Symbols

<table>
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<th>Unit</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>[-]</td>
<td>Association parameter</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>$\mu$</td>
<td>N s m$^{-2}$</td>
<td>Viscosity of a fluid</td>
</tr>
<tr>
<td>$\nu$</td>
<td>m$^3$ mol$^{-1}$</td>
<td>Molar volume of a chemical species</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>m$^3$ m$^{-3}$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\tau$</td>
<td>m m$^{-1}$</td>
<td>Tortuosity</td>
</tr>
<tr>
<td>$\delta$</td>
<td>m</td>
<td>Membrane thickness</td>
</tr>
<tr>
<td>$\theta$</td>
<td>[-]</td>
<td>Dimensionless time</td>
</tr>
<tr>
<td>$\xi$</td>
<td>[-]</td>
<td>Dimensionless distance</td>
</tr>
</tbody>
</table>
1. Background

This report details the derivation and validation of a mathematical model for the transport of lanthanide ions through a liquid membrane. The first part will consider the importance of lanthanides in modern society, industrial techniques for their separation, and an overview of liquid membranes. The second part presents the mathematical modeling of liquid membranes in general and also the proposed model for this report, with assumptions, derivation, and simplifications justified. The third part reviews the validation of the model with experimental results obtained from other researchers and the fourth part consists of appendix and bibliography.

The field is relatively new, and fairly sprawling in terms of the nomenclature used by the various authors. The same holds true for the theories, with many theories targeting different aspects of the process, or employing different assumptions, making comparison difficult [1]. In this report the nomenclature has been chosen, as far as possible, to conform with that of the available literature, where there is consensus regarding naming and symbols, and where the denotations don’t conflict. Decimal points are represented by dots, as Matlab is used for the simulations and Matlab uses decimal points.

1.1 Rare Earth Elements

Generally rare earth element (REE) refers to the fifteen lanthanides as well as scandium and yttrium. The two latter compounds have similar chemical properties and are frequently found in REE ores. Rare earth elements belie their name, in that they are not particularly rare. Five of the lanthanides are, for instance, more abundant than lead. However, they rarely occur in concentrated form and the extraction and purification is very cost and energy-intensive. Of more than 200 ore types only three are considered feasible for extraction. In aqueous solutions, lanthanides typically occur in a trivalent state, as Ln$^{3+}$ [2]. For further information on the physical and chemical properties of rare earth elements, see reference [3].
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Yttrium</td>
</tr>
<tr>
<td>Sc</td>
<td>Scandium</td>
</tr>
<tr>
<td>La</td>
<td>Lanthanum</td>
</tr>
<tr>
<td>Ce</td>
<td>Cerium</td>
</tr>
<tr>
<td>Pr</td>
<td>Praseodymium</td>
</tr>
<tr>
<td>Nd</td>
<td>Neodymium</td>
</tr>
<tr>
<td>Pm</td>
<td>Promethium</td>
</tr>
<tr>
<td>Sm</td>
<td>Samarium</td>
</tr>
<tr>
<td>Eu</td>
<td>Europium</td>
</tr>
<tr>
<td>Gd</td>
<td>Gadolinium</td>
</tr>
<tr>
<td>Tb</td>
<td>Terbium</td>
</tr>
<tr>
<td>Dy</td>
<td>Dysprosium</td>
</tr>
<tr>
<td>Ho</td>
<td>Holmium</td>
</tr>
<tr>
<td>Er</td>
<td>Erbium</td>
</tr>
<tr>
<td>Tm</td>
<td>Thulium</td>
</tr>
<tr>
<td>Yb</td>
<td>Ytterbium</td>
</tr>
<tr>
<td>Lu</td>
<td>Lutetium</td>
</tr>
</tbody>
</table>

Table 1.1: Abbreviations of rare earth elements.
REEs are used in a multitude of modern technical applications, primarily as alloys or additives in batteries, magnets, catalysts, and glass products [4][5]. For details regarding applications, see Table 1.2. As an example, praseodymium (Pr) and neodymium (Nd) are used for making magnets for wind turbines and europium (Eu) and yttrium (Y) is a primary component in liquid crystal displays, commonly referred to as LCD screens [6].

The annual global demand is projected to reach almost 200,000 metric tonnes in 2015. In contrast, the global demand already overshot the availability by 10,000 tons in 2010, with an additional shortfall of 40,000 tons per year projected [6]. This is partly due to increasing global demand, as well as the fact that China controls 95% of the current annual production volume [7]. China’s escalating domestic use of lanthanides, and consequent reduction of exported REEs, has lead to a growing interest in efficient mining and waste products recycling [5][8]. As a result of political developments in China in 2010, the price of several REEs increased by over 300% [9]. Because of the supply situation and the numerous applications central to modern society, both the European Commission and the U.S. Department of Energy have classified rare earth elements as critical raw materials with a high, if not the highest, supply chain vulnerability [10][9].

There is also increasing concern over the health hazards of REEs, as well as the environmental impact of the mining, with tightening regulations and an increasing demand for efficient clean-up processes of waste streams and production processes as a result [2][11].
### Table 1.2: Rare Earth Element Usage

<table>
<thead>
<tr>
<th>Application</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Y</th>
<th>Other</th>
</tr>
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<tr>
<td>Magnets</td>
<td>–</td>
<td>–</td>
<td>23.4</td>
<td>69.4</td>
<td>–</td>
<td>–</td>
<td>2</td>
<td>0.2</td>
<td>5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Battery alloys</td>
<td>50</td>
<td>33.4</td>
<td>3.3</td>
<td>10</td>
<td>3.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Metallurgy</td>
<td>26</td>
<td>52</td>
<td>5.5</td>
<td>16.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Auto catalysts</td>
<td>5</td>
<td>90</td>
<td>2</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FCC[^1]</td>
<td>90</td>
<td>10</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Polishing powders</td>
<td>31.5</td>
<td>65</td>
<td>3.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Glass additives</td>
<td>24</td>
<td>66</td>
<td>1</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Phosphors</td>
<td>8.5</td>
<td>11</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.9</td>
<td>1.8</td>
<td>4.6</td>
<td>–</td>
<td>69.2</td>
<td>–</td>
</tr>
<tr>
<td>Ceramics</td>
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<td>6</td>
<td>12</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>53</td>
</tr>
<tr>
<td>Other</td>
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<td>4</td>
<td>15</td>
<td>2</td>
<td>–</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>19</td>
<td>–</td>
</tr>
</tbody>
</table>

Usage of rare earth elements in percent as of 2008. The numbers are given as an average for the relevant application[^1][^5]. For a list of all common names of rare earth metals see Table 1.1.

[^1]: Fluid Catalytic Cracking, i.e. converting heavy hydrocarbons to lighter ones.
The U.S. Department of Energy points to recycling as one of the main strategies to secure U.S. supply of REEs, but also mentions the lack of a cost and energy-efficient process as the main obstacles in the implementation of REE recycling [9].

Several technologies are currently employed in the extraction of REEs, such as liquid-liquid extraction, flotation, precipitation etc. [13], however, most of the commercially available method are associated with a high operating cost, mainly due to the price, and the large amounts, of extractants necessary [14][15], and the amount of solvent required [14].

In waste stream treatment there is also the problem of entrainment, where organic solvent is lost to the aqueous stream. If the organic solvent is hazardous, which often is the case, the emission problem has not been solved, only shifted [14].

A relatively new method, using so-called liquid membranes (LM), has shown promise as a more cost-efficient and environmentally friendly alternative. The technology centers around using an organic phase as a membrane, separating two aqueous phases.

### 1.2 Rare Earth Element Extraction

The main technique for the separation and purification of lanthanides is liquid-liquid, or “solvent, extraction” [16][13]. Solvent extraction (SX), as it is also called, was first implemented industrially in the nuclear fuel cycle process for the purification of uranium. Since then, it has been adapted to a variety of industrial fields, such as mining, petroleum, and pharmaceuticals. The benefits of SX are high throughput, ease of automatic operation, and high purification potential, but its disadvantages are also many [17].

SX is based on the differences in solubility of a solute between different phases. In rare earth refining the process is as follows:

(i) The rare earth elements are leached out of REE-containing ore using a highly acidic or basic aqueous solvent.

(ii) The solvent is mixed with an organic phase, possibly also containing an extracting agent, and stirred in a mixer.

(iii) Ideally an equilibrium between the phases is formed with regards to lanthanide concentration. In reality, the mass transfer is less than the theoretical maximum, since a complete equilibrium would require infinite mixing time.

(iv) The phases are drained from the mixer into a settler, where the phases separate due to differences in density in the solvents, whereafter the enriched organic phase is separated from the aqueous phase by decantation.

Since the process is limited by equilibrium, this type of mixer-settler equipment is usually operated in series, where the product stream of one unit is the feed stream into the next, enabling high purification rates [18]. The other typical units are column-type contactors and centrifugal devices, both of which can combine several stages in one unit [19]. Several other techniques are also in use to a lesser extent, but each has similar or equivalent disadvantages [13].

All these equipment types share major disadvantages. The amount of solvent required is very large and the number of stages (or size of the unit in single-stage equipment), and hence the capital cost of the facility, is considerable [20]. Moreover, scale-up is difficult, for reasons which will be elaborated below, and the operating expenses are high. Other problems are the need for dispersion and coalescing of the emulsion particles, flooding and loading limits, and the restrictions on the phase liquids, with regards to densities and solubilities [19]. For instance, ion exchangers have been considered, which can quantitatively separate lanthanides from aqueous streams, but they have a very low selectivity, and since most lanthanides are used in purified form, the applicability of ion exchangers is restricted to waste treatment [21]. For many years there has been a large collective effort, on the part of the scientific community, to develop an extraction system with the benefits of SX but without its weaknesses.

### 1.3 Liquid Membranes

A membrane is defined as a semipermeable barrier between two phases. Traditionally, these barriers have been made from inorganic solids or polymers, and are in wide-scale use in applications such as gas separations, water purification, and particle filtration [1].
In a liquid membrane the barrier is, as the name suggests, a liquid which is immiscible, or nearly immiscible, in the two phases it separates. Liquid membranes have been attracting significant scientific attention in the last decades for their advantages over traditional separation methods, which will be described in detail below.

Potential fields of application for liquid membranes range from analytical and organic chemistry, to chemical, biochemical and biomedical engineering. In terms of concrete applications, recovery of toxic or valuable metals, the removal of organic compounds, and development of sensing devices are some examples [1].

Liquid membranes have the advantage that they can combine extraction and back-extraction into a single stage, enabling mass transfer not limited by phase equilibrium in one unit [22]. Furthermore, the diffusion coefficients of solutes are orders of magnitude greater in liquids than in solids [1]. In all LM separation processes the phase from which the solute of interest is to be extracted is denoted the feed, and the other aqueous phase is called the receiving phase. In most cases, the membrane is an organic phase, and the feed phase and receiving phase are aqueous.

Liquid membranes work on the same equilibrium principle as traditional liquid-liquid extraction, in that mass transfer is achieved through a difference in chemical potential between two phases [19]. Since the two aqueous phases are not in direct contact, the transport is not limited by equilibrium, but rather by the rate of mass transfer through the membrane, for reasons which will be explained [18]. Examples of applications where membrane technology could potentially replace existing equipment include pressure driven filtration, reverse osmosis, electrodialysis, continuous deionization, and gas and vapor separations [23].

The first liquid membranes was invented by Norman Li in the sixties, which were to be used for large-scale desalination and hydrocarbon separation [24].

The first commercial liquid membrane process was developed in 1986 in Austria, to separate zinc from textile plant waste stream. But since then, there have been very few attempts at large scale implementation of liquid membrane technology [25]. A few pilot-plants have been constructed with varying success, among them a facility for removing chromium from a surface treatment plant [26].

1.4 Types of Liquid Membranes

There are three main types of liquid membranes: bulk liquid membranes (BLM), emulsion liquid membranes (ELM) and supported liquid membranes (SLM).

In BLMs the membrane consists of an organic phase trapped between two aqueous phases. Variants both with and without a physical membrane separating the phases have been used. They are well suited for experimental lab work when determining rate constants and distribution coefficients of novel extractants, but they have a comparably small surface area to volume ratio, limiting their industrial usefulness [23]. ELMs were the first type of liquid membranes invented, by Li et al. [24]. An aqueous phase is emulsified and trapped in a surrounding organic phase which is then again emulsified in another aqueous phase. This type of LM has a very large surface area, but the recovery and separation of the receiving phase after the extraction is complicated, with multiple steps [23]. Emulsion-type membranes also share some of the downsides of SX, e.g. poor phase separation and solvent entrainment, as well as some stability issues due to swelling and breaking of the membranes [27]. They also require a complicated process. A solution to these problems is to use supported liquid membranes which offer a simpler configuration and process than ELMs [17].

In SLMs the organic phase is immobilized by capillary forces in a thin porous support material which separates the two aqueous phases [28]. Since the organic liquid remains in the porous support only a small amount of membrane liquid is necessary.

The organic phase in the membrane holds the extractant, which is chosen based on its selectivity for the species to be extracted [13]. But since the extractants usually are highly viscous, and viscosity hinders mass transfer, they are generally mixed with a cheap, low viscosity diluent to accelerate diffusion [29][13]. However, high carrier concentrations are usually preferable, since carrier saturation is possible, where all carrier molecules are complexed and the interphase reaction becomes the rate limiting step for mass transfer [30].

Supported liquid membrane systems do not rely on dispersion and coalescence, and flooding and loading limits do not have to be considered as long as the correct relative pressure is maintained, i.e. under the breakthrough pressure of the non-wetting fluid [19]. The breakthrough pressure is the transmembrane pressure at which the aqueous phase starts to displace the organic phase from the support pores.
The importance of liquid membranes is especially pronounced when dealing with large volumes of very dilute solutions which must be processed without secondary waste streams. Liquid membranes have potential as green technology due to their high specificity and intensity as well as low emissions and energy need [25].

1.5 Supported liquid membranes

Although the application of a pressure or temperature gradient, or an electrical field, can intensify the process, the concentration gradient, or rather the difference in chemical potential between the phases is the most efficient driver of the extraction [1][23]. Supported liquid membranes come in various configurations which are detailed below.

1.5.1 Supported Liquid Membrane Configurations

Supported liquid membranes can be designed in a variety of different configurations. The oldest, and simplest, is the flat-sheet configuration, where the membrane phase is held in a porous sheet separating the compartments of the feed and receiving phases, see Figure 1.1. This configuration is simple to construct but has a fairly low surface area. The hollow fibre supported liquid membrane provides much greater interfacial area. A hollow fibre module is built from two sets of porous fibres. These can either be separated into two modules, in which case one would facilitate the extraction and the other the back-extraction, and the membrane phase (outside the fibres) would be circulated between the modules. The other option is to have the feed phase flow through a single set of fibres, immersed in membrane fluid, and having the receiving phase flow on the outside of the fibres. This is sometimes referred to as hollow fibre contained liquid membranes (HFCLMs).
Apart from these, which are the most common, there is a great diversity of modified and hybrid modules, such as flowing liquid membranes, spiral-wound flat sheet liquid membranes, electro-static pseudo-liquid membranes, etc. A complete inventory of all types of liquid membranes is not available in the literature but the nearest thing is the overview published by Román et al. [31].

1.5.2 Advantages of Supported Liquid Membranes

The main advantage in terms of scale-up, with SLM units is that the interfacial area per unit volume, fundamental to the scale-up of extraction equipment, is easy to calculate. In conventional equipment it is only accessible as a product of the area times the overall resistance to mass transfer. This is because the phases are emulsified and the interfacial area is the total area of the emulsion droplets, and the only way to measure the it is by calculating the total mass transfer which is the mass transfer rate times the interfacial area. Since the interfacial area is not known directly, it is difficult to estimate the stirring and amount of solvent needed for a larger process unit. In SLMs the interfacial area is simply the exposed area of the membrane corrected for the porosity [19].

1.5.3 Disadvantages of Supported Liquid Membranes

Industrial applications of supported liquid membranes have yet to materialize on a large scale, most importantly because of problems with the stability of the membranes. For a commercial application a typical life expectancy of a unit needs to be around 3 years, whereas most supported liquid membrane modules have life times shorter than a month [32]. A pilot-plant for the recovery of copper was constructed in 1998, but was decommissioned due to stability problems [17].

An alternative to supported liquid membranes that has been considered by some scientists would be reactive solid membranes, i.e. solid membranes with incorporated extractants, but there are serious doubts within the field as to whether such devices actually can be constructed [32].

There are many factors influencing the stability of a membrane module, and not all factors are universally agreed upon in the scientific community, with regards to their importance. Some of these
factors are: loss of organic membrane fluid to the aqueous phases, progressive wetting of the pores by the non-wetting fluids, too large pressure differences over the membrane and lateral shear stress in flowing membrane modules, such as HFSLMs [21]. For an in-depth study of the stability factors, the reader is referred to the work done by Dreher and Stevens [21]. One specific factor they found to ironically impact the stability detrimentally is the mass transfer itself, which through what is known as the Marangoni effect can cause turbulence, and subsequent solvent loss, at the interphase of the membrane.

The organic liquids used in membranes have a low, but non-negligible solubility in the aqueous phases, and they can be very sensitive to pressure differences between the phases. The thinner the membrane is made, the better the diffusional characteristics, but also the worse the stability due to membrane rupture and interphase solution [21].

Another problem is that it is very difficult to predict phase leakage since the surface properties are difficult to measure and vary with the composition of the feed and receiving solutions. Surfactants, sometimes used to enhance the mixing properties of solvents and extractants, are a particular nuisance, in terms of determining their effects on stability [33].

1.5.4 Mass Transfer in Supported Liquid Membranes

The mass flux of a species is defined as the amount of matter passing perpendicularly through the unit area during unit time [1].

There are four modes of diffusional transport through an LM: passive transport, facilitated transport, and two types of coupled transport. Coupled transport is sometimes referred to as active transport [34]. As with many terms in this field, there is some disagreement about the term active transport, some taking it to mean an extraction driven by a chemical reaction, as with biological membranes, which pump sodium and potassium ions using the reaction of ATP to ADP as fuel [35][36]. However, most researchers use the terms uphill transport, coupled transport, and active transport synonymously.

Passive Transport

Passive transport refers to solutes simply diffusing along their concentration gradient from the feed to the receiving phase, through the membrane. This type of transport is limited by the equilibrium condition between the two aqueous phases, and is mainly used when one species in a liquid mixture is soluble in the organic phase, whereas the other are not, leading to a separation. It also requires the solute of interest to be independently soluble in the organic phase. When this is not the case, such as with metal ions, an extractant, frequently referred to as a carrier (R), is required [37]. This type of transport is called facilitated transport.

Facilitated Transport

Facilitated transport was first discovered in living cell membranes, where sodium and glucose fluxes were observed to be far greater than mere Fickian diffusion would lead one to expect. This was also the case with the flux of oxygen and carbondioxide in blood and amino acids in kidneys and intestines in rats [38]. Four phenomena, which had been previously observed, were explained by the theory of carrier-mediated transport:

![Figure 1.3: Passive transport across a supported liquid membrane](image)
• Fluxes could be very strongly coupled between two or more solutes.
• Fluxes varied linearly in low concentrations, but reached a maximum value for high concentrations.
• Fluxes were much larger than expected.
• Mass transport was observed to be very selective, but could become poisoned.

These results were explicable with the carrier-based transport model, since the carrier could be poisoned by a stronger complexing ion (phenomena (iv)), and the transfer increased linearly, as long as more carrier was available (phenomena (ii)). Phenomena (i), coupled transport, will be explained in more detail below and phenomena (iii) in the next paragraph.

In facilitated transport, the solute reacts with the extractant, forming a carrier-solute complex which then diffuses through the membrane \[34\]. Even though the diffusional resistance is slightly larger for the complex (since it is physically larger), the phase equilibrium can be shifted by several orders of magnitude, leading to a greatly increased overall mass flux \[23\]. The carrier should be soluble in the membrane phase but largely insoluble in the other phases, and the complex formation should be moderate, since back-extraction at the receiving side of the membrane otherwise could become rate-limiting for the mass transfer \[38\].

The carrier reacts on the interface of the membrane following the reaction scheme in equation \[1.5.1\]

\[
S + R \rightleftharpoons SR
\]

(1.5.1)

With certain types of carriers it is also possible to further enhance the efficiency of an LM by coupling the transport of a solute with that of another chemical species.

Coupled Transport

If both the solute and the coupled chemical species diffuse from feed to receiving phase, it is called coupled co-transport, whereas when the coupled chemical species diffuses in the opposite direction, from receiving phase to feed phase, it is referred to as coupled counter-transport. The benefit of coupled transport is that it enables what is known as “uphill” transport, where the solute diffuses against its concentration gradient, because of multi-species diffusional effects \[35\]. If, for instance, the coupled counter ion is hydrogen, the concentration factor will be dependent on the difference in pH between the aqueous phases. In counter-transport the extractant is acidic, and in co-transport the extractant is basic or neutral \[39\].

Separations of metal ions with supported liquid membrane is almost always performed with coupled transport \[21][25\].

In coupled co-transport the transport of the species \(S\) is coupled with the transport of chemical species \(X\) in the following manner:

\[
S + X + R \rightleftharpoons SXR
\]

(1.5.2)

Increasing the gradient of component \(X\) over the membrane forces \(S\) to diffuse against its gradient, i.e. transporting \(S\) from a lower concentration in the feed to a higher concentration in the receiving phase.

Coupled counter-transport is similar, but here the second species is transported in the opposite direction. Two reactions take place, one at the receiving side membrane interphase and the other at the
Figure 1.5: Coupled co-transport (top) and counter-transport (bottom).

feed side interphase. At the feed interphase the carrier reacts with the species to be separated as in facilitated transport:

\[ S + XR \rightleftharpoons SR + X \]  \hspace{1cm} (1.5.3)

and at the other side of the membrane, S dissociates and is replaced by the auxiliary species X

\[ SR + X \rightleftharpoons XR + S \]  \hspace{1cm} (1.5.4)

which is then carried back to the feed side of the membrane. Here the diffusion of S is driven by the gradient of X. The phenomena enables very high purification rates. If, for instance, the counter ion is hydrogen, the equilibrium of the solute over the membrane is dependent on the relative pH-levels. For a pH of 10 in the feed and 0 in the receiving phase, the equilibrium level for the solute in the receiving phase is $10^{20}$ times that of the feed [23].

Supported liquid membranes are the most similar to traditional, solid membranes already in wide-spread use in, for instance, ultrafiltration and gas separations [13], and they possess significant advantages over traditional liquid-liquid extraction techniques.

In summary, SLMs can combine the extraction and back-extraction (the release of the solute into the receiving phase) into one single unit [40], the energy and extractant demands are much lower than for liquid-liquid systems [23], it also has the capability to extract solutes at very low concentrations [41], and it is capable of high separation factors [23]. They also do not have the proclivity of liquid-liquid systems for third phase formation or phase entrainment [29].
2. Modeling

More than 120 different mathematical models for the mass transfer in liquid membranes were put forth in the period 1980 to 1995 alone [33], however the solution-diffusion framework, with or without chemical reactions at the interphases, is the commonly accepted basis for most, if not all, of these [1]. Solution-diffusion means what it says, a solute is first solvated in the membrane phase and then diffuses across the membrane, driven by a concentration gradient to the other side. Usually one or the other, diffusion or the chemical reactions, dominate the process, and hence limit the mass transfer, however, in-between cases of equal reaction and diffusion control are possible. The extraction step determining the overall extraction rate is called the rate-determining step [1].

The models vary greatly in mathematical complexity, some introducing concepts such as Voronoi tesselations or Bessel functions to better model some certain facet of a membrane module or extraction process [42][43], but several authors have been critical of the excessive use of advanced mathematics, claiming it conceals the physical significance of the parameters involved [38][39].

However, one cannot escape the fact that the phenomena involved are quite complex. The theory of membrane separations is bound to involve at least the theory of solution chemistry, chemical thermodynamics, transport phenomena, and chemical kinetics [39], and all of these phenomena have to be represented mathematically in the model equations.

There are two possible set-ups for the phases: either aqueous feed and receiving phases and an organic membrane phase, or organic feed and receiving phases and an aqueous membrane phase. For this part, since a water-organic-water setup is most often used, it will be assumed, without loss of generality, that the feed and receiving phases are aqueous [19]. One of the reasons why this configuration is the most common is that water has a relatively high volatility, making these membranes even more unstable than the organic membranes [23]. This problem could be solved by ionic liquids, but the research into these types of membranes is still embryonic [1].

2.1 Solvent Extraction

The solubilities of the solutes are different for the organic and aqueous phases, leading to an extraction when the the solubility is greater in the membrane phase than in the aqueous phase. Solvent extraction is limited by the equilibrium, and in its most basic form, unaided solvation, the phenomenon can be modeled by equation (2.1.1). The equation describes the distribution of the solute between the aqueous and organic phases.

\[ D = \frac{S_{\text{org}}}{S_{\text{aq}}} \]  

(2.1.1)

In a real-world scenario the distribution factor \( D \) would be modified by a degree of efficiency depending on the application. Using a complexation agent, a so called extractant, can greatly increase the selectivity and efficiency of the extraction [1]. Equation (2.1.1) would then have to be modified:

\[ D' = \frac{S_{\text{org}}}{S_{\text{aq}}} \]  

(2.1.2)

where \( R \) is the extractant.

2.1.1 Phase Equilibrium

The modeling of the phase equilibria at the interphases of the membrane depends on the nature of the chemical reaction (if any) taking place between the solute and the extractant. If the reaction is fast, the solute is often assumed to be in equilibrium at the interphase, even if the bulk phases are not. The general form of the equilibrium constant is given by equation (2.1.4). For a reaction on the form:

\[ aA + bB \Leftrightarrow cC + dD \]  

(2.1.3)

the equilibrium is on the form

\[ K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  

(2.1.4)

For very dilute solutions, the chemical equilibrium can be calculated by the distribution factor, which is assumed to remain constant [22], see equation (2.1.1).
If the reaction is not fast, however, the reaction kinetics must be considered.

2.1.2 Chemical Reaction

The chemical reactions at the membrane interphases play a significant role in the modeling as well as in the physical process.

The main concern is the strength of the formed complex, since a stable complex can limit the mass transfer through the membrane by accumulating at the receiving side interphase instead of decomplexing. If this is the case, an auxiliary, stronger, extracting agent can be added to the receiving phase to accelerate decomplexation. If one of the interfacial reactions is sufficiently slow in comparison with the diffusion, the diffusion can be considered instantaneous and another modeling route must be undertaken [1]. Assuming fast reactions is valid only for large second Damköhler numbers, that is:

\[
\frac{L^2}{Dt_{1/2}} \tag{2.1.5}
\]

where \(t_{1/2}\) is the reaction half-life, meaning, either the reaction has to be very fast or the membrane quite thick. The Damköhler number of a system relates the speed of the reaction to the diffusive mass transfer. For industrial membranes which tend to be at least a few microns, the assumption is approximately true. For a membrane of a thickness 100 Å, the values will be around 10% off for a reaction half-life of a hundred nanoseconds [44][38].

If the reactions are not fast relative to diffusion other equations must be considered, see Cussler [38]. These cases are difficult to model generally, since they are highly dependent on the kinetics of the reactions involved.

With lanthanides, as is the case of study in this report, the reactions are fast with a weakly complexing agent such as DEHPA, but significantly slower with a stronger extractant, such as EDTA [1].

It is assumed that the nature of the membrane phase and support also influence the reactions, but little is known about the impact of physico-chemical surface properties, such as interfacial tension, dielectric constant, viscosity, density, charge distribution, etc [1]. Ho & Sirkar consider the effects of the nature of the membrane support in-depth [19].

It is difficult to formulate a general mathematical model, since the chemical reactions are highly dependent on the chemical species involved in terms of reaction order, reversibility, etc [1]. The reaction might include an adsorption step onto the membrane support. It has even been observed that the chemical reactions must not necessarily take place at the membrane interphase only, but rather, with a slightly hydrophilic extractant, the reactions can occur in the aqueous phase [19][35]. Moreover, some extractants occur primarily in a dimeric form, and with others, both the monomeric and dimeric forms participate in the reaction [39].

The difficulty of modeling the extractive lanthanide reactions are demonstrated by the work done by Wang et al. on yttrium extraction [46]. Their paper describes a kinetically controlled extraction of yttrium, which has been proposed as an alternative method to purifying lanthanide ions.

In this report, the nature of the complexation reaction is assumed to be on the general form of a lanthanide reaction, proposed by Moreno et al. [47]:

\[
\text{Ln}^{3+} + 3HX_2 \rightleftharpoons \text{LnX}_3(HX)_3 + 3H^+ \tag{2.1.6}
\]

A lanthanide, including yttrium and scandium, reacts with three dimers of extractant and forms a complex, releasing three hydrogen ions to the feed phase.

2.2 Mass transfer

The three diffusional processes in a supported liquid membrane system are affected to a varying degree by a large number of factors, including the choices for carrier, solvent, and membrane support. Many of these parameters are difficult, or impossible, to measure directly, and assumptions or estimations must be made [1]. Diffusion coefficients can be measured experimentally in a variety of ways, such as lag-time experiments, pulsed field NMR, and permeability experiments, but estimating diffusion coefficients, which is desirable for a general model where experimental data might not be available, is exceedingly difficult in liquids [1]. The most commonly used method is the Stokes-Einstein equation, which is accurate, on
average, to about 20% [32]:

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi \mu R_0}$$  \hspace{1cm} (2.2.1)

$f$ is the friction coefficient of the solute, $k_B$ is Boltzmann’s constant, $\mu$ is the solvent viscosity, and $R_0$ is the solute radius. This approach is valid for large solutes in small solvents. The other limiting case, where a small solute is diffusing through a solvent of much larger molecules has been investigated by Hiss and Cussler [38]. In the cases studied in this report the first condition applies, exemplified by the yttrium-D2EHPA-complex (172 atoms) diffusing through n-heptane (21 atoms).

The most frequently used improvement on the Stokes-Einstein equation is the Wilke-Chang equation with a reported average error of 10% [49]:

$$\langle D_{k,m} \rangle_{x_k=0} = 7.4 \times 10^{-8} \left( \phi M \right)^{1/2} \frac{T}{\mu m \nu k^n}$$  \hspace{1cm} (2.2.2)

The Wilke-Chang equation describes free diffusion of an infinitely dilute solute in a homogeneous solvent. However, this is not the case with membrane systems. Membranes have physical properties which impact the diffusion of solutes. The definition of the effective diffusion coefficient within the membrane can be found in Ho & Sirkar, which is valid under three assumptions: (1) unhindered diffusion, (2) symmetric, completely wetted membrane, (3) no two-dimensional effects [19].

For unhindered diffusion, the solutes should be at least two orders of magnitude smaller than the pores of the membrane [19]. In order to compensate for the impact of the pores of the membrane on the diffusivity, the diffusion coefficient is multiplied by the porosity and divided by the tortuosity of the membrane:

$$D_e = \frac{\langle D_{k,m} \rangle_{x_k=0} \cdot \epsilon}{\tau}$$  \hspace{1cm} (2.2.3)

This approach is only true for infinitely dilute solutions and only valid for low concentrations of solute. If the concentrations are not low, the binary diffusion coefficients can be estimated using a logarithmic interpolation of the diffusivities for both solutes and solvent as seen in equation (2.2.4), modification by A. Vignes [50]:

$$D_{k,m} = \langle D_{k,m} \rangle_{x_k=1} \cdot \langle D_{k,m} \rangle_{x_m=1}$$  \hspace{1cm} (2.2.4)

### 2.3 Liquid Membrane Extraction

Two principal approaches dominate the field: the membrane, or differential approach, and the integral approach [1].

The membrane approach emphasizes the analogy to mass transfer in solid membranes. All resistance is assumed to lie in the membrane; all other factors are neglected. Constant volumes and ideally mixed aqueous solutions are assumed. The process is reduced to a steady-state diffusion through the membrane with linear concentration gradients, where the concentration at the membrane interphase is equal to the bulk concentration of the respective aqueous phase. In reality, the width of the stagnant aqueous boundary layers nearest the membrane interphase is usually in the range 50–500 micrometers. The boundary layer – or film – thickness varies with the stirring applied in the compartment, and the viscosity and density of the aqueous fluid. For some systems the diffusion through the boundary layers can be rate-determining [1].

The integral approach, on the other hand, considers changes in all three phases in the system, including changes in concentration and volume of the aqueous phases and mass balances of the individual components. These models tend to be complicated, with nonlinear equilibria and phase interactions [1].

The models describing flat sheet SLMs usually accentuate the importance of the chemical reactions at the interphases, since the diffusion is easily accounted for using Fick’s laws. Approximate analytical solutions are available for the extremes of completely diffusion-controlled or reaction-controlled mass transfer. Intermediate cases usually require numerical solutions. Chemical reactions rarely take place within the membrane, since the reason for using a carrier is that the individual compounds are not very soluble in the membrane.

In the integral approach some models take into account the mass transfer resistance in the aqueous phases. Some assume steady-state, linear gradients, and some apply Fick’s second law also to the aqueous phases [22].
For the purpose of extracting metal ions, which are generally insoluble in organic, non-polar solvents, simple diffusion through a membrane is infeasible [37]. The case of simple facilitated transport fails to exploit the main potential advantage of membrane modules, namely non-equilibrium separation characteristics. Disregarding these two transport scenarios there remains two configurations of interest, those of coupled co-transport and coupled counter-transport. The type of coupled transport depends on the extractant used in the system. Basic and neutral extractants support co-transport and acidic extractants favor counter-transport. In co-transport, the chemical reaction is of the type in equation (2.3.1), and with an equilibrium on the form of equation (2.3.2). On the other hand, in counter-transport the type and equilibrium are on the form of equations (2.3.3) and (2.3.4), respectively.

\[
aS^{n+} + bX^m- + cR \rightleftharpoons S_aX_bR_c \tag{2.3.1}
\]

\[
K_{co} = \frac{[S_aX_bR_c]}{[S^{n+}]^a[X^m-]^b[R]^c} \tag{2.3.2}
\]

\[
aS^{n+} + bRX_m \rightleftharpoons S_aR_b + bmX^{\pm+} \tag{2.3.3}
\]

\[
K_{counter} = \frac{[S_aR_b]^{c}X^{\pm+}\quad bm}{[S^{n+}]^a[RX_m]^b} \tag{2.3.4}
\]

In all of the equations (2.3.1) to (2.3.4) \(S^{n+}\) is the solute, \(X^{\pm+}\) the counter-ion, and \(R\) the organic extractant.

The equations above might seem convoluted in their coefficients and exponents, but this is merely for completeness. The usual cases are far simpler, as seen in equation (2.1.6), which illustrates the counter-transport mechanism of a lanthanide in a membrane module with an acidic extractant in dimer form, where the counter-ion is hydrogen. In this case, equations (2.3.3) becomes equation (2.1.6) and (2.3.5):

\[
K = \frac{[LnR_3(HR)_3][H^+]^3}{[Ln^{3+}][HR]^3} \tag{2.3.5}
\]

This is the general equilibrium of a lanthanide-extractant reaction, which is considered fast, and which will be used throughout the rest of this report [47].

2.3.1 Supported Liquid Membrane Separation

The diffusional process for coupled counter-transport in an SLM can be divided into seven individual steps, illustrated in Figure 2.1 [13]:

(i) The solute diffuses from the bulk of the feed to the feed-membrane interphase.

(ii) The solute complexes with the extractant at the interphase and hydrogen is released.

(iii) Hydrogen diffuses from the feed-membrane interphase to the bulk of the feed.

(iv) The solute-carrier complex diffuses from the feed-membrane interphase to the membrane-receiving phase interphase.

(v) Hydrogen diffuses from the bulk of the receiving phase to the membrane-receiving phase interphase.

(vi) The carrier is recovered in the reverse complexation reaction and the solute is released into the receiving phase.

(vii) The solute diffuses from the membrane-receiving phase interphase to the bulk of the receiving phase.
2.4 Mathematical Modeling

The mathematical modeling of membrane mass transfer is essential not only for understanding the underlying mechanisms, but also for control design, cost estimation, and scale-up of extraction processes. Since membrane technology usually compete with traditional, well-understood processes, a reliable model for large-scale implementations is vital to its industrial success. Several different approaches have been investigated by researchers [22][51].

In general, a complete model of a membrane module consists of three sub-models, describing in turn the aqueous feed phase, the membrane and its organic phase, and the aqueous receiving phase. Note that these models may be extremely trivial, i.e. linear gradients or even constant concentrations, but they are necessarily there, even by omission [51].

Roughly, the approaches differ in two ways: the assumed nature of the diffusional process and the reaction rate of the complex formation, which in turn form four categories of:

(i) Steady-state diffusion and fast chemical reaction
(ii) Steady-state diffusion and slow or intermediate chemical reaction
(iii) Unsteady-state diffusion and fast chemical reaction
(iv) Unsteady-state diffusion and slow or intermediate chemical reaction

It can be difficult to determine which regime holds true for a specific system, but in this work the systems investigated will be assumed to follow the third regime [1].

The module configuration to be modeled is also significant, primarily for mass transfer considerations in the aqueous phases. Several articles detailing the modeling of hollow fibre membrane modules are available in the literature [19][22][51]. This report focuses on the modeling of flat-sheet SLMs. Although HFSLMs certainly have a greater industrial potential, FSSLMs are conceptually easier to grasp and provide a good model system in which to highlight the importance of certain details. In the case of this report, that would be the mass transfer resistance in the aqueous phases.

For the first (i), simplest of all cases, a simplified model for steady-state diffusion with fast interfacial reaction was developed by Pier Danesi and has since been adapted for a variety of configurations [52][39]. Assuming linear concentration gradients and a pseudo-steady state system (as well as several other simplifying assumptions) the model is derived from Fick’s first law. Since the mass transfer, across the entire module, is given by equation (2.4.1), the model equation (2.4.2) follows.

\[ N = \frac{dC}{dt} \frac{V}{A} \]  
\[ \ln \frac{C_t}{C_0} = - \frac{A}{V} Pt \]

where \( P \) is a fitted parameter, called the permeability coefficient, defined as \( J/C \). This approach approximates the concentration levels in both feed and receiving phase to be constant. This is a useful
conceptual model for quick calculations, which has been used by a large number of subsequent researchers, however, it lacks generality, severely limited by its assumptions as it is. In order to be able to model a broader scope of operating conditions and model configurations, more rigorous models are necessary. For instance, in order to model the dynamic behaviour of a module to design the control structure and start-up procedure or to implement dynamic optimization, the unsteady nature of the process must be accounted for.

In the second case (ii), the chemical reactions dominate the mass transfer, and the diffusion can be considered instantaneous. The mass transfer is entirely governed by the reaction rate, much like an ordinary solvent extraction process. Cussler provides a schematic for the modeling of these types of systems.

The third case (iii) is the case commonly considered with the integral approach and rigorous models. Most rigorous models base themselves on the mass conservation equations and Fick’s second law of diffusion, along with the necessary boundary conditions.

This can be done either in cartesian coordinates, as is the case for FSSLM, polar coordinates (specially applicable for HFSLMs) or in spherical coordinates, which is applicable to ELM systems.

Many of the numerical models are computationally expensive, whereas the analytical models often neglect more phenomena. A few rigorous analytical models exist, for instance that of Osman Ata.

Case (iv), with unsteady-state diffusion and slow reactions is exceedingly difficult to model accurately, and to the knowledge of the author of this report, a successful model of this kind has not been presented to date.

2.5 The proposed model

The objective of this study is to design a model combining an analytical solution of unsteady-state diffusion through a flat-sheet supported liquid membrane and linear approximations of the gradients in both aqueous phases. The model could be considered a hybrid model, incorporating the integral approach where necessary, however maintaining the overview and clarity of the physical parameters involved.

The model for this investigation is based on a heat transfer analogy and an analytical solution to the flux of heat, as published by Carslaw and Jaeger. Given the mass flux continuum, the mass transfer resistances in the aqueous phases are analytically computable. Since there is no accumulation at the interphase of the membrane, and the concentrations are assumed to be at equilibrium, the mass flux on the aqueous side must equal that on the membrane side of the interphase.

2.5.1 Assumptions

The following assumptions are made:

1. The volume of the feed and receiving solutions are constant. The volume of the solutes is very small compared to the total volume of the aqueous phases, and the aqueous solvents do not diffuse through the membrane.

2. The metal complex reactions at the membrane interphases are fast and reversible. For most lanthanides, this is the case.

3. Complexation reactions occur only on the membrane interphases. Since the metal ions are largely insoluble in the membrane phase, any equilibrium inside the phase would be strongly pushed to the side of the metal complex, in particular since there is very little free solvated hydrogen ions in the membrane phase which could bind to the extractants.

4. The complex concentrations at the phase boundaries are in equilibrium with the feed and receiving solutions. Follows from the previous assumption.

5. The metal complexes diffuse independently. This is more controversial, since it can only be assumed for very low concentrations of ions. However, modeling the interactions of multi-ion complexes would be prohibitively difficult, without a given improvement in the accuracy of the model.

6. Phase polarization effects are not simulated. This is however the subject of further work regarding this model, since little is known about the importance of these effects.
2.5.2 Mathematical Description

The rate of mass transfer in the aqueous phases if proportional to the difference in concentration between the bulk of the phase and the membrane-aqueous phase interphase, which can be written as:

\[ N_k = h_k (C_{B,k} - C_{i,k}) \quad k = 1, 2, \ldots, n \]  

(2.5.1)

where \( N_k \) is the mass transfer coefficient of \( k \), and \( C_{B} \) and \( C_{i} \) are the bulk and interphase concentrations of \( k \), respectively [19].

The change in concentration of the feed and receiving phase can then be modeled as:

\[
V_f \frac{\partial C_k}{\partial t} = -(NA)_\alpha
\]

(2.5.2)

\[
V_f \frac{\partial C_{H^+}}{\partial t} = n \sum_{k=1}^{N} (NA)_\alpha
\]

(2.5.3)

\[
V_s \frac{\partial C_k}{\partial t} = (NA)_\beta
\]

(2.5.4)

\[
V_s \frac{\partial C_{H^+}}{\partial t} = -n \sum_{k=1}^{N} (NA)_\beta
\]

(2.5.5)

The subscripts \( f \) and \( s \) denote the feed and receiving phase, respectively and \( \alpha \) and \( \beta \) the interphases between the membrane and the respective phase. \( N \) is the total number of metal ion species to be transported in the feed. \( V \) is the volume of the given phase.

Within the membrane, diffusion is governed solely by Fick’s second law, since no reaction in the membrane is assumed. That is:

\[
\frac{\partial C_k}{\partial t} = D_e \frac{\partial^2 C_k}{\partial z^2}
\]

(2.5.6)

The solution of this partial differential equation requires one initial condition and two boundary conditions. The initial condition (IC) is given, assuming that the membrane is free of metal ions at \( t = 0 \), and the boundary conditions (BC) stand in relation to the equilibrium constant and the concentrations on the aqueous side of the interphases:

- **IC**: \( C_k(z, 0) = 0 \)  
  (2.5.7)
- **BC1**: \( C_k(0, t) = K_\alpha C_{\alpha,aq} \)  
  (2.5.8)
- **BC2**: \( C_k(\delta, t) = K_\beta C_{\beta,aq} \)  
  (2.5.9)

where \( L \) is the thickness of the membrane and \( K \) is the equilibrium constant at the specified interphase.

In order to simplify the partial differential equation (PDE), it can be rewritten in dimensionless variables as follows:

\[
x_k = \frac{C_k}{C_i}
\]

(2.5.10)

\[
\theta = D_e \frac{t}{\delta^2}
\]

(2.5.11)

\[
\xi = \frac{z}{\delta}
\]

(2.5.12)

**Equilibrium**

Equation (1.5.3) describes as previously mentioned the reaction occurring at the membrane-interphases. The equilibrium can hence be described as:

\[
K = \left[ \frac{[\text{MR}_3 \text{HR}_3][\text{H}^+]^3}{[\text{M}^{3+}][\text{HR}_2]^3} \right]
\]

(2.5.13)

The equilibrium constant depends strongly on the pH of the respective aqueous phase, as can be seen from equation (2.5.13). It is assumed that hydrogen and metal ions do not diffuse independently through the membrane, and that the extractant and the metal complex are completely unsoluble in the aqueous phase. This leads to the modified equation for the equilibrium constant:
\[ K = \frac{[\text{MR}_3]_{\text{org}}[\text{H}^+_{\text{aq}}]^3}{[\text{M}^{3+}_{\text{aq}}][\text{HR}_{\text{org}}]^3} \]  

(2.5.14)

To increase the readability the dimeric form metal-extractant complex and the free extractant remains implicit. The pH and concentrations are easily determined and the concentration of unreacted extractant at the interphases can be written as a function of the concentration of metal complex:

\[(C_{HR})_j = C_{HR,0} - n \sum_{k=1}^{N} C_{MR_k} \]  

(2.5.15)

where \( j \) signifies the interphase of interest. Since the concentration of metal complex is known from the equilibrium, equation (2.5.15) reduces to:

\[(C_{HR})_j = C_{HR,0} - n \sum_{k=1}^{N} K_j C_{MR_k} C_{RH} C_{H^+} \]  

(2.5.16)

This approach is also used by Babcock and Baker [27].

2.6 Other models

Most elaborate models proposed by scientists consider HFSLMs, because of their industrial applicability, and most models are also restricted to a particular system, including module, solvent, extractant, and solute of interest. Only a few general models exist in the literature on FSSLMs, such as the one proposed by Osman Ata [54].

In general, only 13% of the models investigated by Bringas et al. in their overview applied the rigorous approach [22].

Marriott and Sorensen proposed a numerical modeling strategy, geared towards general applicability, with few assumptions regarding the nature of the system, such as isothermal flux, negligible axial diffusion, or other constant physical parameters. All model equations are derived from rigorous mass, momentum, and energy balances. The result is a very general, but computationally complex, model, where a polynomial differential algebraic equation system is solved by numerical methods, where the accuracy of the model is, theoretically, only limited by the uncertainty in the model parameters [53]. The model, which is more of a modeling strategy, can be applied, according to the authors, to any membrane system, but in their paper they exclusively use hollow fibre modules to test the efficacy of the model.

Alhusseini and Ajar proposed models derived from the rigorous mass conservation equations, which also takes into account the mass transfer resistances in the aqueous boundary layers [56]. The model equations were solved using a finite discretization method.

2.7 Solution to the model equations

Following the heat conduction analogy, the system is solved analytically in the way presented by Carslaw and Jaeger [55].

The system represents a boundary value problem (BVP) with non-zero boundaries. In order to solve the PDE, the concentration (or heat in Carslaw and Jaeger) is rewritten as two variables: one representing the steady-state concentration across the membrane and the other representing the transient concentrations.

Solving only for the transient concentrations, the steady-state concentrations are subtracted from the total solution, which reduces the boundary values to zero, and the PDE for the transient is solved with a Fourier series. The number of terms was chosen to 20, after which only negligible changes to the overall profile were observed. The solution for the steady-state concentrations is simply a linear model. The two solutions combined give the overall solution to the PDE on the form:
\[ x_k = x_{k,\alpha} + (x_{k,\beta} - x_{k,\alpha})\xi + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{x_{k,\beta} \cos(n\pi) - x_{k,\alpha}}{n} \sin(n\pi\xi)e^{-n^2\pi^2\theta} + 2 \sum_{n=1}^{\infty} \sin(n\pi\xi)e^{-n^2\pi^2\theta} \int_{0}^{1} g(\xi) \sin(n\pi\xi)d\xi \]  

(2.7.1)

From equation (2.7.1), the boundary values, and hence the mass fluxes, can be derived analytically. At the feed phase-membrane boundary:

\[ \left( \frac{\partial x_k}{\partial \xi} \right)_{\xi=0} = (x_{k,\beta} - x_{k,\alpha}) + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{x_{k,\beta} \cos(n\pi) - x_{k,\alpha}}{n} e^{-n^2\pi^2\theta} + 2 \pi \sum_{n=1}^{\infty} n \cdot \cos(n\pi)e^{-n^2\pi^2\theta} \int_{0}^{1} g(\xi) \sin(n\pi\xi)d\xi \]  

(2.7.2)

and the membrane-receiving phase boundary:

\[ \left( \frac{\partial x_k}{\partial \xi} \right)_{\xi=1} = (x_{k,\beta} - x_{k,\alpha}) + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{x_{k,\beta} \cos(n\pi) - x_{k,\alpha}}{n} e^{-n^2\pi^2\theta} + 2 \pi \sum_{n=1}^{\infty} n \cdot e^{-n^2\pi^2\theta} \int_{0}^{1} g(\xi) \sin(n\pi\xi)d\xi \]  

(2.7.3)

using equations (2.7.2) and (2.7.3), the mass fluxes into and out of the membrane can be calculated. Assuming no accumulation takes place at the interphases, the flux on the membrane side must equal that on the aqueous sides. This results in:

\[ -D_e \left( \frac{\partial C_k}{\partial z} \right)_{\alpha} = h_k(C_{k,B}^f - C_{k,\alpha}) \]  

(2.7.4)

\[ -D_e \left( \frac{\partial C_k}{\partial z} \right)_{\beta} = h_k(C_{k,\beta} - C_{k,B}^s) \]  

(2.7.5)

from equations (2.7.4) and (2.7.5), together with the analytical derivatives (2.7.2) and (2.7.3) the interphase concentrations, hereto unknown, can be calculated.

The problem is of course, that these boundary conditions are incompatible with the solution of the PDE. The process for solving the system must hence be iterative, using the new found boundary concentrations as conditions for solving the PDE until the conditions converge. That is, the new interphase concentrations obtained from equations (2.7.4) and (2.7.5) are used in equations (2.5.7), solving for the same time step with new boundary conditions. This is the process which is repeated until the mass fluxes on both sides of the interphase are within an acceptable margin of error.

In summary, using the known initial concentrations in all three phases, the equilibrium conditions and the resulting instantaneous mass transfer rates are calculated. When the mass transfer rates are known, the linear gradient approximations are used to calculate the interphase concentrations which would result in the same transfer rates. These concentrations are then used in the first calculations to obtain new mass transfer rates, and the process is repeated until the changes in the mass transfer rates are negligible.
3. Evaluation

Evaluating a model is usually difficult and time-consuming. This is usually done by extensive experimental corroborations, analyzing the output of simulations and comparing them to experimental data. However, in order for any conclusions to be drawn, a large number of experiments have to be conducted, under a wide variety of experimental conditions, in order to establish the region of applicability and accuracy of the model. In the writing of this report, neither time nor resources were available for a thorough validation of the model, and hence only a limited analysis of its potential was performed.

3.1 Experimental

A series of experiments were performed concurrently with the development of this model, by another researcher, Samuel Nabile Njie [57]. The equilibrium conditions and the supported liquid membrane extraction of yttrium, neodymium and praseodymium were investigated, using the extractants DEHPA and EHEHPA in solutions of kerosene.

The extraction of the three REEs was tested using both DEHPA and EHEHPA in pure form, as well as a mixture of both DEHPA and EHEHPA. The experiments measured pH levels in both feed and receiving phases, and the metal concentration in the feed phase. From these the extraction efficiencies, molar fluxes, and the mass transfer coefficients were calculated. The initial concentration of extractant was 0.02 M for all experiments and the initial rare earth concentrations varied between 70 and 80 mg l$^{-1}$.

The experiments were carried out in a batch set-up, consisting of two 250 ml compartments separated by a thoroughly wetted membrane. Both compartments were closed to the outside and stirred using magnetic stirrers at a rate of 520 rpm. The duration of the experiments was 6 hours per run.

The membranes, made from polytetrafluoroethylene (PTFE) were supplied by Millipore®. The specifications can be found in Nijes work [57].

For the validation of the model presented in this paper, mainly the equilibrium data, extraction efficiencies and measured pH levels were used.

It is worth mentioning that Nijes work is a study in its own right, whose main findings were that there are synergistic effects in the use of a mixture of DEHPA and EHEHPA for the extraction of rare earth metals. See reference [57] for more details.

3.2 Simulation

In order to evaluate the usefulness and importance of the additions made to the model, i.e. the aqueous boundary layer resistances, simulations were performed. The pertinent experiments performed by Nije were simulated using the model both with and without aqueous resistances, and the relative accuracy was used as metric for the improvements done by the additions.

The simulation conditions were modified to be as similar as possible to the experiments. The volumes of the containers, specifications of the membranes, the initial concentrations of REEs, the concentrations of extractants, and the duration of simulations were all in accordance with their experimental counterparts. The distribution coefficients provided by Nijes work were also used in the simulations. The stirring rate was not used, however, as the methods for calculating the thickness of the boundary layer are quite complex. The computations would be susceptible to measurement inaccuracies in terms of the viscosity and density of the phase liquids. For the purposes of this study it was deemed appropriate to fix the thickness of the boundary layer at 50 micrometers. Varying this within reasonable limits did not alter the results significantly.

All of the simulations were performed in Matlab®.

3.3 Calculations

The distribution coefficients provided by Nije could not be used directly, but were used to calculate the equilibrium constants, which were then used in the model. Using the initial aqueous concentration, the pH at equilibrium and the distribution coefficient the equilibrium constant can be calculated. The equilibrium constant is on the form described in equation (2.1.4). It can be simplified using the distribution factor.

$$ K_{eq} = D \cdot \frac{[H^+]^3}{[HR]^3} \quad (3.3.1) $$
The pH at equilibrium was provided in Nijes data, however the equilibrium concentration of unreacted extractant was not. It can be calculated using the data which is available. The free concentration of extractant can be described by equation (3.3.2).

\[ C_{HR,t} = C_{HR,0} - 3 \cdot C_{MR_3,t} \quad (3.3.2) \]

The concentration of metal complex is related to the free aqueous concentration of metal by the distribution factor and the aqueous concentration can be calculated since the initial concentration is known.

\[ C_{aq,0} = C_{aq,t} + C_{org,t} \quad (3.3.3) \]

Through substitution with the distribution factor the aqueous concentration is obtained.

\[ C_{aq,t} = \frac{C_{aq,0}}{1 + D} \quad (3.3.4) \]

The aqueous concentration then immediately gives the organic concentration at equilibrium, and then the free extractant concentration is calculated. For a table containing the calculations, see Table 4.1 in Appendix 4.1.

Nijes work also presented the feed phase concentrations in terms of pertraction percentages, defined as shown in equation (3.3.5).

\[ Per\% = \frac{C_f^0 - C_f^t}{C_f^0} \cdot 100 \quad (3.3.5) \]

Converting this to concentration is trivial.

### 3.4 Results

The results from Nijes work which were used for the validation were mainly extraction efficiencies and the pH curve for the feed phase presented in his work. The molar fluxes and mass transfer coefficients are not a direct result of the model and would therefore be unsuitable for comparison. Equilibrium data was only available for yttrium, and for yttrium only SLM data with DEHPA as extractant was available.

Simulations without the added aqueous boundary layer gave the results Figures 3.1 and 3.2, and simulations including the aqueous boundary layer yielded the results shown in Figures 3.3 and 3.4.

The most simulations were performed using an aqueous resistance of \( 1 \times 10^{-10} \), an approximate value for most metal ions [58]. In Figures 3.5, 3.6, 3.7, and 3.8, the results of a lower and higher resistance, respectively, is shown.
Figure 3.1: Plot of the feed concentration of yttrium, both experimental and simulated. The simulations do not consider the aqueous boundary layer.

Figure 3.2: Plot of the pH of the feed phase, both experimental and simulated. The simulations do not consider the aqueous boundary layer.

Figure 3.3: Plot of the feed concentration of yttrium, both experimental and simulated, with the impact of the aqueous boundary layer considered.

Figure 3.4: Plot of the pH of the feed phase, both experimental and simulated, with the impact of the aqueous boundary layer considered.
Figure 3.5: Plot of the feed concentration of yttrium, with a low aqueous resistance ($1 \times 10^{-5}$).

Figure 3.6: Plot of the pH of the feed phase, with a low aqueous resistance ($1 \times 10^{-5}$).

Figure 3.7: Plot of the feed concentration of yttrium, with a high aqueous resistance ($1 \times 10^{-15}$).

Figure 3.8: Plot of the pH of the feed phase, with a high aqueous resistance ($1 \times 10^{-15}$).
3.5 Effects of model parameters

In addition to the limited experimental comparison, a number of variations on the model parameters were investigated in order to confirm that the model behave as expected. If the simulation results are plausible, further experiments can be justified.

3.5.1 Amount of extractant

The amount of extractant is known to impact the mass transfer greatly.

![Feed phase with 0.01 M extractant](image1)

**Figure 3.9:** Feed with 0.01 M extractant

![Feed pH with 0.01 M extractant](image2)

**Figure 3.10:** Feed pH with 0.01 M extractant

![Feed phase with 0.05 M extractant](image3)

**Figure 3.11:** Feed with 0.05 M extractant

![Feed pH with 0.05 M extractant](image4)

**Figure 3.12:** Feed pH with 0.05 M extractant

3.5.2 Equilibrium constant

The membrane interphase equilibrium constant varied heavily in the experiments performed by Nije [57], and was therefore subjected to several simulations.
3.5.3 pH levels

One simulation with an increased feed pH level was performed.
3.5.4 Diffusion coefficient

The diffusion coefficient in the membrane was manipulated.

Figure 3.19: Feed with initial feed pH at 5.

Figure 3.20: Feed pH with initial feed pH at 5.

Figure 3.21: Feed with a diffusion coefficient 100 times slower.

Figure 3.22: Feed pH with a diffusion coefficient 100 times slower.

Figure 3.23: Feed with a diffusion coefficient 100 times faster.

Figure 3.24: Feed pH with a diffusion coefficient 100 times faster.
3.5.5 Reaction Mechanism

The ratio of hydrogen to lanthanum was modified to investigate the impact of the reaction mechanism.

Figure 3.25: Feed with the metal to hydrogen ratio at 15.

Figure 3.26: Feed pH with the metal to hydrogen ratio at 15.

Figure 3.27: Feed with the metal to hydrogen ratio at 30.

Figure 3.28: Feed pH with the metal to hydrogen ratio at 30.

Figure 3.29: Feed with the metal to hydrogen ratio at 50.

Figure 3.30: Feed pH with the metal to hydrogen ratio at 50.
3.6 Discussion

Optimally one would have a large data set to validate a model against, since small sample sets are statistically unreliable. Since there has been a very large body of work published over the years, dealing with supported liquid membranes and metal extraction, this should not be a problem. However, the data available is only rarely useful for model comparison. A lot of the work that has been done is concerned with qualitative investigations of parameters affecting the extraction process, and present data which is unusable for quantitative validation, such as the variation of permeability as a function of the pH in the feed phase, or the concentration of extractant in the membrane. Many papers also primarily present initial molar fluxes, proving an extractants efficiency, but this is again not very suitable for validating a proposed model. Indeed, most of the researchers positing mathematical models validate them with their own experiments. This is unfortunate from several points of view. First of all, there is the problem of expectation bias, where researchers, perhaps unwittingly, ignore data contradicting their proposed model. And even if the researchers are perfectly diligent in their presentation, the small amount of data make the validation unreliable. Even the papers publishing validated models rarely adequately present their experimental data. All papers the author of this report examined lacked one or more important variables necessary for a complete simulation of the results, such as the interfacial area, the equilibrium constant or diffusion coefficients of the solutes.

The aim of this report is not to provide yet another model of the extractive process using supported liquid membranes, but to emphasize the need for accounting for the boundary layer resistances in the development of models. Many rigorous models already take these phenomena into consideration, but rarely emphasize their importance. In this report an attempt is made to underline the usefulness of all three submodels of the SLM process, and also to provide an easily implementable model for quick calculations.

3.7 Evaluation of the model

The first obvious problem with the simulations are the negative concentrations displayed in cases where the aqueous boundary resistance is not negligible. The problem probably lies in the nature of the equation system. It is highly non-linear and it is clear that Matlab’s solvers struggle to find a solution. Sometimes they do not find a solution, and the suboptimal value they end up with is used for the calculations. This could contribute to the dramatic decrease in the modeled concentration. In order to evaluate the plausibility of the model, without directly considering the accuracy, it is sufficient to study the results of simulations with variations of the model parameters, see below.

3.7.1 Simulations

In the simulations presented in Section 3.5.1 it becomes clear that the amount of extractant is paramount to the rate of mass transfer across the membrane. This is of course to be expected, since as explained in Section 1.5.4 with small enough quantities of extractant, this becomes the limiting factor. When there emerges a shortage of extractant molecules at the feed-membrane interphase, as in Figure 3.9 no more metal ions can be transported and the rate of mass transfer is severely decreased. It also indicates, since the simulations better approximate the experiments when the amount of extractant is decreased, that this may be a reason for the errors in the simulations. However, it would require a great amount of fine tuning of the extractant concentration to replicate the experimental results, and even then, it seems, the results in pH levels would deviate significantly.

When manipulating the equilibrium constant, which varied quite heavily in the experiments performed by Nije, the results differ only slightly, which is reasonable since there is a trade-off regarding the equilibrium, as explained earlier in Section 2.1.1. If the equilibrium is too strongly driven towards the complex, there will be an accumulation of metal ion-complex at the strip-membrane interphase, limiting the mass transfer.

The pH levels seem to have a very minor impact on the mass transfer since the feed pH level drops very rapidly at the beginning of the simulation. But since the simulation setup is of a batch container, where the hydrogen deficit is quickly filled with migrating ions, the effects could be larger for a continually alkalized setup, where the a base or buffer solution is added to the feed.

Varying the diffusion coefficient through the membrane also greatly affects the simulated mass transfer. Reducing the diffusion coefficient by a factor of 100 puts the simulated results for the metal close to the
experimental ones, but the deviation remains in the pH levels for the feed.

The most interesting round of simulations are the ones with changed reaction mechanisms. Increasing the hydrogen to metal transport ratio markedly changes the picture. A ratio of 50, as seen in Figures 3.29 and 3.30, approximates the experimental results to the greatest degree of accuracy so far. This is of course not plausible, but rather circumstantial evidence that the membrane was ruptured in the experiments which allowed hydrogen and metal ions to seep through faster than would have been otherwise possible.

As seen in the simulations, the model behaves as expected, although with results very different from the observed ones. There are many linchpins in such a complex system as a membrane module, such as the equilibrium, the diffusion coefficient, and reaction mechanisms, which have been commented on above, as well as others, not considered in these simulations, such as membrane and extractant characteristics, as well as the time step used for the solution of the equations. All of these were considered to be of minor importance in comparison with the ones tested, but should be investigated further in future work.

3.7.2 Computational Expense

Comparing the proposed model to other available models from the scientific literature with regards to computational efficiency is difficult, since very few researchers mention the duration of the simulations. Most only present the results. It could be claimed that algorithmic and computational efficiency has lost its relevance with the increasing availability and affordability of high-performance computers, but especially considering simulations of large systems, this need not be true. The model proposed in this work scales really well with the number of solutes as long as the interfacial equilibria remain fairly simple. The main concern is complicated chemical reaction schemes and/or equilibrium equations. These would severely impair the non-linear solvers ability in finding equal mass transfer rates.

The greatest computational effort is spent in the first hundred or so seconds, where the gradients over the feed-membrane interphase are extremely large. After around a hundred seconds the previous solution, which is used as an initial condition for the solver, is very similar to the new solution and the time required to solve the PDE is significantly reduced. It does not, however, come anywhere near the computational time per time step of the model in which aqueous boundary resistance is not accounted for. This could be because of the large amount of function calls, which probably accounts for a minor, but not insignificant, part of the computational demand.

3.7.3 Transport of hydrogen ions

The experimental pH behaviour of the feed phase is puzzling. It seems as though much more hydrogen is transported across the membrane, as compared to what the model would predict. As previously mentioned, this could be due to either a rupture in the membrane, a different reaction mechanism than what has been considered, or a combination of both. As seen from the simulations with modified reaction mechanisms, the deviation would have to be very large in order to account for the observed pH levels. Therefore, the most plausible conclusion is that the membrane was somehow ruptured, or the compartment otherwise contaminated.

3.8 Conclusion

The extraction process for rare earth elements is central to the recycling of these from waste products as well as the mining from ores. The traditional solvent extraction process is wasteful and expensive, and the production could be greatly improved by switching to liquid membrane technology, of which supported liquid membranes have the highest potential. Supported liquid membranes have been used in the academia for several decades, but the industrial introduction has failed to materialize, largely due to stability problems.

Along with the development of sturdier membranes, the accurate and efficient modeling of supported liquid membranes is vital to facilitate the industrial adoption of the technology. Reliable models are necessary for design, control, and cost estimation of liquid membrane systems. This report has highlighted the necessity of incorporating the mass transfer phenomena in the aqueous boundary layer in future models of these systems. The aqueous boundary layer resistances is frequently ignored for approximate models, even though calculations for these could be included with only a little added mathematical effort.
3.8.1 Recommendations for future work

Two things seem imperative to the industrial success of supported liquid membranes: a reasonably stable support material and extractant combination and a unified, and universally accepted, modeling framework. With the large amount of models already available, the latter becomes a question of selection. In order to meaningfully select a few model types to build upon and adapt, there needs to be a large body of specific and comprehensive experimental data, against which to validate a model. Providing this data would be rather tedious, but it is, in the opinion of the author, necessary for further advancements in the field.

Regarding the continuation of the work presented in this paper, the model implementation, i.e. the Matlab code, ought to be scrutinized and perhaps rewritten in order to exclude mistakes and if the problems are not solved, a better solver should be sought for. The influence of the minor parameters discussed in Section 3.7.1 should also be investigated to either be confirmed or rejected as negligible to the simulation outcomes.
4. Appendix

4.1 Equilibrium Constant

The following table provides the data used in calculating the equilibrium constant of yttrium-DEHPA in n-heptane.

<table>
<thead>
<tr>
<th>pH</th>
<th>D</th>
<th>$C_{ex,0}$</th>
<th>$C_{ex,t}$</th>
<th>$C_{aq,0}$</th>
<th>$C_{aq,t}$</th>
<th>$C_{org,t}$</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.61</td>
<td>5.8884</td>
<td>3 x 10^{-2}</td>
<td>1.12 x 10^{-3}</td>
<td>1.63 x 10^{-4}</td>
<td>9.57 x 10^{-4}</td>
<td>2.71 x 10^{-2}</td>
<td>4.36</td>
</tr>
<tr>
<td>1.41</td>
<td>3.7154</td>
<td>3 x 10^{-2}</td>
<td>1.12 x 10^{-3}</td>
<td>2.38 x 10^{-4}</td>
<td>8.83 x 10^{-4}</td>
<td>2.73 x 10^{-2}</td>
<td>10.69</td>
</tr>
<tr>
<td>1.00</td>
<td>1.3490</td>
<td>3 x 10^{-2}</td>
<td>1.12 x 10^{-3}</td>
<td>4.78 x 10^{-4}</td>
<td>6.43 x 10^{-4}</td>
<td>2.81 x 10^{-2}</td>
<td>60.99</td>
</tr>
<tr>
<td>0.59</td>
<td>0.3020</td>
<td>3 x 10^{-2}</td>
<td>1.12 x 10^{-3}</td>
<td>8.60 x 10^{-4}</td>
<td>2.60 x 10^{-4}</td>
<td>2.91 x 10^{-2}</td>
<td>290.36</td>
</tr>
</tbody>
</table>

Table 4.1: Table of measured and calculated values necessary for estimating the equilibrium constant. The pH, D, and initial concentrations were provided by Samuel Nabile Nije and the other values were calculated from these as explained in Section 3.3.

Using the pH and equilibrium data a plot was constructed and a suitable value extrapolated for the appropriate pH levels, see Figure 4.1 below.
Figure 4.1: Plot of equilibrium data with an exponential extrapolation.

\[ f(x) = 2658.4000754885 \exp(-3.928479369 \times x) \]

\[ R^2 = 0.9961186088 \]
Acknowledgements

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Bibliography


