Separation of cesium and strontium from nuclear waste by supported liquid membranes
by John David Parks

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:
High Level Nuclear Waste is an acidic liquid formed from the reprocessing of nuclear fuels. The metals dissolved in the liquid waste consist of approximately 99 wt% stable metals. Cesium-137 and strontium-90 make up the majority of radioactive isotopes in the waste. Thus, it would greatly reduce the cost of permanent storage of the waste if the cesium-137 and strontium-90 could be selectively removed from the mixture.

Separation of metal salts by passive transport through alcohol-supported liquid membranes was investigated. A batch membrane test cell was constructed by placing a liquid membrane between two glass elbows held together with an aluminum flange. On one side, the feed side, the liquid consisted of several dissolved metals in distilled deionized water; on the other side, the strip side, was pure distilled deionized water. Samples were taken from the strip and feed solutions at recorded times and analyzed for metal ion concentrations by ion chromatography. The concentration versus time data provided for the determination of ion permeabilities. Varied experimental parameters include alcohol type, soak time of membrane in liquid, stirring speed, anion type, and run times.

Metal nitrates permeated through octanol membranes in the same order as experimentally determined diffusion coefficients in dilute aqueous solution: Cesium nitrate > sodium nitrate > (calcium nitrate ≈ strontium nitrate) > aluminum nitrate. Cesium nitrate permeability is 1.8 times greater than sodium nitrate, 2.6 times greater than calcium nitrate, and 3.9 times greater than aluminum nitrate. Similar results are observed when 2,3 -dimethyl-4-heptanol and 1-heptanol are used as the membrane liquid.

Metal sulfates also permeated through octanol membranes in the same order as their diffusion coefficients in dilute aqueous solution. Cesium permeability is 1.3 times greater than sodium, and 2.4 times greater than calcium for the metal sulfates.

Experimental passive transport permeabilities of strontium were determined to be more than seven times greater than that reported for facilitated transport of strontium under similar conditions. Facilitated transport, however, exhibits more selectivity than passive transport.

A program written in QBASIC is presented in an attempt to extend permeabilities determined in a batch test cell to user-defined continuous separation processes.

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Date

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ABSTRACT

High Level Nuclear Waste is an acidic liquid formed from the reprocessing of nuclear fuels. The metals dissolved in the liquid waste consist of approximately 99 wt% stable metals. Cesium-137 and strontium-90 make up the majority of radioactive isotopes in the waste. Thus, it would greatly reduce the cost of permanent storage of the waste if the cesium-137 and strontium-90 could be selectively removed from the mixture.

Separation of metal salts by passive transport through alcohol-supported liquid membranes was investigated. A batch membrane test cell was constructed by placing a liquid membrane between two glass elbows held together with an aluminum flange. On one side, the feed side, the liquid consisted of several dissolved metals in distilled deionized water; on the other side, the strip side, was pure distilled deionized water. Samples were taken from the strip and feed solutions at recorded times and analyzed for metal ion concentrations by ion chromatography. The concentration versus time data provided for the determination of ion permeabilities. Varied experimental parameters include alcohol type, soak time of membrane in liquid, stirring speed, anion type, and run times.

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CHAPTER 1

INTRODUCTION

Various technologies are currently under consideration for the removal and concentration of long-lived radioactive metal isotopes from High Level Nuclear Waste (HLW) produced at the Idaho Chemical Processing Plant. The HLW is an acidic liquid formed from the reprocessing of nuclear fuels which is calcined to form a solid waste of approximately 99 wt% stable metal oxides such as CaO, Al_2O_3, ZrO_2, B_2O_3, etc. Cesium-137 and strontium-90 make up the majority of radioactive isotopes in the waste. Thus, it would greatly reduce the cost of permanent storage of the waste if the cesium-137 and strontium-90 could be selectively removed from the mixture. This is especially important since the half lives of cesium-137 and strontium-90 are 30.2 and 28.1 years respectively.

Membrane-based separation may provide a convenient and economical method of removing the radioactive components. Most of the calcined HLW is capable of being redissolved in nitric acid solution, becoming the feed for a membrane process.

CHAPTER 2

RESEARCH GOALS

This project seeks to find a liquid membrane system that maximizes the selective flux of cesium or strontium or both. Effort is concentrated on passive transport systems through supported liquid membranes since passive transport systems have received less attention lately compared to facilitated transport systems.

A second reason for stressing passive transport is that permeation rates are faster in passive transport than in facilitated transport for several reasons:

- Facilitated transport requires permeation of a large carrier molecule with the permeating species; passive transport does not.

- One primary objective of facilitated transport is usually to minimize passive transport. Membrane liquids used to minimize passive transport of ions are usually large hydrocarbon-based molecules such as phenylhexane and isotridecanol which tend to slow diffusion rates. Passive transport experiments may utilize smaller molecules for membrane liquids such as octanol.

- The concentration of the permeating species in a facilitated transport membrane phase is limited to the solubility of the carrier in the membrane phase. Passive transport is not limited in such a way.

The following plans were established in order to complete the objectives:

- Attempt to replicate previous successes at facilitated transport using membrane solvents such as phenolhexane and isotridecanol.

- Run a number of passive transport experiments to determine the permeability of ions through liquid membranes featuring membrane liquids like octanol.

- Create a computer program that may predict results of continuous membrane processes from permeabilities determined by use of a batch test cell.

CHAPTER 3

BACKGROUND

Supported Liquid Membranes

Supported liquid membranes possess many advantages over other types of membranes such as polymer membranes and emulsion liquid membranes [1].

- Diffusion coefficients in liquids are orders of magnitude larger than in polymers, promoting greater fluxes.

- Back extraction is much easier in liquid membranes than in emulsion membranes.

- Special carriers may be added to liquid membranes increasing the selectivity and speed of transport when all other parameters are held constant.

- Flat sheet supported liquid membranes are relatively easy to model compared to emulsion membranes.

The liquid in a liquid membrane system is commonly held in place through the use of a support structure. The supported liquid membrane separates a feed solution high in chemical potential from a strip solution low in chemical potential. Feed and strip solutions are typically not soluble in the membrane phase so that the membrane liquid remains within its support. An example of this is a hydrocarbon based liquid within the pores of a hydrophobic polymeric support separating two aqueous solutions.

Support membranes are chosen based on inertness, surface chemistry, porosity, tortuosity, and thickness [1]. The chemistry should be such that the membrane liquid enters the membrane pores freely while the feed and strip solutions cannot. The pores

must be small enough to prevent membrane liquid loss should pressure gradients occur, yet large enough to allow adequate flux. Porosity should be maximized to increase the area useful for mass transport per total area of membrane surface area. Pore tortuosity should be minimized since the more tortuous the path of the diffusing species, the lower the effective diffusion coefficient.

As previously mentioned, a benefit of liquid membranes is that a "carrier" molecule can be dissolved within the organic membrane phase to facilitate greater selectivity between metal cations. Figures 1 and 2 illustrate the differences between passive transport and facilitated transport. Figure 1 shows simple passive diffusion of a solute down a concentration gradient due to a difference in chemical potential between the feed and strip phases separated by the membrane. Figure 2 illustrates the use of a carrier in facilitated transport. The carrier molecule undergoes a complexation reaction with the solute at the interface between the feed phase and membrane phase. The newly formed complex diffuses across the membrane to the interface between the membrane phase and the strip phase where the reverse reaction occurs. The reformed carrier then diffuses back across the membrane to extract more of the permeating species. The greater the selectivity of the complexation reaction, the more selective the separation. Carrier concentration also plays a large role in facilitated transport since the concentration of the diffusing species within the membrane phase is dependent upon the solubility of carrier in the membrane solvent.
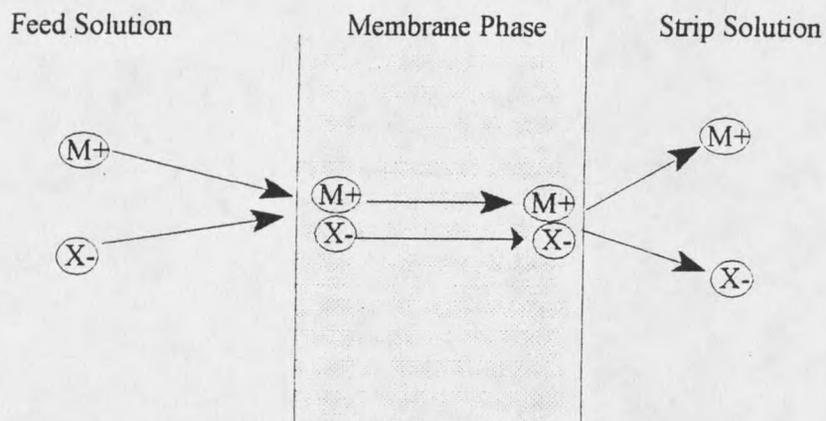
Figure 1. Passive diffusion of an electrolyte through a
supported liquid membrane
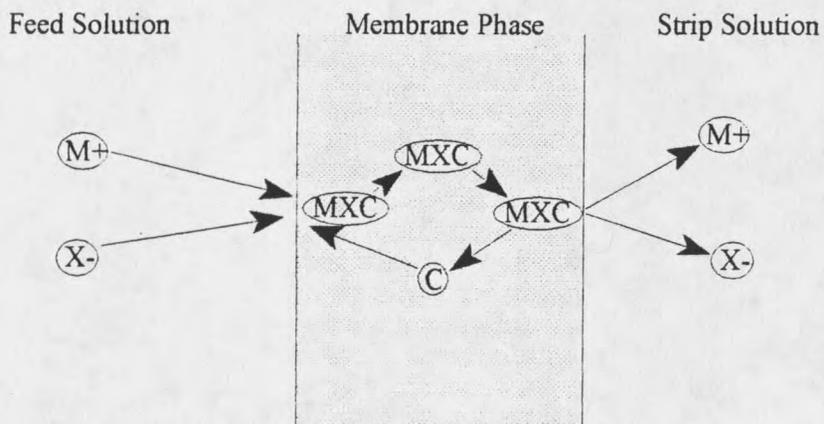
Figure 2. Facilitated diffusion of an electrolyte through a
supported liquid membrane. The carrier is denoted by a "C".

The membrane phase serves a different purpose for passive transport than for facilitated transport. Passive transport requires a membrane liquid that allows quick passive transport of the diffusing species. The selectivity in passive transport is independent of any chemical reactions, but is dependent upon the relative rates of transport between diffusing species. Facilitated transport requires a membrane liquid that prevents passive transport. Selectivity in facilitated transport depends upon the selectivity of the carrier reacting with the permeating species to facilitate a clean separation. Any passive transport usually obstructs the objective of facilitated transport. When a facilitated transport membrane prevents passive transport it is said to be stable. An unstable facilitated transport membrane allows passive transport.

Driving Forces for Mass Transfer Across a Membrane

Mass transfer through membranes occur due to gradients in chemical potential. This chemical potential may be expressed as differences in pressure (either osmotic or applied), electrical potential, and concentration. This study focuses on mass transfer due to concentration gradients.

Fick's Law is used to calculate mass flux due to concentration differences. Fick's law appears below assuming a dilute solution (no convection terms).

$$j = D\frac{dC}{dx} \tag{1}$$

j = Flux of diffusing species due to diffusion (mg/(hr $\cdot$ m^2)

D= Diffusion coefficient (m²/hr)

C = Concentration of diffusing species (mg/L)

x = Position across the thickness of the membrane (m)

Consider diffusion across a thin film. Completing a mass balance on a finite element within the thin film, substituting equation (1), and integrating, results in the equation for diffusion across a thin film [2]:

$$j = \frac{D}{L}(C_f - C_s) \tag{2}$$

The constant L is the thickness of the thin film; C_f and C_s are the concentrations of the diffusing species in the feed and strip solution respectively. Application of equation (2) to a membrane results in:

$$j = [\frac{D_{eff}H}{L}](C_f - C_s) \tag{3}$$

In equation (2), D_{eff} replaces D and is the effective diffusion coefficient [3]. It compensates not only for diffusion through the liquid contained within the membrane, but also the tortuous path of the diffusing molecule through the membrane pores. The higher the tortuosity of the membrane, the lower D_{eff}.

The partition coefficient, H, is defined as the solubility of the diffusing species in the membrane phase, divided by the solubility of the diffusing species in the feed or strip phase [2].

The bracketed term in equation (3) may be replaced with the permeability, P, to yield this form of the membrane transport equation:

$$j = P \ (C_f - C_s)$$
(4)

This is desirable for two reasons. First, convection always accompanies diffusion, and sometimes it is difficult to ascertain whether the convection is negligible or not. Using the permeability encompasses all mechanisms of mass transport across a membrane including convection [4]. Second, it is much simpler to determine the permeability through experiment compared to determining both the diffusion coefficient and the partition coefficient.

Hydration Effects on Diffusion Coefficients of Electrolytes

The CRC Handbook of Chemistry and Physics [5] reveals that a sodium ion has a smaller diffusion coefficient in an infinitely dilute aqueous solution than a cesium ion. This suggests that the sodium ion is effectively larger than the cesium ion in aqueous solution. Franks [6] explains this observation by the amount of hydration that each ion experiences. Although crystallographic measurements in the solid state show the cesium ion is larger, the effective sizes in solution result due to the larger number of hydrated waters associated with the sodium ion.

Table 1 shows experimentally determined diffusion coefficients for a variety of ions in infinitely dilute aqueous solution as published in the CRC Handbook of Chemistry and

Physics [5]. Notice that cesium has the largest diffusion coefficient of all the metals in the

table.

Table 1. Diffusion coefficient for various individual ions in infinitely dilute aqueous
solution [5].

Ion	Diffusion Coefficient (10^{-5} cm^2 s^{-1})
Cs^+	2.056
Ca^{2+}	0.792
Al^{3+}	0.541
Sr^{2+}	0.791
Na^+	1.334
NO_3^-	1.902
SO_4^{2-}	1.065

The diffusion coefficients for a dissolved salt may be calculated by using the

equation below [5]. The diffusion coefficient of the salt is the harmonic average of the

diffusion coefficients of the individual cation and anion [2].

$$D(salt) = \frac{(z_+ + |z_-|)D_+ D_-}{z_+ D_+ + |z_-| D_-}$$

(5)

In equation (5), z_+ and z_- are the charges on the cation and anion respectively; D_+ and D_-

are the individual diffusion coefficients for the cation and anion respectively.

Electrolyte Transport Across Lipophilic Membranes

Figure 1 shows passive transport of electrolytes across a lipophilic membrane. Duffey et al. [7] explains that this electrolyte transport across a membrane of low dielectric constant may occur in two different forms. One form is as dissociated cations with positive charge(s) and dissociated anions with negative charge(s). The other form is as associated ions of no net charge. Even if the ions move as dissociated cations and anions instead of as associated ions, the requirement of electroneutrality dictates that the cation(s) and anion(s) move together. This results in averaging of the diffusion coefficient between the cation(s) and anion(s) as seen in equation (5). Take the case of a large single-charged cation and a small anion. The small anion, which diffuses quicker when alone, attracts the cation thereby increasing the speed of the cation. The slower cation attracts the anion, effectively slowing down the anion.

CHAPTER 4

EXPERIMENTAL

Reagent-grade chemicals were used in all experiments. The metal salts $NaNO_3$, $Ca(NO_3)_2$, Cs_2SO_4, $CsNO_3$, $Sr(NO_3)_2$, $Al(NO_3)_3$, and $CaCl_2$ were obtained from Aldrich; Na_2SO_4 from Matheson Coleman, and Bell; and $CaSO_4$ from Baker. All metals were initially in the feed phase for the various experiments. The feed phase for each experiment usually consisted of three metals in a concentration range between 45 and 300 mg/L as cations. Distilled deionized water served as the strip solution in all experiments.

Octanol (Baker), iso-decanol (Exxon), heptanol (Eastman), and 2,6-dimethyl-4-heptanol (Aldrich) were all used as membrane liquids. The membrane support structure was allowed to soak in the membrane liquids various lengths of time to make the supported liquid membranes.

Celgard 2400® served as the membrane support for all experiments. It is a porous polypropylene flat sheet support membrane obtained from Hoechst Celanese with thickness of 25 μm, porosity of 38% and effective pore size of 0.02 μm according to the manufacturer.

The large test cell (Figure 3) was utilized for all passive transport experiments. The test cell consisted of two 2-1/2" x 3" reducing glass elbows manufactured by Kimax. It contained 800 cm^3 of aqueous solution on each side of the membrane and had a membrane surface area of 45.6 cm^2. A gasket and the membrane are held between the 3" openings by aluminum flanges. Each elbow sets upon a Cole-Parmer stirring motor coupled to a

magnetic egg-shaped stir bar. The elbows are held in place with clamps to a supporting rod. This apparatus enables easy sampling, relatively simple membrane installation, and adequate stirring capability.
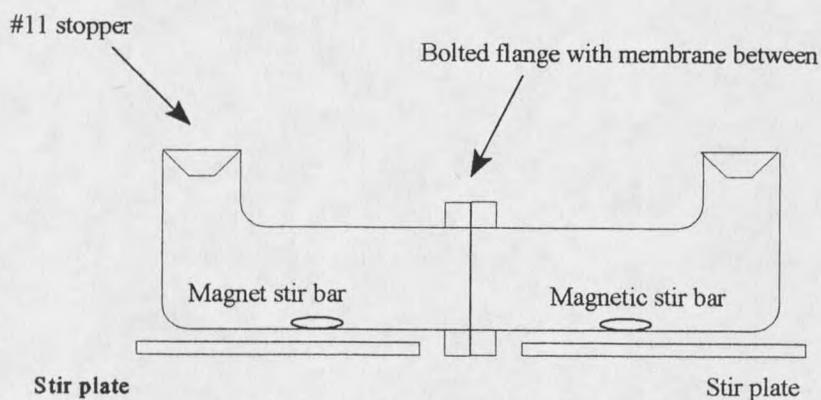

Figure 3. Large Diffusion cell. Each side of the cell holds 800 cm³ of aqueous solution.

Supported liquid membranes were prepared by soaking sheets of Celgard 2400® film in the membrane liquid. The membranes were removed from the membrane liquid, allowed to drip for about a minute, then clamped into place. Prepared aqueous solutions were then poured into each side of the test cell at the same rate to prevent pressure differences from forcing liquid from the membrane pores. Both aqueous solutions were stirred at approximately the same speed based on speed dial position and visual observation. Two milliliter samples were taken periodically from both the source and receiving phases by automatic pipet for analysis.

Analytical

Absolute ion concentrations in the feed and strip samples were determined with a

High Performance Liquid Chromatograph equipped with Shimadzu cation column (model #IC-C2), Shimadzu pump (#LC-10AD), Shimadzu column oven (#CTO-10A) and Shimadzu conductivity detector (#CDD-6A).

The volumetric pump rate was 2.5 ml/min. The conductivity detector was set at a range of 8 or 16, polarity negative, and gain of 1. An oven temperature of 50°C was used with a mobile phase consisting of 5mM tartaric acid and 1mM 2,6- pyridinedicarboxylic acid in distilled deionized water.

Samples required no dilution, concentration, or other preparation prior to injection by syringe into the HPLC sample port. A two way valve determined whether the mobile phase flowed through a 20 μL sample loop or bypassed the sample loop. The sample was injected with the valve set to bypass the mobile phase around the sample loop. Injected sample in excess of 250 μL traveled through the loop into a discard tube. Then the valve position was changed to allow flow of mobile phase into the sample loop, delivering the sample into the cation column. This ensured that the sample size remained consistent for all injected samples.

The recorder integrated and printed areas representing the concentration of each species in each injected sample. A standard solution of 30 mg/L cations was utilized to calibrate areas printed by the recorder into absolute concentrations for each cation.

CHAPTER 5

RESULTS AND DISCUSSION

Experiments were completed to determine permeabilities of metal ions based upon differing membrane liquids, stirring speeds, and soak times of the support structure in the membrane liquid. Experiments were also executed with different anions combined with identical cations to test the effect of the anions on permeabilities. Metal cation feed concentrations ranged from 45 mg/L to 300 mg/L; the strip solution was distilled deionized water in all cases.

Samples taken periodically from both the strip and feed sides of the test cell were analyzed for cation concentration. The feed side gradually decreased in concentration and the strip side increased in concentration as metal ions permeated across the liquid membrane.

Graphical Comparison of Relative Experimental Permeabilities –

Nitrate Salts of Cesium, Calcium, and Sodium

Experiment P features the nitrate salts of cesium, calcium, and sodium as the aqueous feed at concentrations of 50 mg/L, 215 mg/L, and 65 mg/L respectively. Octanol was the membrane solvent. Figure 4 illustrates passive metal ion transport for Test P. It shows concentrations of each cation in the feed and strip solutions as a function of time. It is difficult to judge from this graph which species diffuses most rapidly. Figure 5 shows results of the same experiment with normalization of the concentrations of each metal at