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

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.

# SEPARATION OF CESIUM AND STRONTIUM FROM NUCLEAR WASTE BY SUPPORTED LIQUID MEMBRANES

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# APPROVAL

of a thesis submitted by

John D. Parks

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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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.

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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.

# 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.

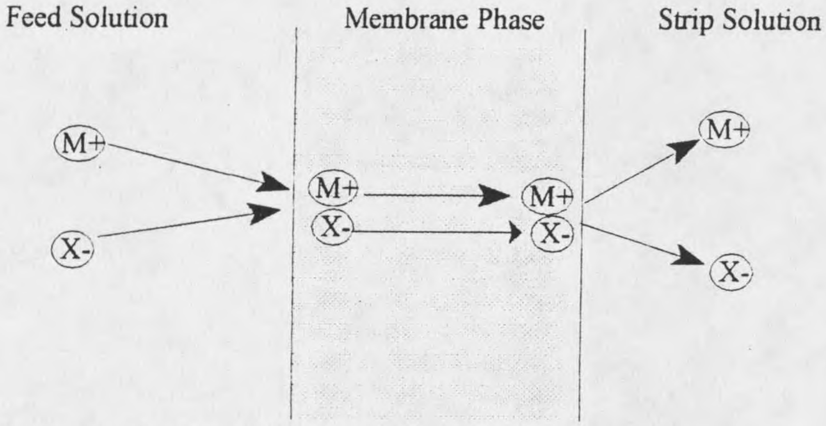

Figure 1. Passive diffusion of an electrolyte through a supported liquid membrane

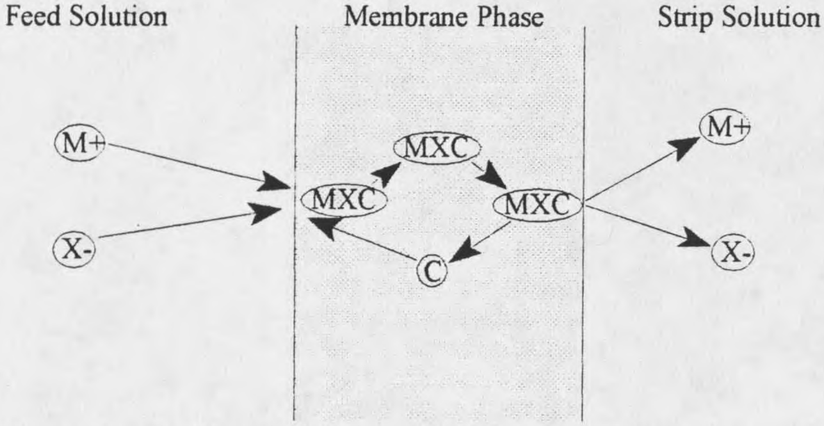

Figure 2. Facilitated diffusion of an electrolyte through a supported liquid membrane. The carrier is denoted by a "C".

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 · m$^2$)

D= Diffusion coefficient ($m^2$/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:

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

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].

$$D(salt) = \frac{(z_+ + |z_-|)D_+D_-}{z_+D_+ + |z_-|D_-} \qquad (5)$$

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 $\mu$m, porosity of 38% and effective pore size of 0.02 $\mu$m 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.

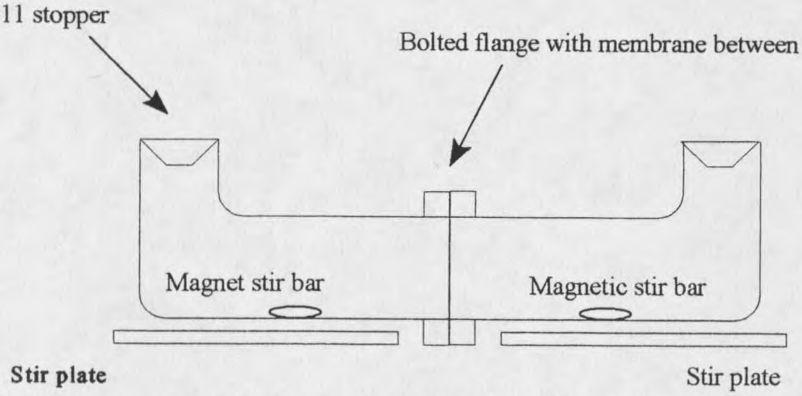

Figure 3. Large Diffusion cell. Each side of the cell holds 800 cm$^3$ of aqueous solution.

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 each sample time. This is done by displaying the concentration of each cation as the percentage of each cation initially charged that is present in the feed and strip solutions at each sample time. It enables graphical comparison of the relative permeabilities of each species. Notice that the cesium nitrate concentration (as percentage of amount charged) decreases more rapidly (has a greater absolute slope) than calcium nitrate and sodium nitrate. This indicates that the permeability of cesium nitrate is greater than that of calcium nitrate and sodium nitrate. Also notice as the experimental time gets large, the system approaches the equilibrium condition where 50% of each of the charged metals exists on each side of the membrane.

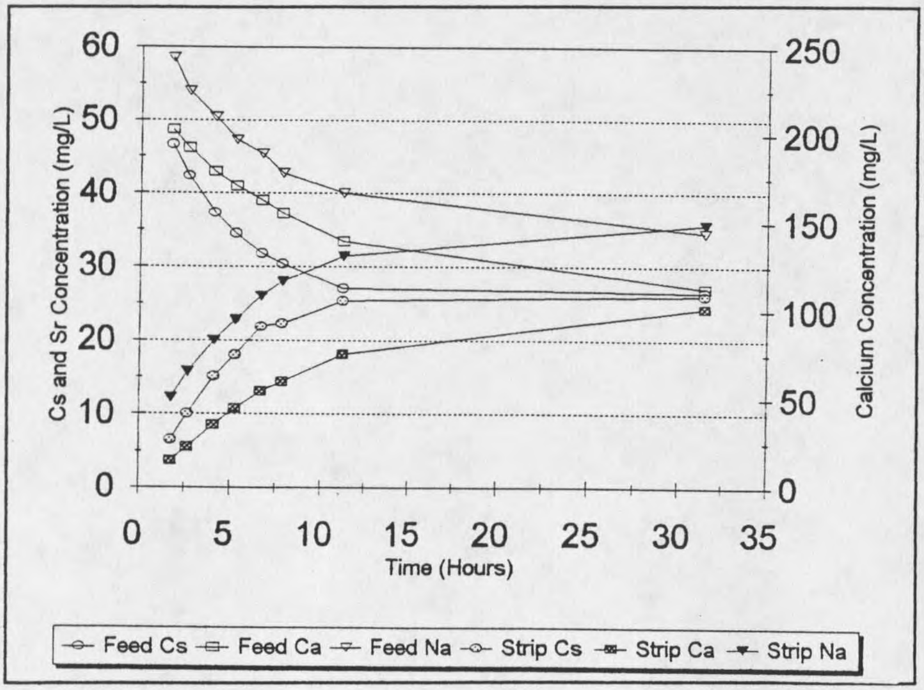

Figure 4. Feed and strip metal nitrate concentrations for Test P. Octanol is the membrane liquid.

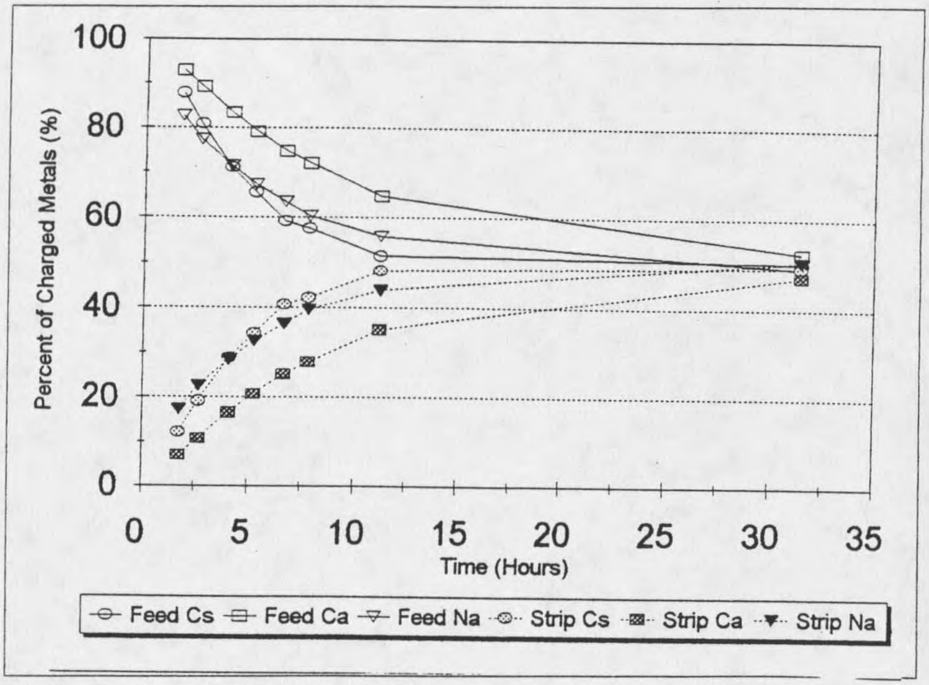

Figure 5. Normalized feed and strip metal nitrate concentrations for Test P. Octanol is the membrane liquid.

## Numerical Determination of Experimental Permeabilities

Numerical permeability values are more useful than graphical comparisons of permeabilities. The concentrations on each side of the membrane as a function of experimental time, along with initial concentrations at arbitrary time zero, may be used to calculate the permeability of each cation by equation (6) from Cussler [2]. Appendix D shows a complete derivation of the equation.

$$-\ln\left(\frac{C_f - C_s}{C_{fo} - C_{so}}\right) = PB(t - t_o) \qquad (6)$$

B= 2A/V is a constant, and a function of the test cell geometry. (1/m)

A= Surface area of the membrane ($m^2$)

V= Volume of one side of the cell ($m^3$)

$C_{fo}$= Initial feed concentration of a specific ion (mg/L)

$C_{so}$= Initial strip concentration of a specific ion (mg/L)

$t_o$= Time at which application of equation (6) is initiated. (h)

P= Permeability (m/h)

A graph of the left side of equation (6) versus ($t-t_0$) provides a straight line so that a linear regression may be performed; the slope being equal to PB. Since B is known from the geometry of the test cell, the permeability, P, may be backed out. Experiment S (Figure 6) is shown because it provides representative results of this technique in practice. Experiment S consisted of cesium, calcium, and strontium nitrates at concentrations of 50 mg/L, 220 mg/L, and 50 mg/L respectively. Isodecanol was the membrane liquid. The filled markers in Figure 6 denote experimental cation concentrations; the straight lines designate the best linear fit to the experimental data for each cation. Time $t = t_0 = 0$ on the graph corresponds to an experimental time of 2-1/2 hours since an initial period of time exists where no transport is observed. This will be explained later under Effect of Isodecanol and Membrane Instability.

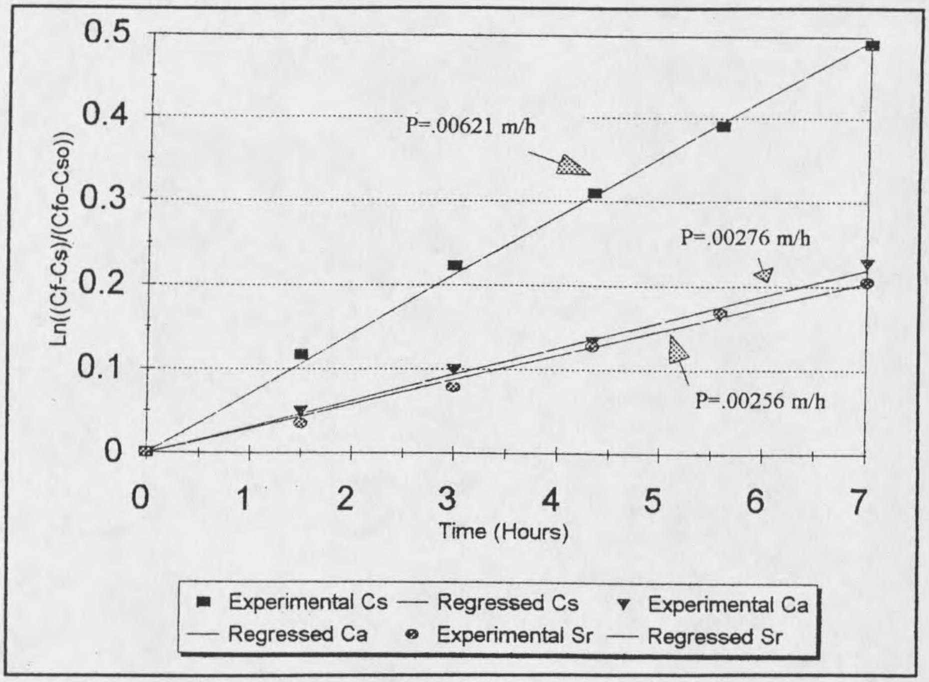

Figure 6. Linear regression of ln $((C_f - C_s)/(C_{fo} - C_{so}))$ versus $(t - t_o)$ for Test S. Isodecanol is the membrane liquid.

The experimental data points in Figure 6 fall on straight lines within a small degree of error. This shows that the permeabilities are constant over the range of concentrations measured. If the permeabilities changed as the feed side gradually decreased in concentration, then a change in slope would occur in a graph of ln $((C_f - C_s)/(C_{fo} - C_{so}))$ versus $(t - t_o)$. Figure 6 proves that this is not the case.

Figure 7 displays a comparison between experimental feed concentrations of cesium in Test S and calculated values using equation (6). A permeability of 0.00621 m/h is used in Figure 7 to determine the calculated values. Figure 6 shows that the permeability of 0.00621 m/h was determined by a linear regression. The calculated feed concentrations fit the experimental data relatively well.

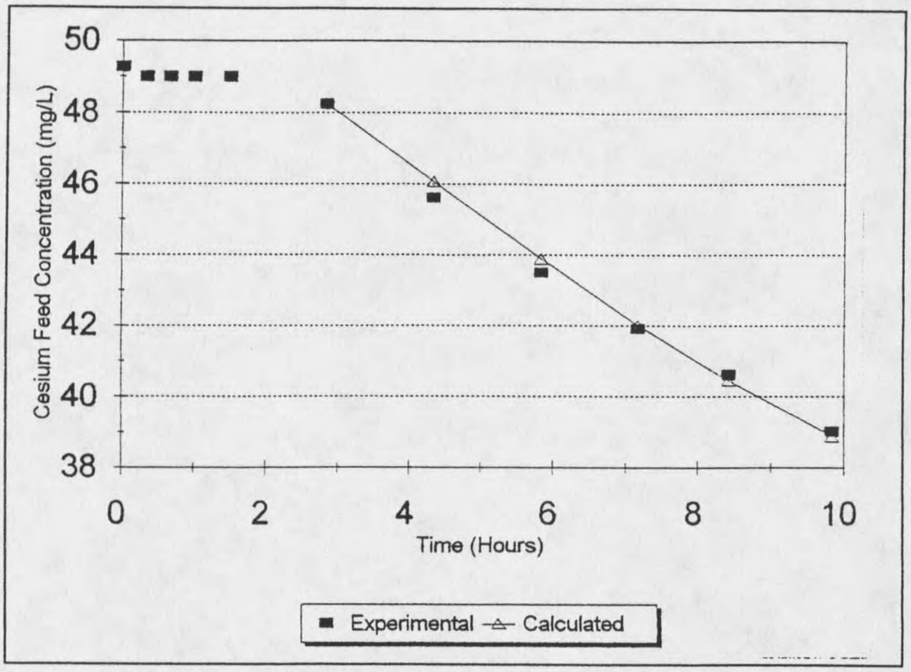

Figure 7. Experimental and calculated cesium nitrate concentrations in the feed solution for Test S. P= 0.00621 m/h for the calculated data.

Figure 8 shows Test U as another example of calculated and experimental feed concentrations. It uses a permeability of 0.0276 m/h to determine the calculated values. Test U utilizes cesium, calcium, and strontium nitrates at concentrations of 50 mg/L, 240 mg/L, and 50 mg/L respectively. Octanol is the membrane liquid. Both Figures 7 and 8 illustrate that feed side concentrations as a function of time are readily predictable using equation (6).

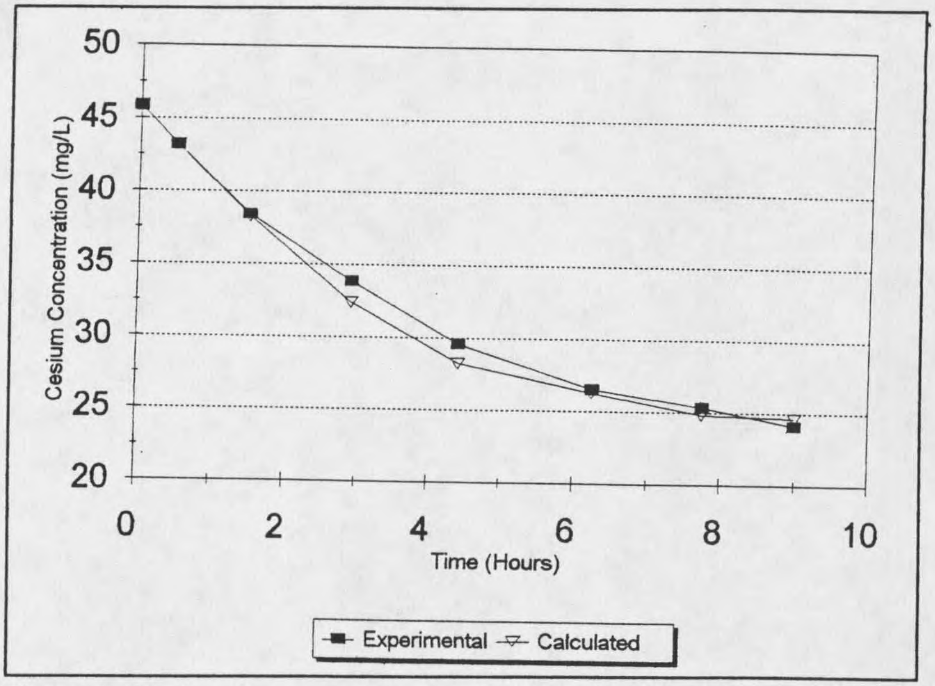

Figure 8. Feed cesium concentration for Test U. P = 0.0276 m/h for calculated data.

## Summary of Permeability Results

Table 2 gives a summary of all the experimental conditions and calculated permeabilities from passive transport experiments. The permeabilities in table 2 are given as the permeabilities of the cation as calculated in the section, Numerical Determination of Experimental Permeabilities. All metal cations are as nitrates unless otherwise specified.

The descriptions “New” or “Reused” in the “Membrane Liquid” column explain whether the membrane was never used, or if it was washed with acetone, rinsed, and reused.

The question marks (?) in the “Soak Time” Column indicate that the soak time was not recorded during the experiment.

Table 2. Passive transport experimental conditions and resulting cation permeabilities calculated from experimental data and equation (6).

| Experiment Number | Feed Phase Ion Concentration | Membrane Liquid | Soak Time | Stirring Speed | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Sr^{++}$ Perm. (m/h) | $Al^{+++}$ Perm. (m/h) | $Na^+$ Perm. (m/h) |
|---|---|---|---|---|---|---|---|---|---|
| 6 | 100 mg/L Cs<br>100 mg/L Ca<br>100 mg/L Sr | None | None | 3 | 0 | 0 | 0 | | |
| 12 | 50 mg/L Cs<br>262 mg/L $CaCl_2$<br>50 mg/L Sr<br>0.0104M $HNO_3$ | Octanol (Reused) | ? | 3 | 0.0165 | 0.00830 | 0.00852 | | |
| A | 49 mg/L Cs<br>259 mg/L $CaCl_2$<br>49 pm Sr<br>0.00013M $HNO_3$ | Octanol (Reused) | 1 Hour | 3 | 0.0229 | 0.0104 | 0.0101 | | |
| C | 50 mg/L Cs<br>260 mg/L $CaCl_2$<br>50 mg/L Sr | Octanol | 1 Hour | 2 | 0.0194 | 0.00888 | 0.00867 | | |
| E | 50 mg/L Cs<br>255 mg/L Ca<br>50 mg/L Al | Octanol (New) | 19 Hours | 3 | 0.0273 | 0.0116 | | 0.00723 | |
| H | 50 mg/L Cs<br>260 mg/L Ca<br>50 mg/L Sr | 1-Heptanol (New) | 24 Hours | 3 | 0.0272 | 0.0107 | 0.0116 | | |
| I | 50 mg/L Cs<br>260 mg/L Ca<br>50 mg/L Sr | Di-4-Hept* (New) | 40 Hours | 3 | 0.0295 | 0.0118 | 0.0120 | | |

| Experiment Number | Feed Phase Ion Concentration | Membrane Liquid | Soak Time | Stirring Speed | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Sr^{++}$ Perm. (m/h) | $Al^{+++}$ Perm. (m/h) | $Na^+$ Perm. (m/h) |
|---|---|---|---|---|---|---|---|---|---|
| M | 50 mg/L Cs<br>250 mg/L Ca<br>50 mg/L Sr | Isodecanol (New) | 24 Hours | 3 | 0.0103 | 0.0062 | 0.00631 | | |
| P | 50 mg/L Cs<br>215 mg/L Ca<br>65 mg/L Na | Octanol (New) | 45 Hours | 3 | 0.0285 | 0.00994 | | | 0.0158 |
| Q | 4000 mg/L Cs<br>4000 mg/L Ca<br>4000 mg/L Sr | None (New) | None | 3 | 0 | 0 | 0 | | |
| S | 50 mg/L Cs<br>220 mg/L Ca<br>50 mg/L Sr | Isodecanol (New) | 35 Minutes | 3 | 0.00621 | 0.00276 | 0.00256 | | |
| T | 50 mg/L Cs<br>235 mg/L Ca<br>50 mg/L Sr | Octanol (New) | 5 Minutes | 3 | 0.0249 | 0.0107 | 0.0103 | | |
| U | 50 mg/L Cs<br>240 mg/L Ca<br>50 mg/L Sr | Octanol (Special) | Special | 3 | 0.0276 | 0.0115 | 0.0126 | | |
| V | 100 mg/L $Cs_2SO_4$<br>100 mg/L $CaSO_4$<br>100 mg/L $Na_2SO_4$ | Octanol (New) | 48 Hours | 3 | 0.0147 | 0.00602 | | | 0.0115 |
| W | 50 mg/L Cs<br>300 mg/L Ca<br>50 mg/L Sr | Decanol (New) | 48 Hours | 3 | Special | Special | Special | | |

* 2,6-Dimethyl-4-Heptanol

## Discussion of Ion Transport in Alcohol

Table 3 shows diffusion coefficients for salts based upon experimentally determined individual ion diffusion coefficients in dilute aqueous solutions [5] from table 1 and applying equation (5). The diffusion coefficient values in the table predict that the order of increasing permeabilities is: Cesium nitrate > sodium nitrate > calcium nitrate. The results of this study for transport across an octanol impregnated membrane follow the same trend as that expected in dilute aqueous solutions as table 3 shows.

Table 3. Theoretical diffusivities of metal nitrates in dilute aqueous solution, experimental cation permeabilities, and experimental permeability ratios.

| Metal Ions | Theoretical Diffusion Coefficient[1] ($10^{-5}$ cm/s) | Theoretical Diffusion Coefficient Ratio (Cs/Metal Ion) | Experimental Cation Permeability (m/h) | Cation Permeability Ratio (Cs/Metal Ion) |
|---|---|---|---|---|
| $CsNO_3$ | 1.98 | 1.00 | 0.0279 | 1 |
| $Ca(NO_3)_2$ | 1.30 | 1.52 | 0.0108[2] | 2.58 |
| $Sr(NO_3)_2$ | 1.30 | 1.52 | 0.0103[3] | 2.42 |
| $Al(NO_3)_2$ | 1.17 | 1.69 | 0.00723[4] | 3.86 |
| $NaNO_3$ | 1.57 | 1.26 | 0.0158[5] | 1.77 |

1. Calculated from individual cation and anion diffusivities [5] and applying equation (5)
2. Experimental permeability from average of Tests E and P.
3. Experimental permeability from Test T.
4. Experimental permeability from Test E.
5. Experimental permeability from Test P

Table 3 above shows that, theoretically, cesium nitrate diffuses 1.52 times faster than calcium nitrate and 1.26 times faster than sodium nitrate in dilute aqueous solution. Assuming that the ion species follow the same path length through the membrane, it is reasonable to predict that the same relationships should represent transport through an octanol membrane. Table 3 also displays typical experimental permeability ratios through an octanol membrane from this study. The experimental permeability ratios are higher than the theoretical diffusion coefficient ratios for all the metal nitrates tested. This observation may be explained two different ways.

Robinson & Stokes [8] suggest that ions traveling through polar solvents, such as the alcohol membrane liquids of this study, cause the solvent particles to rearrange themselves so the negative side is close to the positive ion or the positive side is close to the negative ion, or both. This arranging of polar solvent molecules requires energy and effectively slows the diffusion of the ions. A long chain polar solvent such as octanol requires more energy to rearrange than water, thus slowing down diffusion even more. Further, an ion with a larger charge density such as sodium, is slowed more because it affects a greater number of solvent molecules than an ion with a relatively low charge density like cesium. Cesium nitrate would be less affected than ions like sodium nitrate when permeating though octanol, causing larger diffusion coefficient ratios compared to water.

Another possible explanation is that the partition coefficient (solubility of the metal ions in the membrane phase divided by the solubility of the metal ions in the feed or strip phase) may be greater for ions with lower charge densities than for ions with high charge densities. A greater partition coefficient results in larger permeabilities when all other parameters are held equal. Li and Long [9] reported that hydrocarbons permeate faster through a hydrophobic film like polypropylene, than do polar liquids such as methanol.

This suggests that ions with high charge densities are less likely to enter into the lipophilic membrane than ions with low charge density.

## Discussion of Experiments with No Liquid in Membrane

The Celgard 2400 membrane itself is very hydrophobic. Pouring water on it results in the water forming beads on the membrane and rolling off with no observed penetration into the membrane.

Experiments 6 and Q were run with no liquid in the membrane. No transport at all was detected for either experiment with Test Q providing the longest experimental time of over 92 hours. Evidently the membrane pores were filled with air; water could not enter the membrane pores, hence diffusion of ions could not take place.

## Effect of Isodecanol and Discussion of Membrane Instability

One of the most plaguing problems with facilitated transport is stability of the membrane phase [10]. Stability refers to the ability of the membrane phase to prevent passive transport so that facilitated transport remains the dominant mechanism of mass transport. Appendices A, B, and C examine experiments aimed at facilitated transport of strontium nitrate across various liquid membrane solutions. The overall goal is for the minimization of passive transport across the membrane and maximization of selective facilitated transport. In this way, the carrier molecule selectively reacts with a specific substance on the feed side of the membrane and transports it to the strip side where it is released. Any passive transport is usually contrary to the goals of facilitated transport due to the relatively poor selectivity of passive diffusion. At a certain point in time during the facilitated transport experiments, the membrane becomes unstable. The membrane loses the ability to prevent passive transport of ions, as a rush of ions is observed entering the strip solution. Facilitated transport becomes ineffective since the more non-selective passive transport is typically faster. This rush of ions after the membrane becomes unstable is associated with passive transport instead of facilitated transport for reasons explained in Appendix C.

Isodecanol is regarded as a poor membrane solvent for facilitated transport because it provides a stable membrane for only a short period of time [10]. It is useful for studying the nature of membrane stability, however, because the membrane remains stable for a short time, disallowing any detectable passive transport. Then the membrane becomes unstable as passive transport is observed. The transition time when the membrane changes from stable to unstable is readily observable.

Figure 9 shows the strip phase concentration of metal nitrates as a function of time where passive transport occurs through an isodecanol impregnated liquid membrane. Notice that no detectible transport occurs for the first one and one-half hours since no metals are detected in the strip solution. The ions appear unable to diffuse across the membrane during this period of the experiment. Ion transport through the membrane achieves a constant permeability relatively quickly after what appears to be a short transitional period at two hours. More lipophilic membrane liquids such as phenylhexane, used in the facilitated transport experiments outlined in Appendix C, prevented passive transport of ions for several days. Less lipophilic membrane liquids such as octanol show observable passive ion transport almost immediately. That is why most of the passive transport experiments were run with octanol as the membrane liquid.

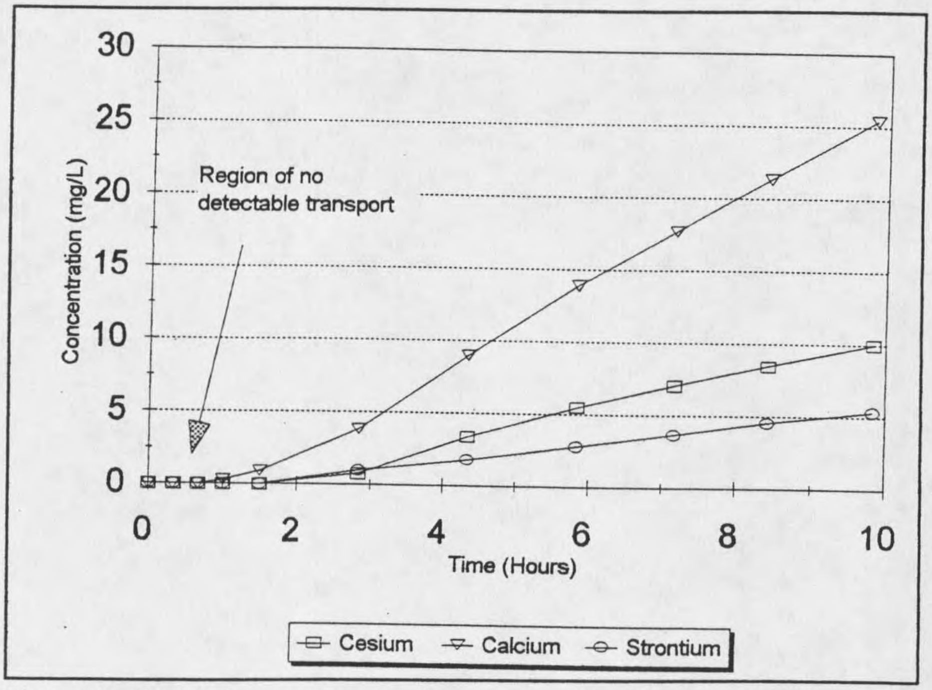

Figure 9. Strip phase concentration versus time for Test S. The membrane liquid is isodecanol.

One possible explanation for membrane instability is that water may enter the membrane to satisfy some sort of equilibrium water concentration between the two aqueous phases and the membrane phase. Danesi [11] briefly mentions that one probable cause of membrane instability is the progressive wettability of the support pores within the membrane. This suggests that the ions cannot diffuse into a relatively lipophilic membrane. The membrane slowly becomes less hydrophobic as water molecules move into the membrane pores. This may occur through a combination of water solvation into the membrane phase; and replacement of the original membrane liquid with water due to osmotic pressure differences, applied pressure gradients, and shear from mixing. It is possible that significant ion transport begins only when the hydrophilicity of the membrane reaches a certain point through addition of water to the membrane phase.

Experiment W was completed to test the idea of water entering the membrane phase through solvation of water into the membrane liquid (decanol). It uses the nitrate salts of cesium, strontium, and calcium at 50 mg/L, 300 mg/L, and 50 mg/L respectively. Before soaking the membrane support in decanol, the decanol was first brought to equilibrium with distilled water in a separating funnel. This experiment yielded no transport for more than eight hours suggesting that ions do not start permeating due to water solvating into the membrane liquid. Experiment W, however, does not rule out the possibility that water entering the membrane enables the permeation of ions. Water may reach equilibrium in the membrane phase through a variety of mechanisms other than solvation. Other methods water may enter the membrane phase include osmotic pressure differences, applied pressure gradients, shear from mixing, and dissolution of the membrane liquid into the aqueous phases. No experiments were run to test these other ideas.

Another possibility is that no water enters the membrane phase, but it simply takes a period of time for the ions to move from one side of the membrane to the other. No experiments were run to investigate this idea.

The process of a membrane becoming unstable may be roughly detected through visual observation. Placing the membrane in the test cell after soaking the membrane in phenylbenzene resulted in an almost transparent membrane. After the membrane was in the test cell for some time, the membrane became cloudy, corresponding to the same time that quick passive transport of ions was detected by HPLC analysis. Soaking the membrane in octanol resulted in a cloudy membrane immediately.

## Nitrate Salts in Octanol

Table 4 shows results of experiments E and P run with various nitrate salts. All parameters were kept constant including octanol as the membrane liquid, equal stirring rates of three on the stirring speed dial, and a long soak time for the membrane in the membrane liquid.

Table 4. Experiments featuring nitrate salts in octanol

| Exper. | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Al^{+++}$ Perm. (m/h) | $Na^+$ Perm. (m/h) | Perm Ratio Cs/Ca | Perm Ratio Cs/Al | Perm Ratio Cs/Na |
|---|---|---|---|---|---|---|---|
| Average of E & P | 0.0279 | 0.0108 | | | 2.61 | | |
| E | 0.0273 | 0.0116 | 0.00723 | | 2.35 | 3.86 | |
| P | 0.0285 | 0.00994 | | 0.0158 | 2.87 | | 1.77 |

Table 4 shows that the permeability for cesium nitrate was greater than all of the other nitrate salts used in experiments E and P. This follows the same trend as the theoretical diffusion coefficients in table 3. Calcium nitrate and strontium nitrate permeabilities were nearly equal which also follows the pattern of theoretical diffusion coefficients in table 3. Finally, aluminum has the slowest permeability in table 4 and the smallest theoretical diffusion coefficient in table 3. The ratios between the experimental permeabilities of cesium nitrate and the other nitrate salts are all greater than the ratios of theoretical diffusion coefficients of ion in dilute aqueous solution displayed in table 3.

## Effect of Soak Time

Soaking the membrane in the membrane liquid for time periods greater than five minutes had little effect upon the permeability. Table 5 below shows comparisons of permeability with soak time. All experiments were carried out with a stirring speed of three. Octanol was the only membrane liquid used for the investigation of soak time effect.

Table 5. Effect of soak time on experimental permeabilities and permeability ratios

| Exper. | Feed Phase Ion Concentration | Soak Time | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Sr^{++}$ Perm. (m/h) | Perm. Ratio Cs/Ca | Perm. Ratio Cs/Sr |
|---|---|---|---|---|---|---|---|
| E | 50 mg/L Cs<br>255 mg/L Ca<br>50 mg/L Al | 19 Hours | 0.0273 | 0.0116 | | 2.35 | |
| P | 50 mg/L Cs<br>215 mg/L Ca<br>50 mg/L Sr | 45 Hours | 0.0285 | 0.00994 | | 2.87 | |
| T | 50 mg/L Cs<br>235 mg/L Ca<br>50 mg/L Sr | 5 Minutes | 0.0249 | 0.0107 | 0.0103 | 2.33 | 2.42 |

Test E and P permeabilities were slightly higher for cesium nitrate than Test T where the membrane was soaked for only five minutes in membrane liquid. These small differences are probably statistically insignificant considering that the calcium permeability does not follow the same trend. Membrane soak time appears to effect cation permeabilities insignificantly.

## Effect of Long Run Times on the Membrane

The section Effect of Isodecanol and Discussion of Membrane Instability suggests that early in each experiment, rapid changes occur within the membrane phase as the aqueous phases appear to approach some sort of equilibrium with the membrane phase. After this initial rapid change, no detectible changes are observed as indicated by constant permeabilities in each experiment. Test T was run to find any relatively long range changes that may be occurring very slowly, and to give an idea of membrane life. A short procedure follows describing Experiment T and Experiment U.

| Date | Event |
|---|---|
| 2/3 | Executed Test T with octanol as the membrane liquid. |
| 2/3-2/7 | The membrane from Test T was left in the test cell with continued mixing on both sides. |
| 2/7 | The aqueous solutions from Test T were dumped out of the test cell, and the test cell was rinsed out while the membrane was left in place. Then Test U was started by pouring a feed solution of 50 mg/L Cs, 50 mg/L Sr, and 240 mg/L Ca as nitrates. |

The permeability increase for each specie is shown in table 6. It shows that the permeabilities increase slightly for each ionic species. This small increase may be statistically insignificant. The permeability ratio for cesium relative to the other cations remains about the same.

Table 6. Effects of long term use of a single membrane

| Exper. (Date of Exper.) | Feed Phase Ion Concentration | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Sr^{++}$ Perm. (m/h) | Perm. Ratio Cs/Ca | Perm. Ratio Cs/Sr |
|---|---|---|---|---|---|---|
| T<br>(2/3) | 50 mg/L Cs<br>235 mg/L Ca<br>50 mg/L Sr | 0.0249 | 0.0107 | 0.0103 | 2.33 | 2.42 |
| U<br>(2/7)* | 50 mg/L Cs<br>240 mg/L Ca<br>50 mg/L Sr | 0.0276 | 0.0115 | 0.0126 | 2.4 | 2.19 |
| Average of E & P | | 0.0279 | 0.0108 | | 2.61 | |

*Mixing of Experiment T aqueous phases continued from 2/3 to 2/6. On 2/7, Experiment U was run with the same membrane used in Experiment T to test the effect of long run times.

Table 6 above suggests that a slow rate of change may occur within the membrane as it is left within the test cell for long periods of time. This is shown by the small increases in permeabilities from Test T to Test U.

Table 6 includes the averages for Tests E and P for comparative purposes. Although the permeabilities increased from Test T to Test U, the permeabilities for Test U were about the same as the average permeabilities of Tests E and P. This indicates that virtually no changes occur in the membrane over relatively long runs.

## Effect of Different Membrane Liquids

The liquid 2,6-dimethyl-4-heptanol was used in a membrane to test the effects of using an alcohol with one more carbon than octanol. Table 7 shows that Test I using 2,6-dimethyl-4-heptanol exhibits slightly higher permeabilities than the average test using octanol. Perhaps the branched nature of 2,6-dimethyl-4-heptanol leads to higher permeabilities. Although it consists of nine carbons, the longest chain is only seven carbons long.

Experiment H was run to test the effects of utilizing a membrane liquid with one carbon less than octanol. Table 7 below shows that 1-heptanol produces permeability results similar to octanol.

Experiments M and S use isodecanol as the membrane liquid. Both tests show marked decrease in permeabilities compared to experiments with other membrane liquids. The calculated permeabilities for Tests M and S also show large differences from one another. Notice that if Test M is neglected, the permeability ratios vary only slightly between all membrane liquids used.

Table 7. Effect of 2,6-dimethyl-4-heptanol, 1-heptanol, and isodecanol as membrane liquids

| Experiment Number | Membrane Liquid | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Sr^{++}$ Perm. (m/h) | Perm. Ratio Cs/Ca | Perm. Ratio Cs/Sr |
|---|---|---|---|---|---|---|
| Test I | 2,6-dimethyl-4-heptanol | 0.0295 | 0.0118 | 0.0120 | 2.50 | 2.46 |
| Average of E, P | Octanol | 0.0279 | 0.01077 | | 2.61 | |
| Test H | 1-heptanol | 0.0272 | 0.0107 | 0.0116 | 2.54 | 2.34 |
| Test M | Isodecanol | 0.0103 | 0.0062 | 0.00631 | 1.66 | 1.63 |
| Test S | Isodecanol | 0.00621 | .00276 | .00256 | 2.25 | 2.42 |

## Experiments 12, A, and C

Experiments 12, A, and C in table 8 used octanol and were run to test effects of acid in the feed, calcium as chloride instead of nitrate in the feed, and lower stirring speeds. All three experiments utilized calcium chloride instead of calcium nitrate, and all three experiments resulted in lower permeabilities and permeability ratios compared to the average of Tests E and P. This could mean that chloride as the anion slows the permeability through an octanol impregnated membrane and decreases the permeability ratio.

Table 8. Experimental permeability results for Tests 12, A, and C

| Test | Calcium Addition | Acid Conc. | Stirring Speed | $Cs^+$ Perm. (m/h) | $Ca^{++}$ Perm. (m/h) | $Sr^{++}$ Perm. (m/h) | Perm. Ratio Cs/Ca |
|---|---|---|---|---|---|---|---|
| 12 | As Chloride | 0.010M | 3 | 0.0165 | 0.00830 | 0.00852 | 1.99 |
| A | As Chloride | 0.00010M | 3 | 0.0229 | 0.0104 | 0.0101 | 2.20 |
| C | As Chloride | 0.0M | 2 | 0.0194 | 0.00888 | 0.00867 | 2.18 |
| Average of E & P | As Nitrate | 0.0M | 3 | 0.0279 | 0.0108 | | 2.61 |

Test C was mixed at a speed of two instead of three. If this is the cause for Test C exhibiting a smaller permeability, then it could indicate that a boundary layer is acting as a resistance to mass transport in addition to the membrane [12, 13]. Permeabilities independent of stirring speed would indicate that boundary layer resistances are negligible and the membrane phase is the only major factor in resistance to mass transport. It is difficult to determine the effects of stirring, however, since Test C permeabilities at a stirring rate of two are greater than Test 12 permeabilities determined at a stirring rate of three.

## Effect of Metal Sulfates

Metal sulfates were employed in Test V instead of nitrates to observe the effect of a divalent anion compared to a monovalent anion. Theoretical diffusion coefficients from equation (5) are shown in table 9 along with theoretical diffusion coefficient ratios of the metal ions in dilute aqueous solution. The permeabilities presented throughout this study are on a cation basis. Table 9 shows permeabilities of sulfates. This means that the permeability of cesium nitrate is one half the permeability of cesium shown in table 8 since two moles of cesium transport across the membrane for every one mole of cesium sulfate.

Table 9. Diffusion coefficients, permeabilities, and ratios of metal sulfates

| Ion | Diffusion Coefficient ($10^{-5}$ cm/s) From Eq (5) | Diffusion Coefficient Ratio (Cs/Ion) | Experimental Cation Permeability (m/h) | Permeability Ratio (Cs/Ion) |
|---|---|---|---|---|
| Cesium Sulfate | 1.57 | 1.00 | 0.00735 | 1.00 |
| Calcium Sulfate | 0.908 | 1.72 | 0.00602 | 1.22 |
| Sodium Sulfate | 1.23 | 1.28 | 0.00575 | 1.28 |

The permeability of cesium as cesium sulfate is only 53% as large as the permeability of cesium nitrate found as the average of Tests E and P. Calcium sulfate permeability is 56% of calcium nitrate, about the same proportion. The permeability of sodium as sodium sulfate is 72% as large as the permeability of sodium nitrate. Therefore, all metal sulfate permeabilities are smaller than metal nitrate permeabilities on an individual cation basis.

All the experimental permeability ratios for the nitrates were larger than the theoretical diffusion coefficient ratios. This is not observed in the metal sulfates. Table 9 illustrates that the cesium/calcium permeability ratio is less than the cesium/calcium diffusion coefficient ratio. Similarly, the cesium/strontium permeability ratio is the same as the cesium/strontium diffusion coefficient ratio.

## Comparison of Facilitated Transport Permeabilities Versus Passive Transport Permeabilities

Dozol, et al. [17] reports strontium permeabilities of 0.78 cm/h using Celgard 2500® as the membrane support, 0.5M dicyclo-hexano-18-crown-6 as a carrier, and hexylbenzene/isotridecanol as the membrane solvent. The passive transport experiments within this study all use Celgard 2400® as the membrane support which has a smaller pore size and less porosity. Passive transport strontium permeabilities of 5.7 cm/h were observed using octanol as the membrane liquid, and applying the same calculation method as Dozol. This demonstrates that the permeability for passive transport is more than seven times greater than facilitated transport.

The selectivity of facilitated transport is usually higher than the selectivity of passive transport. The permeability of calcium in Dozol's report is 0.0045 cm/h yielding a strontium/calcium permeability ratio of 173. The cesium/calcium permeability ratio in this study averages about 2.5. This is a potentially large disadvantage of passive transport.

The flux of ions for passive transport increase linearly with increasing concentration difference across the membrane assuming that the partition coefficient and diffusion coefficient are constant throughout the concentration range. This is in accordance with equation (4). The flux of ions for facilitated transport, however, does not necessarily increase linearly with increasing concentration difference across the membrane.

This is due to solubility limitations of carrier molecules within the membrane solvent. Doubling the feed concentration will not increase flux across the membrane if the amount of carrier complexed to ions does not increase. This is one advantage for passive transport over facilitated transport; much greater fluxes are possible.

## Continuous Process QBASIC Program Model

The batch experiments executed in the test cell show that separation only occurs before equilibrium is reached. At equilibrium in a batch test cell, equal amounts of all solutes exist on each side of the membrane as shown in Figure 5. A continuous process is preferable to reap the benefits of separation before the onset of equilibrium.

A logical progression from batch diffusion using test cells, is a continuous membrane separation process. Figure 10 shows a possible layout of such a process. This process consists of two compartments separated by a membrane. Both the feed and the strip compartments require a stream feeding them and a stream exiting them. The stream to the feed compartment consists of the contaminated liquid; the stream exiting the feed compartment is a stream depleted in the more permeable ion species. The entering liquid to the strip side is pure water; the exiting liquid from the strip compartment is concentrated in the more permeable species. Such a continuous separation cell may be just one of many arranged in series.

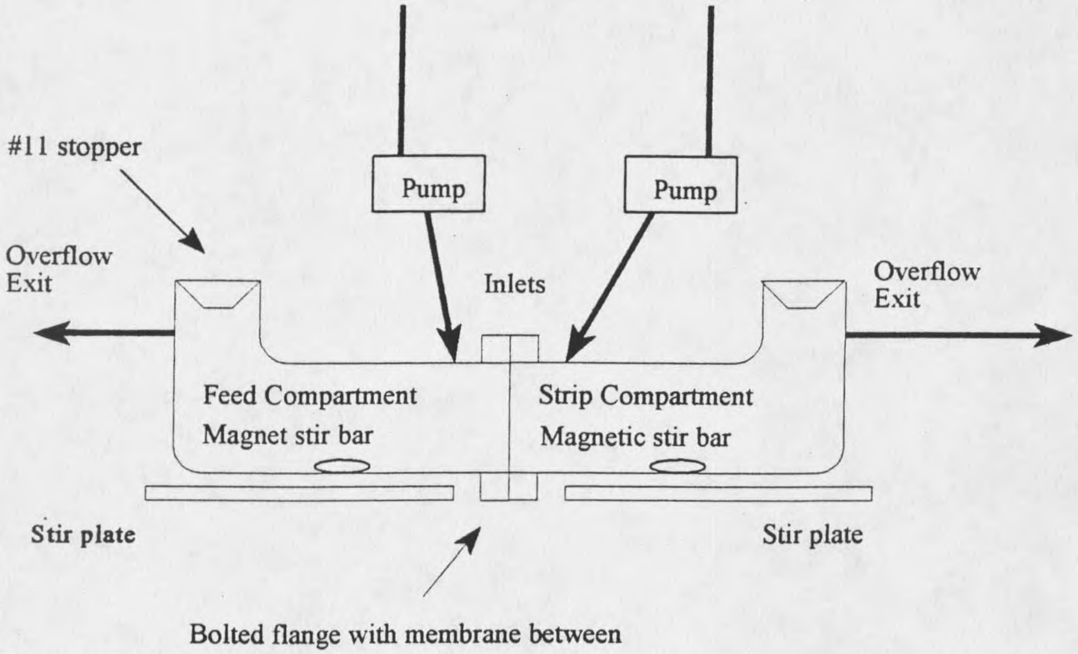

Figure 10. Layout of possible continuous membrane process

The need to predict the outcome of continuous processes from batch experimental permeabilities suggests the need for a computer model of a continuous process. Continuous separation experiments must be conducted in the future to verify such a proposed model.

A proposed computer model has been written in QBASIC to address the problem of applying experimental permeabilities determined from batch test cells to user-defined continuous systems. Assumptions built into the program include a flow pattern such as that in Figure 10 and perfect mixing. The user inputs how many species in the system, feed flow rate, concentration of ions in the stream entering the feed compartment, volume of the feed compartment, volume of the strip compartment, cross-sectional membrane area, strip flow rate, entering strip stream concentration, experimentally determined permeability of each species across the membrane, and differential time basis ($\Delta t$). Then the program calculates the exiting feed and strip compartment concentrations for each species. The QBASIC program is listed in Appendix E.

Equation (4) and mass balances form the theoretical basis of the program. Assume a membrane separates a feed compartment and a strip compartment. The liquid entering the feed compartment contains cesium nitrate and calcium nitrate; the liquid entering the strip compartment is distilled deionized water. A cesium nitrate mass balance around the feed compartment contains one source into it (the entering stream) and two flows out of it (the exiting stream and transport across the membrane). The transport across the membrane remains subject to equation (4). As ions transport through the membrane, they enter the strip compartment. A cesium nitrate mass balance around the strip compartment comprises of one source into it (transport across the membrane) and one flow out of it (the exiting stream). Here again, transport across the membrane remains subject to equation (4). There exists a steady state where the flux and concentration of both compartments do not change as long as the stream flow rates and composition do not change. The program calculates the steady state where mass balances around both compartments and equation (4) are satisfied. It does this through an iterative process.

The user instructs the program to iterate until the problem converges. Here is how the iterations proceed:

1. Calculate the flux of each specie transported through each membrane from the concentration on each side of the membranes and applying equation (4)(Line 1 in program listing, page 62). The feed and strip compartment initial concentrations

are the same as the concentration of the streams entering them.

2. Calculate new concentrations by using the results of step one in a mass balance around the feed compartment and the strip compartment. (Line 3 in program listing, page 62)
3. Calculate new flux values across all membranes from new compartment concentrations and applying equation (4) again.
4. Calculate new concentrations by using the results of step three in a mass balance around both compartments.
5. If the concentrations changed since the previous iteration, then go to step three.
6. If the concentrations are the same as the previous iteration, then the problem is solved.

## Computer Sample Runs

Table 10 shows sample runs using the computer program under differing entering stream conditions. Each run separates two components with permeabilities of 0.025 m/h and 0.010 m/h to simulate experimental permeabilities determined for cesium nitrate and calcium nitrate, respectively. The liquid entering the strip compartment is always pure water, and the cross-sectional area of the membrane is 0.050 $m^2$.

Table 10. Sample runs of QBASIC continuous process model. All concentrations.are in mg/L.

| Run # | Feed Flow Rate (L/h) | Strip Flow Rate (L/h) | Entering Feed $Cs^+$ Conc. | Entering Feed $Ca^{++}$ Conc. | Exit Feed $Cs^+$ Conc. | Exit Feed $Ca^{++}$ Conc | Exit Strip $Cs^+$ Conc. | Exit Strip $Ca^{++}$ Conc. | Diff* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 0.1 | 100 | 100 | 51.9 | 54.7 | 48.1 | 45.3 | 2.8 |
| 2 | 0.4 | 0.4 | 100 | 100 | 56.9 | 64.3 | 43.1 | 35.7 | 7.4 |
| 3 | 0.8 | 0.8 | 100 | 100 | 62.1 | 72.2 | 37.9 | 27.8 | 10.1 |
| 4 | 2.0 | 2.0 | 100 | 100 | 72.2 | 83.3 | 27.8 | 16.7 | 11.1 |
| 5 | 10 | 10 | 100 | 100 | 90.0 | 95.5 | 10 | 4.5 | 5.5 |
| 6 | 1.0 | 2.0 | 100 | 100 | 78.3 | 85.7 | 43.5 | 28.6 | 7.4 |
| 7 | 2.0 | 4.0 | 100 | 100 | 67.7 | 81.8 | 16.1 | 9.1 | 14.1 |

* Difference between Cs and Ca concentrations in the stream exiting the feed compartment.

### Runs 1-5: Effect of Flow Rates to Feed and Strip Compartments

For purposes of this study, the difference between cesium and calcium concentrations in the stream exiting the feed compartment will be a measure of effective separation. The larger the difference, the better the separation.

Runs one through five were executed with all parameters constant except for the flow rates to the feed and strip compartments, which had a large effect upon separation.

It is reasonable that a very small entering flow rate to both feed and strip compartments approximates a batch test cell. Therefore, the steady state concentrations calculated by the program for each side of the membrane would approach equilibrium concentrations in a batch test cell. These equilibrium concentrations are 50% of each charged metal on one side of the membrane, and the remaining 50% on the other side of the membrane. Run #1 shows this effect with a relatively small 0.1 L/h flow rate into each compartment. Notice that the exit concentration of all metals is about 50% of the charged amount of metals. This provides a poor separation.

Increasing the flow rates has the same effect as decreasing the cross-sectional area of the membrane. Gradually increasing the flow rate to 2.0 L/h (Run #4) for both the feed and strip sides resulted in concentrations much different than 50% of each charged metal on each side of the membrane while producing a more favorable separation. The exiting feed compartment concentration difference between cesium and strontium increases from 2.8 mg/L to 11.1 mg/L from Run #1 to Run #4.

Run #5 exhibits flow rates of 10 L/h and shows that the benefits of increasing the flow rates eventually diminish. This is because the feed solution passes through the feed compartment before the ions are able to transport to the strip side of the membrane. Poor separation results.

## Run 7: Effect of Increased Strip Side Flow Rate

Run #7 was executed to test the effects of increased strip side flow rates in comparison to Run #4. Run #7 provides an exiting feed compartment concentration difference between cesium and calcium of 14.1 mg/L while that of Run #4 is 11.1 mg/L. This is partly because the strip flow rate is twice as large as the feed flow rate creating a more dilute strip compartment concentration and increased driving force (concentration gradient) of mass transport.

## Effect of Changing Compartment Volumes

Changing any or all of the compartment volumes produces no effect upon final ion concentrations since changing the volumes does not change any mass balances. This includes the volume of the intermediate compartments between membranes in series. Changing the volumes *does* affect how long the program requires to calculate the final concentrations however. This effect should also be seen in the laboratory as a large volume should take longer to approach steady state. Take the feed compartment for instance. The mass of ions entering the feed compartment is solely dependent upon the characteristics of the entering stream. The concentration of a large feed compartment volume changes more slowly than the concentration of a small feed compartment volume. Eventually all systems reach the same steady state concentrations when only the volume changes.

## Summary of QBASIC Runs

The continuous process QBASIC program model is a preliminary model that is not yet validated by experimental continuous separations. It uses experimental permeabilities determined from batch separations to calculate steady state effluent stream concentrations of a user-defined system. The program achieves this by satisfying mass balances and equation (4). Initial results indicate that the flow rate has a large effect on the separation when all other parameters are held constant. Changing the volume of any or all of the compartments produces no change in the steady state concentrations.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

Metal nitrates permeate through octanol membranes in the same order as their diffusion coefficients measured in dilute aqueous solution: Cesium nitrate > sodium nitrate > (calcium nitrate ≈ strontium nitrate) > aluminum nitrate. The ratios of the diffusion coefficients, however, do not accurately predict the ratio of permeabilities through the membrane. 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 2,6-dimethyl-4-heptanol and 1-heptanol are used as the membrane liquid.

Metal sulfates also permeate through octanol membranes in the same order as their diffusion coefficients in dilute aqueous solution: Cesium sulfate > sodium sulfate > calcium sulfate. Cesium permeability (as cesium) is 1.3 times greater than sodium, and 2.4 times greater than calcium sulfate.

Using isodecanol results in a short period of membrane stability where no transport is detected across the membrane. Then the liquid membrane becomes unstable and passive transport is observed. Passive transport through an isodecanol membrane is slower than that observed through an octanol membrane.

Experimental passive transport permeabilities of strontium were determined to be more than seven times greater than that reported for facilitated transport. This difference should increase with increasing feed concentrations since facilitated transport is limited in the amount of ions in the membrane phase by the amount of carrier in the membrane phase. This is one advantage of passive transport systems over facilitated transport systems. One disadvantage of passive transport is that it is less selective than some facilitated transport systems.

A program was written in QBASIC to extend batch experimentally determined permeabilities to user-defined continuous separation systems. The model must yet be validated through experimentation.

## Recommendations

- Polar liquids other than the alcohols tested may lead to desirable passive transport properties when used as a membrane liquids. A variety of alcohols and other polar liquids with hydrophobic groups attached should be attempted such as butanol, pentanol, 3-octanol, 2-octanone, and hexylamine.
- Liquid membrane stability is a major problem for facilitated transport systems. This may be a big advantage for passive transport systems. The effect of long runs of over a week should be attempted.
- The only way to accomplish separations on a large scale is through a continuous process. Continuous process experiments should be completed to provide information for the development of continuous process models.
- Multiple membrane systems may increase overall separations. Multiple membrane cascades should be tested.
- Many other ions exist in nuclear waste besides those reported in this study.

Experiments should be run to test the permeability of these other metals compared to cesium. For instance, a large permeability ratio should result between cesium and zirconium because zirconium has four positive charges associated with it. This means that it has a high charge density and possibly a large amount of hydration in aqueous solution.

- Devise a method of finding the partition coefficient of specific ions in water/membrane liquid systems.

# APPENDICES

# APPENDIX A

# FACILITATED TRANSPORT INTRODUCTION

The goal of facilitated transport in a liquid membrane system is to transport the permeating species across a membrane faster and more selectively than passive diffusion through the same liquid membrane system. The goal is accomplished through the use of a carrier molecule dissolved in the membrane solvent. The complexation reaction between the carrier molecule and the desired permeating species is important for two reasons: 1) The more selective the carrier species reacts, the cleaner the separation. 2) The carrier must react with the metal cation in such a way that the reaction rate does not limit the flux. This occurs if either the carrier/cation complexation or decomplexation occurs too slowly [14].

Another important property of the carrier is solubility in the membrane solvent versus the feed and strip liquids. The flux of the complexing species has been shown to vary linearly with carrier concentration in flux limited systems [15]. When the carrier dissolves easily into the feed or strip phases, relative to the membrane phase, much of the advantage is lost.

Mobility of the complexed carrier across the membrane is important when the process is flux limited. A low viscosity membrane solvent and small carriers are desired to maximize the diffusion coefficient. Unfortunately, viscous materials are typically used as the membrane solvent to prevent the membrane solvent from being forced out of the pores. This can occur due to applied pressure differences, osmotic pressure differences, dissolution, or shear stresses from mixing.

Dicyclo-hexano-18-crown-6 (DC18C6), shown in Figure 12, and similar derivatives have been applied as carriers within liquid membrane systems to selectively transport strontium from simulated radioactive waste [10,12-16,17,18]. The DC18C6 molecule is ideal for this purpose. The electronegative center of DC18C6 draws cations into it, but selectively combines with strontium since the unhydrated strontium cation fits tightly within the diameter of the DC18C6 cavity.

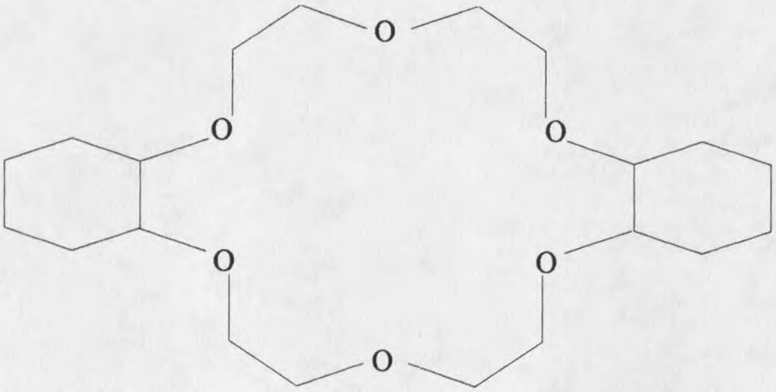

Figure 11. Dicyclo-hexano-18 crown 6

Lamb, et al. [17] observed selective transport of strontium over barium and calcium using 0.5M concentrations of $Ca(NO_3)_2$, $Sr(NO_3)_2$, and $Ba(NO_3)_2$ as the aqueous feed phase and distilled water as the aqueous strip phase. Bis(1-hydroxyheptyl)-dicyclohexano-18-crown-6 was used as the carrier dissolved in phenylhexane at a concentration of 0.05M. Celgard 2400® was used as the support membrane. Twenty-four hours into the experiment, only nineteen micromoles of strontium was reportedly transported to the strip phase versus six micromoles of barium using a membrane 20.67

$cm^2$ in area.

In facilitated transport, a carrier selective to a particular cation, combined with a high concentration of anions in the feed solution provide for interesting results. The anion concentration gradient provides the driving force for metal ion transport "uphill" against its concentration gradient. The result is the possibility of high separation factors with a small strip volume relative to the feed volume.

Dozol, et al. [18] used DC18C6 to extract over 93% of radioactive $^{85}Sr$ spiked into an aqueous feed phase consisting of a mixture of ions and 1.0M nitric acid. A 0.5M solution of DC18C6 in isodecanol/hexylbenzene was impregnated in Celgard 2500® membrane. The nitrate anions apparently drove the transport of strontium ion "uphill" against its concentration gradient. This appears promising, but selectivities and fluxes are not known since the concentration of other metals in the strip were not measured, and the amount of $^{85}Sr$ spiked into the feed solution was unreported.

# APPENDIX B

## FACILITATED TRANSPORT - EXPERIMENTAL

The facilitated transport experiments followed the same basic procedure as the passive transport experiments. One exception is that the carrier molecule (DC18C6 from Aldrich) was dissolved into the membrane solvent before the membrane was allowed to soak in the membrane solution. Membrane solvents consisted of phenylhexane (Aldrich), isotridecanol (Exxon), octanol (Aldrich), and diisopropylbenzene (Aldrich). Vacuum/pressure cycles were applied in some experiments in an attempt to pressurize the membrane liquid solution into the membrane support pores.

The apparatus for facilitated transport experiments was smaller than that for the passive transport experiments. It consisted of two 1" x 2" Kimax® glass reducing elbows with the membrane and a Teflon gasket clamped between the 2" opening to provide a membrane surface area of 20.25 cm$^2$. Each compartment of the test cell contained 260 cm$^3$ of aqueous solution. Another difference is that the stirring motor and stir bars were placed on the ends of the test cell as shown in Figure 13. Two milliliter samples were generally taken between one and three times per day.

All experiments used dicyclo-hexano-18-crown-6 (DC18C6) as the carrier molecule, Celgard 2400® as the membrane support, and distilled deionized water as the receiving phase. All metals used are nitrates unless specified.

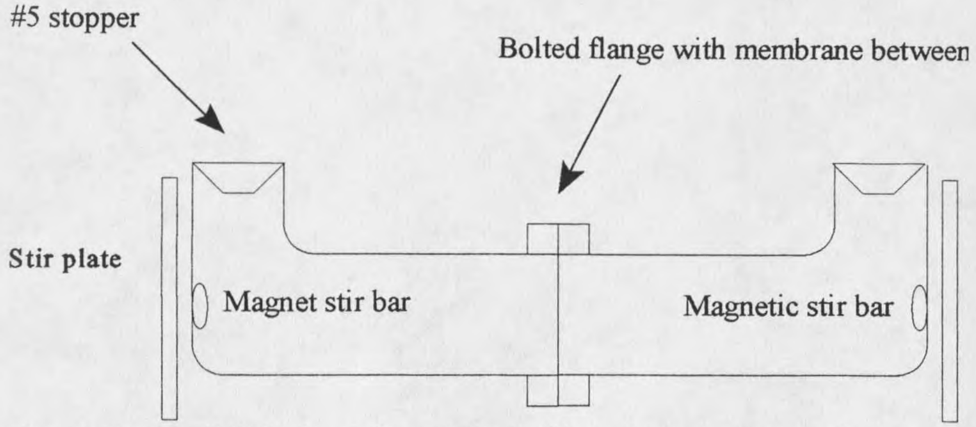

Figure 12. Small diffusion cell used for facilitated transport experiments

# APPENDIX C

# FACILITATED TRANSPORT - RESULTS AND DISCUSSION

Table 11 summarizes the operating conditions over which the experiments were conducted and stability times associated with each experiment.

Table 11. Experimental attempts at facilitated diffusion

| Experiment Number | Feed Phase Ion Concentration | Membrane Makeup | Soak Time and Method | Stirring Speed | Stability Time (Hours) |
|---|---|---|---|---|---|
| 2 | 100 mg/L Cs<br>100 mg/L Ca<br>100 mg/L Sr<br>0.0104M $HNO_3$ | 0.25M DC18C6<br>1-Octanol | 2 Days | 4 | < 3.1 |
| 4 | 100 mg/L Cs<br>100 mg/L Ca<br>100 mg/L Sr<br>0.0104M $HNO_3$ | 0.25M DC18C6<br>0.7M Decanol<br>DB* | 12 Hours of 14" Vacuum | 4 | 71-120 |
| 8<br>First Small Cell Run | 4000 mg/L Cs<br>4000 mg/L Ca<br>4000 mg/L Sr<br>2.0M $HNO_3$ | 0.9M Isotri**<br>0.3M DC18C6<br>DB | ? | 4 | 77-146 |
| 10<br>Small | 4000 mg/L Cs<br>3453 mg/L $CaCl_2$<br>4000 mg/L Sr<br>1.0M $HNO_3$ | 0.9M Isotri<br>0.3M DC18C6<br>DB | Several Vacuum-pressure cycles | 3 | >48 |
| 11<br>Small | 4000 mg/L Cs<br>3453 mg/L $CaCl_2$<br>4000 mg/L Sr<br>1.0M $HNO_3$ | 0.9M Isotri<br>0.3M DC18C6<br>DB | ? | 3 | >77 |
| B<br>Small | 4000 mg/L Cs<br>3453 mg/L $CaCl_2$<br>4000 mg/L Sr<br>No acid | 0.9M Isotri<br>0.3M DC18C6<br>DB | ? | 3 | 55-69 |

| | | | | | |
|---|---|---|---|---|---|
| D<br>Small | 4000 mg/L Cs<br>3453 mg/L $CaCl_2$<br>4000 mg/L Sr<br>No acid | 0.9M Isotri<br>0.3M DC18C6<br>DB | 17 | 3 | 53-76 |
| F<br>Small | 4000 mg/L Cs<br>3453 mg/L Ca<br>4000 mg/L Sr<br>0.0061M $HNO_3$ | 0.9M Isotri<br>0.3M DC18C6<br>DB | 24 | 2 | 99-124 |
| G<br>Small | 4000 mg/L Cs<br>4000 mg/L Ca<br>4000 mg/L Sr<br>0.0061M $HNO_3$ | 0.4M DC18C6<br>DB | 25 | 3 | 43-52 |
| J<br>Small | 4000 mg/L Cs<br>4000 mg/L Ca<br>4000 mg/L Sr | 0.4M DC18C6<br>Phenylhexane | ? | 3 | 70-96 |
| L<br>Small | 4000 mg/L Cs<br>4000 mg/L Ca<br>4000 mg/L Sr | 0.07M DC18C6<br>Phenylhexane | 18 | 3 | >43 |
| O<br>Small | 4000 mg/L Sr | 0.4M DC18C6<br>Phenylhexane | 23 | 3 | >59 |
| R<br>Small | 4000 mg/L Sr<br>4000 mg/L Ca<br>4000 mg/L Sr | 0.4M DC18C6<br>Phenylhexane | 72 | 3 | >174 |

*DB = Diisopropyl Benzene
**Isotri = Isotridecanol

The question marks in the "Soak Time and Method" column indicate that the soak time was not recorded for that experiment. All soak times were in a period between one hour and three days.

The theory was for DC18C6 to selectively complex with strontium on the feed side, then diffuse to the strip side where the decomplexation occurs. Thus selectively transporting strontium from the feed side to the strip side. This was never observed.

The membranes effectively prohibited all transport of ions until the membrane became unstable. The stability time in table 11 is when a tremendous increase of ions into the strip phase was observed. This rapid transport is thought to be passive transport instead of facilitated transport because it occurs much faster than reported facilitated transport, and it is selective for cesium, where facilitated transport using DC18C6 is reportedly selective toward strontium.

The time ranges in the chart indicate that the membrane became unstable at samples taken between the two times. A greater than sign (>) shows that the membrane became unstable later than the last sample of the experiment. A less than sign (<) indicates that the membrane became unstable sometime before the first sample. Table 11 shows that the longest membrane stability times were achieved with phenylhexane; selective strontium transport was not observed.

Figure 14 shows an experimental attempt at facilitated transport. Notice that the first 50 hours show no transport at all. At about 60 hours, the membrane becomes unstable and rapid passive transport occurs.

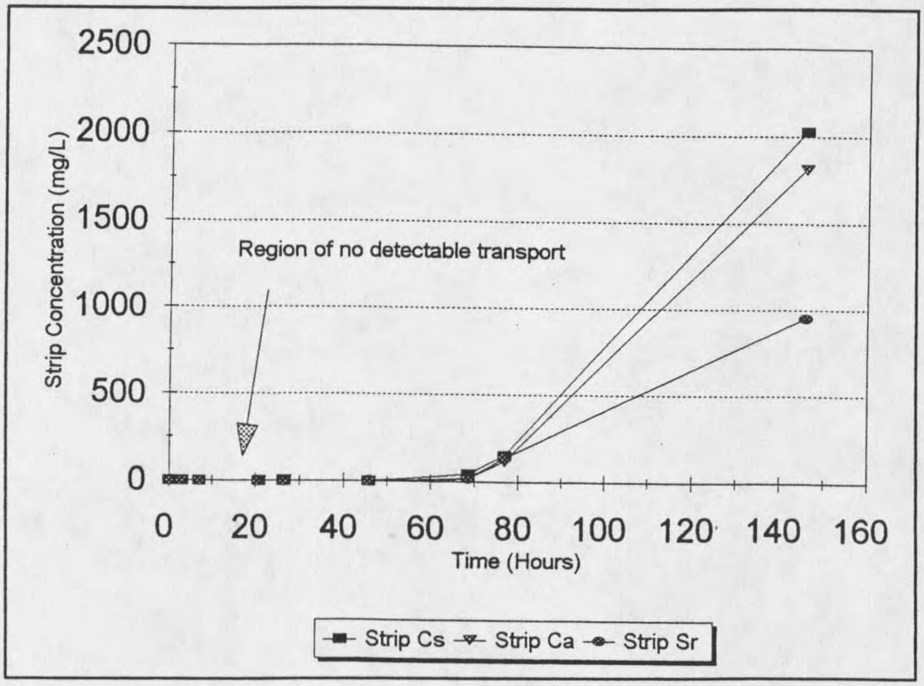

Figure 13. Strip side concentration versus time for Test 8; An experimental attempt at facilitated transport.

The High Performance Liquid Chromatograph (HPLC) used in measuring ion concentrations is capable of measuring down to about 0.1 mg/L of strontium. Only very small random peaks were ever detected in the strip phase before the membranes became unstable. These peaks had to be dismissed as noise. Lack of any consistent peaks when measuring the strip phase indicates that facilitated diffusion was not detectable under the experimental conditions applied.

A few possible reasons why facilitated diffusion did not work are:

- Stirring may have been too turbulent causing water to strip the DC18C6 from the membrane phase. Lack of carrier molecules the membrane phase eliminates the possibility of facilitated transport. One experiment was run at very low stirring speeds.

- A minimal amount of facilitated diffusion occurred that could not be detected by the HPLC.
- The membrane pores may have become clogged by DC18C6 or metal ions falling out of solution or both.

# APPENDIX D

## DERIVATION OF EQUATION (6)

| Variable | Definition |
|---|---|
| $D_{eff}$ | Effective diffusion coefficient |
| Subscript s | Denotes strip side |
| Subscript f | Denotes feed side |
| Subscript 0 | Denotes Initial conditions |
| V | Volume of one side of test cell |
| C | Concentration |
| A | Area of membrane |
| j | Flux of a specific metal salt |
| t | Time |
| L | Thickness of membrane |
| H | Partition coefficient |

A mass balance across the membrane yields:

$$V_s \frac{dC_s}{dt} = Aj \qquad (7)$$

$$V_f \frac{dC_f}{dt} = -Aj \qquad (8)$$

Divide (7) and (8) by $V_s$ and $V_f$ respectively and subtract them:

$$\frac{d}{dt}(C_f - C_s) = \frac{-Aj}{V_f} - \frac{Aj}{V_s} \tag{9}$$

Combining equation (4) and (10) and arranging:

$$\frac{d(C_f - C_s)}{(C_f - C_s)} = -AP\left(\frac{1}{V_f} - \frac{1}{V_s}\right)dt \tag{10}$$

Apply initial conditions and integrate: At $t = t_0$, $C_f - C_s = C_{f0} - C_{s0}$

$$\ln\left(\frac{C_f - C_s}{C_{f0} - C_{s0}}\right) = -AP\left(\frac{1}{V_f} + \frac{1}{V_s}\right)(t - t_0) \tag{11}$$

Substituting $V = V_f = V_s$, and $B = 2A / V$ yields:

$$-\ln\left(\frac{C_f - C_s}{C_{fo} - C_{so}}\right) = PB(t - t_o) \tag{6}$$

# APPENDIX E

## CONTINUOUS MEMBRANE PROCESS PROGRAM LISTING

```
REM *** CONTINUOUS PROCESS, MEMBRANE TRANSPORT SIMULATION

REM *** INITIALIZATION ROUTINE ***
      CLS
      INPUT "How many components in this membrane system "; num
      DIM DHL(num), FConIn(num), SConIn(num), FConOut(num), SConOut(num)
      DIM FConOutInit(num), SConOutInit(num), FMassRateIn(num),SMassRateIn(num)
      DIM flux(num), Con(num)
      PRINT "Enter system parameters unrelated to individual components"
      PRINT : PRINT
      PRINT "Time basis for analysis (h); (values around 0.1 work well)"
      INPUT "If the program doesn't converge however, a lower time basis must be
        chosen"; t
      INPUT "What is the volume of the feed side (L)"; FVol
      INPUT "What is the volume of the strip side (L)"; SVol
      INPUT "What is the volumetric feed rate to the feed side (L/h)"; FVolRate
      INPUT "What is the volumetric rate to the strip side (L/h)"; SVolRate
      INPUT "What is the cross-sectional area of the membrane (m^2)"; Area
      FOR N = 1 TO num
      PRINT
      PRINT "Enter data relative to component # "; N
      PRINT
      INPUT "What is the concentration of stream entering feed side (mg/L)"; FConIn(N)
      INPUT "What is the permeability (DH/l) in m/h"; DHL(N)
      INPUT "What is the Concentration of the stream going to the strip (mg/L)";
SConIn(N)
      NEXT N

REM *** SETTING INITIAL VALUES

      FOR N = 1 TO num
      FConOut(N) = FConIn(N): SConOut(N) = SConIn(N)
      NEXT N

REM *** CALCULATE THE MASSES RATES OF EACH COMPONENT IN   EACH
STREAM ***
```

```
      FOR N = 1 TO num
      FMassRateIn(N) = FVolRate * FConIn(N)
      SMassRateIn(N) = SVolRate * SConIn(N)
      NEXT N

REM *** CALCULATE THE FLUX,  FOR MASS BALANCE PURPOSES

10    FOR N = 1 TO num
1     flux(N) = DHL(N) * (FConOut(N) - SConOut(N) * 1000: REM 1000 is
         1000L/m^3 to change units.

REM *** SET A NEW VARIABLE SO NEW CONCENTRATIONS OUT OF CELL
MAY BE CALCULATED

      FConOutInit(N) = FConOut(N)
      SConOutInit(N) = SConOut(N)
      NEXT N

REM *** MASS BALANCE; CALCULATE STREAM CONCENTRATIONS

      FOR N = 1 TO num
3     FConOut(N) = (FConOutInit(N) * FVol + t * FMassRateIn(N) - t * flux(N, 1) *
         Area) / (FVol + t * FVolRate)
      SConOut(N) = (SConOutInit(N) * SVol + t * SMassRateIn(N) + t * flux(N, stage) *
         Area) / (SVol + t * SVolRate)
      PRINT "Comp #"; N, "FConOut = "; FConOut(N)
      PRINT "Comp #"; N, "SConOut = "; SConOut(N)
      NEXT N

REM *** ASK USER FOR DIRECTION TO TAKE

      PRINT "Press ENTER to continue with next iteration,"
      INPUT "'p' to print results, 'r' to run program over, 'q' to quit"; a$

      IF a$ = "r" THEN RUN
      IF a$ = "p" THEN GOSUB 1000
      IF a$ = "q" THEN END
      GOTO 10

REM *** Print Routine ***

1000   LPRINT "System parameters unrelated to individual components"
      LPRINT
      LPRINT "Number of membranes in series:  "; stage
```

```
LPRINT "Time basis for analysis:          "; t, "hours"
LPRINT "Volume of feed side:              "; FVol, "L"
LPRINT "Volume of strip side:             "; SVol, "L"
LPRINT "Volumetric rate to feed side:  "; FVolRate, "L/h"
LPRINT "Volumetric rate to strip side:  "; SVolRate, "L/h"
LPRINT "X-sectional area of membrane:  "; Area, "m^2"
LPRINT : LPRINT

FOR N = 1 TO num
LPRINT "Results for Component #"; N
LPRINT
LPRINT "Concentration of stream entering feed side:     "; FConIn(N), "mg/L"
LPRINT "Permeability (DH/l) of membrane:                "; DHL(N), "m/h"
LPRINT "Concentration of stream entering strip side:    "; SConIn(N), "mg/L"
LPRINT "Concentration of stream leaving feed side:      "; FConOut(N), "mg/L"
LPRINT "Concentration of stream leaving strip side:     "; SConOut(N), "mg/L"
LPRINT : LPRINT
NEXT N
RETURN
```

# APPENDIX F

## VARIABLES USED IN COMPUTER MEMBRANE MODEL

| | |
|---|---|
| num | Number of components in system |
| DHL(x) | Permeability |
| FConIn(x) | Concentration of component x entering the feed compartment |
| SConIn(x) | Concentration of component x entering the strip compartment |
| FConOut(x) | Concentration of component x exiting the feed compartment |
| SConOut(x) | Concentration of component x exiting the strip compartment |
| FConOutInit(x) | Concentration of component x exiting the feed compartment<br>Used in mass balance to calculate a new FConOut |
| SConOutInit(x) | Concentration of component x exiting the strip compartment<br>Used in mass balance to calculate a new SConOut |
| FMassRateIn(x) | Mass of component x entering the feed compartment |
| SMassRateIn(x) | Mass of component x entering the feed compartment |
| flux(x,y) | Flux of component x through serial membrane number y |
| t | Differential time basis: Ion transported = flux * t * Area |
| Area | Cross-sectional area of membrane |
| FVol | Volume of feed compartment |
| SVol | Volume of strip compartment |
| FVolRate | Volumetric rate of liquid to the feed compartment |
| SVolRate | Volumetric rate of liquid to the strip compartment |

# APPENDIX G

## DERIVATION OF LINE 3 IN PROGRAM MODEL (PAGE 62)

Mass balance of a specific ion around feed compartment:

Mass in entering stream - Mass out exiting stream - Mass out through membrane = Accumulation

$$t * FMassRateIn - t * FMassRateOut - t * flux * Area = \Delta C * FVol$$

Where $\Delta C$ is the change in concentration of the feed over time period t.

$$\Delta C = FConOut - FConOutInit$$

$$FMassRateOut = FConOut * FVolRate$$

Substitution:

$$t * FMassRateIn - t * FConOut * FVolRate - t * flux * Area = (FConOut - FConOutInit) * FVol$$

Solve for FConOut, which is the new concentration of the feed compartment for a specific ion.

$$FConOut = [FConOutInit * FVol + t * FMassRateIn - t * flux * Area] / [FVol + t * FVolRate]$$

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