DIALYSIS FOR CONCENTRATION AND REMOVAL OF INDUSTRIAL WASTES

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DIALYSIS FOR CONCENTRATION AND REMOVAL
OF INDUSTRIAL WASTES

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FOREWORD

The level of organics in water supplies is increasing. Increased con-
centrations of organic pollutants in the Mississippi River have paralleled
closely the explosive development of a petrochemical industrial complex in the
1950s and 1960s. This expansion has resulted in the location of more than 60
major industries between Baton Rouge, Louisiana and the mouth of the river.
Most of these industries discharge their partially treated or untreated wastes
to the river. Industrial expansion is essential to the economy of our community
and nation, but just as critical is the effect that this expansion may have on
our environment. To control environmental pollution that can result as industry
expands, and to mitigate existing problems, it is necessary to establish treat-
ment procedures that will not place undue burden on industrial installations but
will assure a safe environment.

This investigation has studied one process: dialysis applied to treatment
of industrial effluent streams. Plant effluent streams were examined for poten-
tial treatment by dialysis according to the following criteria:
1. Pollution significance
2. Feasibility of treatment by dialysis
3. Industrial interest
The work plan for the project consists of three phases:
1. Selection of 10 waste streams potentially suitable for treat-
ment by dialysis, and a preliminary characterization of
potentially useful dialysis membranes applicable to waste
treatment.
2. A laboratory analysis of several waste-membrane combinations
employing actual waste to determine engineering and transport
data.
3. A semipilot continuous-flow evaluation of one of the optimum
waste-membrane combinations, employing a scaled-up dialyzer to
demonstrate technical and economic feasibility.

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NOMENCLATURE

a	=	chemical activity
A	=	area
C	=	concnetration
$\bar{C}$	=	average concentration in the dialyzer
conj	=	conjugate acid or base
C_o	=	charge concentration
d	=	downstream side of membrane
D	=	diffusion coefficient
f	=	feed (upstream) side of membrane
f	=	Lewis fugacity
G	=	flow rate
H	=	Henry's law constant
i	=	solute i
J	=	Flux
j	=	solute j
K_{eq}	=	equilibrium coefficient
k	=	mass transfer coefficient
k°	=	local mass transfer coefficient for membrane
L	=	thickness parameter
liq	=	liquid phase
l	=	membrane length
M	=	membrane
m	=	membrane phase
N	=	molar flux (moles/cm^{2}sec)
N_{Re}	=	Reynolds number
org	=	organic solute
o	=	at 0 concentration, at initial state, or at length 0
$\bar{p}$	=	specific permeability constant
P	=	partial pressure
P^o	=	vapor pressure in the pure state
prod	=	conjugated product
R	=	gas constant (lit-atm/mole-deg.)
S	=	solubility, or distribution coefficient

T = experimental temperature, $^{\circ}C$

T_g = glass transition temperature

t = time (sec)

U_{liq} = liquid phase mass transfer coefficient

$\bar{U}$ = change in liquid phase concentration

V = volume

v = feed velocity

vap = vapor phase

$$n_1 = \frac{U_{liq}A}{G_{liq}}$$

$$n_2 = \frac{U_{liq}A}{G_{vap}}$$

x_2 = solute mole fraction in liquid

z_2 = solute mole fraction in membrane

Greek Letters

$$\alpha_1 = \frac{\bar{P}S}{L}$$

$$\alpha_2 = \frac{RT\bar{p}H}{L}$$

$$\beta = \frac{\alpha_2}{\alpha_1} = \frac{RTH}{S}$$

γ = activity coefficient

ρ = density

$$\xi = \frac{U_{liq}A}{G_{liq}}\left(1 - K_{eq}\gamma\right)$$

ACKNOWLEDGEMENTS

SECTION I

INTRODUCTION

The objective of this study was to explore the potential of dialysis as a method of secondary water treatment. So far, industrial application of dialysis has been directed primarily toward such operations as caustic recovery in the rayon industry, separation of sulfuric acid from copper and other metals, and separation of sugars from dextrins. In each of these cases dialysis proceeds in response to a difference in chemical potentials of the solutes across the membrane. Dialysis can therefore be classified as a passive process in which the energy necessary to separate the constituents of a solution at a finite rate comes from the free energy present in the system. Dialysis, then, is a process whereby a solution containing a permeating species and separated by a membrane from a solution at lower concentration loses solute through the membrane until the activity of the solute is the same on both sides of the membrane.

A simple illustration of dialysis is shown in Figure 1. A solution containing two solutes i and j is separated from a pure solvent by a membrane M. The solute i is able to pass through the membrane while solute j cannot permeate the membrane and is retained. At the beginning of dialysis the solution containing the two solutes, shown in Compartment 1, is separated from the pure solvent, shown in Compartment 2, by the membrane. As dialysis occurs, some of solute i passes through the membrane into the pure solvent compartment. Because of the chemical activity of the impermeable solutes in the solution, water tends to be drawn into the solution Compartment 1. This movement of water is called osmosis. Over a period of time the composition of solutions in the two compartments change, as represented in Figure 1(b). Solutes i and j both are now in more dilute solutions than the original composite mixture.

The rate of transport of a solute through a membrane depends on several factors: the chemical nature of membrane, the solute, the solvent, the temperature, differences in concentration, interaction of the membrane with solute and solvent, etc. These factors are generally interrelated. In an ideal case, with a given solute, solvent, temperature, and physical arrangement, the rate of diffusion through the membrane can be described by Fick's law of diffusion[1]:

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1. Crank, J. Methods of Measurement. In: Diffusion in Polymers, Crank, J. and G.S. Park (eds.). New York, Academic Press, 1968. p. 1.

Compartment 1

Compartment 2

Solutes
i and j

J_i

Pure
water

J_w

Dialysis membrane M

(a) Beginning of dialysis.

Dialysis membrane M

Compartment 1

Compartment 2

Water and
solute Δi

J_i

Solutes j
and i - Δi

J_w
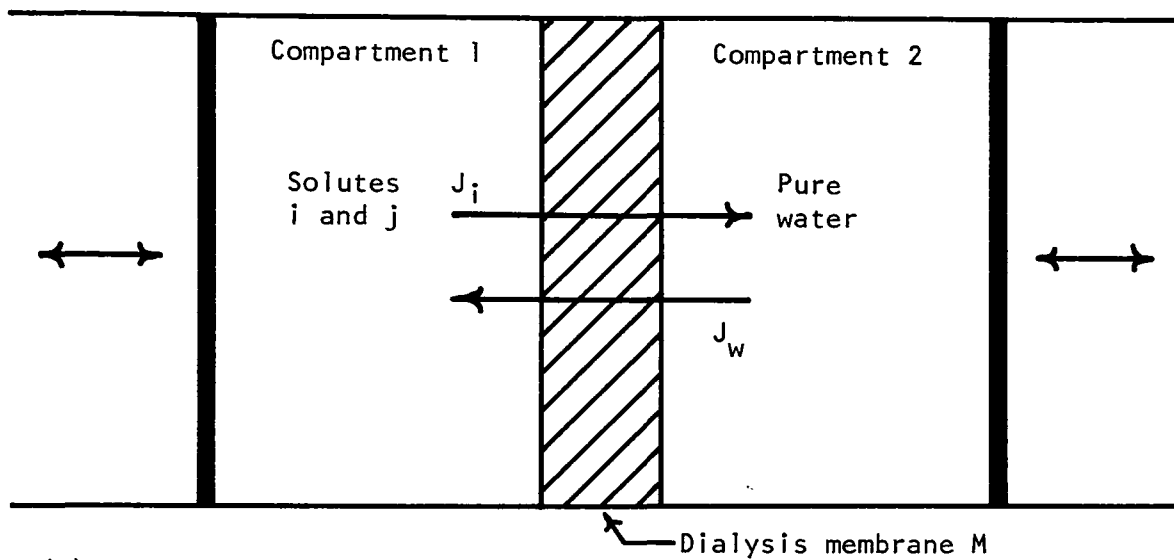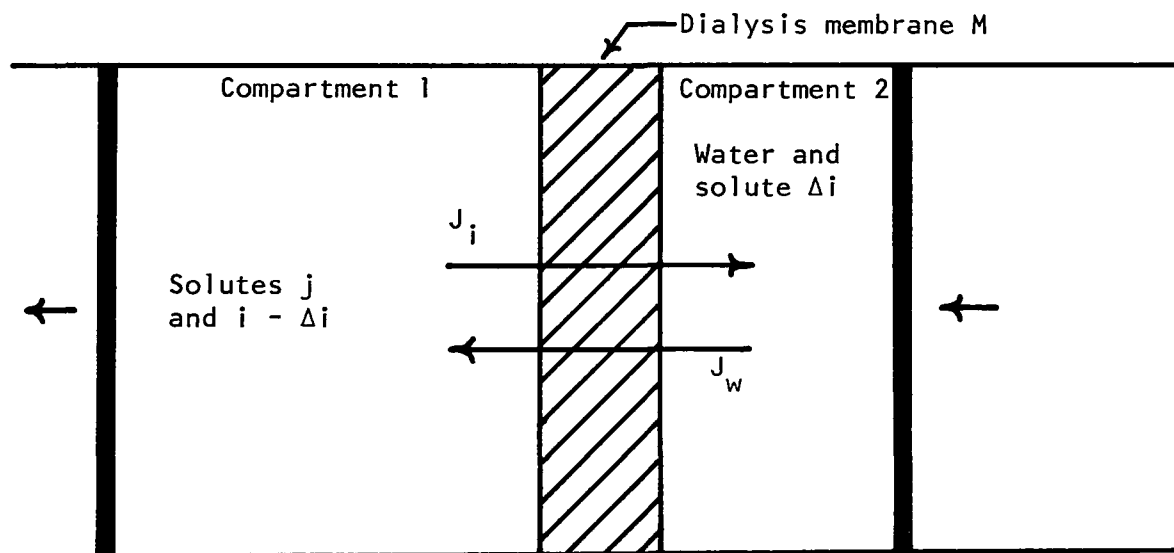
(b) Progress of dialysis after time t.

Figure 1. Dialysis schematic.

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$$\text{Rate of transport per unit area} = -\bar{p}\,dc/dx$$

where $\bar{p}$ is the specific permeability coefficient, and dc/dx the concentration gradient. At the steady or pseudo-steady state, the rate of transport is directly proportional to the difference in concentration across the membrane. It is also proportional to the diffusion coefficient. The permeability coefficient is a property of the membrane and the permeant, as defined by the relation:

$$\bar{p} = D_o S$$

where D_o is the actual diffusivity of solute within the membrane and S is the partition coefficient for solute between the membrane phase and the solutions on either side of the membrane. The membrane determines selectivity by allowing a particular solute to permeate while rejecting others. The membrane also contributes to the rate of transfer because of the interrelation between the membrane structure and the diffusivity of the solute.

A variety of polymeric films or membranes can be used to separate and to purify solutions by dialysis. Choice of the polymeric membrane depends on the chemical nature of the mixture being separated and the stability of the polymer under anticipated conditions of use. One of the solutes to be separated must be permeable to the membrane at an acceptable rate without damaging the membrane. The rate is inversely proportional to the membrane thickness, so it is desirable to employ membranes that are very thin. Thin membranes can be used without concern about changing the value for S, as selectivity is not dependent on film thickness.

The largest industrial applications of dialysis today are the recovery of caustic soda from industrial waste and the refining of crude sodium hydroxide. The press liquors from the viscose rayon process contain 16-17% caustic and some hemicellulose. This solution is dialyzed to obtain a caustic sample which contains 8 to 9% soda but less than 0.08% hemicellulose. The solution can then be reused in the makeup of press liquor or in the viscose steeping process. Waste caustic from the steeping step can also be dialyzed and reused in a similar fashion. Mercerizing liquors, which are composed primarily of caustic soda at a concentration of 20 to 30%, can be similarly treated. The removal of

inorganic impurities, such as chlorides, alumina, silica, and ferric oxide, from crude sodium hydroxide solutions can also be accomplished by dialysis.

Dialysis is employed in separation of sulfuric acid from copper and other metal salts in contaminated copper-plating baths. This separation, accomplished by a difference in diffusion rates of the various ions, results in a product adequately pure for reuse. Another application of dialysis is in the separation of sugars from dextrins in cornstarch conversion. Upon dialysis, dextrins, as well as sugar, pass into the receiving liquid but at different rates. The receiving liquid becomes enriched by the sugar—the faster permeating solute—leaving the dextrin behind in the feed solution.

In the past, dialysis generally has been regarded as a slow and inefficient process. Several factors have limited its development: (1) There has been a small choice of membranes that could perform in the anticipated environment, and these membranes lacked selectivity and uniformity of performance. (2) The operating efficiency of the process has been dependent on the concentration of the diffusible solute. (3) The process rate has been slow compared to other chemical processes. (4) A reasonably large capital outlay has been required for installation of equipment.

All the problems that have been associated with dialysis can now be improved upon or resolved by utilization of up-to-date technology available in areas of membranes and equipment, and by the utilization of up-to-date and precise mass transport technology. To remove, by dialysis, a pollutant at low concentrations in water, it is necessary to maintain the driving force at its maximum value. This can be achieved in the following ways:

1. Organic acids or bases may be dialyzed through hydrophobic membranes. The concentration of the acid or base in the receiving compartment is reduced to minimum by formation of a nonpermeating or conjugate acid or base on the downstream side. Since the concentration of the pure acid or base will be higher in the waste stream, the direction of permeation will be from the waste stream to the recovery stream. Because the concentration of the solute acid will be close to zero, the rate of transfer will be maximized for the system. The conjugate acid and base can be concentrated in the receiving stream for recovery. This method of dialysis is termed "dialysis with conjugation."

2. Dialysis of heavy metals in solution can be accomplished employing hydrophilic membranes. To maintain the maximum driving force and to provide a

means for concentration and recovery of the permeating species, an organic phase containing a chelating or complexing agent can be employed on the downstream side. As in dialysis with conjugation, the free metal ion is removed from the downstream or receiving solution, thus enhancing the driving force. This process of dialysis is called "dialysis with complexing."

3. Organic solutes can be separated from aqueous waste streams by dialysis through hydrophobic membranes into a gas purge stream on the downstream side of the membrane. The gas purge stream removes the permeating species and thus maintains the driving force. The permeating species can then be recovered downstream of the membrane. This process is termed "pervaporation." In each of these cases, complete removal of solute from the upstream side and its collection on the downstream side is theoretically possible.

The present study to characterize these processes was carried out in three phases.

A. SCREENING

A number of organic and inorganic solutes present in industrial waste streams were examined for their susceptibility to separation and recovery by dialysis. The transport rate of each solute was determined in one of the three described dialysis processes. Different type membranes were employed in each of the processes. Where more than one type of membrane was available for a particular process, all were included in the screening. The most promising applications were then selected for further study.

B. CHARACTERIZATION

Process responses of the engineering variables for an ethylene dichloride containing waste stream were studied in a pilot scale pervaporation process. The selection of the pervaporation process and the EDC stream were made on the basis of data gathered in the screening study, namely, with consideration of the pollution significance of chlorinated hydrocarbons in waste water.

C. DESIGN AND PROJECTION

The data from the characterization of the dialysis of the ethylene dichloride stream were used to project the technical and economic feasibility of a full scale plant operation.

SECTION II

SUMMARY

Conventional dialysis across a permselective membrane results in the transport of the permeant to a lower concentration, maintained by simple dilution, on the downstream side of the membrane. Conventional dialysis clearly is not sufficient to remove a very dilute contaminant from a plant's total effluence, unless a solvent completely free of the contaminant is used on the downstream side; but it is possible, by using special techniques such as those enumerated below, to remove certain classes of very dilute contaminants by dialysis without requiring a continual fresh supply of downstream solvent. Three novel techniques were developed and demonstrated as technically feasible in the present study:

1. The use of acid and base conjugation, respectively, on the downstream side of membranes permselective to aniline and phenol.

2. The use of a chelating complex for Al, Cu, and Pb ions.

3. The use of a pervaporation scheme in which a hydrophobic membrane passes volatile contaminants such as nitrobenzene and ethylene dichloride to a downstream vapor purge, which picks up the contaminants substantially free of water.

The pervaporation scheme was applied to a prototype EDC (ethylene dichloride) contaminated industrial waste stream in a pilot process configuration. Economics indicated that while pervaporation is not a particularly inexpensive route with established technology, the use of current improvements in membrane technology could bring costs down into the range of routine process water treatment costs (10¢-50¢ per 1,000 gallons).

SECTION III

CONCLUSIONS

An evaluation of dialysis as an advanced waste treatment process for the removal of selected organics and metallic ions from industrial waste has been performed by Gulf South Research Institute for the Louisiana Department of Commerce and Industry. Dialysis on these industrial waste streams can be both technically and economically feasible when removal of the membrane permeant is supported by special schemes such as acid and base conjugation, complexing, or pervaporation, rather than reliance upon simple dilution to maintain the osmotic gradient. From the study the following conclusions and their close affinities were drawn:

A. The economic removal of dilute contaminants from water by dialysis is dependent upon the driving force of an essentially complete removal of contaminant downstream of the selective membrane. Methods for accomplishing this have been developed and demonstrated in the present study. They include conjugation, complexing, and the removal of the permeant as a vapor on the downstream side of a semipermeable membrane, as follows:

1. Dilute aniline and phenol systems can be stripped of these contaminants using acid and base conjugation downstream of the membrane. With polycarbonate-co-silicone films, specific permeabilities of 3.9×10^{-7} and 2.06×10^{-7} cm^2/sec were obtained for the aniline and phenol respectively. Corresponding values of specific permeability with a styrene-co-butadiene film, Kraton 1101, were 2.5×10^{-7} and 0.71×10^{-7} cm^2/sec. Ethyl cellulose provided a good medium for the phenol service, with a specific permeability of 0.96×10^{-7} cm^2/sec.

2. An effective complexing sink for Al, Cu, and Pb ions permeating a Cuprophan* film exists in bis-(2 ethylhexyl) hydrogen phosphate. Unfortunately, the solute transport rate to the organic receiving phase containing the complexing agent was only 0.56×10^{-7} cm^2/sec. In comparison to transport in a completely aqueous system (where a permeability of 2.58×10^{-7} cm^2/sec was obtained) the resistance to the solute transport to organic receiving phase containing the complexing agent was significantly high. It is believed that

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*Registered trademark of Enka Glanzstoff A.G.

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the major contribution to this resistance came from polarization on the downstream side of the membrane at membrane/receiver interface. Serious attention would have to be given to minimizing this downstream resistance between the aqueous phase and the organic phase before a really attractive process could be claimed. This is the same kind of problem that has hampered the development of liquid-liquid extraction. Because of the work performed in this latter field, it was not deemed feasible to develop a solution to the problem in the context of this study. However, in view of the notoriously small transfer coefficients and tight fluid mechanical constraints experienced in liquid-liquid extraction systems, dialysis through a selective membrane may offer a viable alternative in this extractive process.

3. Pervaporation, based on a vapor-phase sink downstream of any of a number of permselective hydrophobic films, provides an attractive approach for the removal from industrial waste streams of chlorinated hydrocarbons such as chloroform, ethylene dichloride, and other toxic chemicals such as nitrobenzene. In general, the permeants in these applications will have reasonable volatilities. The use of very thin membranes (25 microns or less), high liquid-side velocities, and higher system temperatures is desirable for commercial applications.

B. The pervaporation scheme was used in a larger scale test operation on a stream representative of an ethylene dichloride process plant effluent contaminated largely with ethylene dichloride. This test was at such a scale that the same parameters controlling a large on-site waste treatment unit were applicable, but inordinate capital expenditure was not required. The test provides a credible basis for projecting a treatment cost, based on existing technology, of 90% EDC removal from a stream 0.8% (by weight) EDC in 3.5% HCl. Improvements in membrane transport rates and reductions in membrane costs (such as are feasible in the context of the developing hollow fiber technology) could drop these processing costs to $0.10 - $0.50 per thousand gallons of treated water.

SECTION IV

RECOMMENDATIONS

Field evaluations of two of the processes reported herein are recommended. These field trials should also be supported by background studies concerned with crucial engineering variables such as the following:

A. FOR "CONJUGATE DIALYSIS"

1. A design study to reduce fluid resistances on both sides of the separating membrane.

2. Membrane life evaluation.

3. An evaluation of the use of pretreatment to reduce membrane fouling.

B. FOR PERVAPORATION

1. Development of hollow fiber configurations to provide the requisite area in a simple assembly. A 90% reduction of the 0.8% EDC stream required 450 m^2 of membrane area per gpm of waste flow. This can be accomplished in a simple tube-and-shell assembly occupying a volume of 0.015 m^3/gpm of waste flow.

2. Development of asymmetric fiber structures which could reduce the required membrane areas by a factor of 50.

3. Evaluation of the use of stream pretreatment to prevent fiber occlusions.

4. Design of the EDC recovery system and design of air purge recycling.

C. FOR COMPLEXING

1. Field evaluation of the third process, complexing, is not recommended at this time.

SECTION V

CONTAMINANT SCREENING

In this phase of the project, ten different solutes which presented potential concern as pollutants of the lower Mississippi River water in the New Orleans-Baton Rouge area were screened to test the applicability of dialysis in their concentration or removal from waste streams. These solutes are grouped as:

a) Organic acids or bases: aniline, phenol, ethanolamine.

b) Toxic cations: Al^{+++}, Cu^{++}, Pb^{++}.

c) Volatile refractory organics: nitrobenzene, chloroform, ethylene dichloride, nitrotoluene.

More specifically, the solutions of aniline, phenol, and ethanolamine were dialyzed through hydrophobic membranes aided by the formation of their respective conjugate acid or base on the downstream side in "Dialysis with Conjugation." Solutions of Al^{+++}, Cu^{++}, and Pb^{++} were dialyzed through hydrophilic membranes using an organic receiving phase containing a complexing agent on the downstream side in "Dialysis with Complexing." Nitrobenzene, chloroform and ethylene dichloride solutions were "pervaporated" through hydrophobic membranes.

Our use of conceptual membrane design is based on a unit process technique. The process seeks to sustain itself by taking advantage of the operative chemical and/or physical process to overcome the singular process of dilution. That is, the use of conjugation, complexing, or pervaporation is intended to remove the solutes on the downstream side of the membrane so that the driving force (concentration differences) can be maximized. The removal and/or conversion of the permeating solutes permit a concentration of the product.

Commercially available films including polyethylene (low and medium density), Saran, Cuprophan, and laboratory cast films from Kraton 1101, polycarbonate/silicone and ethyl cellulose were used as membranes in the investigation. Permeability measurements for "Dialysis with Conjugation" and "Dialysis with Complexing" were carried out in a rotating batch dialyzer[2]. The permeability measurements for pervaporation were carried out in a specially constructed Babb &

2. Wendt, R.P., R.J. Toups, J.K. Smith, N. Leger, and E. Klein. Measurements of Membrane Permeabilities Using a Rotary Batch Dialyzer. Ind. & Eng. Chem. 10:406, 1971.

Grimsrud cell (Figure 2), which had previously been used to determine transport properties of hemodialysis membranes. In these previous studies the flow geometry and mass transfer for this cell were defined.

A. THE APPARATUS

1. Rotary Batch Dialyzer

The cell shown in Figure 2 was used to evaluate the membrane compatibility with the solution and its permeability constant. This apparatus is an attractive one because of its ease of operation and construction. It was designed by Regan and co-workers[3], for use in determining true solute permeability through a related membrane. The cell consists of two hollowed-out discs which are clamped together, with the membrane to be tested separating the two halves.

In dialysis there is a flow of permeable components into one side of the membrane. At the other membrane surface there is flow of permeable components out of the membrane and into the layer adjacent to the surface. This process leads to permeant solute concentrations at the interfaces different from the concentrations in the bulk solutions. These differences are great enough to influence the observed mass transfer rate and are normally referred to as boundary layer resistance or concentration polarization. This model has been previously described[2].

In an industrial application the feed solution is pumped past the membrane surface at a high flow rate to reduce the concentration polarization. The greater the feed solution velocity, or Reynolds number, the greater the shear at the membrane surface and the lower the boundary resistance.

For the limited purpose of screening membrane performance, it is not necessary to completely eliminate this boundary effect as long as it is held constant and the magnitude of the effect is relatively small in comparison to the membrane resistance. In the experimental screening of membranes these conditions were achieved with the maximum contribution of the boundary never exceeding 30% of the absolute membrane value. This constant error did not seriously compromise

3. Regan, T.M., W.G. Esmond, C. Strackfus, and A.M. Wolbarsht, Science. 162:1028, 1968.
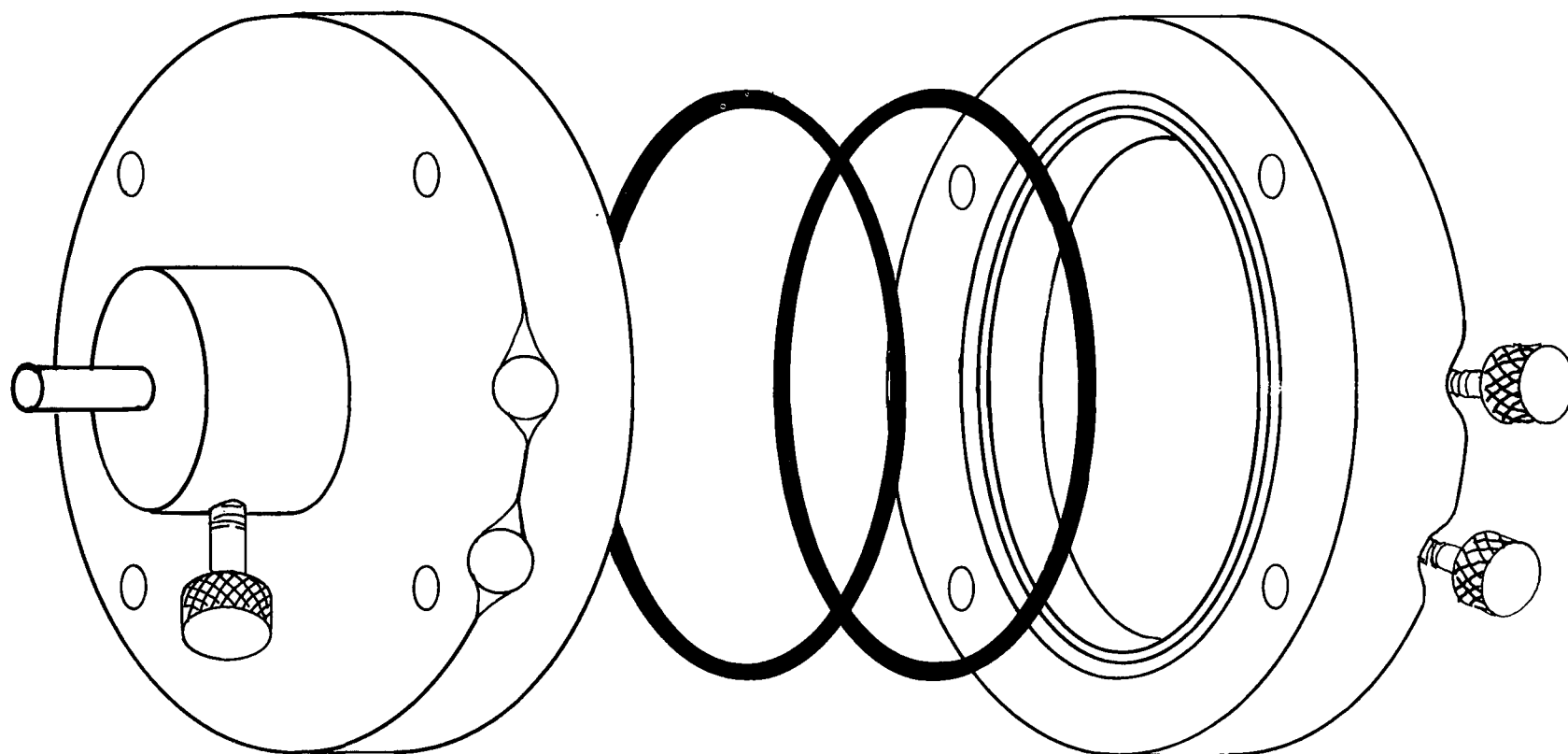
Figure 2. Rotating dialysis cell, disassembled.

the evaluation of relative membrane performance. The error in the permeability obviously becomes less as the membrane resistance becomes large compared to the boundary resistance[4].

The two compartments of the rotary batch dialyzer were filled with 35 cc each of the donor and receiving solutions, and the rotation was started. After selected time intervals, varying from 15 minutes to 60 minutes, the contents of each compartment were drained, neutralized to a common pH, and analyzed by U.V. or atomic absorption. Dilutions were necessary to have concentration levels suitable for analysis. Analyses were performed for solute concentration on both sides of the cell as a check on the mass balance.

2. Pervaporation Test Cell

The pervaporation test cell is made of plexiglass and is shown in Figure 3. Water was circulated through the liquid path (B) between the two membranes, which were held in place by gaskets (E). Air circulated through channels (C) counter current to the water flow around the outside of the membrane compartment. The cell had an "effective" membrane area of 110 square centimeters. By "effective" we mean that area which actually comes in contact with fluids.

4. Klein, E., J.K. Smith, R.P. Wendt, and S.V. Desai. Separation Science. 7(3):285-292, 1972.
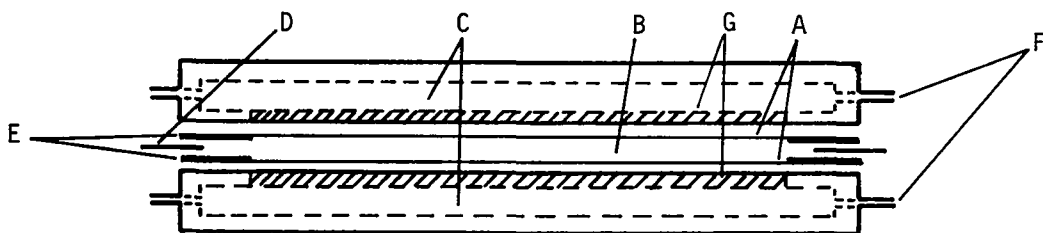
A. Membranes

B. Liquid Channel

C. Air Channel

D. Liquid Ports

E. Gaskets

F. Air Ports

G. Air Channels

Figure 3. Pervaporation test cell (Babb & Grimsrud).

A pervaporation test loop, shown schematically in Figure 4, was assembled to make quick determinations of membrane permeabilities for screening purposes. This apparatus was easily assembled and proved very convenient to operate, rapidly yielding very accurate data. At fixed intervals (varying from 15 minutes to 60 minutes) during the test recirculation runs, samples were drawn from the feed charge for analysis of the solute concentration by gas chromatography. Liquid flow rates of 0.5 to 1 liter/minute and an air flow rate of 12 liters/minute resulted in a slight positive pressure on the liquid side. Air humidity was not a significant factor during these runs since hydrophobic membranes were used and all experiments were done at ambient temperatures.
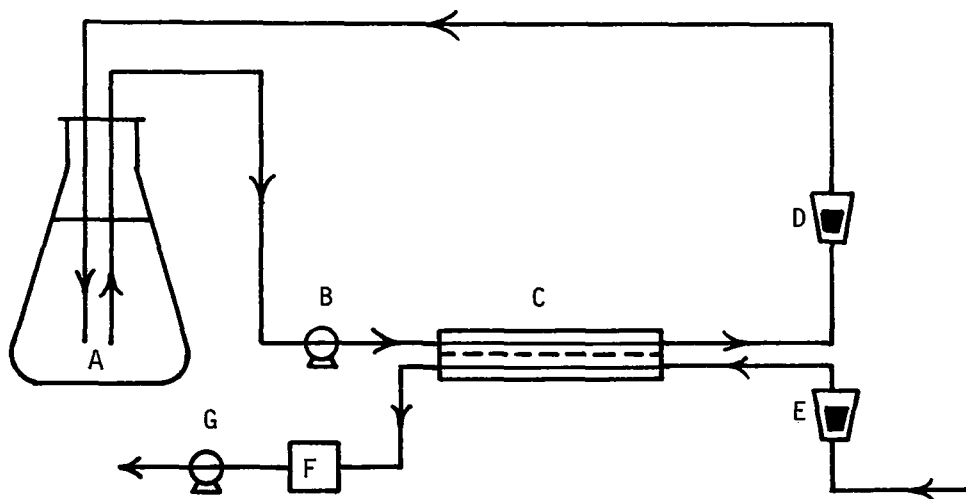
A. Feed Charge

B. Feed Pump

C. Test Cell

D. Liquid Flow Meter

E. Air Flow Meter

F. Trap

G. Vacuum Pump

Figure 4. Pervaporation test loop.

B. MEMBRANES

Membranes were either obtained commercially as films, or prepared by solvent casting on clean glass plates in a controlled environment. (Commercially available polymers were used to make the casting solutions.) The following membranes were used:

1. Commercial Films

a. Polyethylene with phthalate plasticizer.

b. Polyethylene (commercial bag film) without phthalate plasticizer.

c. Saran – A polyvinylidene chloride-polyvinyl chloride copolymer.

d. Cuprophan – A cellulosic hemodialysis membrane.

2. Films Prepared in the Laboratory by GSRI

a. Kraton 1101   A styrene-butadiene block copolymer from
Shell Chemical Company, cast from methyl isobutyl ketone
solutions.

b. XD-7   A polycarbonate-polysilicone copolymer from
General Electric, cast from methylene chloride solutions.

c. Ethyl cellulose, with a high degree of ethyl substitution, cast from
methylene chloride solutions.

These films are not available commercially.

C.   THE PERMEABILITY MEASUREMENTS

Membrane screening was based simply on the experimental determination of an overall solute specific permeability as defined below. The derivations of this equation for the computation of solute permeability constants from the recirculating runs are given in Appendix A and Appendix C (pages 55, and 60, respectively).

The equation is given below:

$$\bar{p} = \left[\frac{V}{A} \cdot \frac{L}{t} \right] \ln \frac{C_o}{C_t} \tag{1}$$

where V = liquid volume (cm^3) of feed or charge solution

C_o = charge concentration (g/cm^3)

A = membrane area (cm^2)

L = membrane thickness (cm)

t = time of run (sec)

C_t = concentration at time t (g/cm^3)

$\bar{P}$ = specific permeability constant (cm^2/sec)

The distribution coefficient S, as previously defined, was determined between the aqueous solution and the membrane phase by use of a chromatographi. method which is also described in Appendix B, page 59.

Pure water permeability of the membranes at $25^\circ C$ was determined using the ASTM Method E 96-63T.

D.   RESULTS

1. Dialysis with Conjugation

The following systems were studied to illustrate the use of conjugation as a permeant sink:

Aniline ---- Initial upstream aniline concentration: 2.98 wt %

Initial downstream H_2SO_4 concentration: 5.33 wt %

Phenol ---- Initial upstream phenol concentration: 0.94 wt %

Initial downstream NaOH concentration: 4.00 wt %

Ethanolamine Initial upstream ethanolamine concentration: 0.5 wt %

Initial downstream H_2SO_4 concentration: 1 wt %

Specific permeability coefficients of aniline and phenol are listed in Tables 1 and 2. The permeation of ethanolamine was too low to be detected. The permeability of the aniline and phenol through the organic polymers was excellent. The best results were obtained with the Kraton and XD-7 films. The observed permeabilities of 2 to 4 x 10^{-7} cm^2/sec compare favorably with commercial dialysis processes where, for example, a value of 6 x 10^{-7} cm^2/sec for the permeability of glucose through uncoated cellophane has been observed[2]. If a

TABLE 1

TRANSPORT OF ANILINE AND WATER THROUGH POLYMERIC MEMBRANE

(Temperature $25^{\circ}C$)

Membrane Designation	Thickness L (microns)	Specific Permeability $\bar{p}$ (cm^2/sec)		Distribution Coefficient $s^{(+)}$
		Water	Aniline	
Polyethylene A	20.0	1.16×10^{-10}	0.44×10^{-7}	
Polyethylene B	13.6	2.32×10^{-11}	0.15×10^{-7}	0.13
Saran	11.9	(*)	0.19×10^{-7}	1.44
Kraton 1101	35.7	3.8×10^{-8}	2.5×10^{-7}	0.765
XD-7	68.3	1.19×10^{-9}	3.9×10^{-7}	2.69

[+] Distribution Coefficient:

$$S = \frac{\text{g of solute per unit volume of swollen polymer}}{\text{g of solute per unit volume of solution}}$$

[*] Transport was so low that the method was not applicable. Estimated to be less than 10^{-12} cm^2/sec

TABLE 2

TRANSPORT OF PHENOL THROUGH POLYMER MEMBRANES
(Temp. 25°C)

Polymer	Thickness L(Microns)	Phenol Specific Permeability $\bar{p}$ (cm^2/sec) x 10^7	Distribution Coefficient S
Polyethylene A (Medium Density)	20	0.5	–
Polyethylene B (Low Density)	14	0.11	–
Saran	12	0.06	0.07
Kraton 1101	41	0.71	0.5
XD-7	68.1	2.06	0.5
Ethyl Cellulose	35	0.96	17.4

correction factor for the error introduced by the boundary layer is applied to the experimental values, these values will be even higher.

A diffusivity for aniline and phenol in the membrane matrix can be estimated from the relationship:

$$\bar{p} = D_o S \qquad (2)$$

where $\bar{p}$ = specific permeability

D_o = diffusion coefficient (cm^2/sec)

and S = distribution coefficient

Tables 3 and 4 list such average diffusion coefficients for aniline and phenol in the membranes tested.

It was observed that choice of solution temperature may be used to advantage in this process. The primary effect of a temperature increase upon membranes operating under a pore-type mechanism is an increase in the permeation rate of the solute in water-filled pores. For diffusive membranes, such as reported here, however, the effect is both to increase the permeation rate in the membrane and to alter the membrane structure.

The polymeric state of the membrane has a pronounced influence on the rate and transport mechanism of a solute diffusing through its matrix. Below the glass transition temperature the membrane is in a glassy state and the polymeric chains are restricted in their ability to move. The membrane may also contain rigid voids which can trap permeant molecules, thereby contributing little to the diffusive process. The restriction in the motion of the polymer chain prohibits activated diffusion. Above the glass transition temperature, however, chain mobility and diffusivity increase. This increased mobility and diffusivity can be visualized as the membrane's becoming more and more rubbery. The polymer films that appear most promising in this present study are all above their glass transitions.

A review by Fujita[5] presents temperature responses for a number of other polymers. His conclusions appear to be applicable in the present work since similar generalizations can be derived from the observed transport rates and the

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5. Fujita, H. Organic Vapors above the Glass Transition Temperature. In: Diffusion in Polymers, Crank, J. and G.S. Park (eds.). New York, Academic Press, 1968. p. 75-106.

TABLE 3

DIFFUSION COEFFICIENTS OF ANILINE IN POLYMERIC MEMBRANES

Polymer	$D_o(cm^2/sec)$
Polyethylene B	11.5×10^{-8}
Saran	1.32×10^{-8}
Kraton 1101	32.7×10^{-8}
XD-7	14.5×10^{-8}

TABLE 4

DIFFUSION COEFFICIENTS OF PHENOL IN POLYMERIC MEMBRANES

Polymer	$D_o(cm^2/sec)$
Saran	8.6×10^{-8}
Kraton 1101	14.2×10^{-8}
XD-7	41.2×10^{-8}
Ethyl Cellulose	$.55 \times 10^{-8}$

difference between experimental and glass transition temperatures
$(T - T_g)$. For example, the plasticized polyethylene, which can be expected to
have a lower T_g, has a greater permeability than the unplasticized polyethylene
membrane. Theory predicts that the higher the temperature above a glass tran-
sition, the greater the transport rate. Obviously a point is reached where the
integrity of the membrane can no longer be maintained or controlled. One solu-
tion to this problem is to use block copolymers, in which the polymer chain is
composed of distinct segments of at least two different polymers. One of these
segments is chosen to be a rubbery polymer above its glass transition and the
other is a crystalline polymer. The crystalline polymer provides the necessary
mechanical properties while transport occurs primarily through the rubbery
material. Examples of such polymers are the polysiloxane/ polycarbonate (XD-7)
and the polybutadiene/polystyrene (Kraton 1101). The polysiloxane copolymer,
whose blocks have a T_g of approximately $-122^{\circ}C$, is the most highly permeable
membrane of all. The butadiene copolymer, with blocks having a T_g of approxi-
mately $-112^{\circ}C$, is the second most highly permeable membrane. From these data we
can expect that both Kraton and the polysiloxane copolymer will increase in
permeability up to the temperature where mechanical structure of the membrane
begins to fail. The block copolymers thus apparently have an advantage of being
able to form large rubbery domains in contrast to cross-linked elastomers which
are relatively constrained by short chains between cross-links. Surprisingly,
the relatively stiff, crystalline ethyl cellulose shows phenol transport rates
higher than those of the butadiene-containing copolymer, Kraton 1101. Since the
apparent permeability values are the average values for the concentration range
of 0.1 molar phenol to infinite dilution, it is possible that the ethyl cellu-
lose membrane was plasticized by the phenol and that its morphology was signifi-
cantly altered in the presence of the permeant. Plasticization increases perme-
ability by reducing cohesiveness between polymer chains, which leads to increased
diffusivity. Alternatively, it is also possible that the 1 molar sodium
hydroxide--an effective swelling agent for the native cellulose--decreased the
ethyl cellulose crystallinity, leading to a more permeable structure.

The transport rates through the two polyethylene film samples are of the
order expected. The less-crystalline, lower density material allows more rapid
transport than the denser, more crystalline membrane. Saran, a copolymer of
vinyl chloride and vinylidene chloride, is a highly ordered polymer. It was

included in the investigation since several of the solutes being screened were chlorinated hydrocarbons. Because of chemical similarity it was expected that these hydrocarbons might distribute favorably in the saran film and thus exhibit an enhanced transport. The saran, however, is apparently unaffected by the phenol and exhibits low permeability, as expected from the chemical nature of this polymer.

The results achieved with aniline and phenol indicate that transport rates of the same magnitude as achieved in commercially-useful dialysis processes are possible, but without the dilutions so notoriously characteristic of ordinary dialysis. The difference between the processes described here and the older processes lies in the availability of new membrane materials which are selective toward organic species coupled with the use of the artificially created chemical potential gradient.

An example of these new membrane materials is the Kraton film, a copolymer of butadiene/styrene. The organic solute material has a high permeability through the mobile or rubbery phase, as discussed above. The ratio of the butadiene to styrene, as well as the thickness of the membrane, can be varied. The composition of the membrane and its amenability to fabrication in various physical configurations make possible permeabilities of the same order of magnitude as those found in other commercial dialyzing processes and in reverse osmosis. These permeabilities can be further enhanced by using solute conjugation in the receiving solution to maintain a maximum chemical potential gradient.

In projecting the use of this process to the concentration of trace contaminants from plant waste streams for later disposal or recovery, consideration of continuous processing will, of course, be required (see Section VII of this report).

For concentration of dilute contaminants, according to the reaction org + conj = prod, one would anticipate that the conjugate acid (or base) would be maintained at a high excess concentration in the receiver compartment, and that the following constraints would apply:

C_{org}^f, the feed concentration = constant (large V_f >>> V_d)

C_{conj}^d, concentration of conjugate acid or base = constant

excess concentration

C_{prod}^d, concentration of conjugated product = K_{eq} C_{org}^d C_{conj}^d

receiver compartment always near equilibrium.

where:

C = concentration

f = upstream (feed) side of membrane

d = downstream side of membrane

org = organic solute

conj = conjugate acid or base

prod = conjugated product

K_{eq} = equilibrium constant

For these constraints it can be shown, by rearranging equation (17), Appendix A, that the accumulation of the organic solute in the receiving compartment of volume V_d will be given by the following:

$$C_{org}^d = C_{org}^f \left[1 - \exp\left(- \frac{A \bar{P} t}{V_d(1 + C_{conj}^d K_{eq})} \right) \right] \qquad (3)$$

where $\bar{P}$ = membrane permeability, cm^2/sec

A = cell cross section, cm^2

t = contact time, sec

The concentration of the organic solute in the receiving phase will attempt to increase until it begins to approach the feed concentration. If it were to reach the feed concentration, the process would, of course, stop, since the driving force would be dissipated. The controlling factors are the membrane permeability and the "sink" for the organic solute given by the product $C_{conj}^d K_{eq}$.

This equilibrium product will predict the amount of the permeating solute that will be present in the receiving phase. In the application of these techniques the concentration of the permeating species is maintained at a very low level by providing a large excess of the conjugating acid or base.

The total amount of organic solute accumulated in the dialysate is the sum of the solute, C_{org}^d and its conjugate C_{prod}^d. The relationship between C_{prod}^d and K_{eq} can be used to find the total quantity of solute transferred:

$$C_{org} = C_{org}^d (1 + K_{eq} \; C_{conj}^d) \tag{4}$$

For reactions with large K_{eq} values, the first term in the brackets reduces to the product $K_{eq} \; C_{conj}^d$, so that one can project that the maximum amount which can be accumulated in the dialysis will approach the product of

$$K_{eq} \; C_{conj}^d \; C_{org}^f, \text{ which is equal to } \frac{C_{prod}^d}{C_{org}^d} \times C_{org}^f \tag{5}$$

The concentration ratio C_{prod}^d / C_{org}^d is thus a measure of the "sink" available for the species to be transferred. The rate at which the process will occur is a product of the membrane permeability times the concentration difference of organic solute. The overall process can then be viewed as a concentration process which can operate up to an amplification ratio established by the equilibrium constant of the species to be transported. If recovery of the product is desired, the dialysis driving force can be enhanced by removing the conjugated product from the sink. Such recovery will, of course, involve the neutralization of the conjugate acid or base. But recovery can be performed in a solution more concentrated than the feed solution.

2. Dialysis with Complexing

The separation of transition metal ions such as aluminum, copper, and lead has been studied, using dialysis with complexing. Permeant cations were complexed on the downstream side of the membrane with soluble impermeable complexing agents of relatively high molecular weight. The cations could thus be concentrated in the receiving phase for more efficient disposal or potential recovery. Hydrophilic membranes and an organic "receiver" solvent were used in this mode

of dialysis. The selection of these membranes and the solvent are discussed below.

Dialysis with complexing has an advantage over simple solvent extraction in that loss of the extracting solvent and/or complexing agent due to partial water solubility and entrainment in the feed stream is eliminated. However, this must be weighed against a potentially slower mass transfer rate common to the dialysis membrane.

a. Choice of Membrane

The selection of Cuprophan for these studies was based on its unique properties: a high water content, good mechanical properties, low cost, and good chemical stability. Since the transport of the metal ions will occur through the water phase within the membrane, there will be minimal interaction between the solute and the polymer. Therefore, membrane selection for dialysis with complexing is based on different criteria than those that pertain to dialysis with conjugation. Other membranes with similar properties could be considered; however, this section of the investigation had as a goal the evaluation of the complexing procedure. Since the properties of Cuprophan had been well documented in other dialysis procedures[6], this membrane was selected in order to eliminate the membrane as an independent variable in this evaluation. (Dialysis membranes are routinely evaluated by GSRI under another program: Membranes and Materials Evaluation, NIH NIAMDD Contract No. 72-2221). There are some experimental membranes that may exhibit enhanced transport for the metal ions under study, however, the chemical and physical stability of these membranes are not competitive, and they are not available commercially. For these reasons they were not included in this evaluation.

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6. Klein, E., J.K. Smith, F.F. Holland, and R.E. Flagg. Membrane and Materials Evaluation; Permeabilities, Physical and Mechanical Properties of Hemodialysis Membranes—Bemberg Cuprophan Pt-150 Membrane. Gulf South Research Institute. Annual Report AK-1-72-2221. Artificial Kidney-Chronic Uremia Program, National Institutes of Health. July 1973. 24 pp.

b.   Selection of Complexing Agents and Solvent Combinations

A number of efficient agents for complexing Al^{+++}, Cu^{++} and Pb^{++} are suggested by Walsh[7]. Based on reported information[8], and the requirement that the systems should be commercially acceptable, some organic phosphorous compounds were chosen for investigation in this study. Those selected were relatively inexpensive, insoluble in water, and compatible with our test system. The following compounds obtained from a local chemical company were tested:

1) Dibutyl Butylphosphonate

2) Tributyl Phosphorothionate

3) Triisooctyl Phosphorothionate

4) Bis (2-ethylhexyl) Hydrogen Phosphate

5) Bis (2-ethylhexyl) Phosphate

A contaminant found in Mississippi River water, Al^{+++}, was used as a representative metal cation of interest. A direct extraction test was run to determine the extraction efficiency of each of the aforementioned compounds. Results obtained appear in Table 5.

Based on this study, bis(2-ethylhexyl) hydrogen phosphate (BHP) was selected for complexing the cations. This complexing agent has low water solubility. It is a colorless, odorless liquid which is slightly lighter than water (specific gravity 0.9). Its cost is about $1.00 per pound. Bis(2-ethylhexyl) hydrogen phosphate dissolves in hexane and in heavy mineral oils, acetone, alcohol, chloroform, etc. Hexane was chosen as the solvent for these trials because, for practical purposes, it is insoluble in water and therefore minimizes the transport of the receiver phase to the feed side.

c.   Results from Rotating Cell Screening Tests

Aluminum System—Aluminum was chosen as a test solute because it is used extensively as a coagulating and/or precipitating agent in waste treatment. Its concentration in natural waters ranges from a few to several thousand micrograms per liter. The toxicity of aluminum has not been well defined, but concern has been expressed about the use of aluminum compounds in the food and cosmetic industries. Data were obtained by dialyzing a 1% aluminum chloride

7.   Walsh, A. Atomic Absorption Spectroscopy. ASTM Special Technical Publication. No. STP 443,31. June 1968.

8.   Marcus, Y. and A.S. Kertes. Ion Exchange and Solvent Extraction of Metal Complexes. London, New York, Sidney and Toronto, Wiley-Interscience, 1969. 1037 pp.

TABLE 5

SINGLE-STAGE EXTRACTION EFFICIENCY

Complexing Agent	Efficiency for Al^{+++} Complexed at pH 3.5 (%)
Dibutyl Butylphosphonate	2
Tributyl Phosphorothionate	31
Triisooctyl Phosphorothionate	35
Bis (2-ethylhexyl) Hydrogen Phosphate	98
Bis (2-ethylhexyl) Phosphonate	43

solution in water. The pH of the solution was maintained between 3-4 to minimize hydrolysis of the $AlCl_3$ during the experiments, which lasted less than 2 hours. The rotating cell was used at 90 rpm, employing 10%, 20% and 30% solutions of bis(2-ethylhexyl) hydrogen phosphate (BHP) in hexane to determine the optimum concentration of the receiver phase. The results obtained are shown in Figure 5.

Several factors can influence the diffusion rate in these experiments. Three factors are present in all membrane processes: (1) the resistance to transport through the aqueous liquid boundary next to the membrane; (2) resistance to transport through the membrane; and (3) a boundary resistance through the organic receiving phase. Figure 5 shows a reduction in the observed diffusion rate with increasing concentration of BHP; this reduction reflects changes in viscosity of the organic receiving phase. For the same rotational cell velocity, a reduced diffusion rate leads to higher boundary resistances in the organic receiving phase. In addition to the three boundary resistances mentioned above, the system has an additional resistance to transport at the interface between the organic and aqueous phases, in this case at the receiver side of the membrane. To delineate the magnitude of this resistance, an experiment was performed using distilled water as a receiver phase. The diffusion rate was found to be 2.58×10^{-7} cm^2/sec, approximately five times higher than that obtained with the complexing agent present in the organic phase. These findings indicate that the rate-determining step is the transition from the aqueous to the organic phase. Previous studies with the rotating cell[4], utilizing turbulence created at 90 rpm as in the present study, have shown that the transport parameter is not likely to improve more than 30% with further increases in turbulence.

The aluminum transport rates for this system are lower than those normally anticipated in dialysis and thus will adversely affect the system's economic attractiveness for industrial applications. However, conventional liquid/liquid extraction processes are similarly burdened with the limiting factor in the transfer from one liquid fraction to the other. Conventional liquid/liquid extractions also suffer from hydraulic constraints and from some loss of solvent and complexing agent due to water solubility and entrainment. The hydraulic problems and loss of solvent and complexing agent would be minimized in the dialysis mode because of the membrane interfacing the two solvents. Thus,
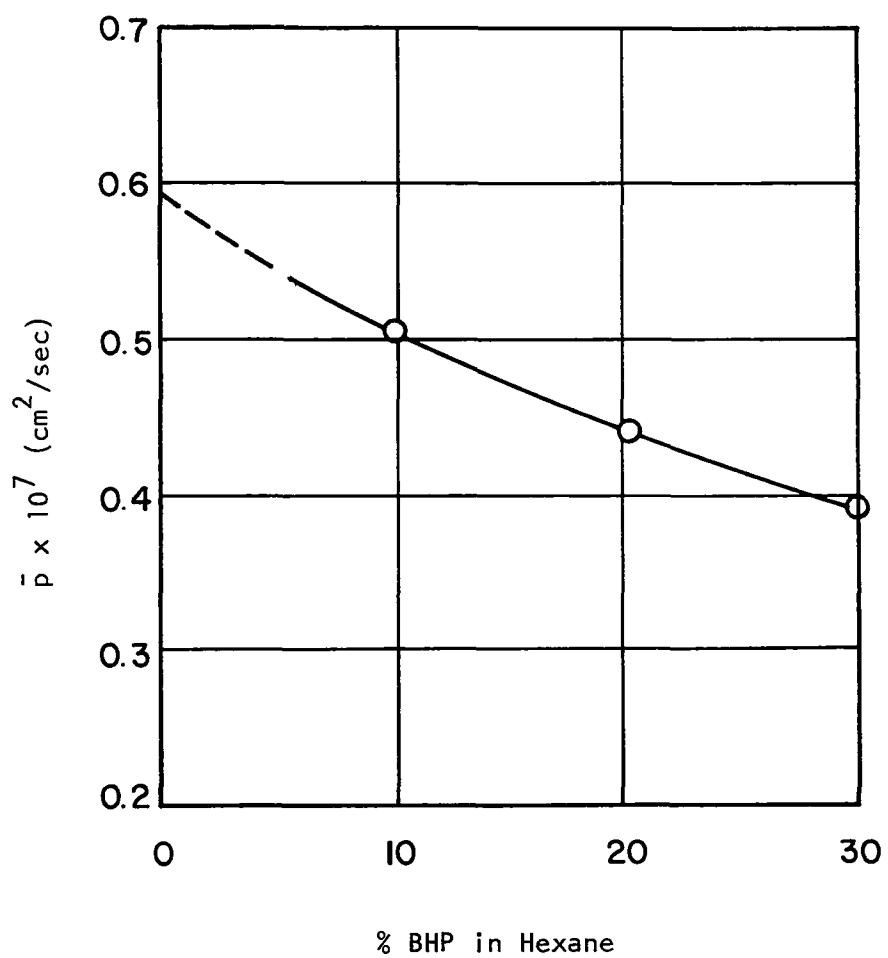
30

Figure 5.   The effect of BHP concentration in the organic phase on
the overall transport rate for Al^{+++}.

dialysis with complexing may prove profitable, compared to liquid/ liquid extraction.

Copper and Lead System—Two additional pollutants found in the Mississippi River, copper and lead, were also screened using this system. With 20% BHP in hexane and at 150 rpm, a 1% aqueous solution of Cu^{++} and Pb^{++} was dialyzed for 2 and 1/2 hours at conditions otherwise identical to those of the Al^{+++} test. No significant transport of copper was observed, indicating that a different receiver phase was needed to achieve usable results. However, in the case of Pb^{++}, the diffusion coefficient D was found to be 0.56×10^{-7} cm^2/sec. This is slightly higher than the corresponding Al^{+++} transport because of increased turbulence at the higher speed. It is our opinion, however, that the transport rate is still low for most industrial applications.

3. Pervaporation

The pervaporation process is similar to classical dialysis in that the feed mixture is placed on one side of a semipermeable membrane, and the product (the permeant) is collected on the other side. The thermodynamic force behind the permeation through the membrane is the difference in chemical potential of the permeant on opposite sides of the membrane. This is accomplished in pervaporation by removing the product from the membrane interface through evaporation. A schematic of a pervaporation cell is shown in Figure 6. The cell interfaces the liquid phase with a thin hydrophobic membrane; the permeant product is removed from the "downstream" side of the membrane as a vapor. The pervaporation process[9] involves the following sequence of steps:

a. Absorption of permeating molecules at the liquid-membrane interface;
b. Diffusion of these molecules through the film;
c. Removal of these molecules from the downstream surface of the film into a vacuum or gas receiving stream.

Pervaporation, as used in this report refers to an activated diffusion process. Such diffusion occurs when there is a chemical interaction which enhances the transport of some components over others in solution. Such membranes are termed permselective. The proper selection of a permselective

9. Binning, R.C. and F.E. James. Petrol. Refiner. 37(5):214, 1958.

Membrane

Liquid in   Air out

Liq.   Air

Liquid out   Air in
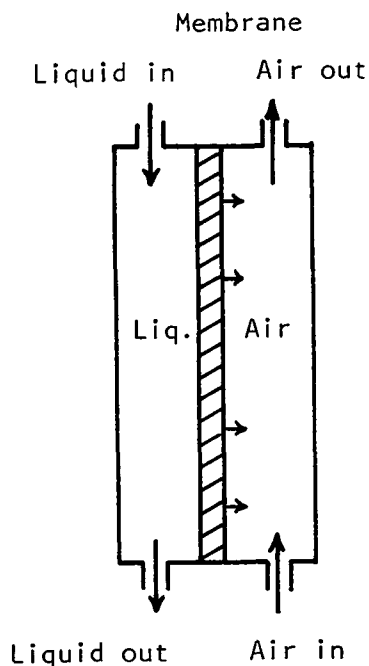
Figure 6. Pervaporation schematic.

membrane and processing conditions such as temperature, fluid flow rates, etc., resulted in an effective separation. The versatility of this process is illustrated in the applications involving the separation of azeotropic mixtures[9], the separation of hydrocarbons[10], and several other applications[11-14].

In this pervaporation process, the solute (with a chemical activity a_1^f in the feed stream) distributes itself between the water and the membrane. The activity of an organic solute at a level corresponding to its solubility limit will approximate that of the pure liquid activity, a_1^o. We can write a distribu-

10. Li., N.N., R.B. Long, and F.J. Henley. Ind. & Eng. Chem. 57(3):19, 1976.

11. Binning, R.C., R.J. Lee, J.F. Jenning, and E.C. Martin. Ind. & Eng. Chem. 53:45, 1961.

12. Binning, R.C. and J.R. Kelly. U.S. Patent 2,913,507. To American Oil Company, November 17, 1954.

13. Choo, C.Y. Advances in Petroleum Chemistry. 6:73, 1962.

14. Sanders, B.H. and C.Y. Choo. Petrol. Refiner. 39(6):133-138, 1960.

tion constant using the approximation

$$a_1^m = S \ a_1^o \tag{6}$$

where a_1^m is the solute activity in the organic membrane phase. On the gas side of the membrane, the solute will attempt to reach its equilibrium partial pressure, i.e., the partial pressure corresponding to a solution of the solute in a fluid having the same activity coefficient as the membrane. This can be approximated by a Henry's law constant

$$H = a_1^m/P \tag{7}$$

The transport equation has been derived for this case by Yasuda[15] and is given by:

$$dP/dt = \frac{\bar{p}H \ (P^f - P^d) \ A}{(1/RT) \ VL} \tag{8}$$

where

$\bar{p}$ = Specific permeability constant (cm^2/sec)

A = Mass transfer area (cm^2)

V = Charge volume (cm^3)

L = Film thickness (cm)

P^f = Partial pressure of the solute on the upstream side (atm)

P^d = Partial pressure of the solute on the downstream side (atm)

P^o = vapor pressure in the pure state

R = Gas Law Constant, lit-atm/mole deg.

T = Temperature

t = time

The equation for our case can be simplified by letting P^d approach zero through rapid gas sweeping. The result indicates that the transport rate will

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15. Yasuda, H. J. of Polym. Sci., Part A. 5, 1967.

34

be directly proportional both to membrane area, and to vapor pressure of the pure solute (from the approximation that P^f at saturation equals P^o).

Thus, compounds having an adequately high vapor pressure, for which one can find the proper membrane, will be suitable for pervaporation separation.

With these criteria in mind, one can choose some likely candidate solute from Table 6, which lists the pollutants detected in the finished water in the New Orleans area. We can reasonably assume that membranes are available with a favorable distribution constant. Thus, the most feasible transport can occur where the highest vapor pressures are present. The level of the "pollution" problem will be related to some extent to the solubility. Some examples of solutes that may be worth considering are chloroform with a 0.82% solubility and 192 mm vapor pressure; ethylene dichloride, 0.81% solubility and 70 mm vapor pressure; and trichlorethane with a 0.43% solubility and 125 mm vapor pressure at 25^oC. All of these solutes have a very strong dependence of vapor pressure on temperature. (An increase of 20^oC will more than double the vapor pressure of ethylene dichloride, for example. The vapor pressure vs. temperature relationship is shown in Figure 7).

Nitrobenzene, chloroform, and ethylene dichloride were selected from this list for screening purposes. Aqueous solutions of these solutes were pervaporated at the following concentrations (by weight):

Nitrobenzene	–	600 ppm
Chloroform	–	8400 ppm
Ethylene dichloride		8000 ppm

These concentrations represent either solubilities approaching equilibrium (chloroform, ethylene dichloride) or the concentration in the local waste streams. In each run 400 ml liquid charge was used. Permeability constants obtained from these runs are listed in Tables 7, 8, and 9.

The membranes listed in these tables are the same as those identified in Section V.B of this report, with two additional membranes: (1) Pliolite (registered trade name of the Goodyear Chemical Co.) is a 50/50 butadiene/styrene resin; (2) Adiprene L-315 (registered trade name of E.I. DuPont deNemours Co.) is a polyurethane resin vulcanized with an aromatic diamine.
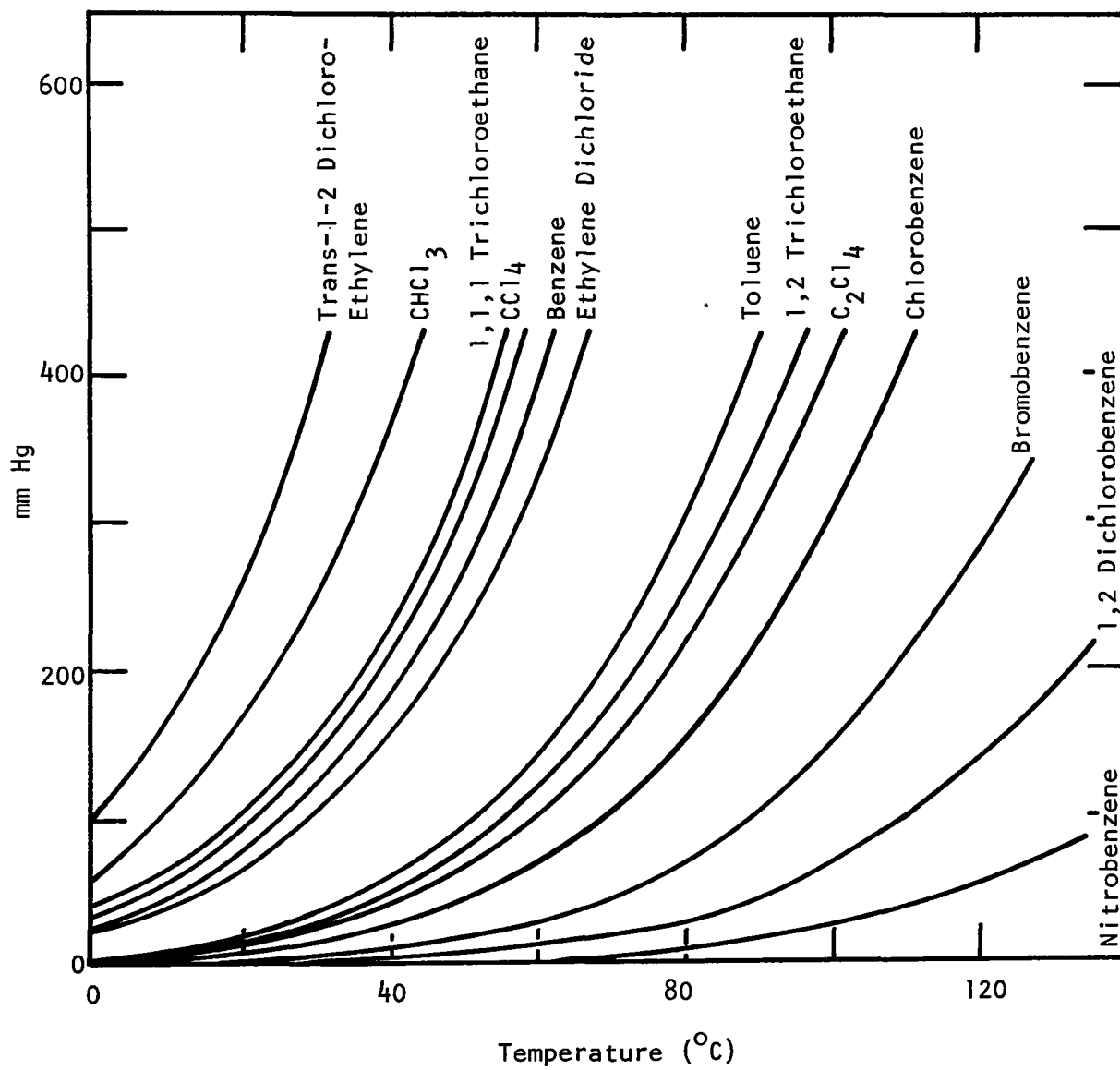
Figure 7. Vapor pressure vs temperature.

TABLE 6

SOLUBILITIES AND VAPOR PRESSURE OF SELECTED ORGANIC SOLUTES
IN WATER

Compound	Solubility wt %	°C	Vapor Pressure Torr (mm Hg) at 25°C
Nitrobenzene	.20	20	0.4
Dinitrotoluene	.03	22	0.2
Chloro Nitrobenzene	.003	17	−
Trichloroethane	.43	25	125
Tetrachloroethylene	.29	25	18
Dichloroethyl Ether	1.1	20	1
Ethylene Dichloride	.81	20	70
Chloro Benzene	.04	25	12
Dichloro Benzene	.02	25	0.7
Chloroform	0.82	20	192

TABLE 7

PERMEABILITY COEFFICIENTS - NITROBENZENE

Liquid Flow: 0.75 lit/min

Air Flow: 12.0 lit/min

Membrane	Thickness (Microns)	$\bar{p} \times 10^7$ ($cm^2 sec$)
Polyethylene (low density)	14.7	6.85
Saran	19.4	6.42
Kraton® 1101	25.0	9.6
Pliolite®	38.0	10.7
Adiprene®	59.0	.13
Polyethylene (Plasticized)	24.4	7.7

TABLE 8

PERMEABILITY COEFFICIENTS - CHLOROFORM

Liquid Flow: 0.75 lit/min

Air Flow: 12   lit/min

Membrane	Thickness (Microns)	$\bar{p} \times 10^7$ (cm^2/sec)
Plasticized Polyethylene	24.4	7.5
Polyethylene	11.0	3.9
Kraton® 1101	29.0	10.1
Saran	16	14.9

TABLE 9

PERMEABILITY COEFFICIENT – ETHYLENE DICHLORIDE

Liquid Flow: 0.75 lit/min
Air Flow: 12   lit/min

Membrane	Thickness (Microns)	$\bar{p} \times 10^7$ (cm^2/sec)
Plasticized Polyethylene	27	5.83
Polyethylene	16	2.1
Kraton®	26	11.45
Saran	16	8.47
Polysiloxane (XD-7)	37	20.5

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SECTION VI

PILOT TEST OF THE PERVAPORATION PROCESS

The results of the contaminant screening experiments using dialysis with conjugation and pervaporation showed good promise for industrial waste stream refinement. Pervaporation, which could be used for the removal of halogenated hydrocarbons and certain other toxic materials like nitrobenzene, is of immediate interest from local water quality considerations. A list of 32 organic compounds which have been identified in New Orleans' finished water supply is given in Table 10. Halogenated hydrocarbons form a major segment of this list. The list also includes nitrobenzene.

An ethylene dichloride (EDC) manufacturer supplied samples from a specific waste stream originating in their ethylene dichloride process. This stream has the following composition:

Ethylene dichloride: 0.8 - 0.9 wt %

Hydrochloric acid: 15 - 20 wt %

Water   balance

(A modified process now under study is expected to decrease the HCl content of this waste stream to 3 - 3.5 wt %).

The objective in the ideal treatment process is total environmental control. Total environmental control means maximum water recycle/reuse and minimum waste production, stressing acceptance of residuals into both raw materials and marketable products. Such control utilizes stabilization techniques for the remainder (minimum) so as to allow for its acceptance into the appropriate environment.

A Kraton 1101 membrane was selected as the test vehicle on the basis of its performance in screening experiments. The cost of this membrane, in addition to its transport properties, was a factor in its selection. Other polymers like polycarbonate/silicone offered higher solute transport but were ten to twenty times more expensive (since they are still in the developmental stage). The polycarbonate/silicone polymer has recently been withdrawn from the commercial market.

TABLE 10

LIST OF ALL ORGANIC COMPOUNDS FOUND IN THE
CARROLLTON WATER PLANT (NEW ORLEANS) FINISHED WATER[*]

acetone	dichloroethyl ether
acetophenone	dimethoxy benzene
benzene	2,6-dinitro toluene
bromobenzene	endo-2-camphanol
bromochlorobenzene	ethyl benzene
bromoform	exo-2-camphanol
bromophenyl phenyl ether (positional isomer?)	hexachlorobenzene
butyl benzene	1-isoprophenyl-4-isopropyl benzene (1,2 isomer)
a-camphanone	isocyanic acid
chlorobenzene	methyl biphenyl
chloroethyl ether	methyl chloride
chloromethyl ether	nitrobenzene
chloroform	o-methoxy phenol
chloronitrobenzene	p-methylphenol
chloropyridine	tetrachloroethylene
dibromobenzene	toluene
dichlorobenzene (positional isomer)	1,1,2-trichloroethane
1,2-dichloro-ethane	vinyl benzene

[*]SOURCE: Industrial Pollution of the Lower Mississippi River in
Louisiana. U.S. Environmental Protection Agency, Region VI, Dallas,
Texas, Surveillance and Analysis Division. PF-611. April 1972. 146 pp.

A.   EQUIPMENT

The loading of a stacked pervaporation pilot unit is shown in Figure 8.
The assembly of the membranes, gaskets, turbulence promoters (a screen matrix
used to improve the mass transfer), and the polypropylene support plates is held
between two metallic frames by anchor bolts.   Polyethylene gaskets (0.15 cm
thick) provide necessary liquid and air passages and also serve as fluid
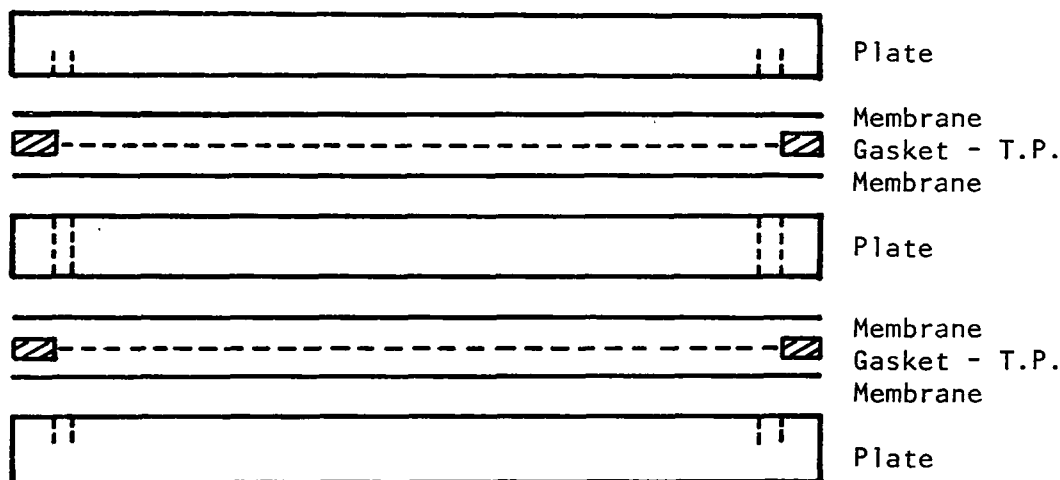distributors.

Figure 8.   Pervaporation unit membrane loading scheme.

Fluid distribution was accomplished by connecting the fluid ports to the
respective passages through grooves etched in the gaskets as shown in Figure 9.
Gaskets No. 1 and 3 distribute water along the membrane while gasket No. 2
distributes air.   Two additional air passages are provided for air flow along
the grooved surfaces of the polypropylene plates.   Figure 10 shows the counter-
current fluid flow pattern in the unit when holes corresponding to the gasket
holes are made on all except the bottom-most membrane and the gaskets are
inserted between them in the order shown.   The bottom-most membrane has only two
openings (for the entrance and exit of the air stream).

The overall experimental setup was identical to that shown in Figure 4
except that the small test cell was replaced with the semipilot unit described
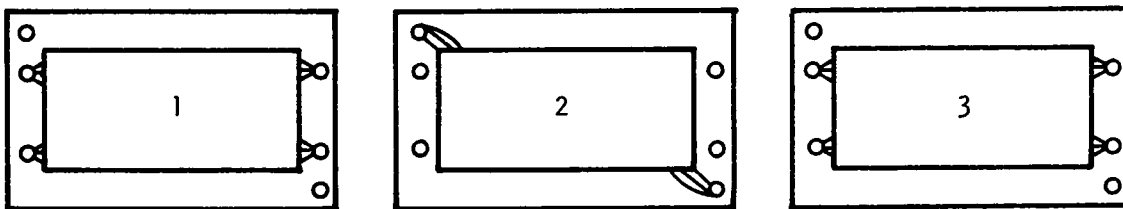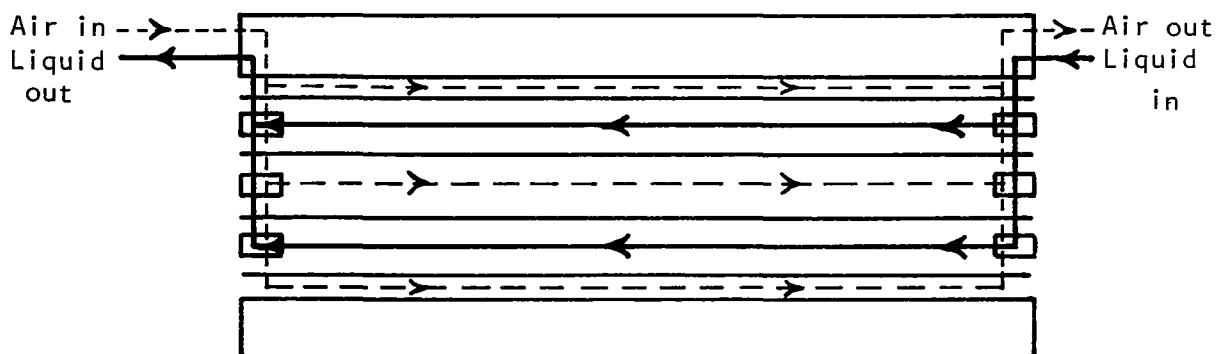above.

Figure 9. Pervaporation unit gaskets.

Figure 10. Pervaporation unit fluid flow pattern.

B. RESULTS

The following process variables were investigated for their effects on the pervaporation rates: feed flow rate, feed temperature, feed concentration, and air flow rate. Each variable was tested at three to four different levels within the available range for its effect on $\bar{p}$, the permeability. These results thus provided a characterization of the design parameters.

1. Effect of Feed Flow Rate

Figure 11 represents the results of a change of feed flow rate from 250 ml/min to 1,000 ml/min. Permeability $\bar{p}$ at 1,000 ml/min increased more than 75% over its base value at 250 ml/min. The increase in the liquid flow velocities

apparently was tending to increase the solute mass transfer through an increased turbulence. Another way to increase the turbulence is to reduce the liquid channel height (consequently the cross section of the flow element) for the same flow of liquid. Channel height is the height of the passage through which the liquid is circulated. Normally, the width of this passage is constant for a particular piece of equipment once it has been selected, but the height is adjustable. The use of channel height adjustment to increase turbulence was restricted, however, by pressure drop considerations. The fluid channel was maintained between 0.07 and 0.20 cm to balance mass transfer and pressure drop considerations.
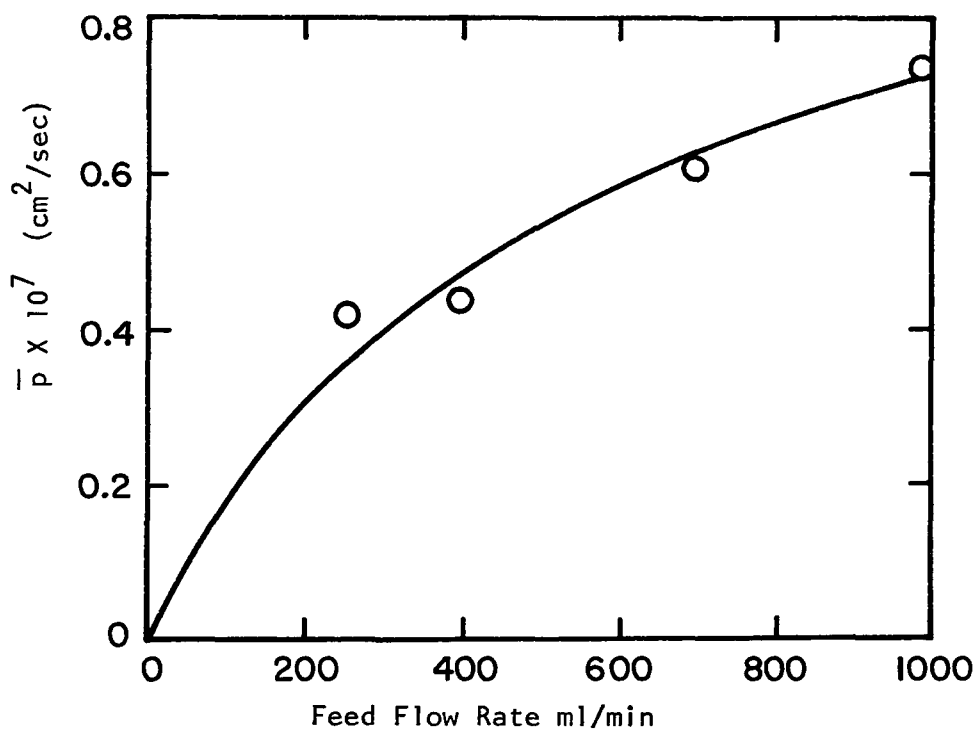

Figure 11. Effect of feed flow rate on permeability.

The permeability of the membrane is increased by an increase in flow rate. This increased permeability is caused by reduction in the boundary layer formation due to the increased turbulence. Note that the relationship, as shown in Figure 11, is not linear.

An analytical expression of the permeability and its flow rate dependence can be established in a Wilson plot[16] (see Appendix E, page 69). The linear dependence found for $\bar{p}$ on $Q^{-0.8}$ is similar to the Gilliland correlation[17], which relates the boundary layer mass transfer coefficient to $Q^{-0.8}$. The Wilson plot thus permits separation of the boundary layer mass transfer coefficient k_{liq} (reflected in the slope) from the membrane diffusion coefficient D (from the intercept). This procedure is simply the graphic representation of the series resistance formulation:

$$\bar{p}^{-1} + \frac{1}{DS} = \frac{1}{Lk_{liq}}$$ (9)

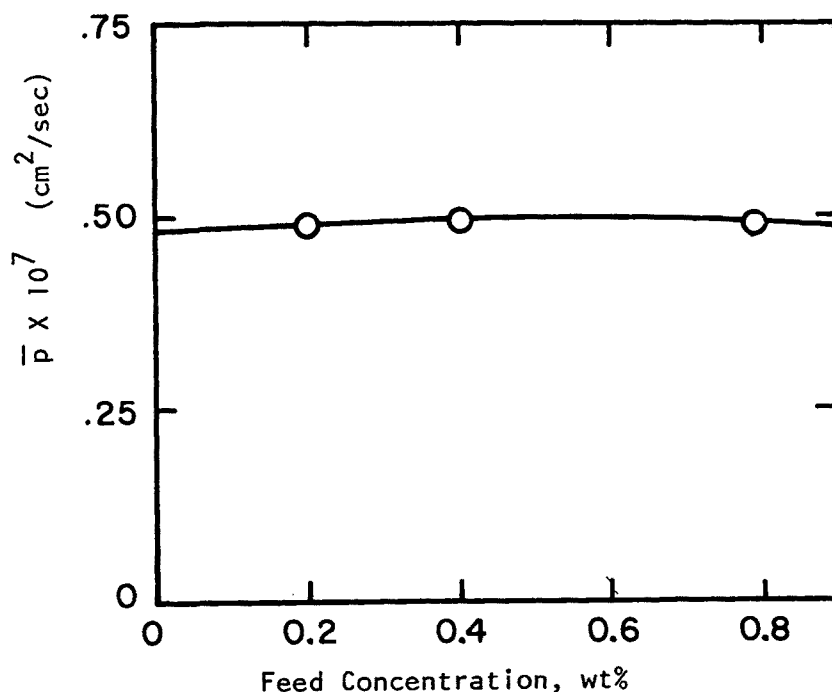Figure 12. Effect of feed concentration on permeability.

16. Wilson, H. Trans. Am. Soc. Mech. Engrs. $\underline{37}$:47, 1915.

17. Gilliland, E.R. Ind. & Eng. Chem. $\underline{30}$:506, 1938.

Figure 12 shows the effect of ethylene dichloride concentration on the membrane permeability. It should be mentioned here that only the ethylene dichloride concentration was changed (from 0.8 wt % to 0.2 wt % in the feed); the HCl concentration remained in each case at 3.5%. No significant change was observed in the permeability constant. This suggests that the parameters in equation (8) are valid and that neither the diffusion coefficient D nor the distribution constant S was affected by the change in the feed solution concentration over the concentration range studied.
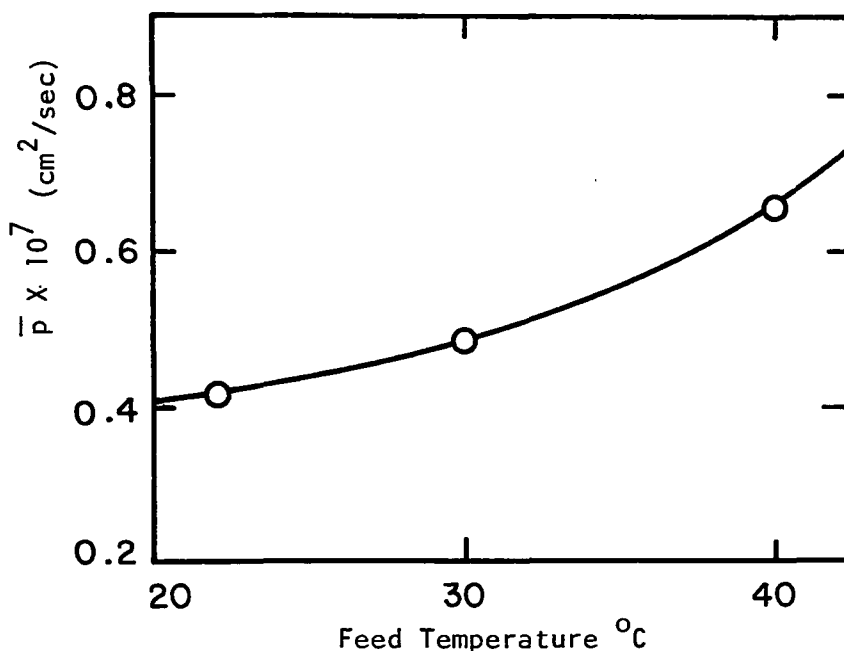
Figure 13. Effect of feed temperature on permeability.

Figure 13 illustrates the effect of temperature on the membrane permeability. An increase in $\bar{p}$ from 0.42×10^{-7} at room temperature ($22^\circ C$) to 0.66×10^{-7} cm^2/sec at $40^\circ C$ amounts to an almost 60% increase in the EDC transport. The increase at higher temperature may be partly attributable to an increase in the membrane diffusion rate but is mostly due to a decrease in the feed viscosity (reducing the boundary layer resistance) and an increase in the feed solute vapor pressure. It is frequently observed that increasing temperature causes a decrease in membrane selectivity. However, in the present application, where the major effect was on the boundary layer, HCl transport through the film remained insignificant.
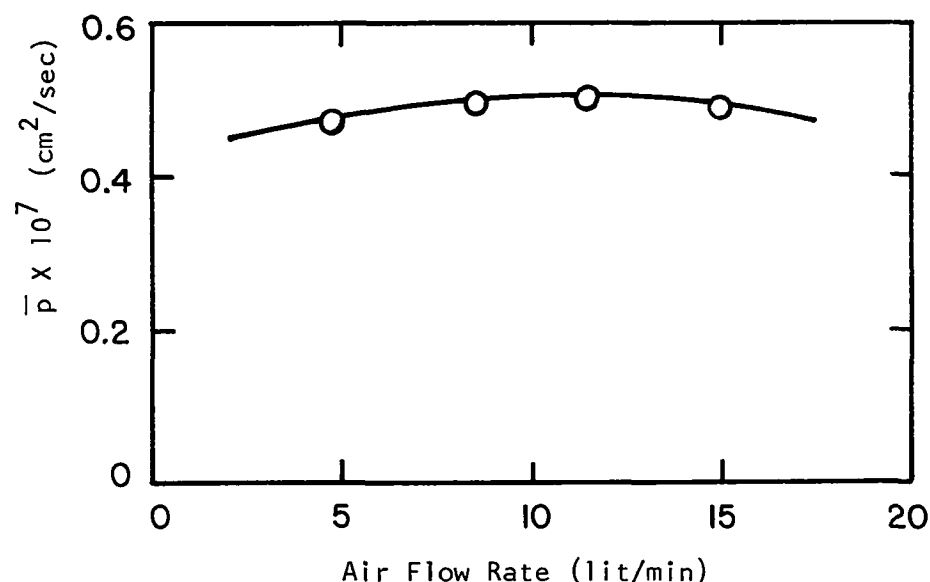
2. Effect of Air Flow Rate

Figure 14. Effect of air flow rate on permeability.

Figure 14 depicts the effect of air flow rate on the permeability of the membrane. The data show that the effect is not significant in the air flow rate range studied. This is consistent with the fact that as long as the permeated solute is removed fast enough from the air side, other conditions being the same, the permeability remains unaffected. It is not unusual for the liquid side coefficient to be the controlling factor as it is here.

3. Effect of Other System Variables

Membrane variables, such as film thickness and structure, will also affect the permeability of the solute. Since the membrane represents the largest resistance in the pervaporative transport, the thinner it is, the less resistance it offers, as illustrated in equation (9). It was also observed, during the experiments, that the plasticized films showed a better permeability than nonplasticized films (see Tables 8 and 9). These increases are mainly attributable to the decrease in the crystallization of the polymer. As discussed above

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in Section V.D.1., plasticization of the membrane lowers the glass transition temperature, leading to enhanced solute permeability. Fujita[5] has prepared a detailed discussion of this phenomenon in the book Diffusion in Polymers, edited by Crank and Park. Those membranes swollen by the pure solute, e.g., Kraton 1101 swollen by EDC, also exhibited better transport properties. These changes can be used judiciously to obtain better transport properties. For example, increasing the polybutadiene portion of the Kraton film would yield an increased transport (though a poorer mechanical structure). The final film selection thus must be based on a balance between physical and chemical properties.

SECTION VII

PROJECTION TO COMMERCIAL OPERATION

A design projection of full-scale operation has been assembled from the
results of the studies reviewed in Section VI. The actual industrial setting
under consideration concerns a feed of 20 gallons per minute containing 0.8 wt %
ethylene dichloride and 3.5 wt % HCl in water (cf. the stream made available by
a chemical manufacturer page 40). Design specifications call for removal of at
least 90% of the chlorinated hydrocarbon from the waste stream. The HCl-
containing residual stream would be treated by conventional neutralization
methods.

A hollow fiber geometry was suggested for this application since hollow
fibers offer better mass transfer characteristics and membrane surface area at
considerable economy. Due to the inherent parallel flow situation in fiber
modules, excessive pressure drops also are avoided. An effective mass transfer
area of 9100 m^2, to be provided in fibers with an inside diameter of 200 microns
and an outside diameter of 250 microns, proves necessary for 90% removal of EDC.
Membranes with higher permeabilities will have proportionately lower area
requirements. Calculations of membrane area requirements for these once-through
configurations, based on the experimentally obtained recirculating data, are
listed in Appendix D and Appendix E.

The economics of this hollow fiber design were evaluated at experimental
permeabilities corresponding to the 28-micron Kraton 1101 membrane (which was
actually studied in the laboratory) and for permeabilities one and two orders of
magnitude higher. The order-of-magnitude projection in permeability improvement
is considered well within the reach of existing membrane technology, since it is
possible to use thinner membranes (e.g. 5 microns vs. the 28-micron Kraton
membrane) and also to operate at higher temperatures (with a 60% increased
permeability observed with an $18^{\circ}C$ temperature increase).

The flow scheme for the proposed process configuration is presented in
Figure 15. The economic analysis is assembled in Table 11. Summary results
for the several cases evaluated are compiled in Table 12.

TABLE 11

ECONOMIC ANALYSIS FOR HOLLOW FIBER UNIT[*]
(Permeability equivalent of $Kraton_2 1101$ membrane)
Membrane area 9,100 m^2

Each plant requires its own economic analysis. Preliminary economic
estimations may, however, be based on the mass balance obtained by the
model discussed in Section VII. Some investment costs such as land cost,
etc., were not assessed since this operation would, in most cases, be
installed in existing plants where these costs have already been amortized.
Because of a small area requirement (6 sq. ft.), building costs also
were excluded. Estimation procedures recommended by Peters[†] and Perry[**]
were followed.

Investment:
Membranes and modules, initial cost $4/$m^2$	$36,400
Pumps and piping	3,000
EDC recovery system installation	5,000
Total Investment........	$44,400

Operating Expenses (Annual):
Membrane maintenance	$ 6,000
Manpower, 1/4 man @ $7,200 for 4-1/4 shifts (vacation, holidays, etc. included)	8,700
Utilities, power $400	400
Total Operating Expense........	$15,100

Capital Cost:
Cost to pay investment in 5 years with profit after 48% tax and 10% Depreciation	$14,000
Capital and Operating Cost	29,100
EDC credit (80% recovery) @ 2-1/2¢/lb.	10,400
Cost of EDC removal $/1,000 gal water	2.16

Payout:
Payout is calculated on the basis of the annual return diminished by a 48%
tax rate, plus allowable depreciation (10-year basis). No provision was
made for interest, since these costs can be included in the risk analysis
calculations. For example, the capital requirement of $44,400 is paid
back by the sum of the depreciation $4,440 plus the net return per year
(100-48%) ($8,538), or:

$$\text{Payout (5 years)} = \frac{\$44,400}{(0.52 \times 8,538) + 4,440}$$

This calculation allows a net 10% return on the investment per year.

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[*] Costs originally projected in 1972.
[†]Peters, M. Plant Design and Economics for Chemical Engineers. New York,
McGraw Hill, 1958.
[**]Perry, J.H. Chemical Engineers' Handbook. New York, McGraw Hill,
Section 26. 4th ed.

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TABLE 12

ECONOMIC ASSESSMENT

Feed: EDC Waste Stream

Processing Capacity: 20 gallons/minute

	$\bar{p} = \bar{p}_K$*	$\bar{p} = 10\ \bar{p}_K$**	$\bar{p} = 100\ \bar{p}_K$
Total Investment	$ 44,440	$ 11,640	$ 8,360
Total Operating Expense	15,100	10,300	9,220
Capital Cost	14,000	3,680	2,640
Capital + Operating Cost	29,100	13,980	11,860
EDC Credit (80% Recovery)	10,400	10,400	10,400
Cost of EDC Removal, $/1,000 gal	2.16	0.422	0.17

* $\bar{p}$ Permeability constant

** $\bar{p}_K$ Permeability constant for lab cast Kraton 1101

Stripped air recycle

Plant Feed Stream

Pervap Unit

P

EDC loaded air

Compressor

Condenser cooling at 15 - 20°C

Aqueous effluent

Possible recycle air blower system as determined by mass transfer requirements.

EDC with some dissolved water for recycle to primary separations unit of plant.
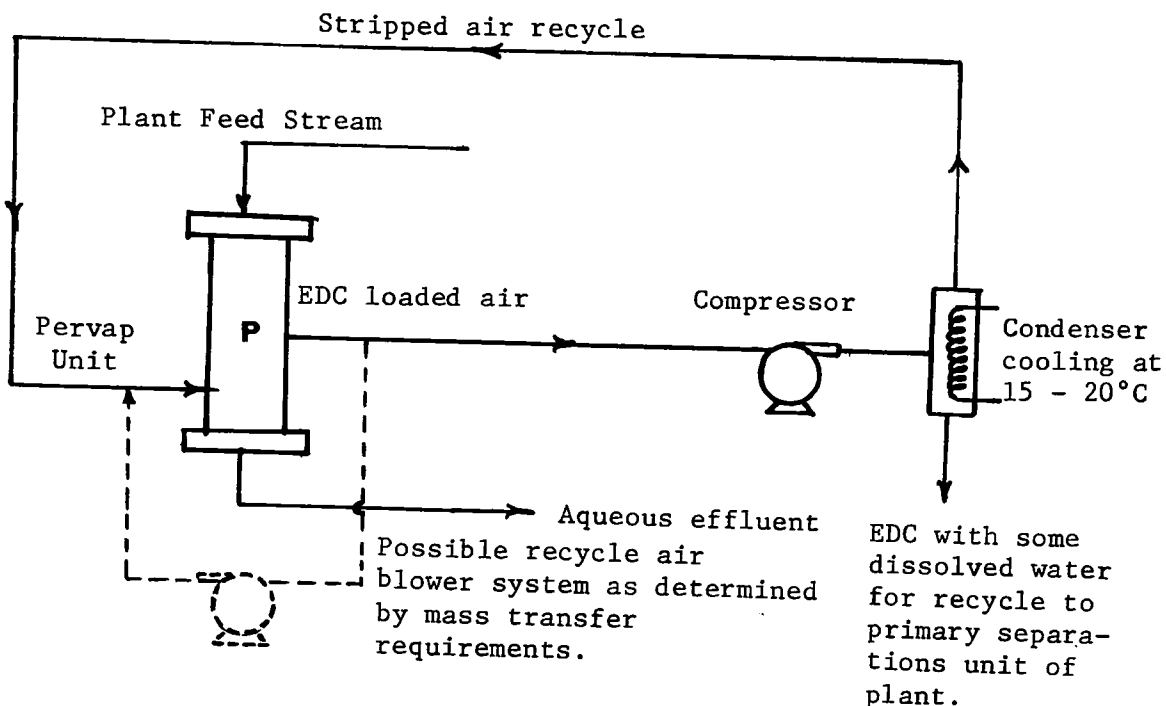
Figure 15. Flow scheme for proposed EDC recovery system.

The question of EDC recovery from the purging air stream is not a trivial one and would not likely be justified purely in terms of the value of recovered product. This necessary recovery operation, to prevent air pollution, in large measure determines the acceptable air flow rate in the pervaporation system. The recovery is aided by low flow rates and high effluent concentrations. Transport across the membrane can be maximized by increasing the stripping gas flow rate to maintain a low concentration in the stripping stream; thus a good concentration driving force for transport across the membrane is maintained. In Figure 14, the lowest flow rate tested appears to be adequate for maintaining the concentration gradient in this particular test configuration. It is significant that the air stream is free from the water pickup that would occur in a straight air-stripping process. The pervaporation process avoids the latent heat load associated with water content and also avoids a decrease in EDC volatility which occurs in the presence of a water phase. The present calculations and economics were based on an air counterflow of 30 lit/min (requiring a

compression to 10-12 atm, given a cooling sink at 15-20°C). A formal optimization on the air-flow specification was not undertaken since the pertinent cost contribution to the overall capital requirements was modest (15%). A definitive design for any given application would, of course, require further consideration.

The following observations are appropriate in reviewing the economic evaluation:

a. The projected cost of pervaporation processing ($2.16/1,000 gallons water) is comparable to the costs of processing by various other advanced waste water treatment processes shown in Table 13. With reasonable improvements in solute flux through the membranes, with larger scale operations, and with parallel reduction in membrane costs, the processing cost by pervaporation can be brought down toward costs associated with process water treatment techniques ($0.10 - 0.50/1,000 gallons)

b. The predominant cost items are the membrane investment and membrane maintenance. These costs are based on the costs of small units (approximately 1 m^2) now commercially available for other applications (e.g., hemodialysis). The actual cost should be much less for the larger installations.

c. The technique of pervaporation is economically very attractive when the recovered product has a high market value. Even for the "distress valued" ethylene dichloride, a substantial portion (33%) of the total cost is recovered in the credit of the recovered product. The product recovery is, therefore, a consequential aspect of the pervaporation economics.

d. Membrane life will depend on the peculiarities of the application; it will typically range between one and two years. A one-year life was assumed for the present evaluation.

e. Overall efficiency of ethylene dichloride recovery was assumed to be 80%. This allows for loss in the condensation system of as much as 10% of the ethylene dichloride removed by the pervaporation. With a recycling air purge, this loss can be significantly reduced.

TABLE 13

COMPARATIVE COSTS OF PROCESSING

Process	Cost per 1,000 gallons[*] (U.S. dollars)
Ultrafiltration	$0.10 to $ 5.00
Reverse Osmosis	.20 to 5.00
Centrifugation	.30 to 10.00
Electrodialysis	.20 to 5.00

[*]Porter, M.C., and A.S. Michaels, Chem. Tech. 55, January 1971.

APPENDIX - A

PERMEABILITY COEFFICIENTS

DIALYSIS WITH CONJUGATION

In Figure 16 is shown the schematic of the dialysis situation, ignoring solution boundary layers for the present. The feed compartment contains water and aniline solution. It is separated from the product (downstream) compartment by a polymeric membrane which has a very low hydraulic conductivity; i.e., convective transport by a pressure gradient is very low. The product compartment contains water, and an excess of acid over that required to establish the equilibrium.
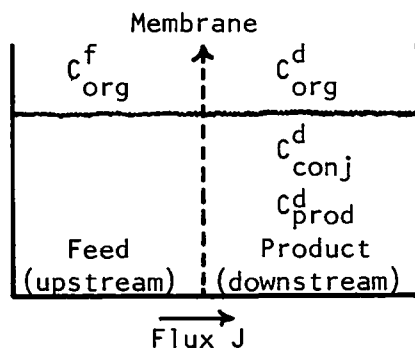

Figure 16. Dialysis scheme.

The concentrations are designated as follows:

C^f_{org} = concentration of organic solute in feed compartment

C^d_{org} = concentration of solute in product compartment

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C_{conj}^d = concentration of acid or base in product compartment

C_{prod}^d = concentration of anilinium or phenolate in product compartment.

The flux of aniline from the feed compartment to the product compartment is given by:

$$J_1 = \frac{-\bar{p}}{L}(C_{org}^d - C_{org}^f) \tag{10}$$

where J_1 is the steady state flux, C_{org}^f and C_{org}^d are the bulk concentrations under zero boundary layer conditions and $\bar{p}$ is a membrane permeability constant, and L is the membrane thickness.

At equilibrium, the relationship between the three components in the product compartment is given by:

$$K_{eq} = \frac{(C_{prod}^d)}{(C_{org}^d) \, (C_{conj}^d)} \tag{11}$$

The boundary conditions for the experiments to be described are:

$$(C_{org}^d)^o = (C_{prod}^d)^o = 0 \quad \text{at} \quad t = o \tag{12}$$

$$(C_{conj}^d)^o \neq 0 \quad ; \quad (C_{conj}^d) \ggg (C_{prod}^d) \tag{13}$$

The zero superscripts denote that the values refer to the beginning of the experiment. The rate equations, relating the changes in concentration in two compartments having volumes V_f and V_d (separated by membrane of thickness L and area A), and containing an excess of acid in the product compartment, are given by:

$$\frac{dC^f_{org}}{dt} = \frac{A\bar{p}}{V_f L} \; (C^d_{org} - C^f_{org}) \qquad\qquad (14)$$

$$\frac{dC^d_{org}}{dt} = -A\bar{p} \; \frac{(C^d_{org} - C^f_{org})}{V_d L} - \frac{dC^d_{prod}}{dt} \qquad\qquad (15)$$

$$= \frac{-A\bar{p}}{V_d L} \; (C^d_{org} - C^f_{org}) - K_{eq} \; C^d_{conj} \; \frac{dC^d_{org}}{dt} \qquad\qquad (16)$$

We assume that equilibrium is attained when C_{org} is consumed by conjugation in the product compartment as rapidly as C_{org} diffuses into the compartment. With the boundary conditions cited, this leads to a discrete expression for the permeability constant in terms of the measurable experimental variables, as follows:

$$\bar{p} = \frac{V_f \; (1 + K_{eq} \; C^o_{conj})L}{At \; (1 + K_{eq} \; C^d_{conj} + V_f/V_d)} \; \ln \; \frac{(C^f_{org})^o}{(C^f_{org} - C^d_{org})} \qquad\qquad (17)$$

Since the equilibrium constant for aniline is known, the experimental data allow the calculation of the permeability constant $\bar{p}$. The form of equation (17) is most useful for application to measurements with a rotating batch dialyzer. The use of equation (17) requires a knowledge of the concentration of the free aniline base in the product compartment. This was calculated from the analysis for total aniline, and a knowledge of the acid concentration and the equilibrium constant. The K_{eq} as designated in equation (17) is 1.9×10^{-4} (cm^2/sec), so that (C^d_{org}) is approximately equal to $(C^d_{prod})/(C^d_{conj}) \times 10^{-4}$, which is much smaller than C^f_{org}. If the product $K_{eq} \; (C^d_{conj}) >>> 1$, and $V_f \simeq V_d$, then the coefficient for the logarithm term of equation (17) can be simplified to:

$$P = \frac{V_f L}{At} \; \ln \; \frac{(C^f_{org})^o}{(C^f_{org} - C^d_{org})} \qquad\qquad (18)$$

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In our experiments (C_{org}^d) was maintained much lower than (C_{org}^f), so that the final expression contained only the term in $((C_{org}^f)^o/(C_{org}^f))$.

APPENDIX - B

DISTRIBUTION COEFFICIENTS

To determine the distribution coefficient of aniline between an aqueous solution and the membrane phase, a gas chromatographic method was used. A small sample of the membrane was equilibrated in a solution of aniline in water over-night. The membrane was blotted to remove surface liquids and then placed into the injection port of a gas chromatograph equipped with a flame ionization detector. The column packing used was a 10% OV-17 silicone on Chromosorb. The method has been published by Dupuy and Fore, et al.[18]. After the injection port is closed, the carrier gas sweeps the membrane sample free of aniline. At the completion of the run the membrane is retrieved and weighed on a microbalance. With the same sensitivity and attenuation settings, a 2.0 microliter sample of the equilibrating aniline solution is also analyzed. The ratios of peak areas are then used to calculate the distribution coefficient with allowances incorpo-rated for the relative densities of the solution and the polymer. The final distribution coefficient is dimensionless; i.e., $(g/cc)_{pol}/(g/cc)_{sol}$, where subscripts pol and sol indicate polymer and solution, respectively.

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18. Dupuy, H., and S. Fore. J. Amer. Oil Chem. Soc. 48:87a, 1971.

PERVAPORATION TRANSPORT ANALYSIS

We will consider the pervaporative membrane transport situation across the membrane M, separating a liquid and a vapor phase. Transport is subject to boundary layer resistances at 1-2 and at 3-4, as follows:
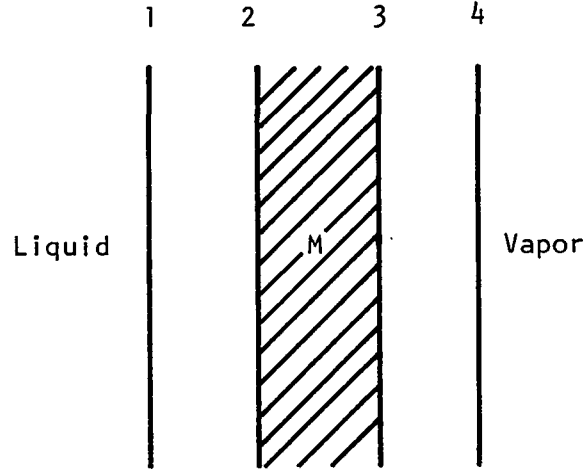

Figure 17. Schematic of membrane transport.

1. FLUX FORMULAS

For a given component i, one can formulate the transport through the three phases (liquid, membrane, vapor) as follows:

$$N_i^m = \frac{\bar{P}}{L} (c_2^m - c_3^m) \tag{19}$$

$$N_i^{liq} = k_{liq} (c_1^{liq} - c_2^{liq}) \tag{20}$$

$$N_i^{vap} = k_{vap} (c_3^{vap} - c_4^{vap}) \tag{21}$$

where N = molar flux (moles/cm^2 sec)

$\bar{p}$ = specific permeability coefficient

L = membrane thickness

m = membrane phase

liq = liquid phase

vap = vapor phase

k = mass transfer constant

C = concentration

Subscripts 1,2,3,4 refer to the boundaries as numbered in Figure 17 above. No convective flow is allowed across the membrane.

2. EQUILIBRIUM CONDITIONS AT THE INTERFACES

The fluxes given above will be equal at steady state and under conditions where accumulations in the membrane and in the boundary layers can be considered negligible. Additionally, one may accept the Lewis interface equilibrium:

$$f_2^{liq} = f_2^m \quad \text{and} \quad f_3^m = f_3^{vap} \tag{22}$$

where f represents the Lewis fugacity.

This leads to the expression:

$$\gamma_2^{liq} P_o \, x_2 = \gamma^m P_o \, z_2 \tag{23}$$

where γ is the solute activity coefficient, P_o is the standard solute vapor pressure, x_2 the solute mole fraction in the liquid, and z_2 the solute mole fraction in the membrane. It is noted that for dilute solutions,

$$C_2^{liq} = \rho^{liq} x_2 \quad , \quad C_2^m = \rho^m \, z_2 \tag{24}$$

Then

$$\frac{C_2^{liq}}{C_2^m} = \frac{\gamma_2^m \rho^{liq}}{\gamma_2^{liq}\rho^m} = S \tag{25}$$

where S is a distribution coefficient, and ρ's are densities.

Similarly at the vapor interface one obtains

$$\gamma_3^m P_o \quad z_3 = f_3^{vap} \simeq P_i \tag{26}$$

$$= C_3^{vap} RT$$

where P_i is partial pressure. From this expression comes:

$$\frac{C_3^{vap}}{C_3^m} = \frac{\gamma_3^m P_o}{RT\rho^m} \tag{27}$$

or a Henry's Law form:

$$\frac{C_3^m}{P_i} \frac{\rho^m}{\gamma_3^m P_o} = H \tag{28}$$

3. REDUCTION OF FLUX FORMULAS TO USABLE FORMS

Membrane concentrations in equation (19) can be replaced using equations (25) and (26) to yield:

$$N_i = \frac{\bar{P}}{L} \left[\frac{C_2^{liq}}{S} - RTHC_3^{vap} \right] = k_{liq} (C_1^{liq} - C_2^{liq})$$

$$= k_{vap}(C_3^{vap} - C_4^{vap}) \tag{29}$$

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To eliminate concentration terms that are not tractable analytically, we eliminate C_2^{liq} and C_3^{vap} algebraically to yield:

$$N_i = U_{liq} \, (C_1^{liq} - \beta C_4^{vap}) \tag{30}$$

where U_{liq} is the liquid phase mass transfer coefficient.

$$U_{liq} = \frac{\alpha_1}{1 + \dfrac{\alpha_1}{k_{liq}} + \dfrac{\alpha_2}{k_{vap}}} \tag{31}$$

$$\alpha_1 = \frac{\bar{p}S}{L} \tag{32}$$

$$\alpha_2 = \frac{RT\bar{p}H}{L} \tag{33}$$

$$\beta = \frac{\alpha_2}{\alpha_1} = \frac{RTH}{S} \tag{34}$$

4. APPLICATIONS TO TEST CELL CONFIGURATIONS

The pervaporation test cell can be used to obtain coefficients in the characterizing equation (30) as follows:

a. Assume that the membrane of area A is used to reduce the concentration in a recirculating liquid sink of volume V, and initial concentration $C_1^{liq}(o)$. The vapor side is maintained everywhere at a concentration C_4^{vap} by fresh supply. The mass transfer of solute is given by:

$$V \frac{dC_1^{liq}}{dt} = -AU_{liq} \, (C_1^{liq} - \beta C_4^{vap}) \tag{35}$$

leading to

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$$- \ln \left[\frac{C_1^{liq} - \beta C_4^{vap}}{C_1^{liq}(o) - \beta C_4^{vap}} \right] = \frac{U_{liq}A}{V} t \qquad (36)$$

on integration.

b. Alternatively, for a long path length, the solute accumulation in the vapor purge stream may not be ignored. For a vapor flow G, along a membrane device of length l and cross-sectional area A', one can write the material balance equation:

$$\frac{\partial (GC_4^{vap})}{\partial l} + U_{liq} (C_1^{liq} - \beta C_4^{vap}) A' = \frac{\partial (V_{vap} C_4^{vap})}{\partial t} \qquad (37)$$

When the vapor flow is fast relative to the liquid flow, then

$$-G \frac{dC_4^{vap}}{dl} = -U_{liq} (C_1^{liq} - \beta C_4^{vap}) A' \qquad (38)$$

and for any given t or C_1^{liq}

$$+ \ln \left[\frac{C_1^{liq} - \beta C_4^{out}}{C_1^{liq} - \beta C_4^{in}} \right] = \frac{-U_{liq}AS}{G} \qquad (39)$$

where A = A' x membrane length l
and

$$N_i = G (C_4^{out} - C_4^{in}) = -U_{liq}A \frac{\beta (C_4^{out} - C_4^{in})}{\ln \frac{C_1^{liq} - \beta C_4^{out}}{C_1^{liq} - \beta C_4^{in}}} \qquad (40)$$

From equation (40) one calculates the concentration in the efflux gas stream:

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$$C_4{}^{out} = \frac{C_1^{liq} + (C_1^{liq} - \beta C_4)\, \exp \dfrac{U_{liq}A}{G}}{\beta} \tag{41}$$

To calculate the change in liquid phase solute concentration, we can now write a material balance based on the change in vapor phase concentration, as follows:

$$V \frac{dC_1^{liq}}{dt} = G\,(C_4{}^{out} - C_4{}^{in}) \tag{42}$$

$$\frac{dC_1}{dt} = \frac{G}{V\beta}\left[C_1 + (C_1 - \beta C_4)\,\exp \frac{U_{liq}A\beta}{G} - \beta C_4{}^{in}\right] \tag{43}$$

$$= \frac{G\,(1 - \exp \dfrac{U_{liq}A\beta}{G})}{VA\beta}\;(C_1 - \beta C_4{}^{in}) \tag{44}$$

$$= \bar{U}\,(C_1 - \beta C_4{}^{in}) \tag{45}$$

which integrates to:

$$\ln \frac{C_1 - \beta C_4{}^{in}}{C_1(o) - \beta C_4{}^{in}} = \bar{U}\,t \tag{46}$$

$$\bar{U} = \frac{G}{VA\beta}\;(1 + \exp \frac{U_{liq}\beta}{G}) \tag{47}$$

APPENDIX - D

PERVAPORATOR ANALYSIS

The performance of a "once-through" pervaporator could be projected based on the following transport analysis. In this analysis, flat sheet membrane geometry, a countercurrent gas-liquid flow and constant fluid rates are assumed. The analysis, as developed, is for dilute solutions.

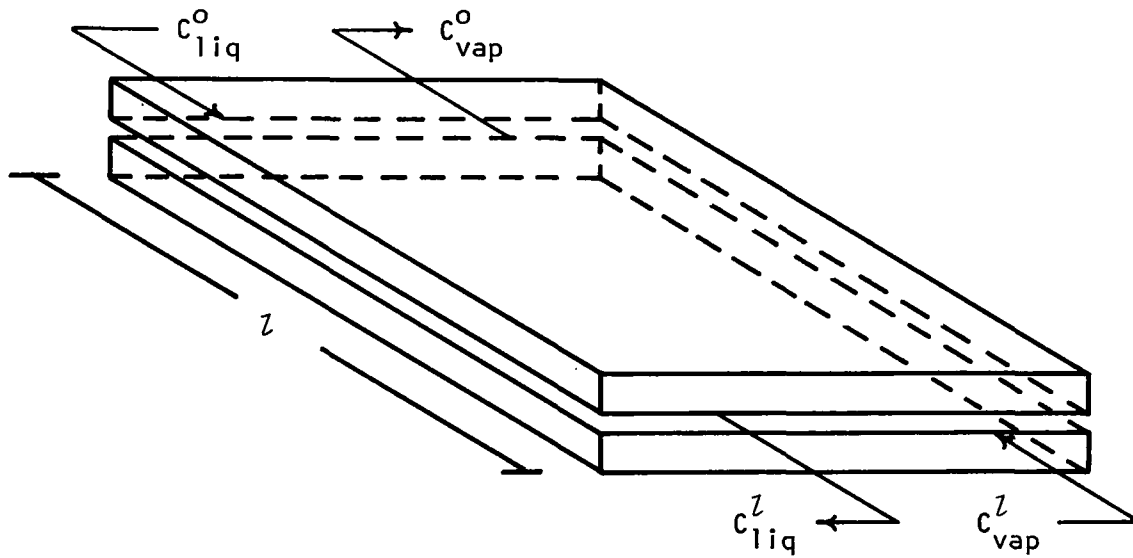Consider a section of stack-loaded pervaporator as shown in Figure 18.

Figure 18. Schematic of stack-loaded pervaporator.

At steady state,

Liquid-side material balance:

$$\frac{d}{d\ell} (G_{liq} C_{liq}) + U_{liq} A (C_{liq} - K_{eq} C_{vap}) = 0 \tag{48}$$

where G = flow rate

    C = concentration

    A = area

    U = mass transfer coefficient

    l = membrane length

    liq = liquid phase

    vap = vapor phase

    K_{eq} = equilibrium constant

    o = length 0

Gas-side material balance:

$$\frac{d}{dl} (G_{vap}C_{vap}) + U_{liq}A (C_{liq} - K_{eq}C_{vap}) = 0 \tag{49}$$

Equations (48) and (49) are a set of linear differential equations. These can be solved simultaneously using Laplace Transforms and known boundary conditions $(C_{liq}^{o}, C_{vap}^{l})$.

Rearranging equations (48) and (49) we have:

$$\left(\frac{G_{liq}}{A}\right) \frac{dC_{liq}}{dl} = U_{liq} (K_{eq}C_{vap} - C_{liq}) \tag{50}$$

and

$$\left(\frac{G_{vap}}{A}\right) \frac{dC_{vap}}{dl} = U_{liq}(K_{eq}C_{vap} - C_{liq}) \tag{51}$$

Thus,

$$\frac{dC_{liq}}{dl} = n_1 (K_{eq}C_{vap} - C_{liq}) \tag{52}$$

$$\frac{dC_{vap}}{dl} = n_2 (K_{eq}C_{vap} - C_{liq}) \tag{53}$$

67

Where $n_1 = \dfrac{U_{liq}A}{G_{liq}}$ (54)

$n_2 = \dfrac{U_{liq}A}{G_{vap}}$ (55)

$\gamma = \dfrac{G_{liq}}{G_{vap}} = \dfrac{n_2}{n_1}$ (56)

Laplace Transformation of (52) and (53) would yield

$$\bar{C}_{liq}s - C^o_{liq} = n_1 K_{eq}\bar{C}_{vap} - n_1 \bar{C}_{liq}$$ (57)

$$\bar{C}_{vap}s - C^o_{vap} = n_2 K_{eq}\bar{C}_{vap} - n_2 \bar{C}_{liq}$$ (58)

In order to evaluate C_{liq} in pure solution (solute mole fraction z = 1), and C_{vap} with no solute present (z = 0), equations (57) and (58) are rearranged and subject to inverse transformation. Whence

$$C^l_{liq} = \frac{[(1-K_{eq}\gamma)\ \exp\ (-\xi l)]}{[\ 1-K_{eq}\gamma\ \ \exp\ (-\xi l)]}\ C^o_{liq}$$

$$+ \frac{K_{eq}[1 - \exp\ (-\xi l)]}{[1-K_{eq}\gamma\ \exp\ (-\xi l)]}\ (C^l_{vap} + \gamma C^o_{liq})$$ (59)

where $\xi = \dfrac{U_{liq}A}{G_{liq}}\ (1 - K_{eq}\gamma)$ (60)

and $C^o_{vap} = C^l_{vap} + \gamma(C^o_{liq} - C^l_{liq})$ (61)

are obtained.

Equations (59) and (61) are used to generate concentration profiles in liquid and gas phases along the length of the stack-loaded pervaporator.

APPENDIX – E

MEMBRANE AREA REQUIREMENT

Plant Capacity   :   20 gallons/minute

Feed Composition   :   0.6 wt % ethylene dichloride

3.5 wt % hydrochloric acid in water

Specification   :   90% removal of ethylene dichloride

Design Parameters : k° (mass transfer coefficient)

D   (diffusion coefficient)

Design parameters k° and D are obtained from the permeability measurements at different flow rates. The overall liquid side mass transfer coefficient is given by:

$$U_{liq} = \frac{1}{\frac{1}{\alpha_1} + \frac{1}{k_{liq}} + \frac{\alpha_2}{\alpha_1 k_{vap}}} \tag{62}$$

where $\alpha_1 = \frac{\bar{p}S}{L}$ (63)

and $\alpha_2 = RTH\bar{p}/L$ (64)

where T is temperature, L is membrane thickness and S is solubility. Since k_{vap} is extremely high, equation (62) can be expressed as:

$$U_{liq} = \frac{1}{\frac{1}{\alpha_1} + \frac{1}{k_{liq}}} \tag{65}$$

but the specific permeability coefficient $\bar{p}$ and U_{liq} are related in the .form

$$U_{liq} = \bar{p}/L \tag{66}$$

Therefore, substituting the relationships (63) and (66) in (65) we get:

$$\frac{1}{\bar{p}} = \frac{1}{DS} + \frac{1}{Lk_{liq}}$$ (67)

However, liquid side mass transfer coefficient is typically related to the feed velocity v (cm/sec) in the form:

$$k_{liq} = k° \; N_{Re}^{0.8}$$ (68)

based on Gilliland correlation[17], where N_{Re} is the Reynold's number.
Substituting (68) for k_{liq} we get

$$\frac{1}{\bar{p}} = \frac{1}{DS} + \frac{1}{Lk° \; N_{Re}^{0.8}}$$ (69)

and, therefore, a plot of $\bar{p}^{-1}$ vs. $N_{Re}^{-0.8}$ (Wilson Plot) would give:

$$Slope = \frac{1}{Lk°}$$ (70)

$$Intercept = \frac{1}{DS}$$ (71)

Since membrane thickness L and solubility S are known, k° can easily be computed.
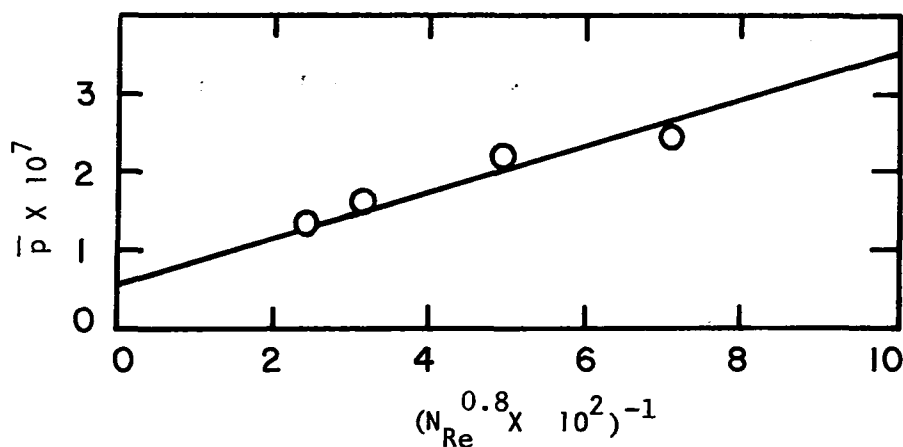

Figure 19. Wilson plot.

Figure 19 shows a Wilson Plot obtained from the experimental data. The slope and intercept are respectively 2.03×10^8 sec/cm^2 and 0.56×10^7 sec/cm^2. Since the film thickness L is 28×10^{-4} cm and S is 50, k° and D are respectively 1.76×10^{-6} and 3.6×10^{-9}, as per equations (70) and (76).

The liquid phase concentration profile (see Appendix D) is given by:

$$C^{l}_{liq} = \frac{[(1-K_{eq}\gamma) \exp(-\xi l)]}{[1-K_{eq}\gamma \exp(-\xi l)]} C^{o}_{liq}$$

$$+ \frac{K_{eq}[1 - \exp(-\xi l)]}{[1-K_{eq}\gamma \exp(-\xi l)]} (C^{l}_{vap} + \gamma C^{o}_{liq}) \tag{72}$$

where $K_{eq} = RTH/S$ \hfill (73)

$$\xi = \frac{U_{liq}A}{G_{liq}} (1 - K_{eq}\gamma) \tag{74}$$

$$\gamma = G_{liq}/G_{vap} \tag{75}$$

$$U_{liq} = \alpha_1/(1 + \alpha_1/k_{liq}) \tag{76}$$

$$\alpha = \frac{DS}{L} \tag{77}$$

Also:

$$\% \text{ Solute Removal} = \frac{C^{o}_{liq} - C^{l}_{liq}}{C^{o}_{liq}} \tag{78}$$

By use of equations (72) and (78), it is possible to determine film area required for a specified solute removal.

As an illustration consider that the module contains 100,000 fibers made of the experimental Kraton 1101 film, each fiber with an inside diameter of 100 microns and an outside diameter of 250 microns. Then for 20 gallons per minute feed flow rate,

$$N_{Re} = 82.3$$

but $k° = 1.76 \times 10^{-6}$ (From Wilson Plot)

Therefore, $k_{liq} = k° N_{Re}^{0.8} = 6 \times 10^{-5}$ cm/sec

$D = 3.6 \times 10^{-9}$ cm^2/sec (Calculated from Wilson Plot)

Therefore, $\alpha_1 = 7.2 \times 10^{-5}$ since S = 50, L = 25×10^{-4} cm

$\gamma = 2.55$

$K_{eq} = RTH/S = 1.95 \times 10^{-5}$

since $R = 0.108$, $T = 298°K$, $H = 3.03\ 10^{-5}$

Therefore, $\xi = 1.21 \times 10^{-5}$

Now,

$C_{liq}^{°} = 0.008$, $C_{vap}^{l} = 0$

Thus if $l = 145$ meters, C_{liq}^{l} from equation (72) is 0.008 and the solute removal is 90%.

Area/meter fiber length = 6.28×10^{-4} m^2/m.

Thus,

Total Membrane Area = $145 \times 6.28 \times 10^{-4} \times 1 \times 10^5$

$= 9.1 \times 10^3$ m^2.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This project evaluates dialysis for its potential for treatment/recovery of a number of organics and inorganics found in industrial wastes along the Lower Mississippi River.

The feasiblity of three membrane techniques was developed.

1. The use of acid and base conjugation on the downstream side of membranes perm-selective to aniline and phenol.
2. The use of a chelating complex for Al, Cu, and Pb ions.
3. The use of a pervaporation scheme in which a hydrophobic membrane passed volatile contaminants such as nitrobenzene and ehtylene dichloride to a downstream vapor purge.,

Rotating batch and mimi-plant plate dialyzers were used. A design projection of full-scale operation was made for pervaporation of ethylene dichloride.

Theoretical and practical aspects of the diffusion phenomena were discussed.

17.	KEY WORDS AND DOCUMENT ANALYSIS		
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