



Temperature effects on the separation of isomeric xylenes using the pervaporation process
by William Blaine Downs

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

The separation of the xylene isomers was investigated by pervaporation using several commercially available polymeric films as membranes. The films were tested with two mixtures of xylene isomers over a range of temperature to determine whether or not the degree of separation was affected. In order to compare results a separation factor was calculated which is analogous to the relative volatility used in distillation. Since para xylene is the most volatile isomer, it was chosen as the basis when calculating the separation factor.

When testing the ortho-xylene, para-xylene mixture a polyimide film gave the highest degree of separation with a separation factor of 2.18 at 132°C. A cellophane film had the lowest separation factor of 0.83 at 132°C indicating that the ortho-xylene was enriched in the product stream. When the meta-xylene, para-xylene mixture was tested a polyvinyl fluoride film gave the highest separation factor of 1.22 at 60°C while a polyethylene film had the lowest separation factor of 1.01 at 26°C. For comparison the relative volatility of the meta-xylene, para-xylene mixture is 1.01. It is 1.08 for the ortho-xylene, para-xylene mixture.

Several membranes had separation factors that increased when the temperature increased, while other films had separation factors that decreased when the temperature increased. A possible mechanism is discussed that may explain this behavior.

Most of the commercially available films tested can be used to enrich the para-xylene isomer in the permeate. In general the degree of separation obtained by pervaporation of xylene mixtures is higher for the ortho-xylene, para-xylene mixture than for the meta-xylene, para-xylene mixture.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

December 1985

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William Blaine Downs

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ACKNOWLEDGEMENTS

I wish to thank Phil McCandless for his guidance and insights during the course of this experimental investigation. Thanks should also be given to the staff and faculty in the Chemical Engineering department for their support in ways too numerous to mention. The financial backing from the guaranteed student loan program made this educational undertaking possible and a word or two is mentioned here in behalf of the continuation of this program. To my parents I want to say thanks, however thanks doesn't adequately express the gratitude and appreciation I have for their warmhearted encouragement and love. In addition, Lyman Fellows should be given mention here as a person who could find or fix a piece of the apparatus in short order when time was pressing.

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TABLE OF NOMENCLATURE

A	Area
C	Concentration
d_0	Diffusivity constant
D	Diffusion coefficient
E	Activation energy
L	Film thickness
p	Pressure
Q	Permeation rate
R	Universal gas constant
S	Solubility constant
T	Temperature
X	Mole fraction of para-xylene in the feed
Y	Mole fraction of para-xylene in the permeate

Greek letters

α Separation factor, relative volatility

Subscripts

1, 2 Component 1 and Component 2

ABSTRACT

The separation of the xylene isomers was investigated by pervaporation using several commercially available polymeric films as membranes. The films were tested with two mixtures of xylene isomers over a range of temperature to determine whether or not the degree of separation was affected. In order to compare results a separation factor was calculated which is analogous to the relative volatility used in distillation. Since para xylene is the most volatile isomer, it was chosen as the basis when calculating the separation factor.

When testing the ortho-xylene, para-xylene mixture a polyimide film gave the highest degree of separation with a separation factor of 2.18 at 132 °C. A cellophane film had the lowest separation factor of 0.83 at 132 °C indicating that the ortho-xylene was enriched in the product stream. When the meta-xylene, para-xylene mixture was tested a polyvinyl fluoride film gave the highest separation factor of 1.22 at 60 °C while a polyethylene film had the lowest separation factor of 1.01 at 26 °C. For comparison the relative volatility of the meta-xylene, para-xylene mixture is 1.01. It is 1.08 for the ortho-xylene, para-xylene mixture.

Several membranes had separation factors that increased when the temperature increased, while other films had separation factors that decreased when the temperature increased. A possible mechanism is discussed that may explain this behavior.

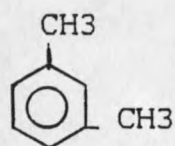
Most of the commercially available films tested can be used to enrich the para-xylene isomer in the permeate. In general the degree of separation obtained by pervaporation of xylene mixtures is higher for the ortho-xylene, para-xylene mixture than for the meta-xylene, para-xylene mixture.

INTRODUCTION AND PURPOSE

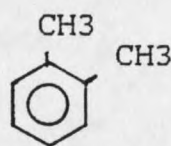
The production of the majority of dimethyl-benzene, commonly referred to as xylene, comes from the petroleum refining industry as a portion of the product of the catalytic reformer [9]. Mixed xylenes which contain the meta, ortho and para isomers along with ethyl-benzene have various compositions depending upon the conditions in the reformer. The structures for these isomers are:



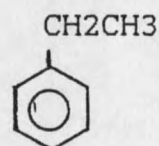
Para



Meta



Ortho



Ethyl-Benzene

This fraction of the reformer product boils over a very limited temperature range with each isomer having a boiling point within that range (Table 1).

Table 1. Physical data for xylenes and ethyl-benzene

C-8 Isomer	Boiling Pt.	Melting Pt.
Para-xylene	138.35 °C	13.26 °C
Meta-xylene	139.1 °C	-47.87 °C
Ortho-xylene	144.4 °C	-25.18 °C
Ethyl-benzene	136.2 °C	-94.4 °C

Mixtures of these xylenes are very difficult to separate by conventional distillation because of the low

relative volatilities between the isomers (Table 2). A large value for the relative volatility implies that it is easier and less costly to separate the components in the mixture. For an azeotropic mixture, the relative volatility is unity indicative of a mixture that cannot be separated by a simple distillation process. Various mixtures of isomeric xylenes have relative volatilities near one indicating the difficulty encountered when undertaking xylene separation by distillation.

Individual xylene isomers that are useful as chemical intermediates require a purity of at least 99.2%, 98.6% and 95.3% for the para, meta and ortho-xylene respectively. The minimum number of plates that are required for a distillation column to achieve this degree of separation for various xylene mixtures are presented in Table 2. Plate efficiencies less than 100% and columns operating without total reflux conditions would increase this number of plates.

Table 2. Relative volatility and the minimum number of theoretical plates required to obtain products of sufficient purity.

Mixture	Rel. Vol. α	Min. # of Theoretical Plates
P-M xylene	1.01	894
P-O xylene	1.08	102
P-xylene ethyl-benzene	1.06	150
M-O xylene	1.105	74

Uses for Xylenes

The mixed xylenes are primarily used to increase the octane number in gasoline and will become more widely used in this capacity as the demand for unleaded gas increases due to federal regulations limiting the use of tetra-ethyl lead [1]. There is the possibility that the demand for mixed xylenes as octane enhancers may cause the price to increase to a point where it is no longer competitive to separate the para-xylene. Para-xylene is the most important isomer with 80% going towards the production of dimethyl terephthalate and terephthalic acid. These chemical intermediates are necessary for the manufacture of polyester fibers useful for household fabrics, carpets and wearing apparel. The remainder is used for polyester

bottle resins and films. Ortho-xylene is in demand as a raw material for phthalic anhydride production and meta-xylene is used to produce isophthalic acid. These chemical intermediates are the basis for pigments, fungicides and unsaturated polyester resins. Current production of para-xylene is 4.4 billion lbs/year and is expected to increase in the future.

Separation Processes Currently in Use

Ethyl-benzene is separated from the mixture by two distillation columns in series that have a combined total of 300 trays which are operated under high reflux ratio. Ortho and meta-xylene are more easily separated due to the 4 degrees difference in boiling points. However, in practice it still requires 150 trays and a high reflux ratio. The meta-xylene, para-xylene separation is not attempted by conventional distillation. At the present time the separation of para-xylene is effected by various crystallization processes that take advantage of the large difference in freezing points. Because of various eutectics that are formed during the crystallization only 60-70% of the para-xylene is recovered per pass.

Adsorption columns containing Zeolite materials are becoming more widely used by industry as indicated by the increasing number of new facilities that have recently been

constructed. One of the xylene isomers is selectively adsorbed on a substrate until the column is saturated. At this point the column is stripped with a liquid that can easily be separated from the xylene and recycled. Adsorption is much more efficient than distillation with a 90-95% recovery per pass. Both of these methods for separating xylene isomers are energy intensive.

The Pervaporation Process

The pervaporation process or liquid permeation is a process where a liquid mixture is brought into contact with a plastic film or membrane and allowed to diffuse through the membrane. The membrane has no pores in it like a molecular sieve but retains its structural integrity as a tangle of long polymer chains. On the down stream side of the membrane the diffusing molecules enter the gas phase with one of the constituents of the mixture enriched in the product stream. This product stream is referred to as the permeate. The gas phase is sustained by maintaining the downstream pressure below the vapor pressure of the permeate vapor. Since a phase change occurs in the pervaporation process, the energy input is at least equal to the heat of vaporization of the permeating mixture.

The pervaporation process has several potential advantages over other separation processes. By using

pervaporation the damaging effects high temperatures have on heat labile compounds are avoided. Proteins, toxins and other biologically active chemicals which are sensitive to heat have the potential of being separated and purified by this technique. Pervaporation also can have the advantage of excellent selectivity for mixtures that are otherwise difficult to separate such as azeotropic mixtures or mixtures of liquids with only small differences in vapor pressures like the xylene mixtures discussed above.

The Purpose for the Experimental Investigation

Although the adsorption process is becoming more popular, pervaporization results for xylene isomers permeating through plastic membranes indicates that an advantageous separation may be obtained by this process. Since the present commercial methods for separating these isomers are very energy intensive, any method that could significantly reduce the operational cost of this separation should be investigated. The purpose of this investigation was to evaluate various commercially available polymer films as pervaporation membranes and to determine the degree of separation of xylene isomers that could be achieved over a range of temperatures.

PREVIOUS RELATED RESEARCH

The earliest research on the membrane permeation process began when researchers found that some gases permeate through a thin sheet of natural rubber. In 1866, T. Graham studied permeation through rubber membranes and concluded that the permeation process was a sequence of, 1) solution in the membrane, 2) diffusion through the membrane and 3) evaporation or desorption at the other side of the membrane [11]. This has been the accepted mechanism for gas permeation since that time.

In gas permeation, solubility in the membrane tends to be low and Henry's Law applies. Permeation essentially follows Fick's first law of diffusion:

$$Q = \frac{DS(p_2 - p_1)}{L}$$

where D is the diffusion coefficient, S is the solubility coefficient, L is the thickness, Q is the permeation rate per unit area and p₁ and p₂ are the pressures on each side of the membrane.

The Liquid Permeation Mechanism

For liquid permeation or pervaporation the diffusing molecules must first dissolve in the membrane, diffuse through the membrane and at some point evaporate into the

gas phase. R.C. Binning et.al. [10] suggested that within the membrane itself there was a liquid-vapor interface dividing a solution phase and a vapor phase zone as depicted in Figure 1. The swollen solution phase of the membrane therefore would have a much different permeability than the membrane in the unswollen state or vapor phase zone. This transition from liquid to vapor may not happen at a well defined interface, but rather across the entire membrane which varies from a swollen to unswollen states. When the diffusing molecules reach the downstream surface they escape from the surface by maintaining a pressure below the vapor pressure of the permeate.

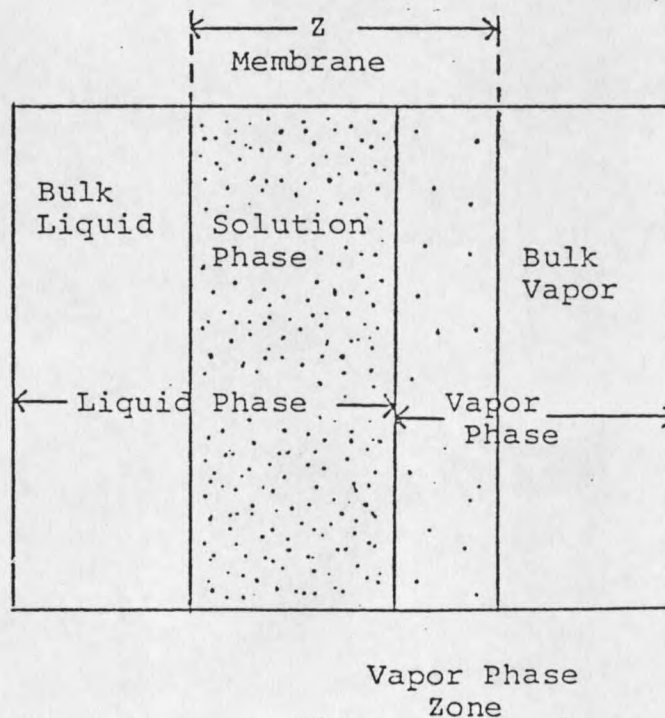


Figure 1. The solution phase and the vapor phase zones within the membrane.

Since the permeability would be different for the vapor phase zone and the solution phase zone, additional variables are introduced into Fick's First Law of diffusion. Obtaining the composition of the permeate at the solution phase zone, vapor phase zone interface is impossible and another method is used to describe the diffusion process. Instead of using separate diffusion rate constants for each zone Binning gives the permeation rate in terms of an overall diffusion rate with the assumption that the controlling rate is in the vapor phase zone [10]. This simpler form of Fick's Law is:

$$Q = \frac{D (C_2 - C_1)}{L}$$

where Q is the permeation rate, C_1 and C_2 are the concentrations on each side of the membrane, L is the membrane thickness and D is an overall diffusion constant.

Membrane selectivity

Binning states that the more permeable molecules are the ones that can more easily diffuse from site to site within the membrane [10]. One molecular species will preferentially permeate through the membrane and become enriched in the permeate as shown in Figure 2. At the end Binning states that the difference in permeation rates, hence selectivity, results from the difference in molecular

size and shape and in the interaction between the permeating species and the membrane materials. Previous research has shown for the para-xylene, meta-xylene mixture or the para-xylene, ortho-xylene mixture, para-xylene is generally the more permeable molecule [4,5,8].

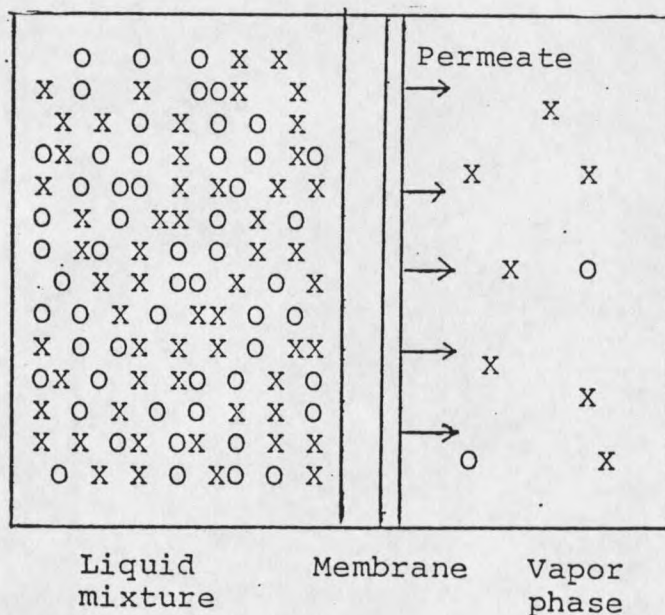


Figure 2. Membrane selectivity

Other researchers [5,8] have indicated that the selectivity of a membrane can be altered by the introduction of plasticizers and by preconditioning the membrane. Sikonia [8] demonstrated that the introduction of clathrates into a poly(vinylidene fluoride) membrane made the membrane permeable to xylenes and selective for para-xylene. The poly(vinylidene fluoride) membrane without any

clathrate addition was very impermeable to xylenes. When these membranes were placed in an oven at elevated temperatures (130-145 °C) prior to being tested, the selectivity for p-xylene varied remarkably. Michaels [8] modeled the structure of a polyethylene membrane as a molecular sieve or screen with amorphous regions (holes) dispersed between interconnected crystalline elements (mesh). By annealing and then recrystallizing the membrane with xylene isomers, the size and distribution of the holes was altered, changing the permeability and selectivity of the membrane.

A polymeric membrane can also be thought of as a tangle of long molecular chains in constant thermal motion with diffusing molecules moving from one position or site to another. A molecule that migrates to a new site must have a site available and an open pathway to that site which in turn depends on the thermal motion of the polymer. For large molecules the size and shape of the diffusing molecule determines the hole size required. If the polymer membrane contains suitable groups that participate in hydrogen bonding, those molecules that readily form hydrogen bonds may diffuse from one bonding site to another. Molecules that cannot form the hydrogen bonds do not diffuse across the membrane by this method [7].

M.H.V. Mudler et.al. [4], studying xylene permeation through cellulose acetate films, gives the molar volumes of

xylenes in increasing order as ortho-xylene < meta-xylene < para-xylene (Table 3). Mudler concludes from his experiments that ortho-xylene is more soluble in cellulose acetate films. This paradox of higher solubility of ortho-xylene in the polymer and selectivity favoring para-xylene had to be explained.

Table 3. Molecular volume and cross sectional areas for xylene isomers.

Compound	Molecular Vol. ³ A	Cross Sectional Area ² A
o-Xylene	59.7	7.65
m-Xylene	59.8	7.20
p-Xylene	59.9	6.92

A.S. Michaels [5] explained that molecules move through a polymer with their major axis aligned and the molecule presenting the smallest cross-sectional area normal to the major axis would diffuse preferentially. The para-xylene isomer permeating through a polyethylene film apparently presents a smaller cross-sectional area normal to the major axis than either ortho-xylene or meta-xylene and therefore permeates faster in spite of its larger volume.

Mudler concluded that permeability is determined by solubility and diffusivity. In the para-xylene and ortho-xylene system, the higher diffusivity of para-xylene more than accounts for the higher solubility of ortho-xylene in the cellulose acetate membrane.

The Separation Factor

A separation factor is used to measure the selectivity of a membrane. The separation factor, α , is defined as the concentration ratio in the permeate divided by the concentration ratio in the feed.

$$\alpha = \frac{X_1/X_2}{Y_1/Y_2}$$

Here X_1 and X_2 are the weight percents of compounds one and two in the permeate and Y_1 and Y_2 are the weight percents of compound one and two in the feed. For isomers the weight percent will equal the mole percent and can be used interchangeably. If only two permeating species are present and the more permeable compound is chosen as the basis for calculation, the separation factor can be rewritten as:

$$\alpha = \frac{Y(1-X)}{X(1-Y)}$$

Here Y is the mole fraction of the component chosen as the basis in the feed and X is the mole fraction of the same component in the permeate. This separation factor is

analogous to the relative volatility encountered in distillation.

Temperature effects

The temperature dependence for this type of activated diffusion is expected to follow an Arrhenius type expression:

$$D = d_0 \exp(-E/RT)$$

where E is the activation energy, D is the diffusivity, R is the universal gas constant, T is the temperature and d_0 is the diffusional rate constant.

Since a phase transition takes place during the pervaporation process there must be an input of enthalpy into the process. Rautenbach and Albrecht [6] have developed a mathematical model for mass transport of mixtures through a membrane based on the sorption, diffusion and desorption model and introduce the corresponding energy balances into their mathematical model. Their conclusions imply that this vaporization results in a temperature drop across the membrane which lowers the permeate flux. The temperature drop can be reduced if the mixture to be separated were circulated past the membrane under turbulent conditions thereby increasing the heat transfer coefficient between the liquid and the membrane.

Hydraulic effects

D.R. Paul [3] proposes that the rate liquids permeate through highly swollen polymeric membranes only depends on the concentration gradient in the membrane. They conducted a series of hydraulic permeation tests on highly swollen rubber membranes in which the volume fraction of rubber ranged from 0.14 to 0.32 and pressure varied between 400 - 500 psi. The same membranes were tested using the pervaporation mode. From these experiments they conclude that there is a ceiling or limit to the hydraulic flux which is nearly identical to the flux obtained by pervaporation. Their conclusion states that the value for the pervaporation flux is the limit for membrane productivity which is approached by the reverse osmosis process operating at extremely high pressures.

For slightly swollen systems, Paul [3] mentions that the ceiling flux for hydraulic permeation would not be significant until much higher pressures were reached. The driving force should be the same regardless of whether pervaporation or hydraulic pressure is used to establish the permeation process. Therefore, the flux is a function of the activities at the surfaces of the membrane and is independent of how these activities are established.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus is depicted in Figure 3. It consisted of the following: (1) Pervaporation test cell and circulating system; (2) Controlled temperature environment; (3) Vacuum system with cold traps; and (4) Permeate composition analysis equipment. Each of these components is discussed in detail below.

Pervaporation Cell and Circulating System

The pervaporation cell is shown in Figure 4. The cell consisted of two 8 cm. dia. stainless steel flat face flanges made by modifying a large pipe union, held together with a large stainless steel nut. Inside one of the flanges was a space large enough to hold a 6 cm. dia. scintered metal disc and filter paper disc for membrane support. This flange was connected to the vacuum system using Swedgelock fittings and 1/2 inch teflon tubing. The other flange had straight threads matching the large nut and had a cylindrical space large enough to allow liquid to circulate past the membrane. The membrane was sandwiched between the two flanges and the large nut was torqued to approximately 300 ft-lb. Offset grooves were cut into the face of each flange for Viton "O" rings which completed the seal.

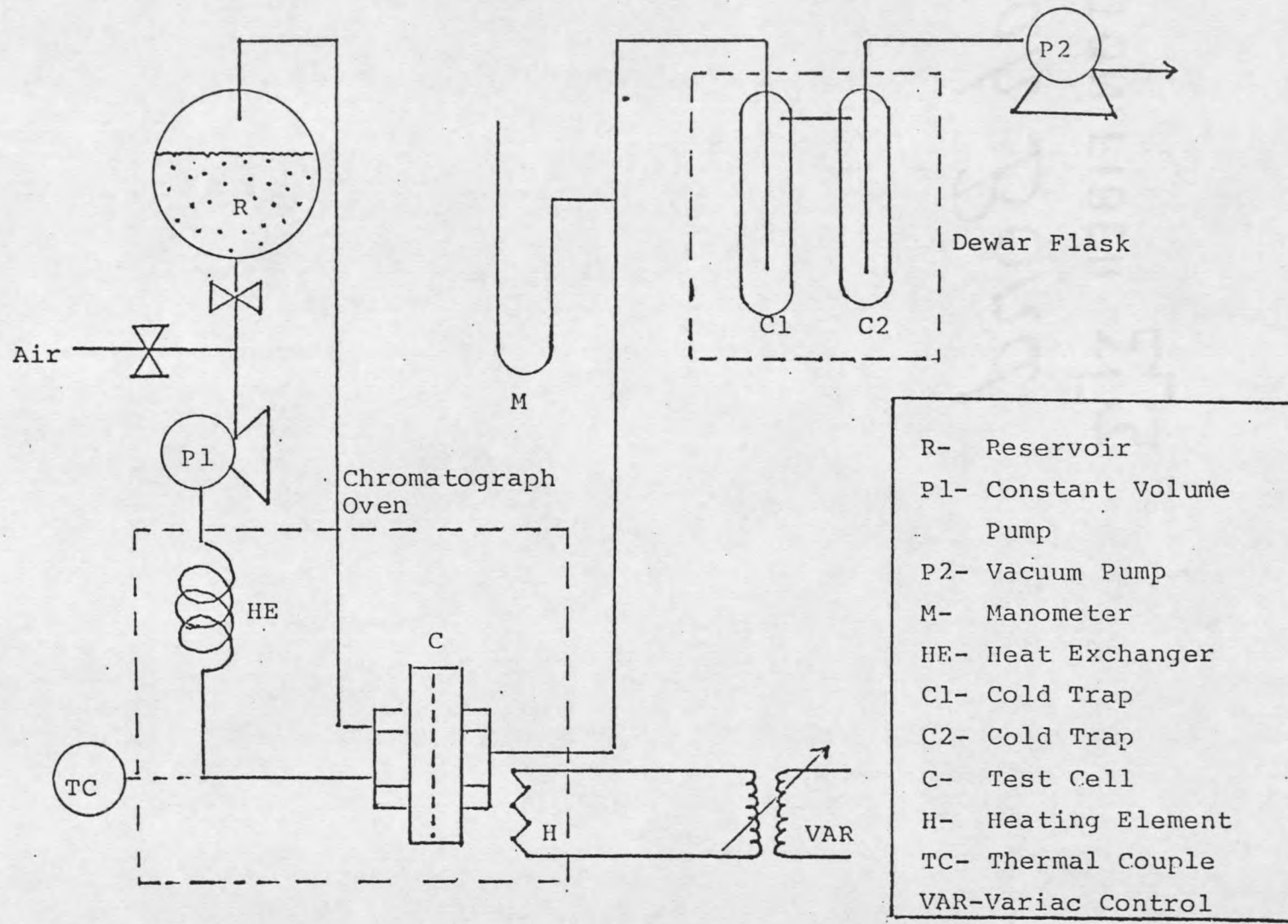


Figure 3. Pervaporation equipment diagram.

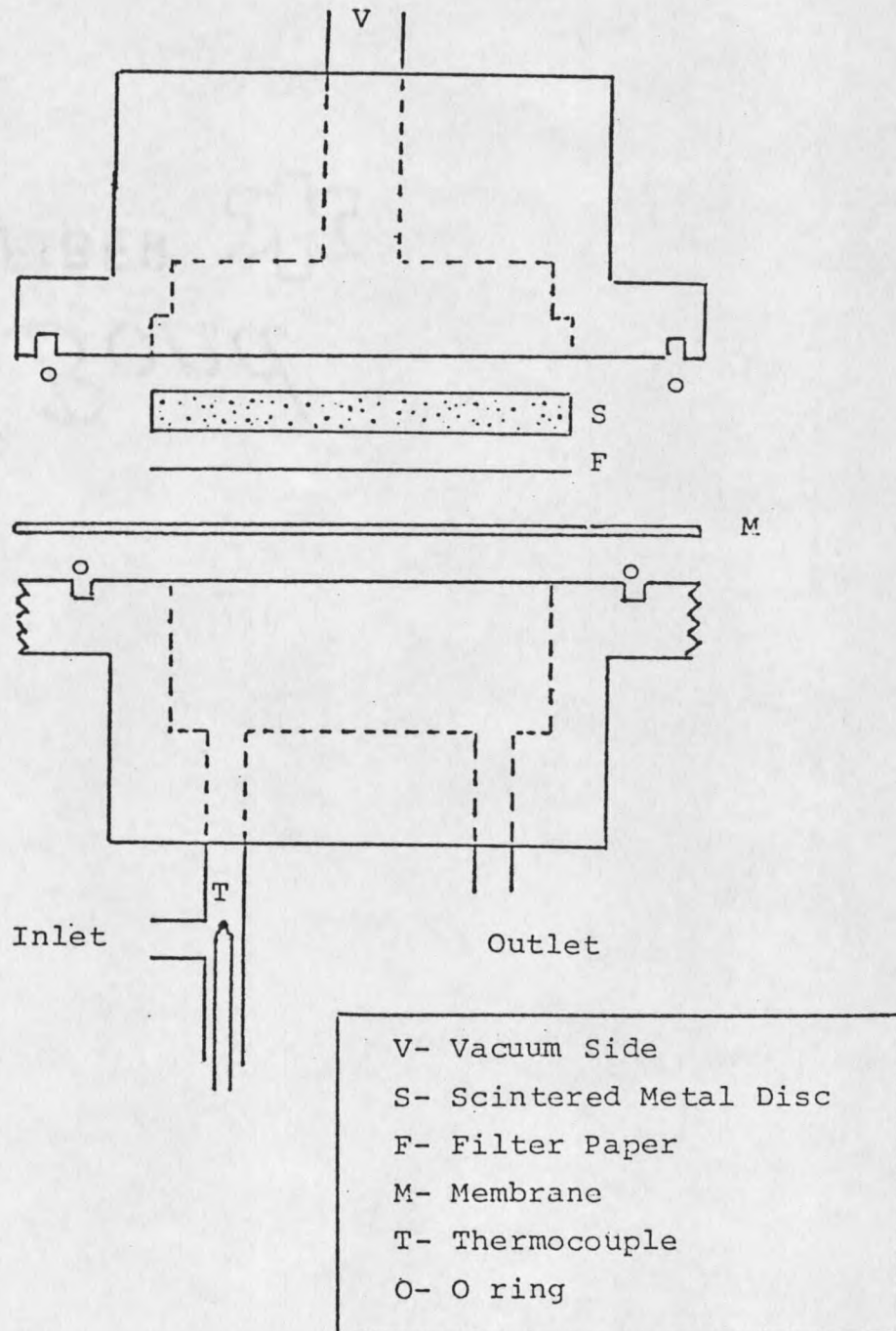


Figure 4. Pervaporation test cell.

Approximately 500 ml of a xylene mixture was stored in a Teflon separatory funnel which acted as the reservoir. At the base of the funnel was a valve to isolate the reservoir from the system. A diaphragm type metering pump circulated the liquid through a heat exchanger, past the membrane and back into the separatory funnel at a rate of 15 ml/min. The heat exchanger consisted of approximately 7.5 meters of 1/8 in. stainless steel tubing that connected directly to the inlet of the test cell. Care was taken to orientate the inlet below the outlet to ensure that there were no gas bubbles in contact with the membrane. Before a new membrane was tested, air was used to purge the system to recover the xylene mixture that remained in the tubing, heat exchanger and test cell.

Controlled Temperature Environment

A chromatograph oven measuring 20 x 26 x 35 cm. was used to house the test cell and heat exchanger. In the base of the oven was a fan for air circulation and a heating element that was controlled by a Variac transformer. Two sections of threaded rod supported the test cell in the center of the oven. The temperature of the stream entering the test cell could be controlled to within 2 degrees celsius and ranged from room temperature to 132 °C depending on the setpoint of the variac. One

eighth inch teflon tubing for the xylene supply stream, the thermocouple wire and the 1/2 inch vacuum line passed through holes in the wall of the enclosure.

Vacuum System & Cold Traps

Two cold finger Pyrex condensers were connected in series to the vacuum line to the test cell using ground glass fittings and spring clamps. One condenser acted as a permeate collector while the other served to prevent back diffusion from the vacuum pump and mercury manometer. The condensers were then placed in a 6 in. Dewar flask which held approximately 5 lbs. of liquid nitrogen. A two stage duo-seal vacuum pump running at capacity provided a vacuum of 200 μ m Hg. The vacuum was monitored by a mercury U-tube manometer and at times a McCloud gauge.

Permeate Composition Analysis

Relative compositions of the permeates were measured by using a Varian Aerograph series 1400 gas chromatograph. Separation of the isomers was effected by using a column packed with Bentone 34 modified with diisodecylphthalate as described by Spencer [2]. Analysis of the permeate typically required 45 minutes to one hour and had an accuracy of $\pm 0.5\%$.

Experimental Procedure

The membranes studied are presented in Table 4. The lip of the flange, coated with a layer of vacuum grease served as the template to cut out a membrane to be tested. The membrane adhered to the base while the matching face of the flange was carefully held to avoid damaging the membrane while the large nut was tightened. The test cell was then placed in the oven and connected to the liquid feed lines and vacuum system.

Table 4. A list of commercial films tested for the permeation of xylene mixtures

Membrane	Manufacturer
Polyethylene Type A	Dupont
Polypropylene	Dupont
Polyimide Kapton ®	Dupont
Polyvinylflouride Tedlar ®	Dupont
Nylon Zytel ®	Dupont
Cellulose Acetate	Dupont
Polyester Mylar Type-S ®	Dupont
Cellophane Type PD-150	Dupont
Capran 77e	Allied Chem.
Parylene N	Union Carbide
Parylene C	Union Carbide

About 500 ml of xylene mixture containing approximately 50% para-xylene and 50% ortho-xylene or meta-xylene was kept in the separatory funnel. When the operation of the metering pump was initiated the connections and lines were checked for leaks. A feed sample was taken for analysis and the Variac transformer was adjusted for the desired temperature. When the temperature of the test cell stabilized, liquid nitrogen was charged to the Dewar flask and the vacuum pump was started.

Generally the apparatus was left unattended for a period of time ranging from 20 minutes to 24 hrs. On occasion the Dewar was recharged with liquid nitrogen and a membrane was tested for as long as 45.5 hours. At the conclusion of a test, the condenser containing the permeate was removed from the Dewar and slowly brought to room temperature. The condenser was weighed and if there was a sufficient amount of liquid it was transferred to a sample bottle. If there was a insufficient amount or no apparent permeate present, the condenser was washed with a small amount of acetone. The acetone-xylene mixture was then put in a sample bottle or analyzed directly.

EXPERIMENTAL RESULTS

For a comparison between pervaporation and distillation processes, a separation factor α was calculated for the membrane that is analogous to relative volatility used in rectification. The ortho-xylene, para-xylene mixture has a relative volatility of 1.08 and the meta-xylene, para-xylene mixture has a relative volatility of 1.01. In both cases the para-xylene is the more volatile compound and is used for the basis when calculating the relative volatility. Para-xylene was used for the basis when calculating the separation factor because para-xylene is generally enriched in the permeate. If either ortho-xylene or meta-xylene is enriched in the permeate, then the value for the separation factor will be less than one.

Test Results for the Ortho-xylene, Para-xylene mixture.

The separation factors for the ortho-xylene, para-xylene mixture and various membranes are presented in Table 5 along with the duration of the test run. Graphical representation of the data is presented in Figure 5. The lowest temperature at which it was possible to collect enough permeate to analyze is presented in Table 5. Many test runs made at the lower temperatures for long periods of time yielded little or no permeate and are omitted from the table.

Table 5. Summary of test results for the ortho-xylene para-xylene mixture. α distillation = 1.08

Membrane	Temperature (°C)	Run Time (hr)	Separation Factor
Polyethylene	24	8.5	1.28
	31	22.5	1.32
Polyimide	132	24	2.18
Polyvinyl fluoride	52	24.5	1.71
	72	17.5	1.33
	102	8.0	1.02
	132	15.0	1.03
	132	3.3	1.08
Zytel Nylon	51	15.5 1	1.23
	128	5.0 1	1.42
Polypropylene	26	23.5	1.30
	52	6.0	1.16
	67	0.8	1.25
	88	0.25 2	1.16
Cellulose Acetate	81	15.5	1.56
	108	8.7	1.52
	134	3.5	1.52
Mylar Polyester	92	29.8 1	1.04
	131	7.5 1	1.23
Cellophane	133	26.0	0.81
Parylene N	39	0.5	1.00
	40	0.1 3	1.00
Parylene C	27	20.0	1.02
	56	27.5	1.00
	106	2.0	1.16
	132	2.0	1.56

1 Acetone wash

2 Above this temperature a full vacuum could not be obtained

3 Vacuum line is filled with permeate. Membrane degradation is evident.

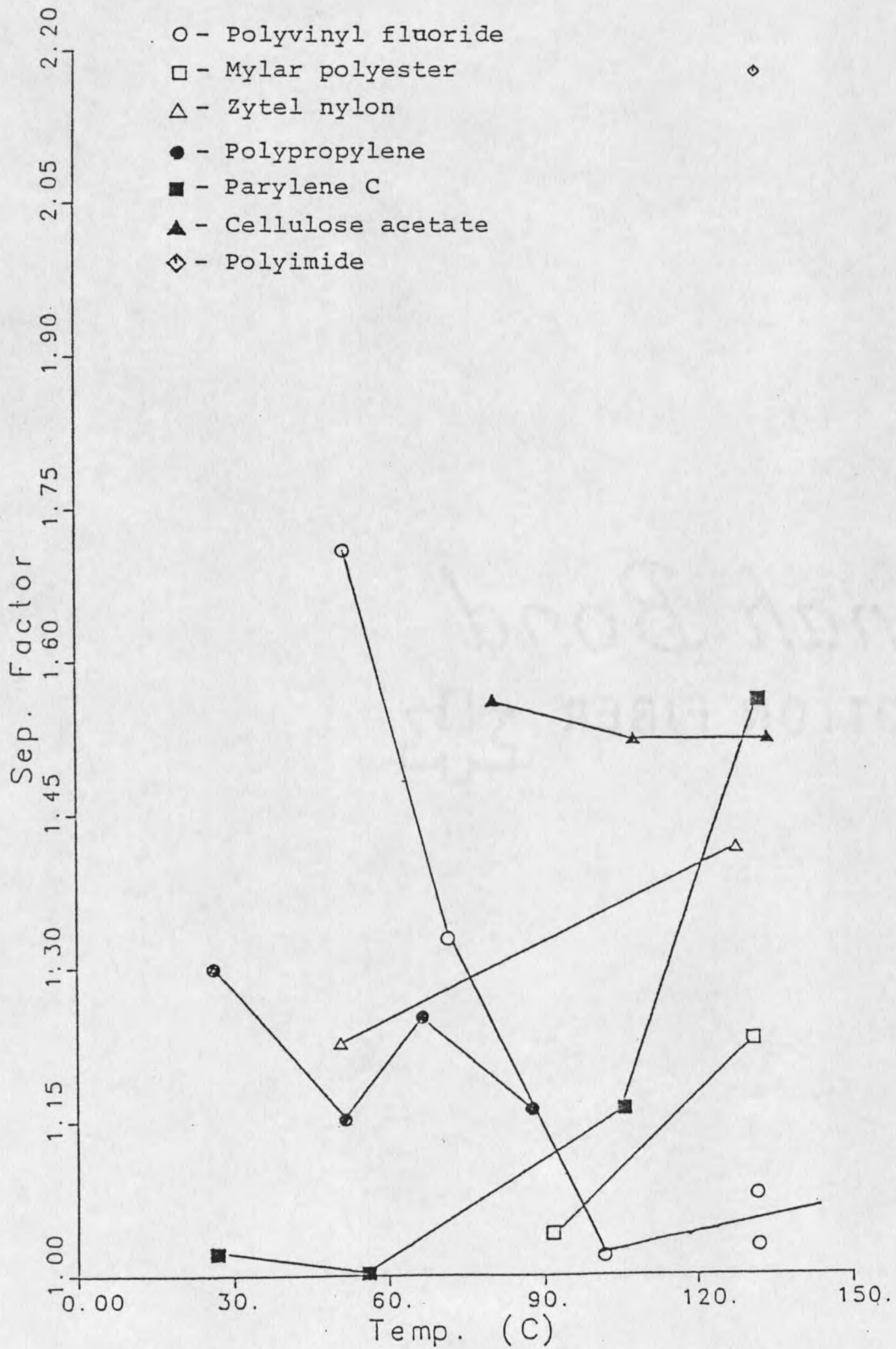


Figure 5. Separation factor vs. temperature for the p-xylene, o-xylene mixture

Of the films tested a polyimide film gave the highest degree of separation with a separation factor of 2.18 at 132 °C. Cellophane gave the lowest factor of 0.83 at 132 °C. Cellophane was the only membrane to give a separation factor less than 1.00 indicating that ortho-xylene permeated preferentially over para-xylene. On one occasion the cellulose acetate film, tested at 60 °C, gave a separation factor of 0.82 but two additional attempts at these conditions failed to produce any value for a separation factor.

The polyethylene film was tested at low temperatures because any attempt to raise the temperature above approximately 40 °C resulted in fluxes so high that the vacuum pump could not pull a vacuum less than ~75 mm Hg. At those elevated temperatures the permeate would condense in the teflon tube ahead of the cold traps and the cold traps would fill rapidly. The Parylene N film exhibited the same type of behavior.

Polyimide, Zytel nylon, Mylar polyester, Capran 77e and cellophane films were the most impermeable to the xylene isomers. Test runs made at the highest temperatures (132 °C) yielded miniscule amounts of permeate that had to be recovered by using acetone. The Capran 77e film did not yield enough permeate to be analyzed even though the acetone wash recovery method was used and the length of the test run at the maximum temperature exceeded 26 hours.

Zytel nylon, Mylar polyester and Parylene C films had separation factors that increased as the temperature increased. The polypropylene and polyvinyl fluoride films had separation factors that tended to decrease as the temperature increased. The cellulose acetate film separation factors tended to remain relatively constant over the temperature range at which they were tested.

Polyethylene, polypropylene, polyvinyl fluoride and the parylene films were more permeable to the xylenes and allowed several grams of permeate to be collected over the duration of a run. These membranes were selected for further testing using the meta-xylene, para-xylene mixture. The Parylene films, developed by Union Carbide and later discontinued, could not be tested with the new mixture because there was not enough film available for further tests.

Test Results for the Meta-Xylene, Para-Xylene mixture.

The permeation results for meta-xylene, para-xylene mixtures are presented in Table 6 and in Figure 6. The polyvinyl fluoride film gave the highest degree of separation with a separation factor of 1.22 at 60 °C. Polyethylene film gave the lowest degree of separation with a separation factor of 1.01 at 26 °C. Para-xylene was enriched in the permeate in every case.

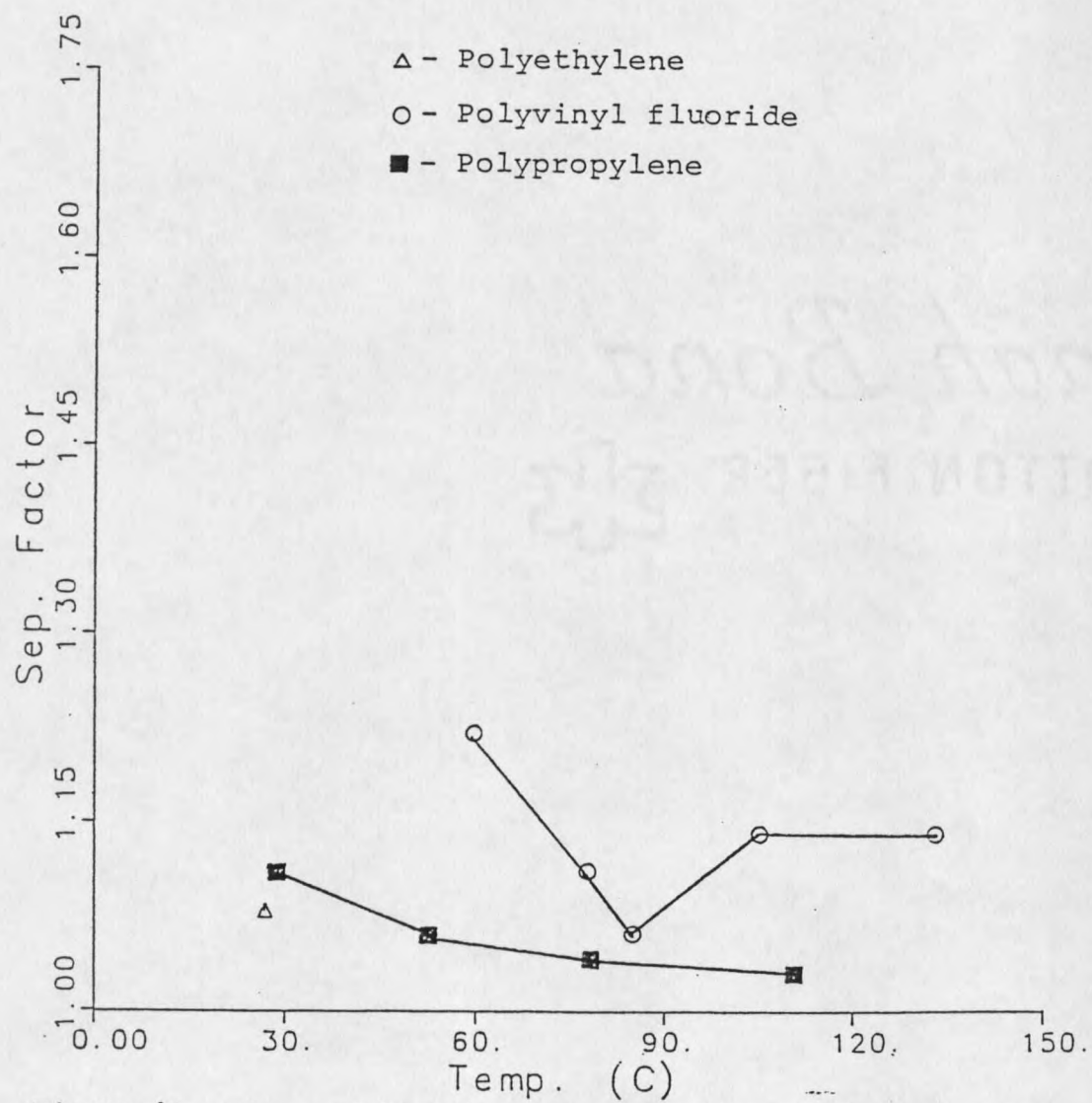


Figure 6. Separation factor vs. temperature for the m-xylene, p-xylene mixture.

Table 5. Summary of test results for meta-xylene, para-xylene mixtures. α distillation = 1.01

Membrane	Temperature (°C)	Run Time (hr)	Separation Factor
Polyethylene	26	23.5	1.01
	27	21.0	1.08
Polypropylene	29	11.5	1.11
	53	4.2	1.06
	79	1.2	1.04
	111	0.2 ¹	1.03
Polyvinyl fluoride	60	26.5	1.22
	78	20.0	1.11
	85	16.0	1.06
	105	25.5	1.14
	133	25.0	1.14

¹ Above this temperature full vacuum could not be obtained

Polyethylene exhibited the same behavior as that encountered with the para-xylene, ortho-xylene mixture. Test temperatures above 40 °C resulted in fluxes that were so high that the vacuum pump could not obtain a vacuum less than ~75 mm Hg.

Both the polypropylene and polyvinyl fluoride films had separation factors that decreased with an increase in temperature. When the polyvinyl fluoride film was tested at temperatures less than 60 °C, there was not enough permeate to be analyzed.

Membranes Tested with Both Mixtures

Polypropylene, polyethylene and polyvinyl fluoride films were tested with the para-xylene, meta-xylene and the p-o-xylene mixtures. When the polypropylene and polyethylene films were tested there was a lower degree of separation when the para-xylene, meta-xylene mixture was used. When the polyvinyl fluoride film was tested there were mixed results. A lower degree of separation was obtained for the para-xylene, meta-xylene mixture at low temperatures and a higher degree of separation at the higher temperatures. These results are depicted in Figure 7 and Figure 8.

Arrhenius Behavior for Pervaporation

To demonstrate that the permeation rate follows Arrhenius behavior, flux data was collected for the polyvinyl fluoride membrane using the meta-xylene, para-xylene mixture. Figure 9 demonstrates that the permeation rate increases with respect to an increase in temperature. When the logarithm of the flux is plotted versus the inverse of the temperature (Figure 10), the slope of the line yields the activation energy. For this system the activation energy is approximately 12 kcal/mol.

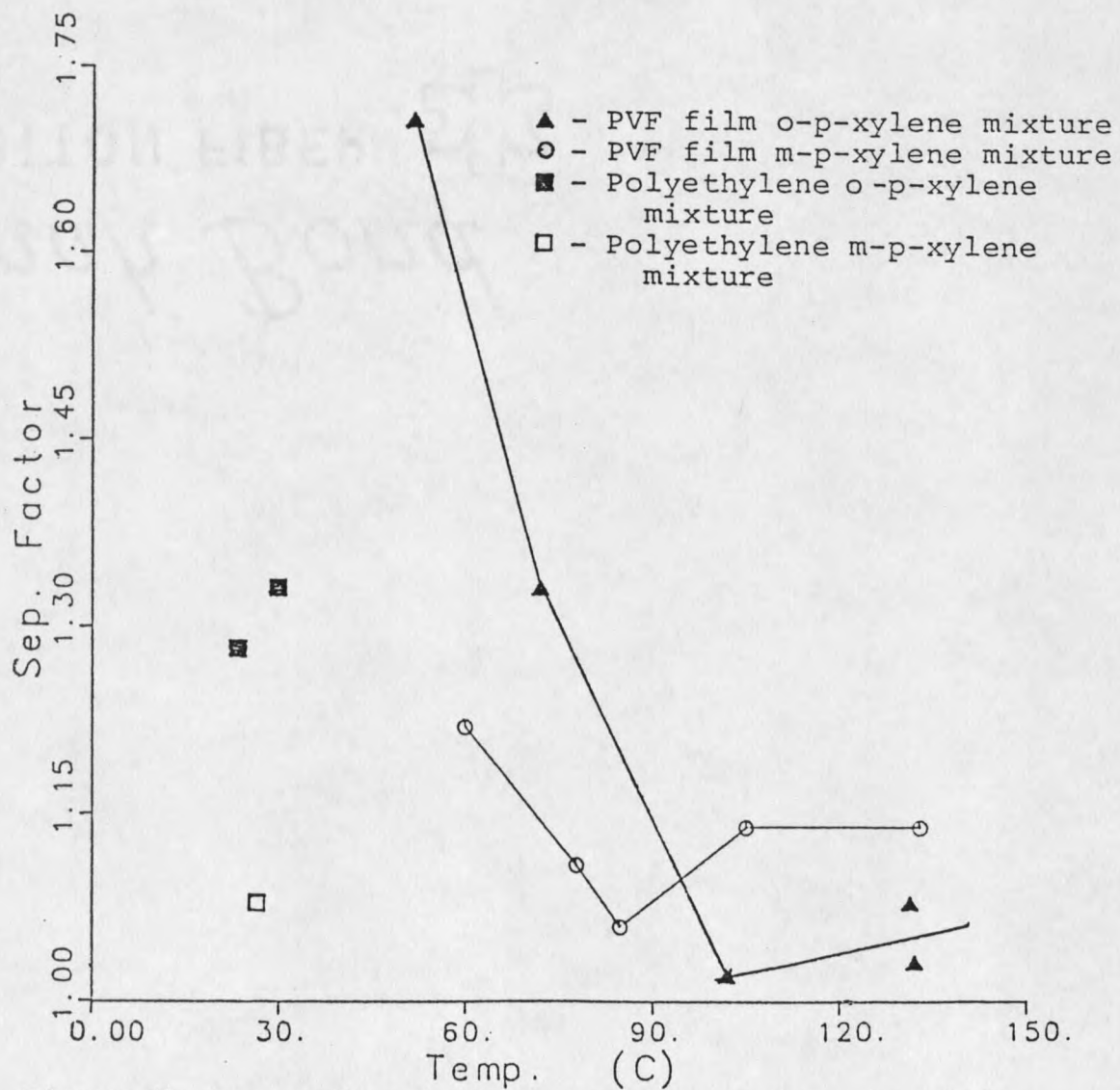


Figure 7. Separation factors vs. temperature for film tested with both mixtures.

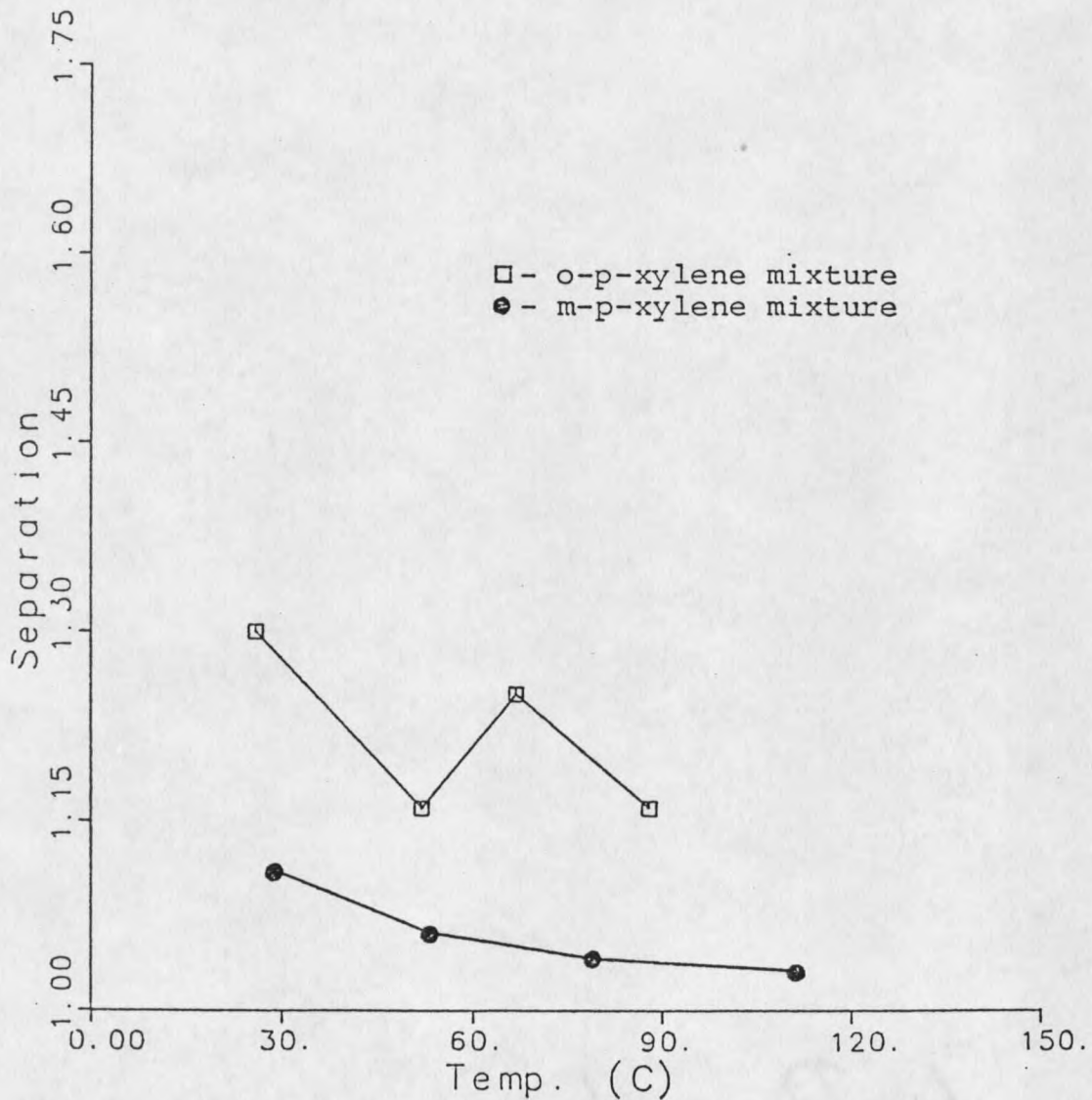


Figure 8. Separation factors vs. temperature for a polypropylene film tested with both mixtures.

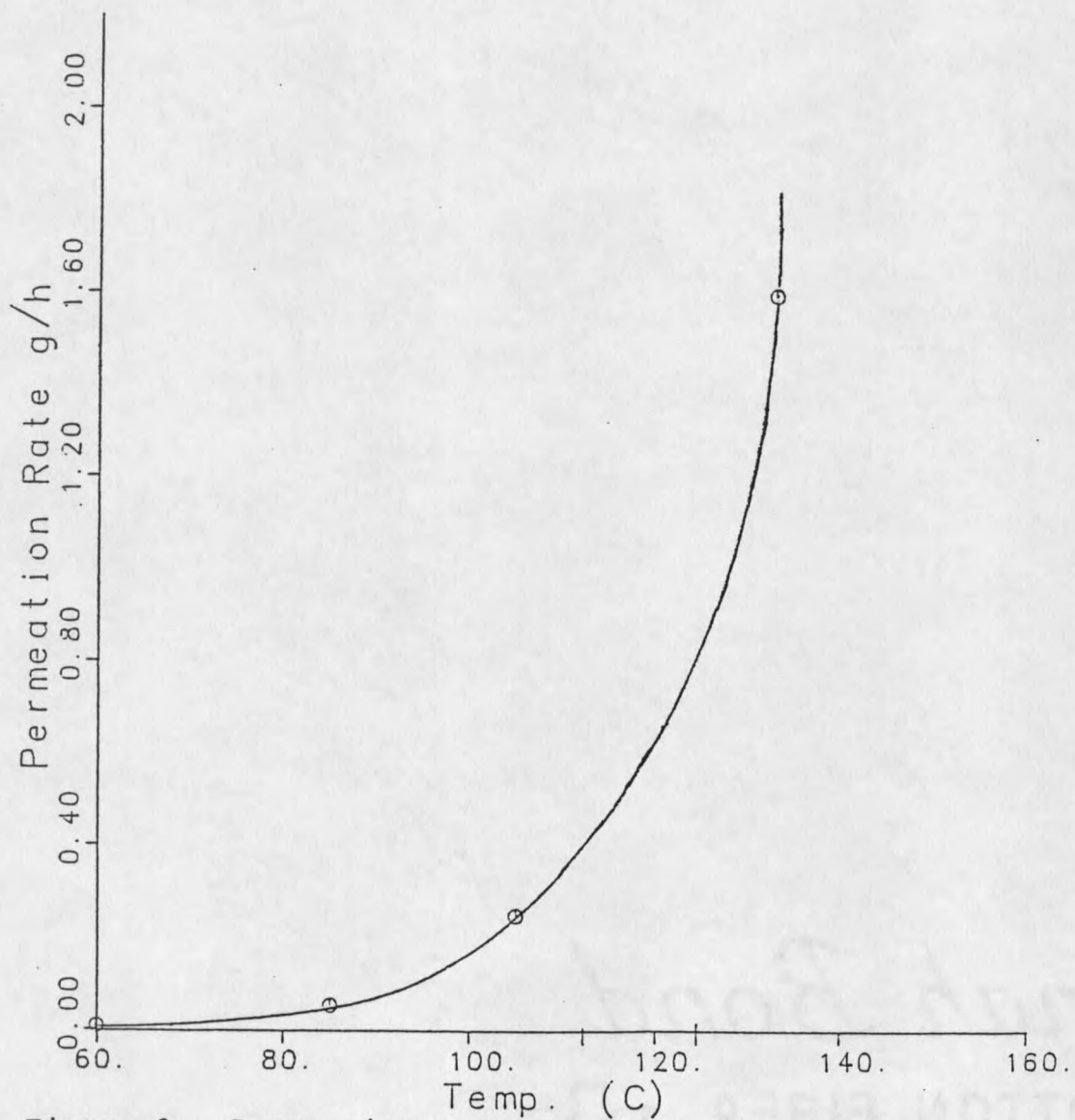


Figure 9. Permeation rate vs. temperature for m-xylene, p-xylene mixtures and a polyvinyl fluoride film

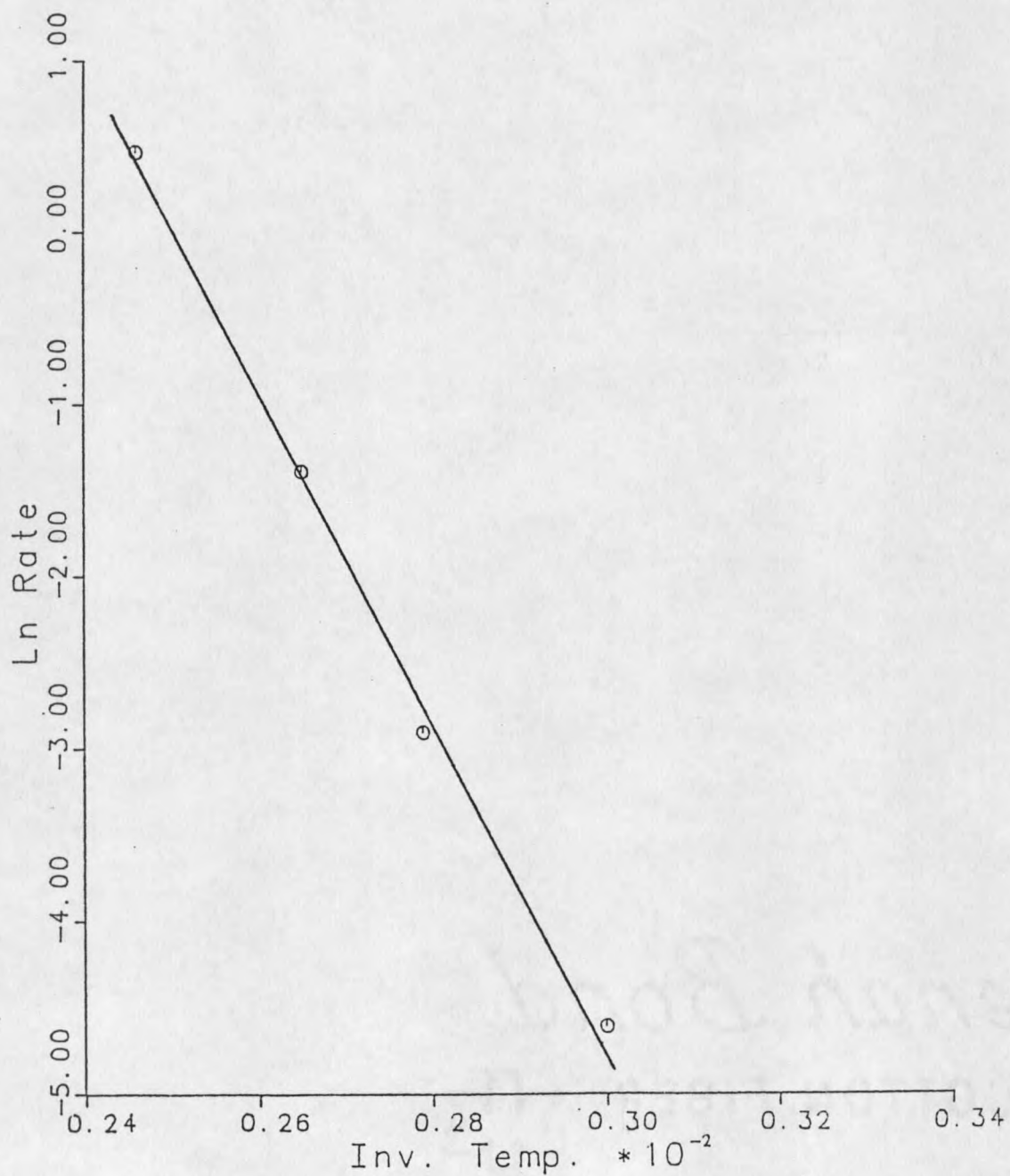


Figure 10. Logarithm of the permeation rate vs. temperature.

DISCUSSION OF THE EXPERIMENTAL RESULTS

Membrane selectivity at different temperatures varied remarkably among the membranes tested. Certain membranes had a wide range of selectivities over the temperature range, while other selectivities varied hardly at all. A few membranes exhibited increasing separation factors with a raise in temperature, while others had a decrease in selectivity with respect to an increase in temperature. A possible explanation for the variety of the results is discussed below.

Increasing Selectivity with Increasing Temperature

Membranes that exhibited this behavior were Mylar polyester, Zytel nylon and Parylene C films. One possible explanation for these results would involve the "mesh" and "hole" mechanism for selectivity. At low temperatures the membrane would be closed or nearly impermeable to any of the xylene isomers. If permeability is determined by solubility and diffusivity and ortho-xylene has a higher degree of solubility, then a low diffusivity of the para-xylene as a result of the low temperature could not offset the higher solubility of the ortho-xylene. The selectivity of the

membrane under these conditions would favor neither of the isomers. As the temperature increased the membrane would begin to open up as the holes increased in size and number. Para-xylene, having the smallest cross sectional area of the xylene isomers, would begin to fill these holes and begin their way through the membrane before the larger isomers. Selectivity would increase until the hole size became large enough to accommodate the larger isomers.

Decreasing Selectivity with Increasing Temperature

Membranes that exhibited this behavior were the polyvinyl flouride and polypropylene films. If these membranes had the proper hole size to allow para-xylene to permeate preferentially at low temperatures, any further increase in hole size would cause the selectivity to decrease. As the temperature increased, the hole size would increase until the larger of the isomers would begin to enter the holes large enough to accommodate their size. Since both permeating species could diffuse through the membrane at higher temperatures the selectivity of the membrane would become less.

Small Changes in Selectivity with Increasing Temperature

If a membrane exhibited increasing selectivity as the temperature increased and then had decreasing selectivity as the temperature increased further, there would be a temperature range over which the selectivity would change very little. The cellulose acetate film exhibited this type of behavior which would indicate that the maximum selectivity for this membrane may have occurred over the temperature range at which it was tested. It is entirely possible that the cellulose acetate film gives a relatively constant degree of separation over a wide temperature range.

Comparison of a Membrane Tested with Both Xylene Mixtures

Polypropylene, polyethylene and polyvinyl fluoride films were tested using the para-xylene, ortho-xylene mixture and the para-xylene, meta-xylene mixtures. A lower degree of separation was obtained when the para-xylene, meta-xylene mixture was used for testing the polyethylene and polypropylene films. The polyvinyl fluoride film exhibited the same behavior at low temperatures, but at higher temperatures higher separation factors were encountered for the para-xylene, meta-xylene mixture than for the para-xylene, ortho-xylene mixture.

It is possible to explain these results based on the cross sectional areas of the xylene isomers. The difference in cross sectional area between the para-xylene and ortho-xylene (0.73 sq A) is greater than that of para-xylene and meta-xylene(0.28 sq A). The rejection of one species by a membrane having a certain hole size distribution would be more difficult when this difference in cross sectional area were small.

CONCLUSIONS

1. Most of the commercially available films tested can be used to enrich the para-xylene isomer in the permeate.
2. In general the degree of separation obtained by pervaporation of xylene mixtures is higher for the ortho-xylene, para-xylene mixture than for the meta-xylene, para-xylene mixture. These separation factors are higher than the relative volatilities encountered in distillation.
3. The degree of separation varies with respect to temperature. For some films the separation factor increases as the temperature increases while in others the degree of separation decreases as the temperature increases.
4. Liquid permeation or pervaporation flux for the meta-xylene, para-xylene mixture follows an Arrhenius type relationship with respect to temperature for the polyvinyl fluoride membrane.

RECOMMENDATIONS FOR FURTHER STUDIES

A range of temperature greater than that of room temperature to the normal boiling point of mixed xylenes should be investigated. This would enable the researcher to determine whether or not films exhibit a maximum selectivity with regards to temperature.

Many tests failed to produce any data because of miniscule amounts of permeate that was collected. This was especially true at the lower temperatures, therefore a more sensitive method for collecting a sample of the permeate should be incorporated into further studies. One way to do this might be to install a long length of tubing ahead of the cold trap which could be periodically isolated from the system. The sample in the tubing could then be pressurized to atmospheric conditions using an inert gas or fluid and injected directly into the chromatograph.

The introduction of time as a variable could be included in future studies to determine whether or not the permeate has an equilibrium composition. Other studies may want to collect the flux data and correlate selectivity with permeability rates. This would be useful for the design of pervaporation units that intend to separate the xylene isomers.

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