Separation of isomeric xylenes by permeation through modified plastic films
by John George Sikonia

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
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Abstract:

The modification of polymer membranes by including various compounds in these films was investigated in order to develop a liquid permeation system which would be selective for one xylene isomer.

These studies were completed using cylindrically-shaped stainless steel permeation cells with an exposed membrane diameter of 7.3 cm and a feed liquid capacity of 400 ml. The upstream pressure was atmospheric while the pressure on the product side of the membrane was maintained at less than 1mm Hg. Feed temperatures ranged from 23 to 130° C.

The liquid permeation membranes were constructed by first combining a solution containing a solvent and either polyvinyl chloride or polyvinylidene fluoride with the additive material, then spreading this casting solution on a glass plate, and finally heating the plate in an oven to evaporate the solvent. The additive materials included complexes of the Werner type, xylene clathrates of these complexes, and various other materials including extractive distillation agents and a plasticizer.

Using membranes of vinylidene fluoride which when unmodified were found very impermeable to the xylenes rather than those of polyvinyl chloride which were found naturally selective, it was concluded that a selectivity for the para-xylene isomer resulted only from the addition of certain materials to the otherwise impermeable films.

The two basic additives investigated were $\text{Ni}(\text{SCN})_2(4\text{-methylpyridine})_4$ p-xylene and $\text{Ni}(\text{SCN})_2(\alpha\text{-methylbenzylamine})_4$ o-xylene. It was found that both of these clathrates made the vinylidene fluoride film selective, but the second compound produced the larger para-xylene separations. The best para-xylene product-feed composition differences obtained were in the range of 8 percent beginning with a feed containing an equimolar mixture of the three xylene isomers. The total product flow rates obtained were about 1 ml/(hr ft²) at the best separations, but ranged up to over 100 ml/(hr ft²).

Studies involving all the components of the clathrates, other types of additives, different feed compositions, and varied treatment conditions revealed that although the selectivity-producing mechanism was not due strictly to the clathration process, some elements of this process appeared responsible for the observed results.

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Bozeman, Montana

August, 1972

ACKNOWLEDGEMENT

The author wishes to thank the staff of the Department of Chemical Engineering at Montana State University for their helpful suggestions made throughout the duration of this project. Appreciation is also expressed to the members of his graduate committee for their time spent reviewing this thesis and performing miscellaneous duties related to this project.

Special thanks goes to Dr. F. P. McCandless, Graduate Advisor, for his patient guidance and contributions throughout the entire endeavor.

The author is grateful for the financial support from an NDEA fellowship for the first three years and a departmental Teaching Assistantship during the last year.

Finally, the author gives his deepest appreciation and thanks to his wife and family for their consistent encouragement and cheerful support.

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ABSTRACT

The modification of polymer membranes by including various compounds in these films was investigated in order to develop a liquid permeation system which would be selective for one xylene isomer. These studies were completed using cylindrically-shaped stainless steel permeation cells with an exposed membrane diameter of 7.3 cm and a feed liquid capacity of 400 ml. The upstream pressure was atmospheric while the pressure on the product side of the membrane was maintained at less than 1 mm Hg. Feed temperatures ranged from 23 to 130° C.

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INTRODUCTION

Among the higher homologs of benzene are the dimethylbenzenes, which are called xylenes. These three compounds have the chemical formula $C_6H_4(CH_3)_2$ and the following structures:

Some selected physical properties of these compounds are given in Table 1.

Table 1. Properties of the Xylene Isomers (1)

	Melting Point °C	Boiling Point °C	Density g/ml
para-xylene	13.26	138.35	0.8611
meta-xylene	-47.87	139.1	0.8642
ortho-xylene	-25.18	144.4	0.8802

Xylenes are recovered as a by-product of coke-oven operations and from petroleum sources, with the latter accounting for over 99 percent of the estimated 439.8 million gallons produced in the United States during 1971 (2). Commercially available xylene has a composition which is dependent on its source. Presently more than 95

percent of the petroleum xylenes are obtained by solvent extraction of reformat. A typical analysis of this product as well as those others encountered is shown in Table 2.

Table 2. Typical C₈ Aromatics Compositions from Various Sources (2)

Isomer	Catalytic Reformat	Steam Cracking	Dispropor- tionation	Coke Oven
Ethylbenzene	17-20%	53%	Nil%	15-23%
Para-xylene	16-20	10	26	15-17
Meta-xylene	35-40	25	50	42-44
Ortho-xylene	19-26	12	24	14-20

In the growing petrochemical industry, xylenes find many uses. As of 1970, approximately 28 percent of the total production was used in solvents, mainly in paint, varnish and lacquers, and pesticides. Some mixed xylenes were blended into motor gasoline for octane control. The major outlets for the xylenes were as separate isomers used as chemical intermediates (2).

Ethylbenzene is converted into styrene and finds its end uses in such things as SBR rubber, polystyrene, plastics, and several other polyesters and plastics.

Para-xylene is in strong demand in world markets as a major raw material for the production of dimethyl terephthalate and terephthalate acid, intermediates used in the production of polyester

fiber and film. Dacron is an important example of a polyester and is polyethylene terephthalate, the condensation product of dimethyl terephthalate and ethylene glycol. Presently the manufacture of polyethylene terephthalate is the major outlet for para-xylene. The world polyester fiber production has grown from 1007 million pounds in 1965, to 3622 million pounds in 1970, a 27.7 percent yearly growth (4).

Meta-xylene, the most abundant xylene isomer contained in the mixed xylenes, has the smallest demand as a separate isomer. Most of the meta-xylene is left in the xylene stream where it is either isomerized, used as a solvent, or used in gasoline blending. The separated meta-xylene is mainly used to produce isophthalic acid which is used to make unsaturated polyesters, alkyd resins, plasticizers, and other esters. The U.S. isophthalic acid production capacity is 135-145 million pounds per year (5).

Ortho-xylene enjoys world-wide demand essentially as a raw material for phthalic anhydride production. Of the 850 million pounds of ortho-xylene produced in the U.S. during 1971, 46 percent was used to manufacture phthalic anhydride and 51 percent was exported (6).

The xylene isomers must be separated in order to be used in their many applications as chemical intermediates. This use demands a commercial para-xylene purity of 99.2 percent, meta-xylene purity

of 98.6 percent, and ortho-xylene purity of 95.3 percent (4,5,6). Some of these separations are conventional but difficult, while others may involve novel and fairly complex processes.

As indicated in Table 1, these isomers are quite identical as far as boiling points are concerned. However, there is enough spread in boiling point, heat of vaporization, and vapor pressure for ethylbenzene and ortho-xylene to be economically fractionated from each other and the xylene stream. Typical ethylbenzene towers are 300 to 400 actual trays with about a 25-50 to 1 reflux to feed ratio. Ortho-xylene fractionators are usually 100 to 150 trays with about a 5-8 reflux to feed ratio. Fairly recent technical developments in the recovery of these two components have been in the design of distillation trays able to operate at high capacity with a relatively low pressure drop (7).

The separation of para-xylene from meta-xylene is the most difficult. Because of the very small difference in boiling points, these two isomers cannot be economically separated by fractionation. However, as a result of the relatively large difference in melting points between para-xylene and the other isomers, low temperature crystallization is the major route in use. Currently there are about a dozen crystallization routes available which differ as follows: direct or indirect cooling; scraped-surface chillers, with separate or built-in crystallizer; pulse purification or conventional second-

stage crystallizer; separation by filtration or use of centrifuge (4). Another unusual crystallization process involves using an "inert" liquid to improve both the purity and recovery of para-xylene (8). In the Japan Gas-Chemical Corporation's process, the classic crystallization process is modified to include selective extraction and isomerization of meta-xylene using HF/BF_3 (9).

A recently developed adsorption process is Universal Oil Products' Parex process. Here para-xylene is recovered from an adsorbent by displacing it with another liquid of different boiling point. The UOP process is so designed to permit efficient use of the adsorbent and desorbent (10). At least four Parex units have been licensed (4). This process and another by Toray Co. (Japan) are thought to rely on potassium- and barium-substituted Type X and Type Y molecular sieves. However, none of these recently patented processes use the "sieve" action, but depend instead on selective adsorption due to preferential attraction (11).

A separation process known as clathration has been of interest for more than ten years. Here para-xylene is separated by a difference in shape from meta-xylene. This process has been developed by the Union Oil Company, but has not been of interest recently (12).

Relatively new works using a variety of plastic membrane systems indicate that significant xylene isomer separation may be obtained by liquid permeation through these films.

Therefore because no one separation process at the present is clearly accepted as the best method of separating para- and meta-xylene and because the demand for high purity para-xylene will increase in the future, more research into this area is certainly appropriate. The object of this particular investigation will be to construct membranes of a plastic or resin material which will also incorporate a xylene-selective clathrate or other suitable compounds and to evaluate their ability to separate the xylene isomers using a liquid permeation process.

TECHNICAL CONSIDERATIONS OF PREVIOUS RELATED WORK

Before dealing with the particular technical background of the problem at hand, it may be constructive to investigate and evaluate membrane separation processes and clathration as they are separately explained in the literature.

MEMBRANE SEPARATION

A membrane is a thin barrier separating two fluids. This barrier prevents all hydrodynamic flow so that transport through the membrane is by a diffusion-like mechanism generally referred to as permeation. The property of the membrane describing its rate of transport is its permeability. A semipermeable membrane is one which transports different molecular species at different rates. This phenomenon is the reason for interest in this process.

Of the permeation processes where the driving force for transport is pressure, this discussion will be limited to those processes in which a liquid feed material permeates through the membrane and leaves as a vapor. First to report that this process had good commercial separation potential, Binning, Lee, Jennings, and Martin called this process liquid permeation (13). Other prominent workers in this field have termed this process "pervaporization" (14). In this report both terms will be used interchangeably. This discussion will be limited to the pertinent material dealing with membranes composed of polymeric

plastic films.

As described by Binning and his coworkers, the liquid permeation process is as shown in Figure 1. Here a liquid feed permeates through the film and leaves as a vapor enriched in one component.

Figure 1. Diagram of the Liquid Permeation Process. In this two-compartment unit, the more permeable molecules are shown as open circles. (13).

Also proposed is a model of the permeation process in which the polymer film is divided into two zones: the "solution phase" and "vapor phase" zones. The majority of the membrane thickness is occupied by the "solution phase" zone in which the polymer is in a highly swollen state due to the high concentration of permeating liquid. The "vapor phase" zone may be considered a region in which permeating molecules are much more dispersed and where the polymer structure more

closely corresponds to that of the dry polymer film. This process is shown diagrammatically in Figure 2.

Figure 2. Polymer Film Under Permeation Conditions as Described by Binning and His Co-workers (13).

As shown above, the permeation process involves three steps: 1) solution of the liquid in the film surface in contact with the liquid charge mixture; 2) migration through the body of the film; and 3) vaporization of the permeating material at the downstream interface where the permeant is immediately swept away. The majority of the selectivity is thought to occur at the interface between the two zones. Subsequent diffusion through the "vapor phase" zone is believed to be the rate-controlling step in the process (13).

Here the films are thought to be non-porous, containing no discrete holes, and not functioning by a molecular sieving action. With

the permeability of a single feed component dependent on the solubility of the charge mixture in the film, it is not possible to predict the permeation rate of a single component from its performance as the sole feed compound. A fundamental form of Fick's first law of diffusion must be used here to describe the liquid permeation process in the steady state:

$$J_1 = D_{1,m}(\Delta C)/L$$

where J_1 is the transmission flux of component 1 through the film (volume/(unit time x unit area)), $D_{1,m}$ is the permeability coefficient for component 1 in the mixture, ΔC is some concentration difference in some appropriate units, and L is the film thickness.

Binning and his co-workers conclude that the size, shape, and solubility of molecules affect their permeability in the following ways: 1) lower molecular weight molecules in a homologous series permeate faster; 2) molecules of smaller cross section with the same molecular weight and chemical nature permeate faster; 3) shape and size factors may predominate for materials with small differences in chemical nature, but molecules with large differences in chemical nature are not as affected by shape and size factors in the range of normally liquid materials (13).

Contrary to Binning's contention that the films are nonporous and do not contain discrete holes or pores and do not function by molecular sieving action; Michaels, Baddour, Bixler, and Choo have proposed a

permeation mechanism which contains these same elements. Based on work with polyethylene film, their model considers the polymer as a simple molecular "sieve" or screen, wherein the "intercrystalline amorphous regions (be they intra- or interlamellar) constitute the "holes" and the extensively interconnected crystalline elements, the "mesh" (14). This model is the result of their extensive research which involved conditioning polyethylene film by swelling it in a xylene isomer and then annealing the film at an elevated temperature.

By carefully controlling the conditions of annealing and recrystallization in the presence of a particular solvating liquid, these experimenters found that it was possible to both narrow the "hole" size distribution and to increase the mean "hole" size over that of the original melt-quenched polymer. Their observation that the permselectivity of the polyethylene to the xylenes was dependent on the configuration of the solvating molecule is provocative in that it implies that these molecules function as templates which control the ultimate intercrystalline spacing or "hole" size. This membrane conditioning scheme is shown in Figure 3.

Also noted in this study by Michaels et al. is that their experimental results when working with mixtures of the three xylenes corresponded well with theoretical results obtained for single compounds. Here the permeability coefficient is defined by the relation:

Figure 3. Schematic Model of Permselective Polymer Membrane Conditioning Given by Michaels and His Co-workers, (14).

$$J = \bar{P}(p_L - p_V)/L$$

where

J = transmission flux
 $\bar{P}$ = permeability coefficient
 p_L = liquid vapor pressure
 p_V = partial pressure of gas phase at downstream film boundary
 L = film thickness

Because of the low pressure on the downstream side of the film, p_V is effectively zero.

Now considering permeation of a xylene mixture, the individual permeability coefficients are used to calculate a single-component flux using the ideal relationship:

$$J_1 = \bar{P}_1 p_1^{\circ} x_1^{\circ} / L$$

where

$$\begin{aligned} J_1 &= \text{transmission flux of component 1} \\ \bar{P}_1 &= \text{permeability coefficient of component 1} \\ p_1^{\circ} &= \text{vapor pressure of pure 1 at the permeation temperature} \\ x_1^{\circ} &= \text{mole fraction of 1 in the feed liquid} \end{aligned}$$

The ratio of any two components in the vapor mixture leaving the film is then related to the feed liquid composition by the following expression:

$$\frac{J_1}{J_2} = \frac{x_1}{x_2} = \frac{\bar{P}_1}{\bar{P}_2} \cdot \frac{p_1^{\circ}}{p_2^{\circ}} \cdot \frac{x_1^{\circ}}{x_2^{\circ}}$$

where

$$\begin{aligned} x_1 &= \text{mole fraction of 1 in vapor product} \\ x_2 &= \text{mole fraction of 2 in vapor product} \end{aligned}$$

These equations produced values which corresponded very well with experimental results obtained using all three xylene isomers in the feed (14).

With the permselectivity defined as:

$$S_{1/2} = \bar{P}_1 / \bar{P}_2$$

Michaels et al. obtained values in the range of 1.2 for para-/meta-, 1.4 for para-/ortho-, and 1.15 for meta-/ortho-.

In contrast to the film-conditioning techniques of Michaels¹, a recent patent granted to A. J. de Rosset (Universal Oil Products) described a membrane of a homogeneous thermoplastic film in which polymer chains are para-xylene structure material connected in head-to-tail

manner giving a repeating polymeric composition. Thus, a polymeric membrane substantially free of cross-linking and consisting of long chains of p-xylene connected by alkyl groups was used to enrich a permeated vapor stream. A competitive permeation gave a selectivity of 1.3:1.0, p-xylene:m-xylene ratio (15).

In several articles by Long, Li, and Henley, it is also proposed that liquid permeation is a special case of ordinary diffusion and can be explained by the classical diffusion model (16, 17, 18). Additionally, the permeability coefficient at a given temperature is exponentially related to the concentration of the liquid in the film. In equation form, this is:

$$\bar{P} = \bar{P}_0 e^{aC}$$

where

$\bar{P}_0$ = permeability coefficient at zero concentration, temperature dependent

a = plasticizing constant, temperature dependent

C = concentration

Then a steady-state, single-component flux is given by (16):

$$J = \bar{P}_0 (e^{aC_1} - e^{aC_2}) / aL$$

where

C_1 = upstream concentration in the film

C_2 = downstream concentration in the film

It is furthermore suggested by these authors that the liquid concentration gradient through the film shows that essentially all resistance to diffusion is at the downstream edge of the film.

Schrodt et al. proposed that hydrogen bonding between the polymer

film and the solvent played an important role in the permeation process (19).

From the preceding discussion, it is apparent that a single permeation mechanism is not clearly established. More experimental work is necessary before any of these suggested mechanisms can be accepted. However, these proposed schemes are of value because they help define the overall permeation process and indicate a direction for further research.

CLATHRATION

As first suggested by H. M. Powell, a structural combination of two substances which remain associated not through strong attraction between them but because strong mutual binding of the molecules of one sort only makes possible firm enclosure of the other should be indicated by the description "clathrate" compound — "clathratus," enclosed or protected by cross bars of a grating (20).

In his book Clathrate Compounds, Vijay Mohan Bhatnagar briefly reviews all areas of clathration and lists a very complete bibliography (21). In this source a clathrate is described as a group of molecules enclosed within a cage from which they can not escape until the structure is destroyed. A clathrate is a single-phase solid consisting of two distinct components: the host and the guest. The guest is retained in closed crystalline cavities provided by the

of the host. Furthermore, the two components do not react chemically with each other, rather very weak forces like those of hydrogen bonds and of the van der Waals type, which normally are not capable of joining molecules together, may contribute to hold the two components in the inclusion compound together. In addition, inclusion compounds are now known in which the bonding principle is a spacial one and depends largely on the geometry of the space.

Of particular importance to this study are a group of inorganic complex compounds which form clathrate compounds with organic compounds. As first reported by W. D. Schaeffer and his co-workers, this class of clathrate formers exhibits a sharp selectivity for forming crystals containing specific isomers of compounds such as the xylenes, cymenes, and methylnaphthalenes (22).

These complexes are of the Werner type and contain three constituents: a metal ion, usually one of the divalent transition elements such as nickel, cobalt, manganese, iron, copper, or zinc; a plurality of neutral molecules (usually four) which in this case may be a variety of basic nitrogen compounds such as the substituted pyridines and quinolines; an anion which may be a simple mono-atomic ion such as chloride or bromide, or a poly-atomic ion such as thiocyanate, formate, cyanate, cyanide, or nitrite.

The preparation of clathrate compounds of these inorganic complexes with many of the organic molecules is very simple. Usually all that is

required is to bring together the components of the complex in an aqueous solution and the Werner complex precipitates immediately as a solid. The reaction times are generally less than five minutes and produce a nearly quantitative yield. As described by Schaeffer et al., "three primary methods may be employed for preparation of the clathrate from the complex and the feed mixture: (1) stirring the complex as a suspension in the liquid feed mixture, (2) contacting of the feed mixture with a solution of the clathrate former in a solvent at an elevated temperature, and (3) contacting a suspension of the complex in an organic fluid (which does not dissolve the complex and does not enter into the clathrating reaction) with the feed mixture" (22).

Another very simple method used in obtaining the clathrate is to form the complex by titration of the metal ion - anion solution with the basic nitrogen compound in the presence of the compounds to be clathrated (23).

When the complexes of metal salts and substituted pyridines are used for clathrating agents, the following reactions may come into play (21):

The symbol Py stands for a substituted pyridine base, M^{++} for a metal ion, and X^- for an anion (21).

Of interest to this study is the result obtained by Schaeffer et al. that these complexes form clathrates which can be selective for particular isomers of xylene. The complex $\text{Ni}(4\text{-methylpyridine})_4(\text{SCN})_2$ prefers p-xylene, $\text{Ni}(3\text{-ethyl-4-methylpyridine})_4(\text{SCN})_2$ prefers m-xylene, $\text{Ni}(4\text{-ethylpyridine})_4(\text{HCO}_2)_2$ prefers o-xylene, and $\text{Ni}(4\text{-acetylpyridine})_4(\text{SCN})_2$ prefers ethylbenzene (22).

These are by no means the only complexes which may be used with good success with each of these isomers. In an article appearing just after Schaeffer's, $\text{Ni}(4\text{-hydroxymethylpyridine})_4(\text{SCN})_2$ is listed as the preferred complex for o-xylene (24).

It is generally noted that changing the components of a complex will change its selectivity in a manner which is unpredictable. Much more information about the selectivity mechanism of clathration is needed before it will be possible to predict the specific compounds which will be selectively clathrated by any given complex.

A new family of Werner complexes displaying a selective clathrating ability has been described by Pierre de Radzitzky and Jacques Hanotier (23). These new complexes have the general formula $\text{Ni}(\text{SCN})_2\text{-(primary substituted benzylamine)}_4$. These complexes and the clathrates they form have very different properties from those previously known.

Contrary to the fact that for ordinary Werner-complex type clathrates where the included compounds can not be removed without dissociating the complex as well, here it is shown that at 60° C the clath-

rate $\text{Ni}(\text{SCN})_2(\text{a-methylbenzylamine})_4$:o-xylene is completely dissociated to the tetramine complex and free ortho-xylene. From a practical point of view this means that it is possible to recover the caged compound while maintaining the tetramine complex for future use without reconstruction (23).

The ability of clathrates to separate xylene isomers has been utilized in demonstration-type commercial operations. Using a process licensed from the Union Oil Company, Cosden Petroleum Company, Big Spring, Texas, produced meta-xylene of 95 percent purity from a feed of C_8 hydrocarbons. The $\text{Ni}(\text{SCN})_2(4\text{-methylpyridine})_4$ complex was used to separate the para- and meta-xylene isomers (25). In another description of this xylene separation process, the following specifications are given (26):

	FEED vol %	CLATHRATE vol %	FILTRATE vol %
m-xylene	81.2	34.4	96.5
p-xylene	14.8	59.3	0.8
o-xylene	0.6	0.3	0.8
ethylbenzene	3.4	6.0	1.9

However, as previously noted, all commercial p-xylene processes currently in operation use methods other than clathration.

Special consideration is due an invention by Raymond N. Fleck and Carlyle G. Wight because it contains some of the features investigated in the present work. Their process centers on a thin diffusion barrier

which is composed of a solid Werner complex immobilized and strengthened by some inert support material. The separation and enrichment of particular components of the feed is presumed due to the occlusion or entrapment of one or another such components within the lattice of the Werner complex to form an association compound of the clathrate type. The difference between this and previous clathration processes is that relatively small quantities of Werner complex are needed to separate large volumes of feed (27). The basic configurations of these diffusion barriers are shown in Figures 4 and 5.

Figure 4. Diffusion Barrier of Fleck and Wight (27).

Figure 5. Diffusion Barrier of Fleck and Wight (27).

This diffusion barrier is incorporated into a separation process as shown in Figure 6. Here the primary driving force for diffusion may be the pressure differential between the feed and product zones. For successful operation it is also necessary to keep the concentration of the more diffusible component at a maximum on the feed zone side and at a minimum on the product zone side (27).

Figure 6. Diffusional Separation Process of Fleck and Wight (27).

A free heterocyclic nitrogen base compound is included in the feed and sweep fluid streams for the purpose of maintaining the activity of the barrier material. This nitrogen base material is generally the same compound as used in the Werner complex. It is claimed

that by changing the Werner complex a change in the selectivity of the diffusion barrier is obtained (27).

No commercial application of this process of Fleck and Wight is known. Although recent literature sources do not confirm the claims of this patent, the basic idea is very interesting and the development of a process which could be called "continuous clathration" is still very attractive.

Work continues throughout the world on optimizing the different clathration separation processes. The Russian experimenters G. M. Panchenkov and A. I. Korosteleva claimed that a single-step para-xylene increase of 21 to 96 percent from a mixture of C_8 hydrocarbons was obtained using $Ni(SCN)_2(4\text{-methylpyridine})_4$ dissolved in 32:56:12 $EtNH_2-H_2O$ -ammonium oxalate (28). Using the same complex, it was also found that the effectiveness of the separation was increased by the addition of $\begin{matrix} COONH_4 \\ COONH_4 \end{matrix}$ and hydroxyethylammonium thiocyanate to the solvent. A common fractionation containing 7.32 percent ethylbenzene, 45.2 percent m-xylene, 19.7 percent p-xylene, and 27.82 percent o-xylene yielded p-xylene of purity in the range 85.3-92.9 percent in one step and 98.25-99.37 percent in two-step clathration (29).

PLASTICIZATION

A plasticizer is defined as a material incorporated in a plastic to improve its workability and its flexibility or distensibility.

These substances extend and modify the natural properties of these resins and may develop new improved properties not present in the original resins. Plasticizers reduce the viscosity of the resins and make them easier to shape and form at elevated temperatures and pressures. Organic plasticizers are usually moderately high-molecular-weight liquids or occasionally low-melting solids. Two cyclic plasticizers used widely are diisodecyl phthalate and the dioctyl phthalates (30).

There are two general theories regarding the mechanism of plasticization. The lubricity theory views the resistance of a polymer to deformation as a result of intermolecular function. The plasticizer acts as a lubricant to facilitate movement of the macromolecules over each other, giving the polymer internal lubricity. The gel theory, devised for amorphous polymers, considers their resistance to deformation to result from an internal, three-dimensional structure, or gel. This gel is formed by more or less loose attachments which occur at intervals along the polymer chains. A plasticizer in a resin having many points of attachment along the polymer chains breaks these attachments and masks the centers of force for polymer-polymer intermolecular attraction by selectively solvating the polymer at these points. However, these plasticizers are not bound permanently (31).

COMBINATION OF SEPARATION TECHNIQUES

It is hypothesized that a combination of the separation techniques of selective permeation through a plastic membrane, clathration, and specialized plasticization can be used to produce films which will show increased selectivity for para-xylene from a mixture of the three xylene isomers.

RESEARCH OBJECTIVES

The objectives of this investigation into the separation of isomeric xylenes using a liquid permeation system included:

A. The determination of the membrane selectivity-pattern response due to:

1. The use of two different plastic resin materials.
2. The inclusion in these plastic films of clathrates of the Werner type which contain different metal ions, different anions, and different basic nitrogen compounds.
3. The inclusion in these plastic films of Werner complexes which contain different basic nitrogen compounds.
4. The formulation of membrane materials containing different relative concentrations of resin solvent, resin, and additive material.
5. The inclusion in the liquid feed of a clathrate solvent or basic nitrogen compound.
6. Different membrane treatment conditions of oven temperature and oven time.
7. Different feed temperatures.
8. Different xylene feed concentrations.
9. The length of permeation time.

B. An estimation of the utility of one of these membrane systems as compared to other experimental and commercial separation processes.

C. The formulation of a well-defined direction for further research using conditioned plastic membranes.

EXPERIMENTAL APPARATUS AND PROCEDURE

In order to investigate the proposed liquid permeation separation processes, it was necessary to design and construct an experimental apparatus and to develop procedures which would yield the appropriate information with the needed accuracy. This experimental apparatus included the membrane-producing equipment, permeation cell, liquid permeation system, and analytical tools. A description of the apparatus and procedures involved in this investigation are given in this section.

APPARATUS

Membrane Producing Equipment. Because the membranes used in this investigation were produced from powdered plastic resins and not from commercially manufactured films, some very simple equipment was used for this purpose. This equipment included several glass plates 8 by 5 by $3/32$ inches on which the casting solution was placed and an electrically-heated oven. The oven cavity was 5.5-inches wide, 8-inches deep, and 4-inches high with essentially no direct ventilation. One small hole (approximately $1/4$ -inch diameter and 2-inches long) projected through the rear wall of the oven. A small hole in the oven door was used to hold a thermometer and another passageway about $3/16$ -inch diameter was provided at the top of the door.

Permeation Cell. The heart of the liquid permeation system is the permeation cell. The two cells used in this investigation were fabri-

cated of stainless steel and were of simple design to eliminate unnecessary complications. The two parts of the cell were cylindrical with an inner diameter of 7.3 cm, the upper part being 10.8-cm long, the lower 2.6 cm, and joined by circular flanges extending 2 cm from the body.

The upper part of the cell held the liquid feed and had a maximum capacity of about 400 ml. For an expected product volume of from 0.1 to 3 ml, the resulting change in one component of the feed was less than 0.1 percent. This small change in feed composition allowed it to be assumed that the distribution of feed components remained constant throughout a run.

The lower part of the permeation cell, through which the product vapor passed, served to contain the film-holding system. The purpose of this system was to support the membrane and allow the vapor to pass freely to the collection point. The components of this system were:

- 1) a metal stand with the circular support disc filled with closely spaced 1/8-inch diameter holes;
- 2) a coarse wire screen mounted on the metal stand;
- 3) a fine wire screen mounted to the stand above the coarse screen;
- 4) a filter paper 9 cm in diameter to cover the screens and to bridge the gap between the screens and the lower part of the cell;
- 5) a gasket of 1/32-inch thick Gylon, marketed by Garlock Inc.;
- 6) three 7-cm diameter filter papers placed inside the Gylon gasket to form a support level with the top of the gasket;
- 7) a 7.5-cm diameter

filter paper placed over the smaller filter papers to bridge the gap between them and the Gylon gasket.

The membrane was placed on this surface and sealed in place with another Gylon gasket by the upper portion of the cell. The two parts of the cell were joined by eight evenly spaced 1/4-inch bolts and nuts. The complete assembly is shown in Figure 7.

The liquid feed material in the upper part of the permeation cell was stirred by a fan-turbine type mixer to keep the flow in the cell turbulent and therefore eliminate the possibility of a concentration gradient of one component forming near the surface of the film. The chief criterion for this type of flow is the tank Reynolds number, defined by (32):

$$N_{Re} = ND_a^2 \rho / \mu$$

where

N = speed, revolutions per second
D_a = impeller diameter, feet
 ρ = fluid density, lb/ft³
 μ = absolute viscosity, lb/ft-sec

For the stirrers used with xylene in this investigation, we have:

N = 6 r.p.s.
D_a = .104 and .125 ft
 ρ = 53.8 lb/ft³
 μ = 3.02x10⁻⁴ lb/ft-sec

With these values, the tank Reynolds numbers of 11,560 and 16,730 were

Figure 7. Permeation Cell with Membrane Support System.

obtained. Both of these values are above the minimum value of 10,000 required for turbulent flow.

It was possible to maintain the liquid feed temperature above that of ambient conditions by slipping a resistance heater over the upper part of the cell. This resistance wire heater was approximately two-feet long and enclosed in ceramic beads and mounted on a chicken wire support. Asbestos insulation tape was wrapped around the heater and then covered with masking tape. The temperature of the liquid was controlled with a Model 63RA, on-off controller manufactured by the Yellow Springs Instrument Company. The liquid temperature was maintained within $\pm 0.5^{\circ}\text{C}$ with a maximum temperature of 130°C .

Liquid Permeation System. The liquid permeation system consisted of the permeation cell with stirrer, heater, and controller; a mercury-manometer vacuum gage; two vapor-collection traps cooled with liquid nitrogen; a vacuum regulator; vacuum pump; safety trap; and connecting tubing.

The permeation cell was connected to the mercury-filled vacuum manometer by way of the safety trap and to the first cold trap with 3/16-inch I.D. Tygon R-3606 tubing. The purpose of the safety flask was to prevent the liquid feed from being drawn into the manometer in the event of a film rupture. A flask with a volume of 125 ml was found satisfactory.

The Tygon tubing was found acceptable when used with the xylene

vapor, but was replaced if contaminated by the liquid xylenes. The softening of the tubing was minimal and contamination of the product from desorption of the xylenes from the tubing was only apparent when unacceptably small amounts of product were collected. That is, when somewhat less than 0.05 ml of product was obtained, the amount thought due to the tubing was less than 5 percent of the total. For normal product volumes in the range of 0.2 to 2.0 ml, this level of contamination was acceptable.

The first cold trap following the permeation cell was used to collect the permeant. The maximum permissible volume of product collected at one time was approximately 20 ml. The second cold trap was used to condense the products which may have been back-diffusing from the vacuum pump. These two traps were connected using a short section of teflon-lined rubber tubing. Black rubber tubing was used to connect the second cold trap with the vacuum regulator and the vacuum pump.

For the majority of the runs, liquid nitrogen was used to cool both cold traps. Although a dry-ice and acetone combination could also have been used, the liquid nitrogen system was not only easier to handle in the laboratory, but also provided an additional margin of assurance that all the permeant was condensed.

Control of the downstream pressure was attained by using a Cartesian-diver type vacuum control, Model C-2100 manufactured by Roger Gilmont Instruments, Inc. When operating the system at the low-

est downstream pressure, this device was not included in the vacuum system.

The low pressure on the downstream side of the membrane was maintained by a rotary, oil-filled, mechanical vacuum pump. This Sargent-Welch Duo-Seal unit was driven by a 1/3 H.P. motor and had a free air displacement capacity of 25 liters per minute.

The assembled liquid permeation system is shown schematically in Figure 8.

Product Analysis. The volume of the product condensed in the first cold trap was determined using a graduated cylinder. The distribution of the components in the permeant and the feed was determined using gas chromatography.

The analytical system used was that proposed by Samuel F. Spencer (33). Here 0.5 gm each of Bentone 34 (an organo clay complex, National Lead Bariod Division) and diisodecyl phthalate were deposited on 9.0 gm of Chromosorb P using the conventional evaporation and slurry technique. This column packing was placed in a 1/8-inch O.D. column 15 to 20 feet long.

The analytical apparatus included an Aerograph 660 flame ionization gas chromatograph equipped with a Sargent 1-mv recorder, Model SR. The operating conditions used were: column temperature, 75° C; injection port temperature, 200° C; detector temperature, 140° C; helium flow rate, 20-30 ml per minute; hydrogen flow rate, 20-30 ml per

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Figure 8. Liquid Permeation System.

minute; air flow rate, 250-400 ml per minute; range, 100; attenuation, 16; sample size for three component liquid, 0.1 μ l.

With these conditions the retention time was approximately 35 minutes for ortho-xylene. The results of a three-component analysis using this system were reproducible to about 0.5 percent. That is, a 95 percent confidence interval for one component would be, for example, 33.5 ± 0.5 percent ortho-xylene.

EXPEPERIMENTAL PROCEDURE

A complete description of the procedures used in conducting this investigation is very important because small changes in technique may greatly influence the observed results. The greatest variation in experimental procedure was found in the methods of producing membranes. Also important were the procedures used in assembling the permeation cell and liquid permeation system, carrying out the run, collecting the product, and determining the analysis.

Membrane Producing Techniques. Because this investigation was concerned with changes in membrane selectivity when used in the liquid permeation system, the procedures employed in making these membranes were of critical importance. The steps involved in the construction of the membranes used in this experiment were: preparation of the resin solution, preparation of additives or film-conditioning agents, combination of the resin solution and additives to form the casting

solution, casting the film, and conditioning the film.

Resin Solution Preparation. The resin solution was made by allowing the powdered resin to dissolve in a suitable liquid. In this investigation two resins were used: polyvinyl chloride (PVC) and polyvinylidene fluoride (VF). The PVC resin used was "Plaskon", Type SR313, Model 81902, manufactured by the Plastics Division of Allied Chemical. A resin solution of PVC was obtained by adding the resin to cyclohexanone and allowing this mixture to stand at room temperature for approximately 24 hours. A clear, colorless solution was formed. The composition of a resin solution is given by a weight ratio; for example, a typical solution might be 6:1 (cyclohexanone, gm:PVC, gm).

The powdered vinylidene fluoride resin used in this study was obtained from Pennwalt Corporation and marketed as "Kynar", Grade 301. Dimethylformamide (DMF) was used to form the plastic solution with the VF resin. This was best accomplished by adding the powdered resin to the solvent and after shaking vigorously, heating gently to form a clear, yellow-brown liquid.

Additive Preparation. The additives included in the membranes were basically of two types: those which required no preparation except in the case of powdering solids and those which were prepared in the laboratory. This latter group included all of the clathrates and complexes.

Although there are several different schemes which might have

been used to form clathrates, the method used in this investigation was that described by de Radzitzky and Hanotier (23). Here the Werner complex was formed by titration of the metal salt with an amine in the presence of the compounds to be clathrated. A typical scheme is shown in Figure 9.

Figure 9. Scheme for the Preparation of the $\text{Ni}(\text{SCN})_2 \cdot (\text{a-methylbenzylamine})_4 \cdot \text{o-xylene}$ Clathrate (23).

The preparation of other clathrates was accomplished using this same scheme with different compounds appropriately substituted. In this study, because the effectiveness of the clathrate process was not the object of investigation, instead of adding a mixture of xylene isomers, only one isomer was clathrated.

The complexes used as additives to the films were prepared in a manner similar to that of the clathrates (23). Figure 10 shows an ex-

ample of the procedure followed in this study. Other complexes were prepared by the substitution of different compounds in this scheme.

Figure 10. Scheme for the Preparation of the $\text{Ni}(\text{SCN})_2$ -(a-methylbenzylamine)₄ Complex (23).

Casting Solution Preparation. Casting solutions were prepared by combining the plastic solution with the additive. This was accomplished by stirring the solution at room temperature if the additives were soluble, or by heating gently and stirring if partially soluble at room temperature. For those additives not soluble in the plastic solution, vigorous stirring was used to uniformly disperse the powdered particles. As with the plastic solution, the additive composition was determined by a weight ratio with the resin.

Film Casting. Once the casting solution had been prepared, it was then cast on a glass plate which had been thoroughly cleaned by washing the casting surface with water and wiping with acetone. The casting process was done in two different ways. For the thin films, with a solvent-to-resin ratio from 6:1 to 20:1, a glass plate with a specified number of masking tapes placed along the long edges was used.

After pouring an adequate amount of casting solution along one end of the plate, it was then spread uniformly over the plate by drawing a stirring rod down the length of the plate at a speed of about 1-inch per second. This process is shown in Figure 11.

Figure 11. Procedure Used in Casting Thin Films.

Thick films were those made from a plastic solution with a solvent-to-resin ratio of 3:1. With high concentrations of additive

material, these casting solutions were very viscous and could not be cast in the same manner as the thin solutions. A uniform film was obtained by spreading the material over a 4.5-inch square area on the center of the glass plate. Upon standing at room temperature for a short time or when initially heated in the oven, the small irregularities in film thickness disappeared.

Membrane Conditioning. The membrane producing process was completed by heating the glass plate on which the film was cast in an oven. This was a very critical step and several different conditions were applied. The oven temperature and the length of time spent in the oven were most important. The object of this step was to drive the solvent from the membrane and impart to the membrane those physical properties of strength and structural uniformity necessary in the liquid permeation process.

For thin films, the usual conditions involved placing the glass plate in the oven initially at approximately 135° C for a period of about 5 minutes. During this time the oven door remain closed. In all cases, because the oven temperature was controlled only by a rheostat, the temperature at the start of conditioning was the critical factor in maintaining uniform treatment conditions for each membrane.

Generally for these thin films, treatment conditions too severe produced membranes with a bright yellow tint instead of the usual light blue or green color. This degradation could be avoided by re-

moving the films from the oven just before all the solvent had evaporated from all portions film surface. Upon removal, the areas still "wet" with the solvent quickly dried.

These thin films were removed from the casting plate by first using a razor blade to cut along the edge of the tape and to lift one edge of the film from the end of the glass. Then by holding the film along the edge loosened from the plate, the remainder of the film was then easily stripped from the plate by gently lifting upward.

For the thick films, very different treatment conditions were needed. To produce membranes which could be tested, treatment conditions ranged from 60 minutes in a 90° C oven to 15 minutes in a 150° C oven. These conditions produced films drastically different in appearance. With the most severe conditions of 15 minutes at 150° C, the film was bright yellow and the exposed surface was completely covered with small craters or indentations. These craters result from the hardening of the film surface as bubbles of gas or solvent burst. Because the high temperature causes the surface of the film to quickly loose the solvent, the casting solution is unable to flow back into these cavities. Although these craters do not extend completely through the film, they do cause the film thickness to vary widely.

For the very mild treatment conditions of 90° C for 60 minutes, the resulting membranes were blue in color, appeared to have the additive evenly distributed throughout, and were very uniform in thickness

with virtually no craters. Treatment conditions midway between the extremes produced satisfactory membranes which were still cratered, but not as deeply as those with the most severe conditions.

Additional factors found important in reducing the cratering with the thick films included allowing the films to stand at room temperature for a few minutes before conditioning and periodically vibrating the glass plates sharply during the first part of the conditioning process. Both of these actions served to rupture the bubbles at a time when the casting solution could still flow into the vacancies.

Permeation Cell Assembly. Before each run the permeation cells were cleaned by flushing with acetone and drying with compressed air.. These procedures were used to insure that no feed or product from previous runs contaminated that of the present run.. The cell assembly procedure was then to: 1) place the metal membrane support with wire screens in the bottom of the permeation cell; 2) place a 9-cm diameter filter paper over the screens; 3) place the lower Gylon gasket on the cell bottom and center with the bolt holes; 4) put three 7-cm diameter filter papers in the center of the gasket; 5) place a 7.5-cm diameter filter paper over the gasket so it overlaps evenly; 6) place the membrane on the lower part of the cell so that all the permeation area is covered; 7) put the upper Gylon gasket on the membrane and center with the holes; 8) carefully position the upper part of the permeation cell on the gasket so as not to disturb the membrane or its supports;

9) after punching holes in the film with a sharp instrument, push the bolts through the holes and secure with nuts.

Liquid Permeation System Assembly. The liquid permeation system was assembled in the following manner: 1) the permeation cell was positioned on its stand; 2) the heating collar was slipped into place on the upper part of the permeation cell and connected to the controlled power source; 3) the stirrer was coupled to its motor; 4) the two cold traps were connected and slowly lowered into the containers of liquid nitrogen; 5) the tubing from the safety trap and product cold trap was connected to the "T" fitting on the lower part of the permeation cell.

Run Procedure. With the liquid permeation system assembled, the following steps were taken before starting an experimental run. First, the liquid feed material was added to the upper portion of the cell. This feed material was mixed from practical-grade stock and was supplied from several different sources. Next the stirrer was activated and the temperature probe inserted in the liquid. After switching on the power to the heating collar, the run time began when the vacuum pump was started.

A run was terminated when the vacuum pump was shut down and the tubing removed from the permeation cell. To complete this process, the power to the heating collar was shut off and the cold traps were removed from the liquid nitrogen. The product cold trap was heated

with warm water to melt the permeant. The liquid feed was poured from the cell to another container and retained for later use.

After being removed from the permeation cell, the used membrane was inspected and kept for comparison with other films.

Product Analysis. The run product volume was first determined quantitatively by pouring it into a graduated cylinder. The product cold trap was then rinsed with approximately 3 ml of acetone (for product volumes less than 10 ml only) to flush any remaining permeant from the cold trap. This liquid was then added to the permeant previously removed and then analyzed for product distribution using the gas chromatograph apparatus previously described. The final analysis of the chromatograms for both the feed and product was done using one of the standard methods of calculating peak area by using the formula: $\text{area} = (\text{peak height}) \times (\text{width at } 1/2 \text{ peak height})$, or gravimetrically determining the peak area by weighing a "cut-out" of the peak, or by calculating the peak area based on the disc-integrator output recorded on the chromatogram. The last method was preferred although all three displayed about the same degree of variation.

The basic elements of the experimental procedure are shown schematically in Figure 12. Variations of this experimental procedure will be fully discussed along with the experimental results for each individual membrane system.

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Figure 12. Basic Experimental Procedure

RESULTS AND DISCUSSION

The purpose of this section will be to present the important results of the experimental work and to discuss these results in order to better understand the role of the conditioned membranes in the separation of the xylene isomers using the liquid permeation process. The presentation of these results will include graphical displays of membrane-performance parameters as well as analyses of the controlling mechanisms involved.

These results included those from the polyvinyl-chloride film studies, vinylidene-fluoride film studies, and the final system performance studies along with many subdivisions under each topic.

PVC FILM STUDIES

The membranes made with PVC as the resin were those initially investigated. This investigation included some preliminary runs to generally determine the response of this system to changes in film-modifying variables and later three more carefully constructed experiments to more fully define the response of this membrane system to a variety of membrane modifications.

In these studies and those that follow, the selectivity of the films for the para-xylene isomer will be indicated by the difference between the percentage composition of para-xylene in the product and

the percentage composition of para-xylene in the feed. This scheme gives a good indication of the overall film performance because with a feed mixture containing all three xylene isomers in approximately equal proportions, the products were found to contain an increased amount of para-xylene, a decreased amount of ortho-xylene, and approximately the same amount of meta-xylene.

Because this method requires no "back-calculating" to show what happened to the compound of interest, it was preferred for comparing results on a daily basis. Evaluations and comparisons of membrane performance based on other methods of defining selectivity are shown later.

Preliminary PVC Film Studies. The first preliminary study with PVC film involved the modification of the membrane by adding the $\text{Ni}(\text{SCN})_2(4\text{-methylpyridine})_4$:p-xylene clathrate. To a 6:1 (cyclohexanone: PVC) plastic solution was added 0.05 to 0.5 gm of clathrate. With an approximately equimolar feed at room temperature and with the downstream pressure less than 1 mm Hg, these thin films with the clathrate additive produced a moderate increase in the para-xylene selectivity over the unmodified PVC films. Whereas these unmodified PVC films produced a para-xylene product-feed composition difference of 2.5 percent, the maximum difference for the modified film in this instance was 4.8 percent. As shown in Figure 13, a fairly well defined maximum in selectivity occurred when approximately 0.05 grams of clathrate

were added per gram of resin.

An examination of the product flow rate through these films, as presented in Figure 14, reveals that the xylene isomers are relatively soluble in the unmodified PVC film. The slight decrease in permeability with increasing amounts of clathrate added is unusual and not displayed by other film systems.

Other preliminary runs with this same membrane system, but also including a small amount of 4-methylpyridine in the feed, or ethylbenzene in the feed, or a small amount of para-xylene in the casting solution revealed no drastic change in membrane performance. However, as a result of these runs, the operating characteristics of the thin PVC films were adequately defined to permit the use of a more sophisticated experimental design.

PVC Factorial Studies. In order to examine the effects of varying two or more variables simultaneously, a factorial experimental design was employed. Here it was possible not only to assess the effect of one variable independently of the others, but also to determine the magnitude of the interactions between variables. In this research effort, three variables, each at a high and low level, which were thought to affect the membrane performance were investigated together. Factorial experiments of higher order than this 2^3 factorial were avoided because of the lack of experimental experience necessary to insure the optimum use of the time available. Because only the results of these

Figure 13. Para-Xylene Selectivity with Different Amounts of a Para-Xylene Clathrate Added to a Thin PVC Film.

Figure 14. Total Product Flow Rate with Different Amounts of a Para-Xylene Clathrate Added to a Thin PVC Film.

experiments will be presented, the reader may consult one of the references given to more fully understand the theory and mechanics of this statistical tool (34,35).

Three separate factorial studies were completed using the PVC films. The first investigated the effects of changing the plastic solution composition ratio, the amount of clathrate added to the plastic solution, and the addition of the appropriate basic nitrogen compound to the feed. The second study examined the effects of clathrate type, and the conditioning factors of oven temperature and oven time. In the third, the effects of clathrate type and the addition of the appropriate nitrogen compound to both the feed and film were determined.

In these experiments, two runs were made at each of the eight treatment combinations. The order of running the sixteen parts of the experiments was chosen at random to confound the effects of any factors introduced by unplanned variations of experimental technique.

The object of the first study was to determine the effects of changes in the solvent-to-plastic ratio, the level of clathrate addition, and the addition of a basic nitrogen compound to the feed material on the membrane performance as judged by the para- and ortho-xylene product-feed differences and the magnitude of the product flux. The fixed factors for this experiment included:

plastic resin : PVC

solvent : cyclohexanone
film additive : $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$
feed additive : a-methylbenzylamine
feed temperature : 30° C
feed composition : approximately equimolar with p-,
m-, and o-xylene
downstream pressure : <1 mm Hg
film conditioning temperature : 130° C
film conditioning time : 2.5 minutes
film casting thickness : 1 tape

The three variables with the high and low levels were:

	Low Level	High Level
solvent-to plastic ratio	6:1	20:1
plastic-to-clathrate ratio	1:0.25	1:1.0
feed additive	0 %	3 % of total

The results of this factorial study included the following:

1) The level of clathrate addition to the film was the most significant factor in determining the para-xylene composition of the product. The effect of increasing the clathrate level from 0.25 to 1.0 grams per gram of resin was to decrease the percentage composition in the product by 2.2 ± 0.22 with 90 percent confidence.

2) The selectivity of the membrane was not significantly influenced by the film thickness as determined by the solvent-to-plastic ratio. However, the total product flow rate appears to be inversely proportional to the film thickness as determined by the solvent-to-plastic ratio. This result corresponds with the Fick's law diffusion expressions in which the flux is inversely proportional to the distance of diffusion.

3) The addition of the basic nitrogen compound part of the clath-

rate to the feed failed to influence the membrane selectivity. This result seemingly contradicts that reported in the literature that the inclusion of the nitrogen compound found in the clathrate as part of the feed helps maintain the selectivity of the membrane (27).

4) The best increases of para-xylene were obtained with films containing the low level of the clathrate and with the feed containing no a-methylbenzylamine. With these conditions, a para-xylene product-feed difference of 4.5 ± 0.9 percent with 90 percent confidence was obtained at a product flow rate of up to 440 ml/hr ft².

The object of the second PVC factorial study was to determine the effects of the film conditioning factors of oven temperature and oven time on films containing different clathrates. The fixed factors for this experiment were:

plastic resin : PVC
solvent : cyclohexanone
feed temperature : 30° C
feed composition : approximately equimolar with p-,
m-, and o-xylene
downstream pressure : <1 mm Hg
film composition : 6:1:0.25 (solvent:resin:clathrate)

The three variables at the high and low levels were:

	Low Level	High Level
clathrate type	Ni(SCN) ₂ (a-MeBzAm) ₄ · o-xylene, 1 tape	Ni(SCN) ₂ (4-MePy) ₄ · p-xylene, 2 tape
oven temperature	120° C	155° C
oven time	2.5 minutes	5.0 minutes

Two tape thicknesses were needed when casting films with the para-xylene clathrate because this additive, which is much more insoluble

in the plastic solution than the other, would quickly form relatively large solid particles in the plastic membrane. The extra tape thickness provided the additional strength needed for this system.

The results of this factorial study included the following:

1) The permeation rate was significantly affected only by the amount of time the film spent in the oven. The effect of increasing the oven time from 2.5 to 5.0 minutes was to decrease the flux by 72 ± 21 ml/hr ft² with 90 percent confidence.

2) The expected para-xylene composition varied ± 0.9 percent at the 90 percent confidence level at a given treatment combination. The effect of increasing the oven time was to slightly reduce the para-xylene selectivity of the membrane. An interaction significant at the 95 percent level between the film composition and oven temperature was the result of poor para-xylene selectivity of the membranes containing the para-xylene clathrate and conditioned at 155° C. The best separation was obtained with the films containing the ortho-xylene clathrate which were conditioned at 120° C for 2.5 minutes. The 4 percent para-xylene increase was obtained with a product flow rate of about 80 ml/hr ft².

3) The inclusion in the film of two clathrates, each selective for a different xylene isomer, did not greatly influence the selectivity of the membrane. With the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ clathrate strongly selective for ortho-xylene and the $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4$ clathrate selective

for para-xylene, the results of this study suggest that the selectivity for para-xylene imparted to the membrane was due to a mechanism not exactly like that of the clathration process alone.

The object of the third factorial study was to determine the effects of adding the appropriate basic nitrogen compound both to the feed and to the film when used with films containing the two clathrates previously used. For the membranes containing the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ ortho-xylene clathrate, a-methylbenzylamine was the compound added; for the $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4$ para-xylene case, 4-methylpyridine was the compound used. The fixed factors for this experiment included:

plastic resin : PVC
 solvent : cyclohexanone
 feed temperature : 30° C
 feed composition : approximately equimolar with p-,
 m-, and o-xylene
 downstream pressure : <1 mm Hg
 film composition : 6:1:0.1 (solvent:resin:clathrate)
 oven temperature : 135° C
 oven time : 4 minutes
 nitrogen compound additives : a-methylbenzylamine and 4-methyl-
 pyridine

The three variables at the high and low levels were:

	Low Level	High Level
clathrate type	$\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ o-xylene	$\text{Ni}(\text{SCN})_2(4\text{-MePy})_4$ p-xylene
nitrogen compound in film	None	6:1 (solvent:BNC)
nitrogen compound in feed	None	5 %

The results of this third factorial study included:

- 1) Although there was a significant interaction between the addi-

tion of the nitrogen compounds to the feed and to the film, this effect did not greatly influence the maximum para-xylene selectivity obtained. This was due to the small variations in values due to different treatment combinations and the variation of repeating values in each treatment combination. With 90 percent confidence, the maximum para-xylene product-feed difference was 4.0 ± 1.0 percent.

2) A significant interaction between clathrate type and the addition of the nitrogen compound to the feed was the result of high permeation rate values for the system with 4-methylpyridine added to the feed. The total product flow rate was quite variable at 200 ± 10^4 ml/(hr ft²).

3) The addition of the appropriate basic nitrogen compound to the casting solutions appears to have little effect on the membrane selectivity.

4) In this study, as in the second, the added selectivity imparted to the film by including the different clathrates was not the result of these clathrates operating independently of the film system. Both clathrates increased the selectivity for the para-xylene isomer by amounts not significantly different from each other.

PVC System Summary. The preliminary and factorial studies of the membrane systems using PVC as the resin and the clathrates Ni(SCN)_2 -(a-MeBzAm)₄:o-xylene and Ni(SCN)_2 (4-MePy)₄:p-xylene as the main film additives showed that it was possible to significantly increase the

natural ability of the films to separate para-xylene from a xylene mixture.

Also demonstrated was that the type of clathrate added to this film system had little effect on the para-xylene selectivity whereas the amount added was important. The addition of the nitrogen compound found in the clathrate to either the feed or the film casting solution had little effect on the membrane selectivity. The film conditioning factors of oven temperature and oven time were both found important in determining the overall performance of the PVC membranes.

Although the PVC system has provided valuable information concerning the modification of plastic films to increase their ability to selectively permeate one xylene isomer, this system appears unsuitable for more extensive research into the mechanism of this selectivity increase and for liquid-permeation system optimization studies because the natural selectivity of the PVC for para-xylene may mask the true contributions of the film additives and conditioning modifications.

VF FILM STUDIES

Vinylidene-fluoride resin was chosen as the base for liquid permeation membranes because it is very impermeable to the xylene isomers. Any ability of this film material to naturally select one isomer over the others was insignificant because of the extremely small rate of permeation. Therefore, it was concluded that any selectivity imparted

to this type of film was due only to the materials added to the film and the methods of conditioning.

The VF membrane systems investigated included both thick and thin films. In the thick films the effects of adding different clathrates and complexes were investigated along with the effects of adding nitrogen compounds to the feed or film, adding a clathrate solvent to the feed, including para-xylene in the film, using different components in the included clathrates, using different film treatment combinations, and different feed compositions. The thin film studies involved adding extractive distillation agents to the film, including a plasticizer in the film, changing the feed temperature, adding a nitrogen compound to the feed, completing two factorial studies, running selectivity studies, and determining the effects of feed composition and temperature.

Thick VF Films with Clathrate Addition. Preliminary work with thin VF films with relatively high clathrate-to-resin concentrations showed that it was very difficult to obtain cast membranes without small holes. This was most apparent with $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4 \cdot \text{p-xylene}$ as the additive. In an attempt to overcome this problem, the additive materials were combined with a thick plastic solution having a resin-to-solvent ratio of 3:1.

After initial runs in which the casting procedure and film treatment conditions were established, the first study compared the para-

xylene selectivity changes resulting from the addition of either the $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4 \cdot \text{p-xylene}$ or the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate to the thick VF films. As shown in Figure 15, the addition of the clathrate material to the film produces an increase in para-xylene selectivity. In both cases this increase passes through a single maximum value.

Contrary to the results shown in the PVC studies, there appears to be a significant difference in selectivity due to the type of clathrate added. This difference was shown by this study to be one due to the particular composition of the clathrate added and not due only to the amount added. Also shown was that in this film system the clathrates incorporated into the membranes produced the resulting selectivity by some mechanism other than that of classical clathration. This conclusion was obvious because the higher para-xylene selectivity was obtained with the clathrate which was reported to be highly selective for the ortho-xylene isomer.

The great difference in performance of these two additives was also shown by the values obtained for total product flow rate. As represented in Figure 16, the flow rates for the films with the ortho-xylene clathrate rise very slowly throughout the greater part of the addition range and then sharply increase at the high values. Those for the para-xylene clathrate show a more unusual pattern and appear to decrease at intermediate levels before sharply increasing at the

Figure 15. Para-Xylene Selectivity with Different Amounts of Clathrate Added to Thick VF Films.

Figure 16. Total Product Flow Rate with Different Amounts of Clathrate Added to Thick VF Films.

high level. The increase in flux at high clathrate addition levels along with the loss of selectivity is thought due to a weakened membrane structure.

It must be noted that even though the values plotted in Figure 15 are averages of three experimental points, subsequent to this study it was not possible to obtain values of para-xylene product-feed differences as large as those shown with the same system. However, the overall effects of this clathrate addition study were obtained in other studies with the only difference being the magnitude of the para-xylene increase. This lack of reproducibility between studies was also to occur in other film systems and was thought due to unnoticed changes in experimental film-casting and film-conditioning techniques.

In an attempt to improve the performances of the thick VF films containing the clathrates, the effects of adding the appropriate nitrogen compound to both the feed and film were investigated. As shown in Figure 17, the effect of adding the nitrogen compounds to the feed was to decrease the para-xylene separation. With the $\text{Ni}(\text{SCN})_2$ - $(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate added to the film, the selectivity decrease was quite variable and relatively small over a large range of feed-addition levels. In the para-xylene clathrate case, virtually all of the decrease occurred at the 3 percent 4-methylpyridine level. The total product flow rate remained almost constant at 0.4 ml/(hr ft²) throughout the entire addition range for the a-methylbenzylamine case.

Figure 17. Para-Xylene Selectivity with Different Amounts of Nitrogen Compound Added to the Feed Used with Thick VF Films Containing Clathrates.

With the 4-methylpyridine addition to the feed, the flux was highly variable and ranged between 1.3 and 4.3 ml/(hr ft²). This study also demonstrated the difference in performance of this membrane system due to different clathrate additions.

In later studies of this film system with the clathrates added to thick VF films, the effects of adding the appropriate nitrogen compound to the casting solution were investigated. Here it was found that for the addition of *a*-methylbenzylamine to the casting solution, a small increase in selectivity at a level of 1:1 (clathrate:nitrogen compound) was followed by a small decline at higher levels. For the addition of 4-methylpyridine to the casting solution containing the para-xylene clathrate, no increase was noted. These effects are illustrated in Figure 18.

The effect on the product flow rate of modifying the casting solution containing the clathrate by adding the nitrogen compounds is shown in Figure 19. For the *a*-methylbenzylamine case, the rate of permeation appears to be an exponential function of the amount of nitrogen compound added to the casting solution. For the 4-methylpyridine addition, the values for product flux were approximately ten times as large and widely variable with no simple relationship apparent between flow rate and addition level. The results of this study showed that it was much more difficult to produce uniform membranes which contained the $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4 \cdot \text{p-xylene}$ clathrate than with the other

Figure 18. Para-Xylene Selectivity with Different Amounts of Nitrogen Compound Added to Casting Solutions for Thick VF Films Containing Clathrates.

Figure 19. Total Product Flow Rate with Different Amounts of a-Methylbenzylamine Added to Thick VF Films Containing a Clathrate.

clathrate used. This lack of uniformity is believed a result of the low solubility of the para-xylene clathrate in the casting solution in contrast to the high solubility of the ortho-xylene clathrate.

In a similar attempt to increase membrane selectivity, a clathrate solvent was added to the xylene feed. Instead of adding a component necessary to form the clathrate, it was thought that the solvent might allow the clathrates to release the included compounds and the permit them to reform. To test this idea, ethylene glycol, mono-methyl ether (Dow Chemical's "Dowanol-EM"), which had been found to be an acceptable solvent by Schaeffer et al., was chosen as the feed additive (22). The overall effect was similar to that of adding the nitrogen compound to the casting solution. For films with the ortho-xylene clathrate, a slight increase was noted throughout a broad addition range. With the para-xylene clathrate, the addition of only one percent produced a para-xylene product-feed difference decrease of over one percent. As shown in Figure 20, it appears possible to productively modify the performance of the films containing the $\text{Ni(SCN)}_2 \cdot (\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate by the addition of an agent to the feed which acts on the selectivity-producing compounds.

The response of the product flow rate to the clathrate solvent addition is shown in Figure 21. Here the flux appears to be a linear function of the amount added to the feed rather than the exponential function shown previously for the addition of the nitrogen compound to

Figure 20. Para-Xylene Selectivity with Different Amounts of Methyl Cellosolve Added to Xylene Feed Used with Thick VF Films Containing Clathrates.

Figure 21. Total Product Flow Rate with Different Amounts of Methyl Cellosolve Added to Xylene Feed Used with Thick VF Films Containing Clathrates.

the casting solution.

In order to test a selectivity-increasing mechanism like that used by Michaels et al. (14) in studies with polyethylene film, para-xylene was used as the sole feed component for a run period equal to that of one which followed using a xylene feed mixture and the same membrane. For films in which both clathrates were included as in previous runs, no increase in para-xylene selectivity was noted after the residual para-xylene left in the film from the first run was removed.

Another study involved adding para-xylene to the casting solution in resin-to-para-xylene ratios of 4:1 and 4:2 for thick VF films with a composition of 12:4:1 (solvent:resin:clathrate). In all cases, no significant increase in para-xylene was noted although the permeation rate was increased.

Metal Ions in Clathrates with Thick VF Films. Schaeffer and his co-workers reported that some of the transition elements were suitable for the metal ion constituent of the Werner complexes investigated. In particular, nickel, cobalt, manganese, iron, copper, and zinc were tested. These researchers found that the nickel and cobalt complexes produced superior results for para-xylene recovery as compared to the iron and manganese compounds. This sensitivity was termed remarkable when considered in the light of the principal apparent variable, the effective radii of the metal ions. Octahedral radii of manganese, iron, cobalt, nickel, copper, and zinc range only from 1.23 through

1.39 Å, a total range of only 0.16 Å (22).

In order to test this effect in the thick VF film system, clathrates of the type $X(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$, where "X" is a metal ion, were incorporated in the membranes with the composition ratio 12:4:0.5 (DMF:VF:Clathrate). After conditioning in the oven for 20 minutes at 130° C, these films were handled in the usual manner.

Using the method of Radzitzky and Hanotier previously outlined, the following metal salts were used in the preparation of the clathrates: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (the usual salt), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and ZnCl_2 . It was found that no clathrates were formed with the iron, manganese, and zinc salts. The volume of the dark blue clathrate formed with the copper salt was approximately one-half that of the light blue clathrate formed with the nickel salt. The clathrate formed with the cobalt salt was a gray color and appeared to decompose on exposure to air. The volume of this clathrate was also about one-half that which included the nickel.

The results of this study in which three runs were made with each clathrate were that virtually no changes in selectivity and product flow rate were found due to the presence of different metal ions in the membrane. These results also indicate that in this membrane system the selectivity is not a result of clathrate action only.

Anions in Clathrates with Thick VF Films. Among the anions given by Fleck and Wight (27) as suitable for use in complexes which may

separate the aromatic compounds desired in this study were thiocyanate (SCN^-), cyanide (CN^-), cyanate (OCN^-), and acetate ($\text{C}_2\text{H}_3\text{O}_2^-$). The effects of incorporating these different anions in the $\text{Ni}(\text{Y})_2(\text{a-MeBz-Am})_4$:o-xylene clathrate, where "Y" is an anion, were investigated.

Using the procedure previously outlined, the following salts were used to provide the anions in the clathrates: KSCN, KCN, KOCN, and $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$. The clathrate formed with the cyanide anion was of small volume and light blue. That with the cyanate anion was light green and also of small volume when compared to the clathrate containing the thiocyanate anion. No clathrate was formed with the acetate anion.

The influence on para-xylene selectivity of the type of anion in the clathrate was shown to be significant. As represented graphically on Figure 22, three distinct selectivity-response patterns were evident. Almost no separation was obtained with the clathrate containing the cyanide anion. The thiocyanate- and cyanate-containing membranes both produced approximately the same maximum selectivity for para-xylene, but the films with the cyanate anions lost their selectivity at higher clathrate addition levels much faster than those with the thiocyanate anions.

The difference in performance of these film systems was also shown by the product flow rates. Figure 23 shows that the permeation rate in all cases appears to be an exponential function of the amount of clathrate added to the casting solution. The difference in slopes

Figure 22. Para-Xylene Selectivity with Ortho-Xylene Clathrates Containing Different Anions Added to Thick VF Film.

Figure 23. Total Product Flow Rate with Ortho-Xylene Clathrates Containing Different Anions Added to Thick VF Film.

between the thiocyanate and cyanate systems represents a ten-fold product flow rate difference at the high clathrate addition level.

Contrary to the results of the study in which different metal ions were substituted in one clathrate, this study which substituted different anions showed a behavior much like that of a true clathrate system; that is, changes in any component may affect the ability of the clathrate to select one compound over another. It should also be noted here that the exponential dependence of the product flow rate on the amount of clathrate added to the casting solution shown here contrasts with the result shown in Figure 16. As mentioned previously, along with the higher flow rate in this study went an overall decrease in selectivity when compared with the previous study even though the shapes of the selectivity-response curves remained similar.

Included Compounds of Clathrates in Thick VF Films. The effects of included compounds on membrane performance were investigated in two studies. In the first study using the ortho- and para-xylene clathrates of $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ in films of composition 12:4:0.5 (DMF:VF:Clathrate) which were conditioned at 130° C for 20 minutes, it was found that the para-xylene clathrate gave a para-xylene product-feed difference 1.5 percent lower than with the ortho-xylene clathrate.

In a more complete study, the ortho- and para-xylene clathrates of $\text{Ni}(\text{OCN})_2(\text{a-MeBzAm})_4$ were compared throughout a broad range of clathrate addition levels. As shown on Figure 24, the difference in

para-xylene selectivity shown by the two additives appears to be significant. The inclusion of the para-xylene appears to depress the selectivity and broaden the range of maximum selectivity. The product flow rates of these films were nearly identical. The ortho-xylene case is shown on Figure 23.

Treatment Conditions of Thick VF Films with Clathrates. The thick VF film treatment conditions of 130° C and 20 minutes which were used in the studies previously described were not chosen arbitrarily and seemed adequate, but they were not chosen as the result of systematic experimentation. In order to determine the effects of oven temperature and time on films of composition 12:4:0.5 - 3.5 (DMF:VF: $\text{Ni(SCN)}_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$), the performances of the films with treatment conditions of 90° C - 60 minutes, 110° C - 40 minutes, 130° C - 30 minutes, and 150° C - 20 minutes were compared with films treated at 130° C for 20 minutes.

These treatment conditions do not represent all the possible combinations of time and temperature that could provide films suitable for use in the liquid permeation system, but do represent different conditions in the neighborhood of those used previously. The films were all cast in the same manner and with the given oven temperature being that at the start of conditioning.

The treatment conditions included two more severe than the standard and two less severe. The conditions of 130° C for 30 minutes and

Figure 24. Para-Xylene Selectivity with Clathrates
 Containing Different Included Compounds Added to Thick VF Films.

150° C for 20 minutes were those more severe. The membranes treated under these conditions were more pitted and yellow than those conditioned for 20 minutes at 130° C. As shown in Figure 25, the para-xylene selectivity was decreased under these conditions throughout the entire range of clathrate addition. Figure 26 shows that even though the films conditioned at 130° C for 30 minutes were less permeable at the low clathrate addition levels, the rate of permeation increased much more rapidly at higher levels than for the films conditioned at 130° C for 20 minutes. This ten-minute difference in oven time appears to cause the increase in flow rate by excessively drying and then degrading the film materials.

The treatment conditions of 110° C for 40 minutes and 90° C for 60 minutes appeared to be less severe than the standard conditions of 130° C for 20 minutes. The films conditioned at the lower temperatures were much more uniform in thickness and texture with almost no cratering.

The response of para-xylene selectivity to increased levels of clathrate in the films treated under the less severe conditions was very different from those with the standard conditions. As shown in Figure 27, the results from both the 90° C - 60 minute and 110° C - 40 minute conditions were very similar. The effect of both of these mild treatments was to maintain the selectivity throughout a much larger range of clathrate addition.

Figure 25. Para-Xylene Selectivity with Different Treatment Conditions Applied to Thick VF Films Containing an Ortho-Xylene Clathrate.

Figure 26. Total Product Flow Rate with Different Treatment Conditions Applied to Thick VF Films Containing a Clathrate.

Figure 27. Para-Xylene Selectivity with Different Treatment Conditions Applied to Thick VF Films Containing a Clathrate

Although displaying about the same selectivity, the total product flow rates for these two mild treatment conditions were quite different. As illustrated on Figure 28, the membranes conditioned at 90° C for 60 minutes gave results in the neighborhood of those obtained from films conditioned at 130° C for 20 minutes. In contrast to this, the films conditioned at 110° C for 40 minutes were less permeable and did not show the exponential dependence of the flow rate on the level of clathrate addition until the higher levels.

This study demonstrated the importance of the treatment factors of oven temperature and time on the performance of the membranes. For treatment conditions which allowed the films to dry without cratering and degradation, the para-xylene separation was maintained over a broad range of clathrate addition levels. Although not investigated here, there are many other factors which may have an important role in conditioning the membrane. Among these could be the temperature change during conditioning and the environment of the oven cavity with regard to solvent removal.

Feed Composition for Thick VF Films with Clathrates. Works by other researchers have indicated that the selectivity of a membrane may or may not be dependent on the feed composition. To determine the selectivity response of the thick VF films containing the $\text{Ni}(\text{SCN})_2 \cdot (\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate to feeds containing all three xylene isomers and only para- and meta-xylene, runs were completed at four

Figure 28. Total Product Flow Rate with Different Treatment Conditions Applied to Thick VF Films Containing a Clathrate

different clathrate levels.

To compare any difference in the selectivity of the membrane for the para isomer over the meta, the selectivity was computed in a manner similar to that of a relative volatility. For this method of computation, the selectivity is given as:

$$S_1^i = \frac{x_1/(1 - x_1)}{x_1^o/(1 - x_1^o)}$$

where

S_1^i = permselectivity of component 1

x_1 = mole fraction of 1 in vapor product

x_1^o = mole fraction of 1 in feed liquid

As shown in Figure 29, the selectivity of this membrane system for the para-xylene over the meta-xylene was increased throughout the entire clathrate addition range when the ortho isomer was included in the feed. These results indicate that for this system the permeation through the film was not a case of classical diffusion where the xylenes form ideal solutions in the polymer phase. Rather, some interaction between the feed components and the film material was indicated. This conclusion agrees with that reached by Binning (22).

The maximum selectivity value of 1.43 shown on Figure 29 corresponds to a value of 1.18 as computed by the permselectivity given by Michaels et al. (14). The total product flow rates with either feed were nearly identical and agreed with values obtained previously.

Figure 29. Selectivity for Para-Xylene Using Different Feeds with Thick VF Films Containing a Clathrate.

Thick VF Films with Complex Addition. The diffusional separation of aromatic compounds revealed by Fleck and Wight was accomplished using a barrier composed in part of a solid Werner complex (27). For the most part their diffusion barriers preferentially passed the para-xylene isomer; however, it was claimed that by suitably modifying the structure of the barrier the selectivity preference could be changed in favor of the other two isomers. In order to determine the behavior of the present system with complexes rather than clathrates added to the film, three studies were conducted. The first looked only at adding the complexes to a thick VF casting solution and the other two examined the effects of adding the appropriate nitrogen compound to either the feed or the casting solution.

Using complexes as described previously, the casting solutions for the thick films containing the complexes were prepared in exactly the same manner as for those containing the clathrates. The para-xylene selectivity imparted to these films with the complex addition was in some ways similar to those containing the clathrates and in other ways quite different. The maximum para-xylene product-feed difference obtained with the inclusion of either the $\text{Ni(SCN)}_2(\text{a-MeBzAm})_4$ or $\text{Ni(SCN)}_2(4\text{-MePy})_4$ complex was about the same at 3.5 percent. This value is much lower than the best values achieved with clathrate addition, but roughly corresponds with lower values obtained in other studies. Some differences between this system and the other are that both complexes

produced about the same maximum selectivity and that the addition of the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ complex extended the selectivity at very high complex addition levels. The selectivity was maintained at its highest level at complex addition levels which were approximately eight times the level of clathrate added to the VF film to obtain maximum selectivity. These selectivity effects are shown in Figure 30. As shown in Figure 31, the total product flow rates for this system also displayed an exponential dependence on the additive quantity in the casting solution and generally agreed with those values produced by the clathrate system.

This study showed that the addition of a complex to the VF film produces an increase in para-xylene selectivity. Even though the maximum selectivity obtained was about the same in both cases, examination of the performance of the membranes throughout a broad range of complex addition revealed that the two complexes which differ only in the nitrogen compound constituent reacted very differently. This difference in performance was attributed to the greater solubility of the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ complex in the VF casting solution.

The effects of adding the appropriate nitrogen compound to the xylene feed were also investigated for these thick VF films which contained complexes. a-Methylbenzylamine was added to the feed used with the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ complex and 4-methylpyridine with the $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4$ complex. As shown on Figure 32, the para-xylene

Figure 30. Para-Xylene Selectivity with Different Amounts of Complex Added to Thick VF Films.

Figure 31. Total Product Flow Rate with Different Amounts of Complex Added to Thick VF Films.

product-feed difference decreased with the addition of 4-methylpyridine to the feed in a manner similar to that for films containing the clathrate. The selectivity response to the α -methylbenzylamine addition was also similar to the response shown in the clathrate system, but with the overall values lower in the present case.

The total product flow rate with the 4-methylpyridine added to the feed was variable and averaged about $1.5 \text{ ml}/(\text{hr ft}^2)$. Whereas the VF films containing the clathrate produced a constant flow rate of approximately $0.4 \text{ ml}/(\text{hr ft}^2)$, with the α -methylbenzylamine added to the feed used with films containing the complex, the flux appeared directly proportional to the addition level. This effect is shown in Figure 33.

The effects of adding the appropriate nitrogen compounds to the casting solutions containing the complexes were very similar to those observed for the cases in which clathrates were included. As shown in Figure 34, the addition of α -methylbenzylamine produced a small increase in para-xylene selectivity while the added 4-methylpyridine produced a decrease. Because of the rather large variations in permeation rates at a given addition level, no graphical representation of these results will be given. The values ranged from $0.3 \text{ ml}/(\text{hr ft}^2)$ at the low α -methylbenzylamine addition level to $2.8 \text{ ml}/(\text{hr ft}^2)$ at the high level and from $0.4 \text{ ml}/(\text{hr ft}^2)$ at the low level of 4-methylpyridine addition to $7.0 \text{ ml}/(\text{hr ft}^2)$ at the high level.

Bentone 34 Addition to Thick VF Films. Bentone 34 is an organo-

Figure 32. Para-Xylene Selectivity with Different Amounts of Nitrogen Compound Added to the Feed Used with Thick VF Films Containing Complexes.

Figure 33. Total Product Flow Rate with Different Amounts of a-Methylbenzylamine Added to the Feed Used with Thick VF Films Containing a Complex.

Figure 34. Para-Xylene Selectivity with Different Amounts of Nitrogen Compound Added to Casting Solutions of Thick VF Films Containing Complexes.

clay complex and was used as one constituent of the stationary phase in the gas chromatograph column used in the product analysis. Because of its ability to separate para- and meta-xylene, and because it is structured differently from the other film additive previously investigated, its performance was of interest.

Using the thick VF plastic solutions, the Bentone was added in the resin-to-Bentone ratios of 1:0.5, 1:1, 1:1.5, and 1:2.0. Casting solutions with more Bentone than the maximum given were unacceptable because the extremely thick mixtures would not dry uniformly. A para-xylene product-feed difference of 2 percent was obtained at all addition levels with very little variation. The product flow rates ranged from 1.5 to 8.9 ml/(hr ft²) with large variation and with no obvious relationship to addition level.

By using a compound different from the clathrates and complexes previously used as additives, this study showed that the action of these agents was not only due to the modification of the VF film to make it more permeable, but also to some special interaction which greatly increased the selectivity for para-xylene.

Thick VF Film Summary. The studies conducted in which a thick VF plastic solution (3:1, DMF:VF) served as the basic film material were very important in revealing information about this liquid permeation system. With this plastic solution which itself is very impermeable to the xylene isomers, it was determined that the addition of two differ-

ent clathrate materials both produced significant para-xylene selectivity increases, but at different levels. It was further learned that although the metal ion constituent of the clathrates did not influence the membrane performance, the type of anion, nitrogen compound, and included compound were all shown to have significant effects on the membrane permeability. It was shown that the addition of *a*-methylbenzylamine to either the feed or film produced small increases in selectivity for the membranes containing either the clathrate or complex of which it is a part, whereas the addition of 4-methylpyridine to either the feed or film produced only decreases in selectivity for membranes containing this compound in a clathrate or complex. The addition of an organo-clay complex which was unlike the other additives produced a very different selectivity response.

It was concluded that the selectivity imparted to the films by the clathrate additives was not the result of a classical clathration process, but was rather due to a combination of increased solubility of the xylene feed in the membrane and some selectivity-producing mechanism possessing some of the characteristics of a clathration process.

Thin VF Films Containing Extractive Distillation Agents. In an attempt to understand more about the action of increasing membrane selectivity by combining various additives with the VF film system, the effects of including two extractive distillation agents in the thin

films were investigated. Two compounds suggested as being worthy of investigation were 1,2,4,5-tetrachlorobenzene and pentachlorophenol. Of these two compounds, 1,2,4,5-tetrachlorobenzene was the more soluble in the VF plastic solution.

The effect of including these compounds in the thin films was to make the films moderately selective for para-xylene. As shown in Figure 35, both agents produced approximately the same increase. This was somewhat unusual because the product flow rates for films containing these additives were quite different. In Figure 36, it is seen that the less soluble agent had a much greater flow rate throughout the entire addition range.

Thin VF Films Containing Diisodecyl Phthalate and Bentone 34. The effects of adding diisodecyl phthalate and Bentone 34 to the thin VF films were of interest because these two compounds are components of the stationary phase of the gas chromatograph column used to separate the xylenes and diisodecyl phthalate is a widely used plasticizer.

As shown on Figure 37, the addition of diisodecyl phthalate to the thin casting solutions produced a para-xylene selectivity response similar to that of the extractive distillation agents, but about 0.5 percent lower. This result seems to indicate that the selectivity increases due to the addition of non-clathrate compounds is caused by some type of plasticizing action. These compounds modify the internal structure of the films in such a way as to increase the solubility of

Figure 35. Para-Xylene Selectivity with Different Amounts of Extractive Distillation Agents Added to Thin VF Films.

Figure 36. Total Product Flow Rate with Different Amounts of Extractive Distillation Agents Added to Thin VF Films.

Figure 37. Para-Xylene Selectivity with Different Amounts of Diisodecyl Phthalate and Bentone 34 Added to Thin VF Films.

the xylene feed in favor of the para-xylene isomer.

The inclusion of equal amounts of diisodecyl phthalate and Bentone in these films produced a decrease in para-xylene selectivity as the addition level increased. This decrease was attributed to the weakening of the thin membrane by including more of the solid Bentone. This action is shown in Figure 38 by the significantly higher product flow rates obtained by including the Bentone in the films. The exponential dependence of permeation rate on the addition level was maintained in these film systems.

Thin VF Films Containing Clathrates. The studies of the thin VF films containing the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate included one to determine the effects of adding a-methylbenzylamine to the xylene feed, two factorial studies to examine the effects of six experimental factors, and finally studies to investigate the effects of feed composition, temperature, and film durability for one system.

Using a very thin casting solution of composition 20:1:1 (DMF:VF: $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$), a-methylbenzylamine was added to the feed in amounts of 1, 3, 5, and 10 volume percent. It was found that for these films conditioned at 130° C for 3.0 minutes with 2 tapes, with the feed at 60° C, a para-xylene product-feed difference of 3 percent was obtained at the 3 percent addition level. At all other addition levels, the increases were constant at about 1 percent. The total product flow rate at the 3 percent addition level was 40 ml/(hr ft²).

Figure 38. Total Product Flow Rate with Different Amounts of Diisodecyl Phthalate and Bentone 34 Added to Thin VF Films.

The object of the first VF factorial study was to determine the effects of the film composition factors of solvent-to resin and resin-to-clathrate ratios along with the effect of nitrogen compound addition to the feed on membrane performance. These factors have previously been shown to have important effects on experimental results; therefore, the purpose of this investigation was to examine the interactions between these factors and quantitatively determine the magnitude of their effects. The fixed factors for this experiment were:

plastic resin : VF
solvent : DMF (dimethylformamide)
feed temperature : 60° C
feed composition : approximately equimolar with p-,
m-, and o-xylene
downstream pressure : <1 mm Hg
film conditioning : 135° C, 5 minutes
film casting thickness : 2 tape
film additive : $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$
feed additive : a-methylbenzylamine

The high and low levels of the three variables under investigation were:

	Low Level	High Level
solvent-to-resin ratio	6:1	9:1
resin-to-additive ratio	1:0.25	1:0.5
feed additive	0 %	3 % of total

After completing two runs at each of the eight different treatment combinations, the results of this study included the following:

1) With these thin VF films containing the o-xylene clathrate, the unexplained variation in experimental values was smaller than that observed in the PVC studies. With 95 percent confidence, the least

significant difference between two treatment combination values for product para-xylene composition was only 0.64 percent.

2) The film thickness as determined by the solvent-to-resin ratio was not found to have a significant effect on membrane selectivity. This result agrees with that generally accepted for membrane separation processes.

3) Using the para- and ortho-xylene product compositions as the experimental values, it was found that there was a significant interaction between the amount of clathrate added to the membrane and the presence of the nitrogen compound in the feed. This interaction, averaged over the solvent-to-resin ratio, is shown in Figure 39.

The addition of the α -methylbenzylamine to the feed appears to have acted to increase the para-xylene selectivity in the case with the low level of clathrate addition by enhancing the selectivity-producing ability of the included clathrate. For the case with the high level of clathrate addition, the action of the nitrogen compound was to increase the xylene solubility to the point of weakening the membrane structure and thus allowing a significantly higher permeation rate with a subsequent decrease in selectivity. In the range of clathrate addition levels investigated in this study, increased amounts with no nitrogen compound added to the feed resulted in significantly higher para-xylene selectivities.

4) For all treatment combinations except that with both the high

Figure 39. Interaction Between Level of Clathrate Addition and Nitrogen Addition to the Feed.

level of clathrate addition and nitrogen compound included in the feed, the total product flow rates were on the order of 0.6 ml/(hr ft²). For the exceptions, the average rates were approximately 4.5 ml/(hr-ft²). No conclusions were reached concerning the effects of the variables on the permeation rates because the errors involved in collecting the small volume samples were greater than the differences shown

by the variables.

5) The best increases of para-xylene were obtained with films of composition 9:1:0.5 (DMF:VF:Ni(SCN)₂(a-MeBzAm)₄:o-xylene) with no a-methylbenzylamine added to the feed. With these conditions, a para-xylene product-feed difference of 3.5 ± 0.5 percent with 90 percent confidence was obtained at flow rates of approximately 0.6 ml/(hr ft²).

The object of the second factorial study was to begin with the film composition determined above and examine the film casting and conditioning effects of oven temperature, oven time, and film thickness. The fixed factors for this experiment included:

plastic resin : VF
solvent : DMF
film additive : Ni(SCN)₂(a-MeBzAm)₄·o-xylene
film composition : 9:1:0.5² (solvent:resin:clathrate)
feed temperature : 60° C
downstream pressure : <1 mm Hg
feed composition : approximately equimolar with p-, m-,
and o-xylene

The three variables at the high and low levels were:

	Low Level	High Level
oven temperature	135° C	145° C
oven time	6 minutes	8 minutes
film casting thickness	2 tape	3 tape

The results of this study included the following:

1) Under the conditions of the sixteen runs of this investigation, the unexplained variation in para-xylene product composition was slightly larger than that in the first study. With 95 percent confidence, the least significant difference between two treatment combina-

tions was 0.73 percent.

2) With the para-xylene results, the interactions between oven temperature and oven time, and oven temperature and film thickness were highly significant. In Figure 40 it is seen that: 1) at the high temperature all the results are close together with little effect of performance at the lower temperature; 2) at the lower temperature it appears that the thicker membranes produced the higher selectivity values.

These results indicate that the film performance is not inversely proportional to the severity of film conditioning. Rather, it appears that an optimum film "dryness" which is much more dependent on the oven temperature than the oven time is most critical. The difference in selectivity shown by the film casting thickness is thought due to the rate and manner in which the solvent was driven from the casting solution and not due to the resulting thickness alone.

3) For all treatment combinations, the average permeation rate was $0.32 \text{ ml}/(\text{hr ft}^2)$. In this study, none of the variable factors was shown to have an effect significant at the 90 percent level.

4) The best selectivities shown for para-xylene were from the thick films conditioned at 135° C for 6 minutes. At these conditions, the para-xylene product-feed difference was 6.9 ± 0.5 percent with 90 percent confidence at a flow rate of $0.62 \pm 0.32 \text{ ml}/(\text{hr ft}^2)$.

Figure 40. Oven Temperature Interactions with Oven Time and Film Thickness.

Feed Composition for Thin VF Films with Clathrates. In order to determine the effect of feed composition on the performance of the thin VF films containing the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate, two different experimental schemes were examined. In the first, the performance of the films were compared using the ternary xylene feed and

each of the binary feed combinations. In the second, one feed with only para- and meta-xylene, and the other feed with all three isomers were tested with the para-xylene concentrations varying between 10 and 90 percent.

The first study tested films of composition 9:1:0.5 (DMF:VF:Ni-(SCN)₂(a-MeBzAm)₄·o-xylene) which had been cast with 3 tape thicknesses and conditioned at 135° C for 6.5 minutes. With a feed containing approximately equal amounts of all three isomers, the permselectivities computed in the manner of relative volatilities were: $S_p' = 1.22$, $S_m' = 0.99$, and $S_o' = 0.83$. These results indicate that the films were selective for the para-xylene isomer, had very little effect on product meta-xylene composition, and acted against the permeation of ortho-xylene. The results for the binary feed mixtures which were about equimolar were: 1) with para- and meta-xylene feed, $S_p' = 1.10$; 2) with para- and ortho-xylene feed, $S_p' = 1.11$; 3) with meta- and ortho-xylene feed, $S_m' = 1.09$.

The results of this first study agreed with the similar study conducted using the thick VF films. The selectivity of these membranes has been shown to be dependent on the composition of the feed. In particular, the inclusion of ortho-xylene in the feed containing para- and meta-xylene significantly increased the selectivity for the para-xylene isomer. It was also found that the selectivity for para-xylene in binary feed mixtures was independent of the other component in the

feed. These findings further support the contention that in this liquid permeation system, the permeation of the feed compounds through the membrane can not be described by the classical diffusion mechanism.

The second part of this composition study was completed using films like those of the first, but with the oven time shortened to 6.0 minutes. The five basic feed solutions prepared containing para- and meta-xylene had para-xylene compositions of approximately 10, 30, 50, 70, and 90 percent. After two runs with each feed had been completed with the feed temperature of 60° C, one run with each feed was conducted with the feed at 90° C. Finally, after adding enough ortho-xylene to each feed to account for approximately 28 percent of total volume, one run with each of these feeds was completed using a feed temperature of 90° C. The results of these runs are shown in two different ways on Figures 41 and 42.

As shown on Figure 41, the para-xylene product-feed difference appears to go through a maximum at about the 50 percent level with the binary feed. The 30° C feed temperature difference caused little variation in the values for the binary feeds. With the ortho-xylene added to the feeds, the product composition was similar to that with the binary feed mixtures up to the 50 percent para-xylene level. At larger para-xylene values, the product-feed difference increased sharply.

By plotting the results as the relativity volatility type of selectivity, S_p^1 , the overall shapes of the curves shown on Figure 42

Figure 41. Para-Xylene Selectivity with Different Feed Compositions Used with thin VF Films Containing Clathrates.

Figure 42. Para-Xylene Selectivity with Different Feed Compositions Used with Thin VF Films Containing Clathrates.

are much like those on the previous figure. Here the selectivities for para-xylene obtained with the feeds containing ortho-xylene again were similar to those with the binary feeds at the low, para-xylene concentrations, but rose rapidly at higher values. For the two cases with the binary feeds, the calculated selectivities did not go through a maximum and were relatively constant about a value of 1.10.

The results of this second composition study confirm the difference in film performance caused by the presence of ortho-xylene in the feed. Additionally, this study showed that the para-xylene selectivity was dependent on the ratio of para- to meta-xylene in the feed. Both of these results indicate the formation of non-ideal solutions between the feed compounds and the membrane.

Feed Temperature for Thin VF Films with Clathrates. The object of this study was to determine the effect of a broad range of feed temperatures on membrane selectivity and product flow rate. The membranes used were of composition 9:1:0.5 (DMF:VF:Ni(SCN)₂(a-MeBzAm)₄·o-xylene) which were cast 3 tapes thick and conditioned at 135° C for 6.5 minutes. Two runs were made at each of the feed temperatures of 45, 60, 75, 90, 110, and 130° C. The values from a run conducted at 30° C were discarded because the total product volume was too small for the product analysis to be reliable. In the present system, the feed temperature of 130° C was the maximum value attainable.

The temperature dependence of the permeation constant is usually

given by an Arrhenius relationship. This type of relationship was verified by this experiment and is graphically shown on Figure 43. Here a straight line was obtained by plotting the logarithmic, total product flow rate versus the inverse of the absolute feed temperature. Agreement was very good except at the lowest temperature. Experimental difficulties in obtaining the product volumes were probably responsible for the low value given.

This flow rate dependence on temperature was also shown in another study in which films of composition 20:1:1 (DMF:VF:Ni(SCN)₂(a-MeBzAm)·o-xylene) which had been cast 1 tape thick and conditioned at 130° C for 3 minutes were used with a xylene feed at temperatures from 30 to 70° C. In this study, the addition of a-methylbenzylamine to the feed in amounts of 1, 3, 5, and 10 percent did not change the general relationship, but did alter the slopes and intercepts in a manner not fully investigated.

The ability of the film to select one isomer over another was influenced in a more unusual manner by changing the feed temperature. Instead of a constant selectivity decrease with increasing temperature, a well defined maximum was obtained at about 90° C. As shown on Figure 44, the values plotted are averages of two experimental points. The variance for this study was quite small with the difference between the high and low points shown being significant.

In the similar but less extensive study using the films of compo-

Figure 43. Total Product Flow Rate Dependence on Feed Temperature for Thin VF Films Containing a Clathrate.

Figure 44. Para-Xylene Selectivity Dependence on Feed Temperature for Thin VF Films Containing a Clathrate.

sition 20:1:1 and 20:1:2 instead of the 9:1:0.5 in the present case, a similar result was obtained. Increasing the feed temperature from room temperature to 60° C produced an increase of 2 percent in the para-xylene product-feed difference.

This selectivity response pattern is thought due to two different factors. At temperatures above that with the maximum selectivity, the selectivity decrease appears to be the result of a weakened film structure and the greatly increased feed solubility caused by the higher feed temperatures. This effect is similar to that shown by including too much clathrate or complex in a casting solution.

The decrease in selectivity at low feed temperatures is somewhat harder to explain. It is hypothesized that at temperatures less than that of maximum selectivity, the membrane is too "tight" due to the decreased solubility of the feed in the membrane. This does not allow the permeating compounds to be influenced by the selectivity-increasing additives.

Membrane Durability for Thin VF Films with Clathrates. The object of this study was to determine the effect of the length of permeation time on membrane performance. The membranes used were of composition 9:1:0.5 (DMF:VF:Ni(SCN)₂(a-MeBzAm)₄·o-xylene) which were cast with 3 tapes and conditioned for 6.0 minutes at 135° C. Two membranes were prepared. These membranes were installed in the permeation cells in the usual manner and remained in place throughout the total time period.

At 12-hour intervals, the vacuum pump was shut down and the product cold trap was removed from the system. After removing the sample in the usual manner, the system was assembled and re-started. The total down time for the apparatus between runs was approximately 20 minutes.

The para-xylene product-feed composition differences for these films are shown on Figure 45. It was noted that for films with the lower permeation rate which was constant at about $0.74 \text{ ml}/(\text{hr ft}^2)$ for the entire run, the selectivity values varied randomly about a value of approximately 2.6 percent. For the other membrane which had a constant flow rate of approximately $2.04 \text{ ml}/(\text{hr ft}^2)$, the para-xylene selectivity started at a very low value of 1.2 percent for the first 12 hours, but then approached the values of the other film after about 36 hours. Therefore, it appears that at least for this film system, the para-xylene selectivities and product flow rates are relatively unchanged by the length of the run time.

Figure 45. Para-Xylene Selectivity with Different Run Times Used with Thin VF Films Containing a Clathrate.

CONCLUSIONS

It had been hypothesized that a combination of the separation techniques of selective permeation through a plastic membrane, clathration, and specialized plasticization could be used to produce films which would show increased selectivity for para-xylene from a mixture of the three xylene isomers. The results obtained in this investigation support this hypothesis.

The two different plastic resins used as the basic membrane materials produced different responses to the liquid permeation of the xylene feed. The xylene compounds were shown to permeate through the unmodified PVC film at moderate flow rates ($40 \text{ ml}/(\text{hr ft}^2)$) and display a selectivity for the para-xylene isomer. Films of unmodified VF were found very impermeable to the xylene feed even at elevated feed temperatures. It was concluded that for the purposes of investigating the mechanism of producing selectivity for a xylene isomer by including materials in the membrane, the VF film was the more satisfactory. With the VF membranes it was decided that any observed selectivity and permeation was the result of only the film additives and not the resin.

Considering all the different film systems investigated, it was concluded that those containing clathrates produced the greatest improvement in para-xylene selectivity. In particular, it was found that the most effective additive to the VF films was the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4$ -

o-xylene clathrate. The other film additives were valuable in contributing to the understanding of this liquid permeation process.

The addition of different clathrates to the VF membranes produced different selectivity and flow rate results. Because both the $\text{Ni}(\text{SCN})_2 \cdot (4\text{-MePy})_4$:p-xylene clathrate and the $\text{Ni}(\text{SCN})_2 \cdot (\text{a-MeBzAm})_4$:o-xylene clathrate showed a selectivity for the para-xylene isomer, it was concluded that the selectivity-producing mechanism was not strictly that of the clathration process. Further investigation into the nature of the selectivity increase caused by the inclusion of the clathrate compounds involved looking at all the components of the additives.

The substitution of different metal ions for the nickel usually used, had little effect on the membrane performance. This result is contrary to that generally observed with the clathrates in question which often show large changes in selectivity under these conditions.

The results of this investigation did show changes in membrane performance due to the inclusion of different anions, nitrogen compounds, and included compounds in the clathrates. With work putting the complexes rather than the clathrates in the membranes, it was also concluded that the presence of different nitrogen compounds had a significant effect on membrane performance. These findings all indicated that even though the selectivity producing action was not shown to be the result of a strictly clathration process, some of the characteristics of this process were present.

Further evidence to support the presence of some special action of the clathrates in the membranes came from two other studies. In the first it was observed that the addition of materials not like the clathrates to the film produced different results. In particular, the addition of an organo-clay complex, Bentone 34, to the film caused the membrane performance in terms of selectivity response and total product flow rate to be unlike that found with clathrate addition. Also, the addition of extractive distillation agents and diisodecyl phthalate to the thin VF films showed that although the films were made more permeable to the xylene feed, the maximum values for para-xylene selectivity shown in the best runs with films containing the clathrates were more than twice those obtained from these non-clathrate systems.

Perhaps more importantly, it was concluded from the results of the feed composition studies that the xylene permeation through the films containing clathrates was non-ideal. That is, the selectivity for para-xylene was found to be influenced by the presence of a third xylene compound in the feed. Although this was noted in some processes involving liquid permeation through polymer films and not in others, in the present case the non-ideality comes not from the polymer film, but from the xylene interaction with the clathrates included in the film.

The description of this interaction seems most easily accomplished in terms of what it is not. It was concluded that the mechanism of increased para-xylene selectivity was not due to clathration in the

classical sense, to the "sieve" or hole theory of diffusion through a polymer film, or to different xylene solubilities in the VF film. Rather, the mechanism may involve some of the weak forces and geometric factors thought present in the clathration process.

The results of this investigation also indicated that the form in which the additive appears in the conditioned membrane was an important factor. This final form was thought to be determined by the degree of solubility of the clathrate in the plastic solution. In particular, it was found that the $\text{Ni}(\text{SCN})_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate was much more soluble in the plastic solution than the $\text{Ni}(\text{SCN})_2(4\text{-MePy})_4 \cdot \text{p-xylene}$ clathrate. The greater solubility of the ortho-xylene clathrate seemed responsible for the more uniform distribution of the solid material in the conditioned membrane.

For the addition of clathrate-like materials to the film systems investigated, it was concluded that there existed a value of clathrate addition which produced a single maximum value of para-xylene selectivity. In almost all cases examined, regardless of the solvent-to-resin ratios, the resin-to-additive ratios were in the range 1:0.25 to 1:1.

The response of the total product flow rate to changes in clathrate addition level was in most cases defined by an exponential dependence on the amount added. This result agreed at least in form with the relationship given by Long, Li, and Henley presented earlier in which the diffusivity of a single component was shown exponentially

dependent on the concentration of the solvent in the film (16). The difference shown was that what might be called changes in xylene solubilities or concentrations in the films of other systems was found due to changes of clathrate concentration in the films of the present investigation.

The film conditioning factors of oven temperature and oven time were also found important in influencing the membrane performance by controlling the character and distribution of the additive materials. In some systems these two factors were found to interact and influenced the results of the liquid permeation process in an unusual manner. It is believed that the majority of the unexplained variation in the experimental results was caused by uncontrolled changes in these factors from one run to the next. Even though a large range of values for these film conditioning factors was investigated, it was not concluded that the conditions used for the different studies were the optimum combinations of these factors.

It was concluded that variations in the solvent-to-resin ratio produced films which were not only different appearance, but also different in performance. As expected in the thin film systems, the total product flow rates were found to be approximately inversely proportional to the film thickness. The differences found in resin-to-additive levels used to produce the best para-xylene selectivity were thought due in part to the different ratios of solvent-to-resin used. This effect

appeared most strongly when considering the best resin-to-additive ratios of 1:0.125 and 1:0.5 used with VF casting solutions with solvent-to-resin ratios of 3:1 and 9:1, respectively.

It was concluded that changes in feed temperature affected the total product rates in the manner usually found in liquid permeation systems. The permeation rates were found to be exponentially dependent on the feed temperature as predicted by an Arrhenius-type relationship. For the systems investigated, it was found that using a range of feed temperatures from 23 to 130° C the changes produced in membrane selectivity could not be described simply. It appeared that rather than producing the maximum selectivity at a low temperature, the best separation values were obtained from an intermediate temperature in the range from 60 to 90° C.

It was concluded that although the optimum combination of the experimental factors of solvent-to-resin ratio, resin-to-additive ratio, casting thickness, oven temperature, oven time, feed temperature, and film-drying environment was probably not obtained, the best values of para-xylene selectivity obtained with the VF film system containing the $\text{Ni(SCN)}_2(\text{a-MeBzAm})_4 \cdot \text{o-xylene}$ clathrate are in the same range as those reported by other researchers. The best values of para-xylene selectivity obtained with the thick VF films when computed in the manner of Michaels were in the range of 1.15 to 1.3. These values compare favorably with those computed in that study involving polyethylene film (14).

However, the product flow rates of the present work were often more than ten times less than those found in the work of Michaels et al. The selectivity values given by de Rosset (15) of approximately 1.3 for the selectivity of para-xylene with respect to meta-xylene when computed in the manner of a relative volatility are in the same range as those obtained in the present work. No specific results for selectivity or permeation rate were listed by Fleck and Wight for their diffusional separation process. (27).

The commercial potential of the liquid permeation process investigated in the present is uncertain for several different reasons. In the operation of this process in a continuous manner, the conditioned membrane is contacted with feed in the feed zone and allows a portion of the feed to permeate through the membrane. The feed mixture not permeating the the film is removed from the feed zone enriched in the less selectively permeated component. It is believed that a series of membranes may be arranged in a staged manner to accomplish the further enrichment of both the feed and permeated vapors. Because it is believed that there exist no commercial applications of the xylene separation processes of the liquid permeation type including those of the other researchers previously mentioned, the desirability of using the process investigated here must be considered doubtful in its present stage. Although at times giving exceptional values for para-xylene selectivity, the inability to consistently reproduce the best results

must be rectified before a detailed economic analysis of the present system is possible.

It was therefore concluded that the outstanding result of this research effort was that it was found possible to impart a selectivity for the para-xylene isomer to a polymer film which itself had no natural tendency to selectively permeate any of the xylenes by adding to the film specified quantities of a clathrate or clathrate-like compound. It was also concluded that the selectivities obtained by this novel, liquid permeation system compared favorably with those of other xylene separation processes which used a polymer film naturally selective for the para-xylene isomer.

RECOMMENDATIONS FOR FUTURE STUDY

The present investigation showed that it was possible to modify an impermeable polymer film by including certain compounds in its structure to both increase the permeability and impart a selectivity for one component of the liquid feed. The recommendations for future study include those to improve the experimental techniques in order to make the results more reproducible and those to expand the scope of this study to encompass a broader range of additive materials and film conditioning factors. These recommendations are listed below.

- 1) One factor believed most responsible for variations in results with identical film casting solutions is the oven temperature during membrane conditioning. It is recommended that future work include equipment modifications necessary to enable the experimenter to accurately control the oven temperature. This control should include provisions for maintaining a constant temperature or allowing the temperature to increase or decrease at a controlled rate.

- 2) The method of product collection should be revised to improve the accuracy of determining the quantity of total product obtained during a run. It is recommended that this be accomplished by revising the experimental procedure. To eliminate the majority of the condensed water in the product trap and the initial permeation product, the experimental apparatus should be assembled in the usual manner, but

started with the product cold trap out of the liquid nitrogen bath. After a short period of time when the system is evacuated and running at steady state, product collection could begin by immersing the product cold trap in the liquid nitrogen. After a run was completed, the product cold trap could be isolated from the system and weighed to determine the amount of product collected. The distribution of the products could then be determined in the usual manner.

3) The substitution of glass tubing throughout the system is also recommended to eliminate the absorption and desorption of the feed components from the plastic tubing used in this investigation.

4) It is recommended that polymers different from those investigated here be included in future work. In particular, a polymer such as polypropylene might be used in place of the VF. If the conditions of strength and ease of fabrication are satisfied, film materials such as polypropylene which are naturally selective for para-xylene may be successfully used with the modification system investigated in the present work. Of interest may be the determination of whether the two effects which increase selectivity are additive.

5) It was concluded that the solubility of the additive materials in the plastic solution influenced the appearance and performance of the conditioned membrane. Therefore, it is recommended that different solvents be used in the formation of the plastic solutions to determine if the type of solvent plays a significant role in the preparation

of a membrane. In particular with the VF system, a polar organic solvent such as dimethylacetamide may be substituted for the dimethylformamide previously used.

6) To extend the scope of future investigations, there are scores of possible additive materials to be examined. In particular, there are many different clathrates and complexes which may be worthy of investigation. Because it appeared that the nickel-thiocyanate combination was the most suitable, future work should be directed toward the investigation of the effects of different nitrogen compounds. Two large groups of nitrogen-containing compounds may be considered. As given by Fleck and Wight (27), a particularly preferred class of bases comprises the hetero-cyclic resonance-stabilized compounds which contain one to three hetero-N atoms. Examples include pyridine, the picolines, pyrrole, pyrazole, triazole, quinoline, the quinaldines, isoquinoline, pyrimidine, pyrazine, pyridazine, and the substituted derivatives of these compounds. Of this class, a sub-group thought to be of particular interest includes the 3-substituted, 4-substituted, and the 3,4-disubstituted pyridines. A second group of nitrogen compounds includes the substituted primary benzylamines. Hanotier and de Radzitzky list many possible compounds (23). Obviously there are also other types of compounds which could be included in the plastic solution, but it is believed that those of the clathrate-type containing nitrogen compounds of the two groups given are the most likely to yield the desired

results.

7) The film conditioning factors of oven temperature, time, and environment were found important in influencing film performance. It is recommended that in addition to more accurately controlling these conditions, that they be extended to include more of the combinations which would provide acceptable membranes. This would include low oven temperatures used with long retention times as well as combinations throughout the intermediate range. The oven environment during conditioning should also receive attention with particular interest focussed on the ventillation in the oven cavity. It is believed that the degree of movement of the heated vapors in the oven cavity during conditioning affects the rate and manner of solvent evaporation from the cast membrane. Also worthy of careful investigation are other conditioning factors such as the temperature and length of time the membrane spends outside the oven before conditioning and the length of time the membrane spends after conditioning and before use. Because many of these factors were found to interact with each other, the experiments must be designed with enough sophistication to enable the experimenter to clearly distinguish between results which are due to one effect only and those due to the interaction of two or more variables.

8) This study was primarily directed toward the investigation of the selectivity responses of the conditioned membranes. In future work it is recommended that with the goal of the optimization of a liquid.

separation process using the conditioned membranes, the selectivity achieved must be balanced by and considered in the light of the permeation rate obtained.

9) It is recommended that more compounds be considered as feed materials for this system. Although the present work considered only the xylenes, by using such compounds as benzene, toluene, ethylbenzene, and the tri-methylbenzenes in the feed, it may be possible to learn more about the nature of this separation process and possibly find a new area of utilization.

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NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
a	plasticization constant
C ₁	upstream concentration in the film
C ₂	downstream concentration in the film
ΔC	change in concentration
D _a	impellor diameter
D _{i,m}	permeability coefficient for component i in the mixture, volume/(concentration unit x length x time)
DMF	dimethylformamide
J _i	transmission flux of component i, volume/(unit time x unit area)
L	film thickness
m	meta isomer
M ⁺⁺	metal ion
α-MeBzAm	α-methylbenzylamine
4-MePy	4-methylpyridine
N	stirrer speed, revolutions per second
N _{Re}	tank Reynolds number
o	ortho isomer
p	para isomer
$\bar{P}_i$	permeability coefficient of component i
$\bar{P}_0$	permeability coefficient at zero concentration, temperature dependent

NOMENCLATURE (Continued)

<u>Symbol</u>	<u>Definition</u>
p_i°	vapor pressure of pure i at the permeation temperature
p_L	liquid vapor pressure
p_V	partial pressure of gas at the downstream film boundary
PVC	polyvinyl chloride
Py	pyridine
$S_{i/j}$	permselectivity of component i with respect to component j, $\bar{P}_i/\bar{P}_j$
S_i'	permselectivity of component i with respect to the feed mixture, computed in the manner of a relative volatility
VF	vinylidene fluoride
X^-	anion
x_i	mole fraction of component i in the vapor product
x_i°	mole fraction of component i in the feed liquid
ρ	fluid density, lb/ft ³
μ	absolute viscosity, lb/(ft sec)

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Separation of
isomeric xylenes by
permeation ...

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