



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

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

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

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

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

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

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William Blaine Downs

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TABLE OF NOMENCLATURE

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

Greek letters

α Separation factor, relative volatility

Subscripts

1, 2 Component 1 and Component 2

ABSTRACT

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

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

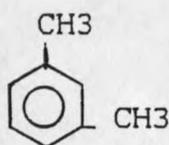
Most of the commercially available films tested can be used to enrich the para-xylene isomer in the permeate. In general the degree of separation obtained by pervaporation of xylene mixtures is higher for the ortho-xylene, para-xylene mixture than for the meta-xylene, para-xylene mixture.

INTRODUCTION AND PURPOSE

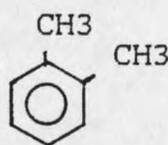
The production of the majority of dimethyl-benzene, commonly referred to as xylene, comes from the petroleum refining industry as a portion of the product of the catalytic reformer [9]. Mixed xylenes which contain the meta, ortho and para isomers along with ethyl-benzene have various compositions depending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



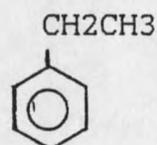
Para



Meta



Ortho



Ethyl-Benzene

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

Table 1. Physical data for xylenes and ethyl-benzene

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

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

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

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

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

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

Uses for Xylenes

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

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

Separation Processes Currently in Use

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

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

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

The Pervaporation Process

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

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

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

The Purpose for the Experimental Investigation

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

PREVIOUS RELATED RESEARCH

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

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

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

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

The Liquid Permeation Mechanism

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

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

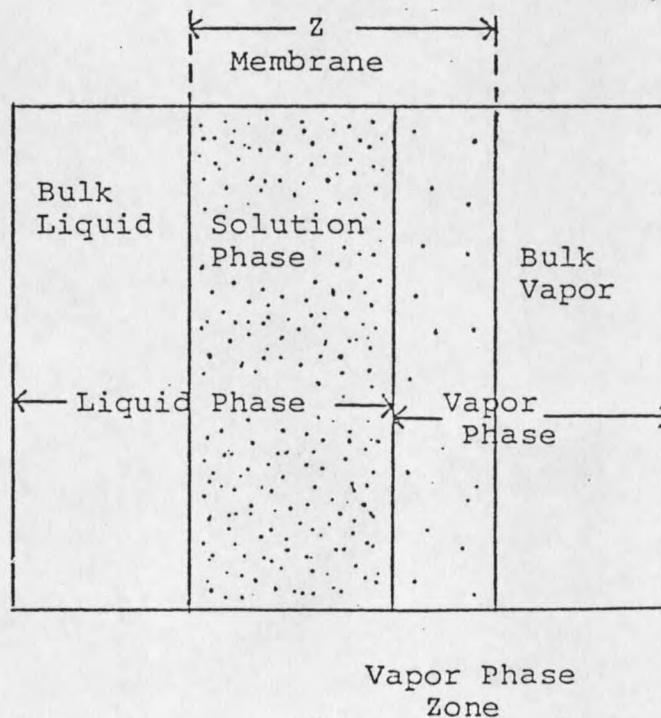


Figure 1. The solution phase and the vapor phase zones within the membrane.

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

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

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

Membrane selectivity

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

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

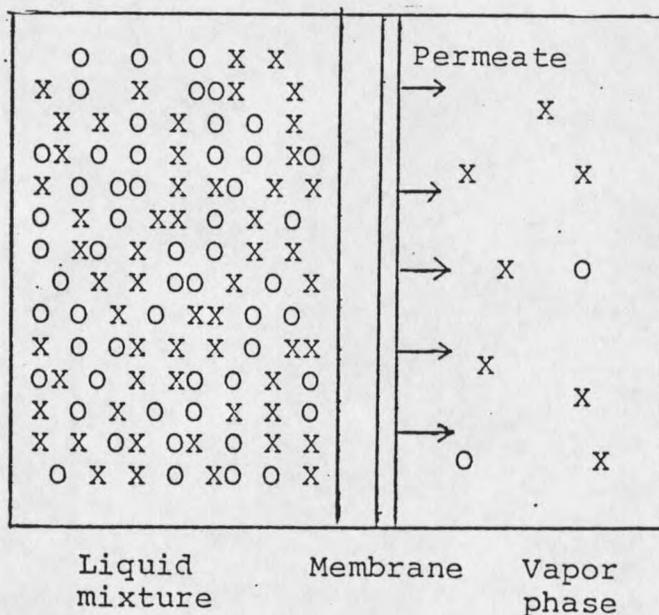


Figure 2. Membrane selectivity

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

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

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

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

