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FINAL REPORT

PURIFICATION OF ORGANIC COMPOUNDS BY MEMBRANE PERMEATION

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Prepared by: John L. Eisenmann

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SUMMARY

This report presents data obtained during a study of liquid-phase membrane permeation in which the effects of various operating conditions, charge mixtures, and film properties were examined. Selected binary mixtures were permeated through thin, non-porous, plastic films and the permeation rate and selectivity of the system recorded. It was found that perm-selectivity increased and permeation rate decreased as the crystallinity or density of hydrocarbon films was increased. The effect was most consistent when hydrocarbon binaries were used. Permeate pressure was found to have a marked effect on selectivity and some influence on rate. Permeant pressure also affected selectivity and rate but less than permeate pressure and apparently depended on some critical downstream pressure. The magnitude and direction of both of these pressure effects varied with the type of film employed.

1.0 INTRODUCTION

This is the Final Report to the Army Chemical Center on Contract DA-18-108-Cml-6626, Purification of Organic Compounds by Membrane Permeation. In general, membrane permeation is understood to mean the transfer of a liquid, a vapor, or a gas through a thin, non-porous, polymeric or plastic film, the so-called membrane. In this study, however, the term membrane permeation is restricted to refer to a liquid-phase permeation system in which a liquid charge called the permeant (either pure or a mixture) is maintained in contact with one side of the membrane and permeated material (the permeate) is collected on the opposite or downstream side of the membrane.

The rate of permeation and the perm-selectivity towards a given mixture depends on the nature of the membrane and the operating conditions of the system. The permeate is removed from the downstream face of the membrane as a vapor and collected by condensation. Rapid permeate removal is generally desirable and to accomplish this the permeate chamber is usually kept under reduced pressure. A second removal technique requires that the downstream membrane face be continually swept with a stream of inert gas. The permeant is usually at atmospheric pressure but super-atmospheric pressure can be used to increase the permeation rate if suitable equipment is available. The upper temperature limit for permeation is governed by the thermal stability of the individual film and its solubility in the charge at the permeation temperature. It will be shown later in this report that film solubility is greatly influenced by other operating conditions.

2.0 BACKGROUND

For gases, the possibility of membrane permeation through plastic films has been known for over a century [1,2], as has the fact that some gases will permeate a given membrane faster than others. Relatively recently it has been suggested that this difference in gas-phase permeability could be applied to the commercial separation of gaseous mixtures [3,4]. Weller and Steiner have discussed the fractionation of air by permeation through a film of ethyl cellulose and have also examined polystyrene membranes for separation of helium or hydrogen from mixtures of gases. Brubaker and Kammermeyer have also investigated the possible use of membranes for separation of gaseous mixtures. They looked principally at polyethylene film because of its general chemical stability, and tried various mixtures of hydrogen, helium, carbon dioxide, oxygen and nitrogen. Gas transmission rates were relatively low even for the "fastest" films, and while vapors exhibited much higher permeability rates, gas or vapor separation by membrane permeation was judged uneconomical. Applications appear remote without extensive research into the production of "faster" films.[4] Compounding or film processing techniques were suggested as means for obtaining films with higher permeability rates and better selectivity. Higher temperatures and pressures are known to increase the rate of gas permeation but these techniques require films with good thermal and physical stability and cause concomitant loss of selectivity.

Recently, however, a successful liquid-phase permeation process has been developed [5,6] which can achieve rapid rates of permeation and, like gas permeation, function as a separation process if the charge is a mixture of liquids. Besides faster permeation rates, the most important difference between gas and liquid permeation is the fact that in the liquid phase system it is not possible, at the present time, to calculate the composition of the permeate from a knowledge of charge composition and the independently measured permeation rates of the pure components.[6]

A laboratory scale permeation cell has been developed [7,8,9] for exploratory research and film screening and, in at least one instance,

development has rreached the point where an automated continuous-process pilot plant [10] has been designed and started-up.

As mentioned above, membrane permeation, as defined in this report, seeks to separate a liquid mixture by selectively permeating one component of this mixture through a plastic membrane. These membranes are nonporous, i.e., do not contain discrete holes or pores, and they do not function by a molecular sieving action. [11] Obviously the membranes must not have any pinholes and must be protected against punctures by sharp or pointed objects. Under these conditions a membrane life of several months is possible. Actual permeation through the membrane is believed to involve three steps:

1. Solution of the liquid charge into the upstream film surface.
2. Diffusion of molecules through the membrane.
3. Evaporation of permeated molecules from the downstream face of the membrane.

The efficiency of a given permeation system is judged by the permeation rate and the selectivity as determined by comparison of charge and permeate compositions. The selectivity can be expressed simply as the percent of preferentially permeated material in the permeate or in terms of a separation factor, α ,

$$\alpha = \frac{Y_B}{Y_A} \Big/ \frac{X_B}{X_A} = \frac{Y_B}{Y_A} \cdot \frac{X_A}{X_B}$$

where: Y_B = concentration of B in permeate

Y_A = concentration of A in permeate

X_B = concentration of B in charge

X_A = concentration of A in charge

For a given film the important variables affecting rate and selectivity are charge and permeate pressure, temperature, film thickness, and the properties of the permeating molecules. The available data relating to these factors are discussed briefly below. A useful review article, emphasizing engineering and economic aspects of membrane permeation has appeared recently.[9]

Binning et al [6] have reported the data in Table I for a 50-50 volume % n-heptane/isooctane mixture permeated through a 1 mil film at 100°C. These results indicate that varying the charge pressure from 1 to 8 atmos-

TABLE I

Charge Pressure, psi	Permeate Composition Vol % heptane	Permeation Rate gal/hr-ft^2 x 10^3
15	75	140
115	75	140

pheres had no detectable effect on either the rate or selectivity of the permeation. In another series of experiments using pure n-heptane as the charge, at 99°C., the charge pressure was held constant at one atmosphere while that on the permeate side of the film was varied from 20 to 500 mm. of mercury in eight steps, thereby creating a pressure differential ΔP across the film. As long as the pressure on the permeate side permitted rapid removal of the permeated product, no affect on the rate was noted between $\Delta P = 740$ to $\Delta P = 260$, and it was concluded that the permeation rate is independent of the pressure differential across the film.

No data was presented relating permeate pressure or ΔP to selectivity, however, and it would be pertinent to repeat this experiment using a binary mixture as permeant to determine if these parameters have any influence on selectivity.

The effect of temperature on rate of permeation was also investigated by Binning and coworkers with films of four different thicknesses. Again, they used a 50-50 volume % n-heptane/isooctane mixture with the charge at atmospheric pressure and the permeate zone pressure at 35mm Hg.

Their results are shown in Table 2.

TABLE 2

Film Thickness	Permeation Temp. °C	Permeate Comp. Vol % heptane	Rate gal/hr-ft^2 x 10^3
0.8	70	79	78
	80	78	105
	90	76	144
	100	75	205
1.0	70	77	58
	80	77	80
	90	75	112
	100	75	156
1.4	70	76	33
	80	77	50
	90	75	69
	100	75	93
1.9	70	76	22
	80	76	33
	90	77	47
	100	75	66

It can be seen that a substantial increase in rate occurred as the temperature was increased. Binning et al also consider that a significant decrease in selectivity occurred during the temperature rise at each film thickness. However, he used the same data to determine the effect of film thickness and concluded that while rate decreased with increasing thickness at a given temperature, selectivity remained essentially constant at all four thicknesses. Since, at some temperatures, the variation in

"constant" selectivity between thicknesses was as great as it was for temperature changes within a given film thickness, some additional work appears to be needed to confirm the effect of film thickness.

Other data on the effect of temperature and film thickness has been obtained by Michaels and Choo.[12,13,14] They found that the permeation rate of both ortho and para xylene increased with increasing temperature when 1 mil polyethylene was used as the permeation membrane. With one, two and three mil polyethylene films at 25° the rate decreased and the selectivity remained constant. These results tend to support Binning's contentions although they were obtained at lower temperature ranges and with an especially preconditioned film.

On the basis of the postulated permeation steps mentioned above, rate and selectivity differences may arise from either solubility or diffusivity differences between permeants. The former is determined primarily by differences in chemical nature of the permeating molecule, while the latter is controlled largely by the size and shape of the molecules and by the degree of aggregation among the diffusing species. Bent and Pinsky[15] have related the shape factor of a molecule to the "diffusional cross section" $(\bar{V}/\bar{L})$, where $\bar{V}$ is the molar volume and $\bar{L}$ is the maximum linear dimension of the permeant molecule. If it is assumed that the permeating molecules move through the polymer matrix with their major axis aligned with the direction of diffusion, the "diffusion cross section" represents the molecular cross section normal to the direction of movement. A smaller cross section should be indicative of faster diffusion. This is borne out experimentally in data given by Michaels and Choo [12,13,14] in Table 3 and by calculations based on Binning's results [6] and presented in Table 4..

TABLE 3

Permeant	$\bar{V}/\bar{L}$	Rate, lb/hr-1000 ft^2
o-xylene	13.9	57.6
m-xylene	13.2	79.3
p-xylene	12.8	101

TABLE 4

Permeant	$\overline{V}/\overline{L}$	Rate, lb/hr-1000 ft^2
n-hexane	12.1	68.7
2-methylpentane	13.9	20.7
2,2-dimethylbutane	16.3	0.71

Molecules of similar cross-section like the homologous normal alkanes have been shown to permeate according to the length of the molecules. Bent and Pinsky [15] observed decreasing permeation rates in the order n-pentane, n-heptane, n-decane, n-tetradecane, and Binning et al [6] obtained similar results with n-hexane > n-heptane > n-octane > n-nonane. The latter workers also reported that the olefins 1-hexene and 2-heptene permeated much faster than their saturated analogs. This difference may well be due to the differing chemical nature between olefinic and aliphatic hydrocarbons while the previously discussed permeability changes can be attributed to diffusion of molecules of similar chemical reactivity but different shapes and sizes. Another example [15] of chemical nature affecting permeation is shown in Table 5. It should be pointed out that Bent and Pinsky's data were obtained by determining the weight loss - with time - of polyethylene bottles standing at atmospheric pressure and filled with the liquid under study - relatively static conditions compared to continuous vacuum evaporation of the permeate.

TABLE 5

Permeant	$\overline{V}/\overline{L}$	Rate, lb/hr-1000 ft^2
benzene	12.7	209.0
butyraldehyde	10.4	8.7
phenol	10.3	0.43

In most of the publications on membrane permeation discussed above no mention was made about the composition of the polymer films used. Only Michaels [13,14], Choo [12] and Bent and Pinsky [15] have described their membrane material and in each case polyethylene film was employed. This is obviously a good membrane material for hydrocarbon permeation and, since these investigators were primarily interested in hydrocarbon separation, it was the film of choice. Availability of polyethylene in a wide number of thicknesses and densities probably was also a factor in its selection. Recently, however, Schrodt et al [16] have presented some of their work on the selectivity of various film types. They have looked at the separation of several binary mixtures using cellophane, saran, polyethylene, teflon, nylon, mylar, polyvinyl alcohol and polyvinyl chloride, and use their data to support a theory of membrane selectivity based on hydrogen bonding, in which the more highly bonded permeant diffuses slower and, therefore, concentrates in the non-permeate. Schrodt did not study any of the operating variables and considerable scatter was present for runs on which duplicate permeations were made. The best separation achieved was a 100% permeate concentration of acetone from a charged 61:39 weight percent acetone/chloroform mixture. Usually, however, the permeate was enriched about 10-20% over the non-permeate.

Several patents have now issued as a result of the work of the Binning group which also describe specific films, claimed useful for potential commercial applications of membrane permeation. One [17] describes a method for increasing the octane rating of the product from an alkylate process by permeation through cellulose type films such as cellulose acetate butyrate and ethyl cellulose. Three related patents [18,19,20] deal with separation of hydrocarbons by permeation through films cast from these and other similar esters and ethers of cellulose. Various azeotropic mixtures are claimed [21] to be broken by permeation through membranes of cellulose esters, nylon, polyacrylonitrile and polyvinyl alcohol. Hydrolyzed polyvinyl acetate is employed [22] as a membrane to selectively permeate water from a reacting esterification mixture and thus drive the reaction to completion. One hundred percent esterification of acetic acid by n-butanol

is claimed by this technique. Other reversible reactions which produce water as a product may also be forced to completion by continuous permeation of the water formed during the course of the reaction. Catalytic reactions such as alkylation, polymerization, etc., may be subjected to permeation in order to free the product of catalyst. The catalyst is retained in the reaction zone or upstream side of the permeation system while the products and unreacted starting materials comprise the permeate. Conventional separation techniques are then employed to enable recycle of recovered starting materials. Of course, if such a permeation is also capable of selectively permeating the product as formed, the process is even more favorable. Catalysts claimed susceptible to this treatment are BF_3, $AlCl_3$, H_3PO_4, and similar Friedel-Crafts type catalysts [23]. Membranes used include polyethylene, polyvinyl chloride, polyacrylonitrile and others. Some of these patented processes have been discussed in more detail by the inventors.[24,25]

From the foregoing discussion it is apparent that membrane permeation is a relatively new process which, so far, has attracted the attention of only a few research groups, understandably interested only in specific aspects of the process. Considerable work needs to be done, especially on the changes in selectivity produced by alteration of permeate and charge pressures and by differences in film thickness. The mechanism of the permeation process has not been established. Schrodt [16] has suggested a hydrogen bonded process and Binning [6] has proposed that selectivity occurs at an interface between a "vapor phase zone" and a "solution phase". Before either mechanism - or a third one - can be accepted, more experimental work is necessary.

Another problem is the fact that permeation rates of individual components cannot yet be used to give reliable estimates of the separation to be expected for mixtures. Sweeney and Rose [26,27], in work done for the Chemical Corps, have noted that the permeation rate and perm-selectivity for a binary does not follow from a simple law of independent rates, i.e., the two components evidently affect one another when mixed. For example, in the permeation of certain binaries through saran type films, the observed separation was the reverse of that expected from consideration of their independent rates. Binning et al [6] have attributed this discrepancy to differences in the condition of the swollen membrane when it is in contact with and dissolves the pure compounds, and when a mixture is present.

3.0 DISCUSSION OF PRESENT WORK

From the point of view of the evaluation of films for use in the separation of organic mixtures, the non-correlation between permeation rates of individual compounds and the observed degree of separation of these mixtures means that, at present, suitable films must be found empirically for each separation of interest. Only limited information is available on such tests, and this ranges quite widely with respect to charge mixtures and operating conditions. For this reason we decided to confine our experiments during the first part of this study to an investigation of a series of binary mixtures in which one component was held constant and the other varied with respect to its size, shape and chemical nature as compared to the control component. The influence of these parameters on the perm-selectivity of the particular film under test could then be determined. A series of three hydrocarbon films was selected for these initial tests and n-heptane was selected as the standard substance because it is non-reactive, non-polar, and a simple linear molecule of convenient size. In a later phase of the work, we intended to look at the effect of the operating variables of temperature, charge pressure and permeate pressure on some of these same systems and to extend the work to other film types. Some of the work discussed has been reported earlier.[28]

All permeation runs were done in a permeation cell manufactured by Ionics' Incorporated[7,9]. This cell consists of a stainless steel vessel, open at the bottom, but designed so that it may be closed by the film under investigation. The film is supported by a porous stainless steel disc which, in turn, rests on the film holder. The film holder is cut with channels, to allow withdrawal of vapor from the downstream side of the porous disc, and provided with an outlet for attachment to a vacuum train. To seal the vessel, the film holder assembly is bolted over the open bottom, the periphery of which is provided with the gasketing necessary to ensure a vacuum-tight seal. The top of the vessel carries a stirrer, thermometer, and inlet and outlet valves. Heating is by an electric mantle. The cell is mounted between two metal uprights which enables it to be pivoted to an upside-down position for charging and film installation. A collection train with dry-ice acetone or liquid nitrogen traps is used to collect the permeate fractions. Analyses were performed by gas-liquid chromatography on a Perkin-Elmer Vapor Fractometer, and the amount of each substance calculated from the peak areas. The calculated values were corrected from calibration curves constructed for each mixture. Chemicals used were C.P. grades from Distillation Products, Inc. or Phillips Petroleum.

3.1 Hydrocarbon Films - Density Variations

The films chosen for our initial tests were a group of hydrocarbon films: Ludlow Plastic polypropylene (PP) of density 0.90, Dupont medium density (MD) polyethylene of density 0.92, and Phillips "Marlex" high density (HD) polyethylene of density 0.96. Films of this type are readily available in many different modifications designed to give physical and thermal stability, and in various densities. Film density has been shown to be proportional to crystallinity and slight changes in density produce large alterations in physical properties. A valuable correlation is the "polyethylene density spectrum", shown in Figure 1, adapted from a Phillips Chemical Company technical bulletin.

Before deciding on these three hydrocarbon films the following polymers were screened and found unsatisfactory for permeation of a 50-50 pentane-heptane mixture:

1 mil polystyrene - no product, membrane ruptured at 70°C.
1 mil Aclar (a polyfluorohalocarbon film) - no product at 100°C, 200 mm. permeate pressure.
1 mil Mylar - no product at 150°C, 55 mm. permeate pressure
1 mil Saran - no product at 120°C, 80 mm. permeate pressure

A study of the selected films would show the variation in permeability with density and therefore crystallinity, and indicate how the membranes should be modified, or which varieties of the available standard film used, in order to increase permeability and selectivity. These hydrocarbon films also have excellent chemical stability which gives them potential usefulness as perm-selective membranes for many types of permeation mixtures.

Examined first was the effect of changing film density on the permeation rate and perm-selectivity for several binary mixtures of heptane and various other hydrocarbons. Tables 6, 7, 8 give the results of experiments with pentane/heptane mixtures and Table 3 presents a summary of the average data for these runs. In Table 8 the average of fractions two and three are shown in parenthesis and were used as more representative of the HDPE results since fraction one appeared anomalous. This is probably because

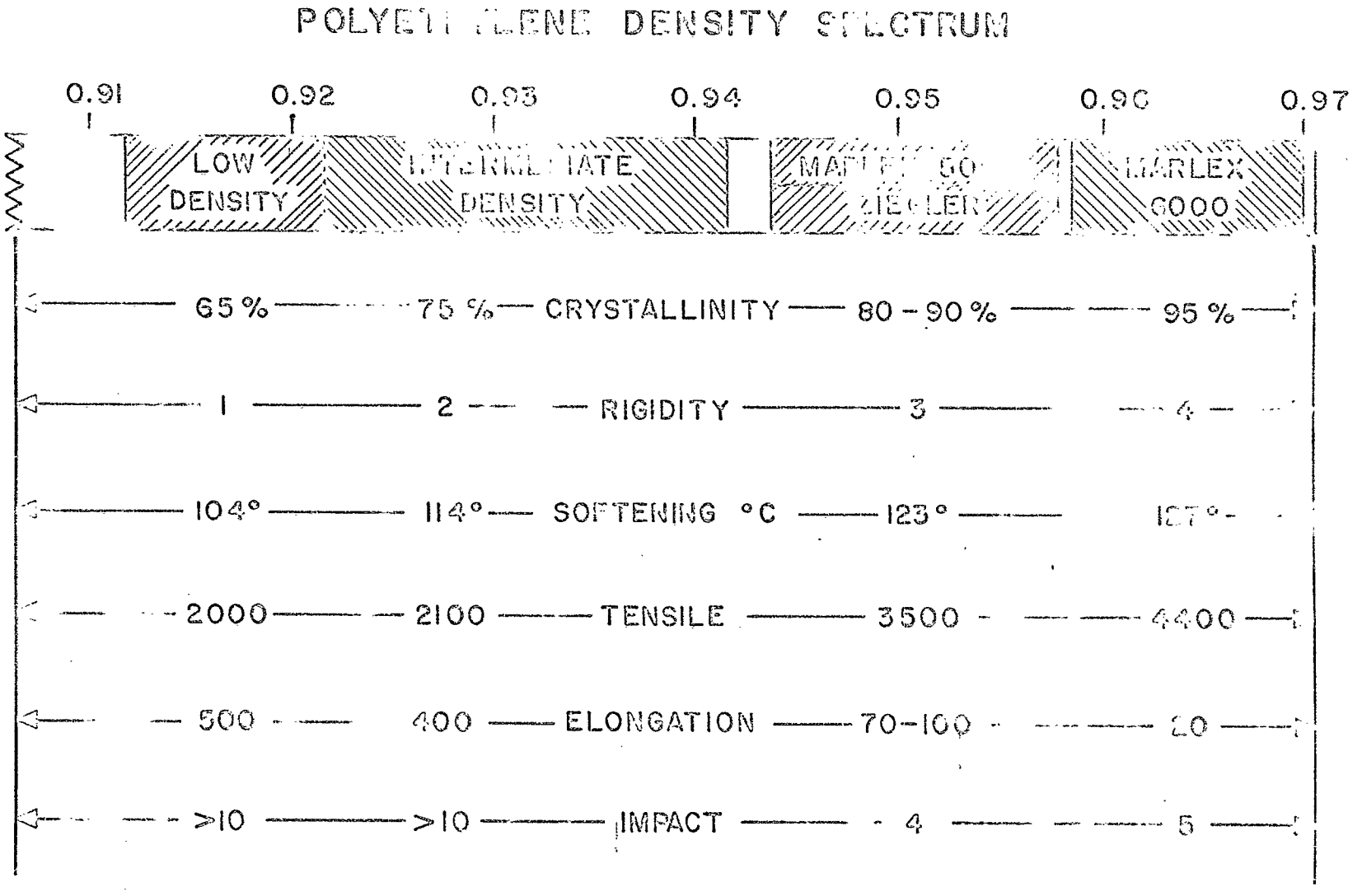

POLYETHYLENE DENSITY SPECTRUM
0.91
0.92
0.93
0.94
0.95
0.96
0.97
LOW DENSITY
INTERMEDIATE DENSITY
MARLEX 6000
65 %
75 %
CRYSTALLINITY
80 - 90 %
95 %
1
2
RIGIDITY
3
4
104°
114°
SOFTENING °C
123°
2000
2100
TENSILE
3500
4400
500
400
ELONGATION
70-100
20
>10
>10
IMPACT
4
5

FIGURE I

no forerun was collected for the permeation through HD polyethylene, and it has been our experience that in many instances some forerun is necessary in order to allow the membranes to reach an equilibrium or steady state with the change mixture. The permeated material collected as forerun is not necessarily representative of the bulk of the permeate. Fraction one was therefore considered the forerun.

As seen in Table 9, the permeation rate decreased and the perm-selectivity for pentane increased from MD polyethylene to polypropylene to HD polyethylene. Temperature, film thickness, and charge and permeate pressure were the same for all these runs.

TABLE 6

n-pentane:n-heptane; 200g (48:52 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	20 min	6.8	55	.164
1	20	10.2	53	.200
2	10	5.3	59	.207
3	10	5.5	54	.214
4	10	5.9	56	.229
5	10	6.0	60	.234
6	10	10.7	45	.418
		ave.	55	.250

$\alpha = 1.3$

TABLE 7

n-pentane:n-heptane; 200g (51:49 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	1.6	63	--
1	20 min	2.3	70	.044
2	20	3.5	63	068
3	20	6.6	59	.129
4	10	3.2	60	.126
5	10	3.2	58	.126
6	10	3.3	61	.131
7	10	3.4	61	.131
			ave. 62	.108

$\alpha = 1.6$

TABLE 8

n-pentane:n-heptane; 200g (44:56 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	0	0	--
1	60 min	1.2	43	.009
2	60	4.0	57	.026
3	60	4.0	56	.026
			ave. 52 (57)	.020 (.026)

$\alpha = 1.4$

$(\alpha = 1.7)$

TABLE 9

Permeation of Binary Mixtures of n-heptane/n-pentane
60°C, 1 mil films, 760 mm charge pressure, 25 mm permeate pressure

Film	Charge % Pentane	Permeate % Pentane	α	Rate g/hr-cm^2
MD polyethylene	48	55	1.3	0.25
Polypropylene	51	62	1.6	0.11
HD polyethylene	44	57	1.7	0.03

Table 10 through 13 present similar data for the heptane/cyclohexane binary, where again it can be observed in the summary in Table 13 that the rate decreases, with selectivity increase, in the order MDPE > PP > HDPE. A negligible forerun was obtained from the experiment shown in Table 12, but the conclusions are the same even if the first fraction is omitted from the calculations.

TABLE 10

cyclohexane:n-heptane; 200 g (51:49 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C.

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2
1	20 min	5.7	52	.112
2	20	10.3	49	.196
3	20	13.5	50	.248
		ave.	50	.185
				α = 1.0+

TABLE 11

cyclohexane:n-heptane; 200g (50:50 wt.%)
1 mil polypropylene
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate $g/hr-cm^2$
Forerun	-	7.2	54	-
1	60 min	11.0	53	.072
2	60	12.6	52	.082
3	60	12.4	55	.081
4	60	12.3	55	.080
		ave.	53	.079
			$\alpha = 1.1$	

TABLE 12

cyclohexane:n-heptane; 200g (49:51 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr-cm^2$
1	60 min	1.5	64	.010
2	60	2.3	58	.015
3	60	2.6	57	.017
		ave.	60	.014
			$\alpha = 1.4$	

TABLE 13

Permeation of Binary Mixtures of n-heptane/cyclohexane
60°C, 1 mil films, 750 mm charge pressure, 5 mm permeate pressure

Film	Charge % Heptane	Permeate % Heptane	α	Rate $g/hr\text{-}cm^2$
MD polyethylene	49	50	1.0+	0.19
Polypropylene	50	53	1.1	0.08
HD polyethylene	51	60	1.4	0.01

Tables 14 through 21 give the results for heptane/cyclohexene and heptane/hexene binaries with Tables 17 and 21 presenting the results in summary form. Once again the rate decreases and the selectivity improves in the order MD polyethylene-polypropylene-HD polyethylene. For the heptane-cyclohexene mixtures, very little separation took place with any film but what small selectivity was exhibited was reversed between the polypropylene (Table 15) and HD polyethylene (Table 16) film. The polypropylene membrane preferentially permeated heptane while cyclohexene was favored by HD polyethylene. All the films permeated hexene in preference to heptane.

In Table 16 with HDPE, the selectivity observed in the forerun with heptane/cyclohexene was reversed during the remainder of the experiment. This is similar to the effect noted in Table 8 when a pentane/heptane mixture was permeated through high density PE and the forerun was so anomolous that it was rejected. It may be that a highly crystalline polymer like HD polyethylene changes its structure under the permeation conditions used and produces a corresponding selectivity change. Such a behavior may be worth looking into in the future as a technique for obtaining better perm-selective membranes or as a method for inducing crystallinity in films.

TABLE 14

cyclohexene:n-heptane; 200g (56:44 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate$_2$ g/hr-cm^2
Forerun	-	5.4	40	-
1	20 min	9.1	41	.178
2	20	16.5	44	.323
3	20	20.7	44	.405
4	20	20.5	46	.400
			ave. 44	.327
				α = 1.0

TABLE 15

cyclohexene:n-heptane; 200g (52:49 wt.%)
1 mil polypropylene
charge pressure; 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $_2$ g/hr-cm^2
Forerun	-	1.5	46	-
1	60 min	12.3	46	.080
2	60	11.9	50	.077
3	60	12.1	58	.078
			ave. 51	.078
				α = 1.1

TABLE 16

cyclohexene:n-heptane; 200g (50:50 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% cyclohexene in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	-	2.6	47	-
1	60 min	4.7	52	.031
2	60	5.4	53	.034
3	60	5.7	53	.037
		ave.	52	.034
			α = 1.1	

TABLE 17

Permeation of Binary Mixtures of n-heptane/cyclohexene
60°C, 1 mil films, 760 mm charge pressure, 5 mm permeate pressure

Film	Charge % Heptane	Permeate % Heptane	α	Rate $g/hr\text{-}cm^2$
MD polyethylene	44	44	1.0	0.33
Polypropylene	48	51	1.1	0.08
HD polyethylene	50	48*	1.1	0.03

* Note that this means cyclohexene rather than heptane was preferentially permeated in this experiment.

TABLE 18

Mixed hexenes:n-heptane; 200g (51:49 wt.%)

1 mil polyethylene - medium density

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Hexenes in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	-	5.6	47	-
1	20 min	6.6	54	.129
2	20	17.7	51	.348
3	10	15.0	50	.588
		ave.	53	.355

$\alpha = 1.1$

TABLE 19

Mixed hexenes: n-heptane; 200g (55:45 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Hexenes in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	-	0.8	54	-
1	60 min	8.8	58	.057
2	60	12.8	59	.084
3	60	12.8	57	.083
		ave.	58	.075

$\alpha = 1.1$

TABLE 20

mixed hexenes:n-heptane; 200g (45:55 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Hexenes in permeate	Rate g/hr-cm^2
Forerun	--	1.6	50	--
1	60 min	2.2	53	.014
2	60	3.0	52	.020
3	60	3.5	56	.023
			ave. 54	.019
				α = 1.4

TABLE 21

Permeation of Binary Mixture of n-heptane/n-hexenes
60°C, 1 mil films, 760 mm charge pressure, 5 mm permeate pressure

Film	Charge % Hexenes	Permeate % Hexenes	α	Rate g/hr-cm^2
MD polyethylene	51	53	1.1	0.36
Polypropylene	55	58	1.1	0.08
HD polyethylene	45	54	1.4	0.02

The set of Tables 22 through 25 again illustrates the familiar pattern. For the heptane/benzene binary, benzene permeates preferentially and the rate decreases and the selectivity increases from MD polyethylene to HD polypropolene to HD polyethylene.

TABLE 22

benzene:n-heptane; 200g (52:48 wt.%)

1 mil polyethylene - medium density

charge pressure: 760 mm; permeate pressure; 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Benzene in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	6.3	64	--
1	40 min	26.3	59	.256
2	20	20.2	55	.396
3	10	10.1	51	.394
			ave. 55	.349

$\alpha = 1.1$

TABLE 23

benzene:n-heptane; 200g (50:50 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Benzene in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	7.6	60	--
1	60 min	14.0	61	.091
2	60	15.8	59	.103
3	60	16.3	53	.107
			ave. 58	.100

$\alpha = 1.4$

TABLE 24

benzene:n-heptane; 200g (49:51 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Benzene in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	4.1	66	--
1	60 min	5.8	65	.038
2	60	6.8	64	.044
3	60	6.6	64	.044
4	60	10.3	60	.067
			ave. 63	.048

$\alpha = 1.8$

TABLE 25

Permeation of Binary Mixture of n-heptane/benzene
60°C, 1 mil films, 760 mm charge pressure, 5 mm permeate pressure

Film	Charge % Benzene	Permeate % Benzene	α	Rate $g/hr\text{-}cm^2$
MD polyethylene	52	55	1.1	0.35
Polypropylene	50	58	1.4	0.10
HD polyethylene	49	63	1.8	0.05

For the permeation of the n-heptane/di-n-butyl ether binary through the three membranes under investigation, there was, as usual, a marked decrease in rate over the membrane trio MDPE-PP-HDPE but the expected increase in selectivity was not observed, $\alpha = 1.8$ being obtained for HDPE, $\alpha = 1.9$ for PP, and $\alpha = 1.7$ for MDPE. This data is shown in Tables 26 through 29. Overall, the heptane/butyl ether runs gave very little variation in

selectivity with the different hydrocarbon films; a result possibly connected to the fact that this was the only non-hydrocarbon binary tested, thereby allowing polarity effects to come into play. Such polar effects apparently outweigh both film density and size differences in determining selectivity.

TABLE 26

di-n-butyl ether:n-heptane; 200g (47:53 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	0.8	8.2	--
1	60 min	1.4	74	.009
2	60	2.1	70	.014
3	60	2.0	71	.013
			ave. 72	.012
			α = 1.8	

TABLE 27

di-n-butyl ether:n-heptane; 200g (51:49 wt.%)
1 mil polypropylene
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	1.6	80	--
1	60 min	4.9	66	.032
2	60	7.4	68	.048
3	60	7.6	62	.049
			ave. 65	.043
			α = 1.9	

TABLE 28

di-n-butyl ether:n-heptane; 200g (41:59 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2
Forerun	--	0.8	82	--
1	60 min	1.4	74	.009
2	60	2.1	70	.014
3	60	2.0	71	.013
			ave. 72	.012
				α = 1.8

TABLE 29

Permeation of Binary Mixtures of n-heptane/di-n-butyl ether
60°C, 1 mil films, 760 mm charge pressure, 5 mm permeate pressure

Film	Charge % Heptane	Permeate % Heptane	α	Rate g/hr-cm^2
MD polyethylene	53	65	1.7	.12
Polypropylene	49	65	1.9	.04
HD polyethylene	59	72	1.8	.01

In all six of these organic binaries, the same trend in rate of permeation was observed. However, the order of the relative permeation rate is surprising since polypropylene, the film of lowest density, gives the intermediate rate. Barrie and Platt [29] have shown that the presence of crystallinity causes a reduction in the permeability of hydrocarbon vapors through peroxide-cured natural rubber and since, in this instance, crystallinity increases from PP <MDPE <HDPE we might expect the permeation rates to

decrease in the same order. Apparently any correlation of decreasing permeability with increasing crystallinity holds only within a given polymer type and the presence of methyl side chains may account for the relative permeability of polypropylene. This is what van Amerongen [30] found in an investigation of the influence of the structure of elastomers on their permeability to gases. From his results he was able to propose a general rule that pendant methyl groups in the polymer molecules bring about low permeability. While any such correlations between data on gas and/or vapor permeability on the one hand, and liquid permeability on the other, must be regarded with caution; the fact that some liquid permeation results can be discussed in terms of results obtained from gas permeation experiments indicates that some of the more general conclusions derived from gas permeation work may be useful in giving direction to research in the newer liquid permeation technique.

In regard to perm-selectivity, all six binaries showed the same trend in their increase in alpha (α) from MD polyethylene through polypropylene to HD polyethylene. However, the incremental increases in α's between the films were not equal nor were they the same for all six pairs of compounds. The heptane binaries with cyclohexane, cyclohexene, hexenes, and benzene gave comparable α's slightly better than one using MD polyethylene and polypropylene, while a significant increase occurred for permeation through HD polyethylene. Heptane/pentane showed the largest increase between MDPE and PP, with HDPE giving about the same separation as PP. The binary with di-n-butyl ether gave virtually the same separation factor for all three films.

There does not appear to be any published data concerning the perm-selectivity of gas mixtures through chemically similar films of varying density, crystallinity, or number of pendant methyl groups to which our data can be compared, as was the case for permeation rates. Michaels and co-workers [14] have presented some data on the liquid phase permeation of xylenes through low and high density polyethylene membranes, but they were especially preconditioned by solvent annealing.

From the foregoing data, it can be concluded that for the same film type, the permeation rate will decrease with increasing percent of crystallinity or with density, where this property can be used as a criterion of crystallinity. Methyl side goups also decrease permeation rates and may compensate for lower percent crystallinity. The selectivity of such a membrane is, in general, increased by these same film properties which cause the permeation rate to decrease. Probably both the higher ordered

crystalline regions of the polymer and the methyl group both act by offering greater resistance to the passage of the permeating molecules and imposing restrictions on their size and shape.

The improved separation ability of HD polyethylene can be counteracted by operating at higher temperatures, a phenomenon common to other films used for liquid-phase permeation. Table 30 shows the results of a pentane/heptane permeation run at 90°C, and in Table 31 is compared to the 60°C permeations through MD polyethylene and 1 mil HD polyethylene.

TABLE 30

n-pentane:n-heptane; 200g (46: 54 Wt.%)
2 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 25 mm; 90°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$	Rate per 1 mil
Forerun	--	0.31	61	--	--
1	60 min	1.7	53	0.011	.022
2	60	3.2	55	0.021	.042
3	60	3.5	46	0.023	.046
		ave.	51	0.018	.037
			$\alpha = 1.2$		

TABLE 31

Permeation of pentane-heptane mixtures
charge pressure: 760 mm; permeate pressure: 25 mm

Film	Temp. °C	α	Rate per 1 mil $g/hr\text{-}cm^2$
1 mil MD polyethylene	60	1.3	0.25
1 mil HD polyethylene	60	1.7	0.03
2 mil HD polyethylene	90	1.2	0.04

Alpha is now no better than for the MD film. Film thickness is probably not a critical factor since earlier workers have presented evidence that

selectivity is independent of this property. Table 30 also illustrates the fact that the rate per unit thickness can usually be considered constant, the rate through the 2-mil film being approximately one-half that of 1-mil polyethylene. Another feature of Table 30 is the non-representative selectivity of the forerun; a characteristic which has been observed previously for HD polyethylene permeations.

We have also looked at the ability of the three test films to separate molecules which are similar chemically and in shape but differ in size. Binary mixtures of heptane with pentane, decane and dodecane were used. Tables 32 and 33 record the results for the heptane/decane and heptane/dodecane permeation with MD polyethylene film and in Table 34 they are collected with heptane/pentane results already mentioned. As one might expect the separation factors increase with the difference in size.

TABLE 32

n-heptane:n-decane; 200g (54:46 wt.%)
2 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 5 mm; 90°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2	Rate per 1 mil
Forerun	--	1.5	90	--	--
1	20 min	1.3	88	.025	.050
2	20	1.9	83	.038	.076
3	20	2.1	81	.042	.084
4	20	2.4	76	.047	.094
5	20	2.7	79	.053	.106
6	20	2.9	73	.058	.116
7	20	2.7	74	.053	.106
8	20	3.0	75	.059	.118
9	20	3.0	72	.062	.124
10	20	1.5	70	.060	.120
			ave. 77		.099

α = 2.9

TABLE 33

n-dodecane:n-heptane; 200g (46:54 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	-	2.3	99	-
1	60 min	12.6	99	.082
2	60	13.7	98	.088
3	60	12.8	99	.084
		ave.	99	.085
			$\alpha = 84$	

TABLE 34

Permeation of binary mixtures of n-heptane
MD polyethylene film, d = 0.92 g/cc; charge at 1 atm.

Cpd.	Charge % Heptane	Temp. °C	Permeate Pressure, mm	Permeate % Heptane	α	Rate for 1 mil $g/hr\text{-}cm^2$
n-pentane	52	60	25	45	1.3	0.25
n-decane	54	90	5	77	2.9	0.10
n-dodecane	54	60	5	99	84	0.09

With polypropylene as the membrane, Tables 35 and 36, compared to heptane/pentane in Table 37, the separation again increases with difference in size to the same value for the heptane/dodecane mixture, but the heptane/decane separation is considerably better, and HD polyethylene, in Tables 38,39 and 40, gives excellent separation of the heptane/decane binary in spite of the higher permeation temperatures used in this run. The relative permeation rates among all three films are, in general, consistent with the data previously discussed except for a reversal of the MDPE-PP rates with the heptane/decane mixture.

TABLE 35

n-heptane:n-decane; 200g (53:47 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 5 mm; 85°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	2.8	92	--
1	15 min	2.9	88	.076
2	15	3.0	88	.073
3	15	3.0	87	.078
4	15	5.4	85	.140
5	15	5.4	85	.140
6	15	5.4	82	.140
7	15	5.8	78	.150
8	15	6.8	79	.180
9	10	4.6	79	.180
10	10	4.9	78	.190
			ave. 83	.135

$\alpha = 4.3$

TABLE 36

n-dodecane:n-heptane; 200g (46:54 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2
Forerun	--	0.8	99	--
1	60 min	2.8	99	.018
2	60	4.3	99	.028
3	60	4.8	99	.031
4	60	5.2	98	.034
			ave. 99	.028

α = 84

TABLE 37

Permeation of binary mixtures of n-heptane

Polypropylene film, d = 0.90 g/cc., charge at 1 atm

Cpd.	Charge % Heptane	Temp. °C.	Permeate Pressure, mm.	Permeate % Heptane	α	Rate g/hr-cm^2
n-pentane	49	60	25	38	1.6	0.11
n-decane	53	85	5	83	4.3	0.14
n-dodecane	54	60	5	99	84	0.03

TABLE 38

n-decane:n-heptane; 200g (50:50 wt.%)

2 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 5 mm; 95°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$	Rate for 1 mil film
Forerun	60 min	neg.	--	--	--
1	60	0.6	99	.004	.008
2	60	1.5	95	.010	.020
3	60	2.1	90	.014	.028
			ave. 95	.009	.019

α = 19

TABLE 39

n-heptane:n-dodecane; 200g (53:47 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	1.2	97	--
1	60 min	2.3	98	.015
2	60	2.6	99	.017
3	60	2.7	99	.018
			ave. 99	.017

α = 88

TABLE 40

Permeation of binary mixtures of n-heptane
HD polyethylene film, d = 0.96 g/cc.; charge at 1 atm

Cpd.	Charge % Heptane	Temp. °C	Permeate Pressure, mm.	Permeate % Heptane	α	Rate g/hr-cm^2
n-pentane	56	60	25	43	1.7	0.03
n-decane	50	95	5	95	19	0.02
n-dodecane	53	60	5	99	88	0.02

These three hydrocarbon films did not manifest such large differences in selectivity toward mixtures containing molecules of similar size (molecular weights) but different shape. The heptane/isooctane series presented in Tables 41, 42 and 43 shows this. The data are summarized in Table 44. Alpha increases by a factor of about 1.5, while in the heptane/decane series alpha increases seven times going from MD to HD polyethylene. This is in agreement with Bent and Pinsky [15], who found that size is more important than shape in the permeation of pure liquids through polyethylene. It should be noted that the selectivity increase and the rate decrease occurred despite an increased charge temperature (necessary to maintain permeation), a condition which usually decreases selectivity and increases the rate. Permeate pressure changes of the order of magnitude shown in Table 44 would not be expected to affect the rate (see ref. 6) and do not seem to influence the selectivity since a very similar permeation using MDPE at 25 mm., shown in Table 45, gave an identical separation factor and a comparable rate.

TABLE 41

isooctane:n-heptane; 200g (47:53 wt.%)

1 mil polyethylene - medium density

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr-cm^2$
Forerun	--	4.0	74	--
1	60 min	15.7	70	.102
2	60	19.4	64	.126
3	60	10.6	64	.127
			ave. 66	.118
				α = 1.7

TABLE 42

n-heptane:isooctane; 200g (53:47 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr-cm^2$
Forerun	--	8.8	69	--
1	15 min	7.3	65	.190
2	6	3.4	66	.214
3	30	14.7	66	.191
4	9	4.9	66	.212
5	9	4.6	65	.199
6	9	5.5	64	.238
7	9	4.6	64	.208
8	9	4.8	63	.206
9	9	5.6	63	.242
10	9	4.8	62	.210
			ave. 64	.211 α = 1.6

TABLE 43

n-heptane:isooctane; 200g (54:46 wt.%)
1.8 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 5 mm; 95°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$	Rate per 1 mil
Forerun	50 min	2.7	73	.021	.038
1	20	1.0	73	.019	.034
2	20	1.1	73	.021	.038
3	20	1.0	72	.020	.036
4	20	1.0	72	.020	.036
5	20	1.1	73	.022	.040
6	20	1.1	72	.022	.040
		ave.	73		.037

α = 2.3

TABLE 44

Permeation of heptane-isooctane binary
1 mil films; charge at 1 atm.

Film	Charge % Heptane	Temp. °C	Permeate Pressure,mm.	Permeate % Heptane	α	Rate $g/hr\text{-}cm^2$
MD polyethylene	53	60	5	66	1.7	0.12
Polypropylene	53	60	25	64	1.6	0.21
HD polyethylene	54	95	5	73	2.3	0.04

TABLE 45

n-heptane:isooctane; 200g (53:47 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 25 mm; 50°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2
Forerun	63 min	2.8	64	.030
1	20	3.4	65	.066
2	20	4.5	64	.088
3	20	4.9	64	.097
4	20	5.1	64	.100
5	10	2.6	64	.102
6	10	2.6	65	.103
7	10	2.8	65	.109
8	10	2.7	64	.104
9	10	2.5	66	.098
10	10	2.5	65	.099
			ave. 65	.097

$\alpha = 1.7$

It was remarked above when discussing the effects of size variations in binary mixtures that the heptane/decane mixture reversed the expected relative permeation rates between MD polyethylene and polypropylene films. These data are collected in Table 46.

TABLE 46

Permeation of heptane/decane binary - 5 mm. permeate pressure

Ref.	Rate/1 mil g/hr-cm^2	α	T, ^oC	Film
Table 32	.10	2.9	90	2 mil MDPE
Table 35	.14	4.3	85	1 mil PP
Table 38	.02	19	95	2 mil HDPE

The selectivity changes are in the order usually observed for these three films. The permeation characteristics for this binary were reexamined and the results shown in Tables 47, 48 and 49 obtained. In this new series the rates are in the "normal" order, i.e., MDPE > PP > HDPE, but the selectivity properties of the polypropylene and HD polyethylene films have been drastically reduced to a point where seems to be little difference among the three films. The only obvious difference between the original and the new series of permeations is the temperature, which was approximately 30^o lower in the second set of experiments. This, of course, should increase the selectivity according to the information available from the literature. An explaination may lie in some property of decane itself or in the particular binary formed, which causes a decrease in decane solubility or diffusion at higher temperatures. Other indications that decane may be an unusual permeant may be seen in Tables 32 and 35, which show heptane/decane permeations in which numerous fractions were collected for analysis. The rate tends to increase gradually during the course of the run in contrast to other similarly performed experiments (as, for example, heptane/isooctane in Tables 42 and 43). This could be the result of some sort of "film conditioning" effect which allows permeation of increased amounts of decane. The smaller heptane molecule creating an enlarged channel which permits passage of a larger molecule

of the same shape but normally too large to pass easily. Increase in permeation temperature would disrupt this mechanism and interfere with decane permeation. Unfortunately, we have not been able to explore this area further during the course of the work.

TABLE 47

n-heptane:n-decane; 200g (50:50 wt.%)

1 mil polyethylene - medium density

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	--	86	--
1	60 min	14.2	80	.093
2	60	19.6	74	.13
3	60	18.9	72	.12
		ave.	75	.11

$\alpha = 3$

TABLE 48

n-heptane:n-decane; 200g (47:53 wt.%)

1 mil polypropylene

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	2.5	78	--
1	60 min	4.3	71	.028
2	60	5.7	66	.037
3	60	5.9	68	.038
			ave. 68	.034
				α = 2.4

TABLE 49

n-heptane:n-decane; 200g (48:52 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	0.53	95	--
1	60 min	1.1	89	.007
2	60	1.7	73	.011
3	60	1.8	68	.012
			ave. 77	.01
				α = 3.6

Several times in the literature it has been mentioned that film thickness has little or no affect on selectivity and that the permeation rate per unit thickness is constant. We have confirmed this by permeating a pentane/heptane mixture through a dual film composed of two layers of medium density polyethylene. As seen in Table 50, the rate is one-half that for permeation through a single thickness, as reported in Table 6, and the selectivity is identical for the two runs.

TABLE 50

n-pentane:n-heptane; 200g (50:50 wt.%)
1 mil polyethylene - medium density (two layers of film used)
charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	10.4	71	--
1	60 min	16.4	57	.107
2	60	18.8	57	.123
3	60	18.8	54	.123
			ave. 56	.118
				α = 1.3

An interesting extension of this technique would examine perm-selectivities of dual films formed from two dissimilar membranes.

3.2 Hydrocarbon Films - Permeate Pressure Changes

We also wished to include in this study some work on the effect of changing the operating variables for a given permeation system. One of the most important of these variables is the permeate pressure. Binning et al[6] have reported that changes in charge pressure have no effect on selectivity or rate and likewise that the pressure differential across the film (varied by changing the permeate pressure) does not alter the rate. He gave, however, no data describing the effect of permeate pressure on selectivity.

We have found that changes in this parameter can, at least with some permeating systems, cause favorable modifications in selectivity. This is illustrated in Tables 51, 52 and 53, in which heptane/pentane mixtures were permeated through MD polyethylene at permeate pressures of 50 mm., 100 mm., and 200 mm. Alpha, in all cases, was enhanced over the 25 mm. permeation (Table 26), the separation increasing more than five-fold in going from 25 mm. to 200 mm. pressure on the downstream side of the membrane. At 50 mm., no increase over the 25 mm. run was apparent from the averages, but closer examination of the data disclosed the possibility that the average alpha may have been affected by the fact that a larger fraction of the total charge mixture was permeated in this experiment than in the 25 mm. run, which significantly depleted the concentration of pentane in the charge during the latter part of the permeation. The rapid increase in observed permeation rate may indicate a leak, which would affect alpha, but examination of the membrane after the run did not reveal any visible rupture. If, however, a leak did develop, the later fractions may not be representative. A corrected separation factor based on the first fraction only, gives $\alpha = 1.4$, slightly greater than the run at 25 mm. permeate pressure. Table 54 summarizes this data on permeate pressure variations for the heptane/pentane system. Note that there is an initial decrease in rate with increase in permeate pressure, but the rate then remains constant.

TABLE 51

n-pentane:n-heptane; 200g (42:58 wt.%)

1 mil polyethylene - medium density

charge pressure: 760 mm; permeate pressure: 50 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	15.4	53	--
1	60 min	26.6	51	.173
2	60	29.8	46	.194
3	60	73.8	39	.481
			ave. 45	.283

α = 1.1

(First Fraction only) (α = 1.4)

TABLE 52

n-pentane:n-heptane; 200g (48:52 wt.%)

1 mil polyethylene - medium density

charge pressure: 760 mm; permeate pressure: 100 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	5.4	82	--
1	12 min	4.0	67	.129
2	3	1.3	66	.167
3	3	1.3	65	.169
4	3	1.3	70	.173
5	3	1.4	68	.183
6	3	1.6	68	.209
			ave. 67	.172

α = 2.2

TABLE 53

n-pentane:n-heptane; 200g (51:49 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 200 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	1.1	94	--
1	3 min	1.1	89	.146
2	3	1.2	89	.155
3	3	1.3	87	.168
4	3	1.3	87	.169
5	3	1.4	81	.179
6	10	4.5	82	.177
		ave.	86	.166

$\alpha = 5.9$

TABLE 54

Permeation of heptane-pentane mixtures: effect of permeate press.
1 mil MD polyethylene, d = 0.92 g/cc.

Reference	Charge % Pentane	Temp °C	Permeate Pressure	α	Rate $g/hr\text{-}cm^2$
Table 6	48	60	25	1.3	0.25
Table 51	42	60	50	~1.4*	~0.17*
Table 52	48	60	100	2.2	0.17
Table 53	48	60	200	5.9	0.17

* Based on incomplete experiment

A duplicate permeation of heptane/pentane at 200 mm. permeate pressure, Table 55, confirmed the improved separation at higher permeate pressures although the average selectivity did not march exactly the original 200 mm. experiment. This indicates that more precise control over operating conditions and film properties should be an important consideration in any future work in this area.

TABLE 55

n-pentane:n-heptane; 200g (44:56 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 200 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	3.7	61	--
1	60 min	10.2	85	.067
2	60	20.1	68	.131
3	60	23.4	59	.153
			ave. 71	.117
				α = 3.1

Tables 56 through 59 give the results of permeating pentane/heptane mixtures through high density polyethylene at downstream (permeate) pressures of 25, 100, 200, and 300 mm. of Hg. The selectivity is seen to increase and the permeation rate to decrease with increasing permeate pressure, similar to the results recorded above for MD polyethylene film. However, the permeation at 200 mm. permeate pressure gave $\alpha = 21$, much higher than the other separation factors obtained with HDPE film and apparently indicates that an optimum selectivity can be obtained as a function of permeate pressure in this system. No such maximum was observed with the MD polyethylene film in the 25 to 200 mm. Hg range although additional work might reveal such a point. The permeation rate also seems to increase to a low maximum at 200 mm. permeate pressure.

TABLE 56

n-pentane:n-heptane; 300g (45:55 wt%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr \cdot cm^2$
Forerun	--	0.3	57	--
1	60 min	1.9	52	.012
2	60	1.4	52	.009
3	60	2.1	50	.014
		ave.	52	.012
			$\alpha = 1.3$	

TABLE 57

n-pentane:n-heptane; 300g. (51:49 wt%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 100 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	60 min	0.1	84	--
1	60	0.9	79	.006
2	60	1.4	74	.009
3	60	1.6	71	.011
			ave. 75	.009

$\alpha = 2.9$

TABLE 58

n-pentane:n-heptane; 200g (48:52 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 200 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	-	0.83	85	--
1	60 min	1.7	96	.011
2	60	1.8	94	.012
3	60	1.9	94	.012
			ave. 95	.012

$\alpha = 21$

TABLE 59

n-pentane:n-heptane; 300g (49:51 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 300 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	60 min	Trace	--	--
1	60	0.6	88	.004
2	60	0.7	89	.005
3	60	0.8	88	.005
			ave. 89	.005
				$\alpha = 8.4$

Tables 60, 61, 62 and 63 show the results of four additional experiments permeating a heptane/pentane binary through 1 mil HD polyethylene film at four different permeate pressures. This series of experiments was run to confirm the first series of HD polyethylene runs in which the permeate pressure was varied and Figure II is a plot comparing the two sets of data. The second series does indeed confirm the fact that increasing the permeate or downstream pressure increases the perm-selectivity, but the maximum alpha is displaced toward higher pressures, being at least 350 mm. Elucidation of the reason for this displacement will have to wait for a more detailed examination of the permeate pressure effect, but it probably lies in variations within the film itself. The permeation rate does not exhibit a corresponding maximum.

TABLE 60

n-pentane:n-heptane; 300g (51:49 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 150 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	--	0.4	70	--
1	60 min	1.5	63	.010
2	60	1.9	61	.013
3	60	2.2	60	.014
			ave. 61	.012
			α = 1.5	

TABLE 61

n-pentane:n-heptane; 300g (51:49 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 200 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	--	0.6	--	--
1	60 min	1.6	75	.011
2	60	2.1	78	.014
3	60	2.1	76	.013
			ave. 76	.013
			α = 3.0	

TABLE 62

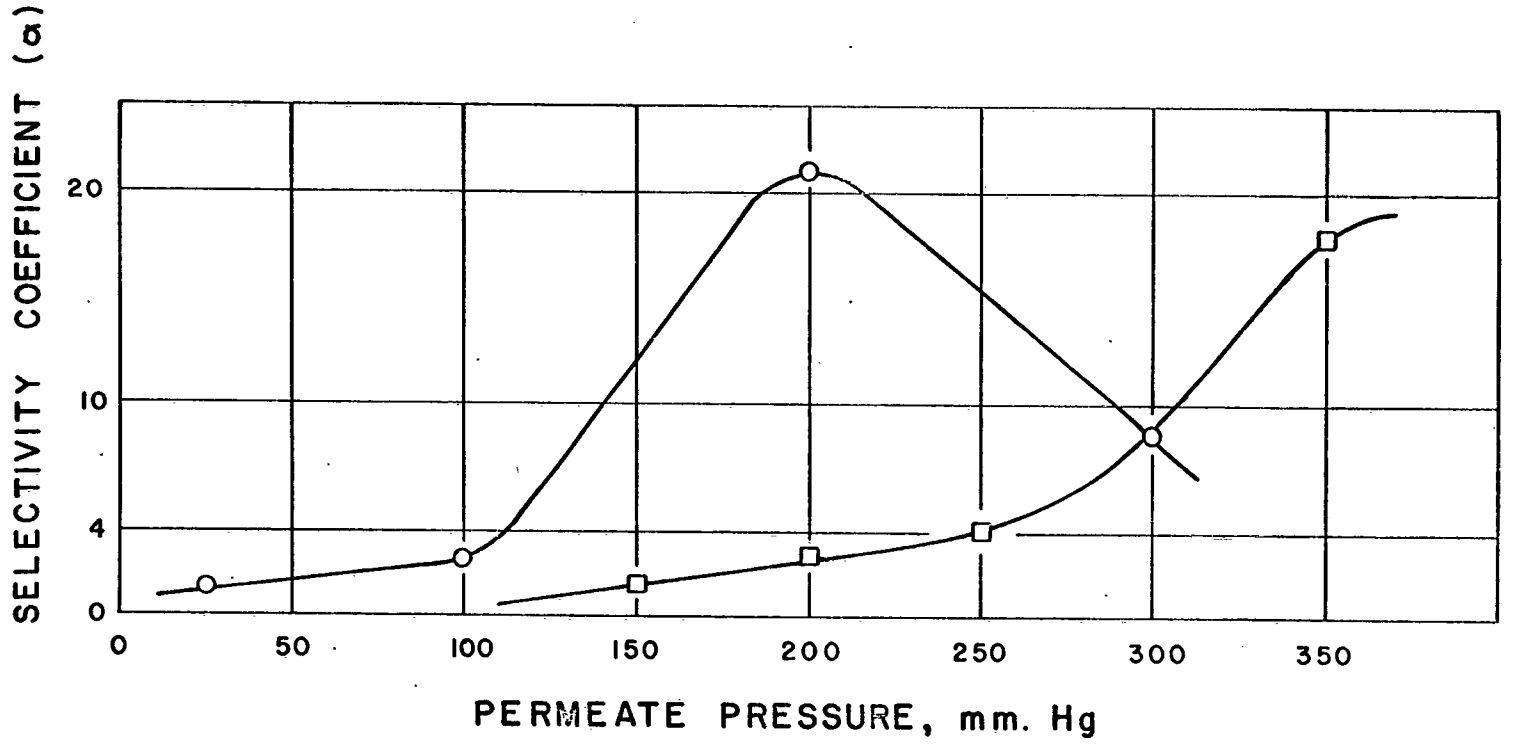
n-pentane:n-heptane; 300g (49:51 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 250 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	0.3	--	--
1	60 min	1.1	80	.008
2	60	1.5	80	.010
3	60	1.7	80	.011
			ave. 80	.010
			$\alpha = 4.2$	

TABLE 63

n-pentane:n-heptane; 300g (52:48 wt.%)
1 mil polyethylene - high density
charge pressure: 760 mm; permeate pressure: 350 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	--	--	--
1	60 min	0.9	95	.006
2	60	1.4	95	.009
3	60	1.3	96	.008
			ave. 95	.008
			$\alpha = 18$	



PERMEATION OF 50:50 PENTANE / HENTANE
THROUGH HIGH DENSITY POLYETHYLENE AT 60°C

FIGURE II

To determine if the permeate pressure effect exists with other binary mixtures, heptane/cyclohexane (twice) and heptane/cyclohexene mixtures were permeated through MD polyethylene, at 200 mm. permeate pressure, 60°C, and 760 mm. charge pressure. This is in contrast to the 5 mm. downstream pressure used in our previous experiments with these binaries. In all runs the film dissolved before any permeation occurred. A re-run of the heptane/cyclohexane permeation at 5 mm. permeate pressure with MDPE at 60°C is shown in Table 64, and produced no visible film damage after a total permeation period of approximately three (3) hours. This was three times longer than the previous successful heptane/cyclohexane run at 5 mm., and the results were similar. We conclude that at suitable (presumably low) permeate pressures successful permeations can be made through films which would dissolve in the charge mixture under normal conditions. Heating samples of the film in beakers containing 50:50 mixtures of the charge did, in fact, dissolve the film by the time the temperature used for permeation was reached. Alternately, it will require a membrane of relatively high chemical stability to allow observation of the effect of high permeate pressure on certain permeant mixtures of interest.

TABLE 64

cyclohexane:n-heptane; 200g. (48:52 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	--	55	--
1	60 min	26.3	53	.171
2	60	39.0	52	.254
3	50	44.7	53	.350
			ave. 53	.258

$\alpha = 1+$

Tables 65 and 66 show data for permeation of heptane/isooctane charge mixtures through medium density polyethylene at 100 mm. permeate pressure and 1300 mm. charge pressure. For this pair of organics, the charge pressure had little effect on selectivity and the high permeate pressure decreased selectivity compared to the 5 mm. run (Table 41). The rate remained relatively constant.

TABLE 65

isooctane:n-heptane; 200g (47:53 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 100 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
1	60 min	5.8	54	.038
2	60	21.1	58	.137
3	60	21.8	58	.142
			ave. 57	.102
			α = 1.2	

TABLE 66

isooctane:n-heptane; 400g. (46:54 wt.%)
1 mil polyethylene - medium density
charge pressure: 1300 mm; permeate pressure: 5 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Heptane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	--	5.2	69	--
1	60 min	18.3	71	.119
2	60	25.7	67	.168
3	60	22.6	66	.147
			ave. 68	.144
			α = 1.8	

Another example of the critical nature of the downstream pressure can be seen in the data on permeation of a heptane/decane mixture, shown in Table 67. Permeation of this charge through 1 mil polypropylene film at 15 mm. pressure on the permeate side yielded an alpha of 6.2, significantly higher than $\alpha = 2.4$ for permeation at 5 mm., Table 48. The last two fractions collected showed a large increase in rate and may indicate a rupture in the membrane, although on examination after the run it appeared to be intact. The "film conditioning" effect may also be operating here.

TABLE 67

n-heptane:n-decane; 300g. (54:46 wt.%)
1 mil polypropylene
charge pressure: 760 mm; permeate pressure: 15 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2
Forerun	--	1.5	92	--
1	60 min	4.9	92	.032
2	60	14.0	90	.091
3	60	11.4	83	.075
			ave. 88	.066
			α = 6.2	

Finally, the selectivity of MDPE for the n-butyl ether/heptane system remained constant when the permeate pressure was increased from 5 mm. to 50 mm., although the rate decreased markedly. Tables 26 and 68 illustrate this.

TABLE 68

di-n-butyl ether:n-heptane; 200g. (54:46 wt.%)
1 mil polyethylene - medium density
charge pressure: 760 mm; permeate pressure: 50 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Heptane in Permeate	Rate g/hr-cm^2
1	60 min	10.1	57	.066
2	60	13.4	62	.088
3	60	10.2	52	.067
			ave. 57	.074
			α = 1.6	

It is apparent that permeate pressure has an important affect on the perm-selectivity of a membrane. Appropriate pressures can permit use of films which are soluble in the charge mixtures under normal conditions and can alter the selectivity of films within the ranges of permeate pressures where they remain stable. From the preliminary data obtained, it cannot be determined what the direction and magnitude of this selectivity change will be with a particular film or whether it will be favorable or unfavorable with a given pair of permeants.

How the permeate pressure induces the observed changes in the perm-selectivity and rate of permeation of a membrane cannot yet be established with certainty. The different pressures probably cause alterations in the internal structure of the film which interfere with the normal (i.e., originally observed) movement of the individual molecules. The proposed "vapor phase zone" of the membrane should be most affected by these changes.

Ionics has also encountered permeation rate effects caused by downstream pressure variations in some of its company-sponsored membrane research. These were mostly observed in the area of low permeate pressure, however. For instance, with certain film-charge combinations used for water/organic separation, rate changes like the following were observed:

Permeate Pressure, mm.Hg	Rate, g/hr-cm^2
1	0.20
5	0.32
10	0.33
15	0.29

This data indicates that re-examination of permeation rates in the low downstream pressure region may be in order and that precise pressure control should be maintained.

3.3 Non-hydrocarbon Films - Effect of Permeate Pressure and/or Charge Variations

In addition to the work described above concerning the effect of variations in film density and permeate pressure for permeations through the three hydrocarbon films studied, it seemed desirable to obtain an idea of the influence of operating variables over a wider range of film types and charge mixtures. For this purpose, a series of experiments were set up in which HD polyethylene, cellulose acetate butyrate (CAB), and polyvinyl alcohol (PVA) were each to be examined for permeability to binary charge mixtures of pentane/ethyl ether, pentane/butanol, and ethyl ether/butanol. Use of these three binary mixtures for permeation experiments, since they are composed of molecules of approximately the same size and shape, will allow evaluation of the parameters of interest for pairs of molecules with different polarity and solubility. Use of the three different films will allow us to determine if any observed perm-selectivity or rate changes are affected by film type. The inclusion of pentane and HD polyethylene in the permeant and film series will permit the results to be related to our earlier work on the permeation of hydrocarbons through polyolefin films.

Tables 69 through 71 show the results of permeating these three mixtures through HD polyethylene. In Table 69, the ether/pentane permeation run, little separation was observed between the two molecules of similar size and shape although polarity and solubility differences exist. The ether was preferentially permeated in spite of the fact that it is a more polar molecule permeating through a non-polar film. With the pentane/butanol mixture, Table 70, the pentane was very selectively permeated, α being 35.

A mixture of two polar molecules, butanol and ethyl ether, was not effectively separated by the non-polar polyethylene film and the rate was extremely slow. In fact, the permeate fractions were so small manipulation was a problem. Table 71 gives the data from this run. Table 72 shows an attempt to increase the separation factor for ethyl ether/pentane through HD polyethylene by using a higher permeate pressure. No improvement was observed, although under similar conditions the separation of the pentane/heptane binary was markedly increased (see Table 58).

TABLE 69

n-pentane:ethyl ether; 300g. (50:50 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	-	0.4	47	-
1	60 min	1.9	44	.012
2	60	2.7	45	.018
3	60	2.3	44	.015
			ave. 44	.015
				$\alpha = 1.3$

TABLE 70

n-pentane:n-butanol; 300g. (48:52 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 25 mm; 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	-	-	-	-
1	60 min	0.8	97	.005
2	60	0.9	95	.007
3	60	1.2	97	.008
			ave. 96	.007
				$\alpha = .35$

TABLE 71

n-butanol:ethyl ether; 300g. (50:50 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 25 mm,; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	-	0.1	-	-
1	60 min	0.4	51	.003
2	60	0.4	56	.003
3	60	0.3	39	.002
		ave.	49	.003

$\alpha = 1.1$

TABLE 72

n-pentane:ethyl ether; 300g. (50:50 wt.%)

1 mil polyethylene - high density

charge pressure: 760 mm; permeate pressure: 200 mm; 60°C

Fraction	Time	Wt. Permeate,g.	Wt.% Pentane in Permeate	Rate $g/hr-cm^2$
Forerun	-	0.6	-	-
1	60 min	2.3	52	.015
2	60	3.0	49	.019
3	60	3.1	49	.021
		ave.	50	.018

$\alpha = 1$

Tables 73 and 74 record data for the permeation of pentane/ethyl ether and butanol/ethyl ether through 1 mil cellulose acetate butyrate film. The permeate pressure was varied for each fraction taken during these runs in order to determine the effect on the rate and selectivity of permeations with this film. For pentane/ether, Table 73, very little separation was observed in the 300-500 mm. Hg range of downstream pressure. However, the lower pressures did product the greatest separation of those observed and also a significant increase in rate. An optimum permeate pressure may exist for this system just as it does for HD polyethylene but was not bracketed by the operating conditions used. Table 74 presents a similar experiment run with a butanol/ethyl ether charge mixture. In this experiment alpha increased with increasing permeate pressure to a point where permeation ceased, while the rate continually decreased.

TABLE 73

n-pentane:ethyl ether; 300g. (38:52 wt.%)
1 mil cellulose acetate butyrate
--- charge pressure: 760mm; 25°C

Fraction	Time	Permeate Pressure mm Hg.	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$	α
Forerun	35 min	300	6.6	37	.087	1.6
1	30	500	1.3	44	.016	1.2
2	30	500	1.1	47	.014	1.1
3	30	500	1.0	46	.013	1.2
4	30	400	2.5	41	.033	1.3

TABLE 74

n-butanol:ethyl ether; 300g (52:48 wt.%)
1 mil cellulose acetate butyrate
charge pressure: 760 mm; 25°C

Fraction	Time	Permeate Pressure mm Hg.	Wt. Permeate, g.	Wt.% Et_2O in Permeate	Rate $g/hr\text{-}cm^2$	α
Forerun	60 min	100	28.2	90	.185	9.5
1	30	500	neg	-	--	--
2	30	400	neg	-	--	--
3	60	300	6.0	93	.039	17.4
4	60	300	5.5	93	.036	18.0

The results of a second butanol/ethyl ether permeation through cellulose acetate butyrate are presented in Table 75. This experiment extended the permeate pressure range examined from 5 to 500 mm. and confirmed that high permeate pressures vastly improve the selectivity but severely reduce the permeation rate. These effects are analogous to those observed for heptane/pentane permeation through polyethylene. Attempts to repeat these experiments with cellulose acetate butyrate at 60°C caused rupture of the film.

TABLE 75

n-butanol:ethyl ether; 600g. (49:51 wt.%)

1 mil cellulose acetate butyrate

charge pressure: 760 mm; variable permeate pressure; 19°C

Fraction	Time	Wt. Permeate, g.	Wt.% of ether in Permeate	Permeate Pressure mm Hg.	Rate $g/hr\text{-}cm^2$	α
Forerun	60 min	0.20	-	400	-	-
1	30	2.5	99	300	.033	95
2	15	1.3	99	300	.034	95
3	5	2.3	99	200	.178	95
4	5	2.2	98	200	.174	47
5	5	2.9	98	150	.229	47
6	5	3.5	97	100	.277	31
7	5	4.1	97	50	.325	31
8	5	4.6	83	25	.364	4.7
9	5	4.4	72	5	.350	2.5

Attempts were also made to permeate the three binaries of interest through polyvinyl alcohol film. Both the pentane/butanol and pentane/ether charge mixtures gave no product when run at 60°C for 4 and 2 hours respectively. Butanol/ether did permeate, but at a low rate, which appeared to decrease with time. Fair separation was obtained. Table 76 shows the data on this run. No further attempt was made to use polyvinyl alcohol as a perm-selective membrane.

TABLE 76

n-butanol:ethyl ether; 300g. (52:38 wt.%)
1 mil polyvinyl alcohol
charge pressure: 760 mm; permeate pressure: 25 mm: 60°C

Fraction	Time	Wt. Permeate, g.	Wt.% Et_2O in Permeate	Rate $g/hr\text{-}cm^2$
Forerun	60 min	3.4	73	.022
1	60	3.5	77	.023
2	60	1.2	70	.008
3	60	0.5	69	.003
		ave. (excluding forerun):	72	.011
			$\alpha = 2.8$	

The available data on the permeation rates and selectivities for the three binary mixtures and the three films just discussed are collected in Figure III. A more extensive compilation of the results of charge variations was not made because we were diverted by the permeate pressure effect observed with cellulose acetate butyrate membranes, Tables 73 and 74, and wished to explore this effect further with a second film type. It is possible that a more detailed chart of representative films and charge mixtures, extending Table III, will permit accurate initial selection of appropriate films and operating conditions for separation of a given mixture.

FIGURE III			
	High Density Polyethylene 1 mil	Polyvinyl Alcohol 1 mil	Cellulose Acetate Butyrate 1 mil
Pentane and Ethyl Ether	Ether α = 1.3 Rate = 0.015 60°C 25 mm Hg DSP*	No Permeate 60°C 25 mm Hg DSP	Ether α = 1.2 Rate = 0.016 60°C 500 mm Hg DSP
Pentane and Butanol	Pentane α = 35 Rate = 0.007 60°C 25 mm Hg DSP	No Permeate 60°C 25 mm Hg DSP	
Ethyl Ether and Butanol	α = 1.1 Rate = 0.003 60°C 25 mm Hg DSP	Ether α = 2.8 Rate = 0.011 60°C 25 mm Hg DSP	Ether α = 9.5 Rate = 0.19 25°C 100 mm Hg DSP
* DSP = downstream (permeate) pressure			

3.4 Effect of Permeant and Permeate Pressure Variations

Investigation of the effect of high upstream (permeant) pressures on perm-selectivity and rate was begun with the n-butanol/ethyl ether binary. Tables 77 and 78 show data for the permeation of this charge mixture through 1 mil cellulose acetate butyrate for upstream pressures between atmospheric and 160 psig of nitrogen. In Table 77 the permeate pressure was held constant at 300 mm. while in Table 78 the permeate pressure was maintained at 200 mm. In both cases the excellent selectivity originally observed with this permeating system (Table 74) was maintained.

In Table 77 at 300 mm. permeate pressure, the permeation rate is seen to increase with increasing upstream pressure. Some changes in alpha also occurred but the separation obtained under all operating conditions was so great that they are not a significant measure of variations in perm-selectivity. However, the trend appears to be toward greater selectivity with higher pressure. The observed change in rate with upstream pressure was unexpected in light of literature reports [6,9] that this parameter has no effect on either rate or selectivity.

At 200 mm. permeate pressure, Table 78, variations in the upstream pressure over the range 1-160 psig nitrogen overpressure did not produce the changes in permeation rate observed in the first set of data. Comparing these two runs, it would appear that the importance of the upstream pressure on rate is a function of the permeate pressure, with a maximum critical downstream pressure needed before any effect is noted. However, both temperature and permeate pressure changes seem to have a more pronounced effect than high overpressures and are easier to realize experimentally. For example, a threefold increase in permeate pressure decreased the rate by one-fifth while an 80X increase in overpressure was needed to increase the rate by the same amount.

TABLE 77

n-butanol:ethyl ether; 300g. (50:50 wt.%)
1 mil cellulose acetate butyrate
permeate pressure: 300 mm; 18°C

Fraction	Time	Wt. Permeate,g.	Wt. % Ether	Upstream Pressure,psig	Rate $g/hr\text{-}cm^2$	α
Forerun	60 min	1.8	97	160	.012	32
1	60	3.2	97	160	.021	32
2	60	3.7	97	160	.024	32
3	60	3.1	97	160	.020	32
4	60	0.4	96	1 atm	.002	24
5	60	0.2	96	1 atm	.002	24
6	60	0.3	96	1 atm	.002	24
7	60	3.6	97	160	.023	32
8	60	1.9	97	80	.013	32
9	60	1.2	96	40	.008	24
10	60	3.4	97	120	.022	32

TABLE 78

n-butanol:ethyl ether; 300g. (51:49 wt.%)
1 mil cellulose acetate butyrate
permeate pressure: 200 mm; 18°C

Fraction	Time	Wt. Permeate,g.	Wt. % Ether	Upstream Pressure,psig	Rate $g/hr\text{-}cm^2$	α
Forerun	22 min	6.3	99	1 atm	.113	102
1	9	2.4	99	20	.107	102
2	6	1.6	99	40	.107	102
3	5	1.3	99	60	.104	102
4	5	1.3	99	100	.104	102
5	5	1.3	99	140	.106	102
6	5	1.3	99	160	.102	102

The effect of high permeant pressures on the permeation rate in the butanol/ethyl ether binary-CAB system was corroborated by the data shown in Tables 79 and 80. In both of these runs, the permeate pressure was held at the critical 300 mm. Table 79 records a second run with upstream pressures between atmospheric and 160 psig, while Table 80 extends the over-pressure to cover the 160 to 250 psig range. In both sets of data the permeation rate is seen to increase consistently with increasing permeant pressure, and to be reproducible at all pressures for a given film sample. There is, however, a difference in the range of permeation rates realizable by different samples of the same film type.

TABLE 79

n-butanol: ethyl ether; 300g. charge
1 mil cellulose acetate butyrate
permeate pressure: 300 mm; 18°C

Fraction	Time	Wt. Permeate,g.	Upstream Pressure,psig	Rate $g/hr\text{-}cm^2$
Forerun	--	0.4	1 atm	.005
1	30 min	3.4	160	.044
2	30	3.4	120	.045
3	30	2.5	80	.032
4	30	1.6	40	.021
5	30	1.1	20	.014
6	30	0.5	1 atm	.006
7	30	3.7	160	.048
8	30	3.4	120	.044
9	30	2.5	80	.032

TABLE 80

n-butanol: ethyl ether; 300g. charge
1 mil cellulose acetate butyrate
permeate pressure: 300 mm; 15°C

Fraction	Time	Wt. Permeate, g.	Upstream Pressure, psig	Rate $g/hr\text{-}cm^2$
Forerun	22 min	2.1	160	.038
1	15	1.6	160	.043
2	10	1.0	160	.039
3	10	1.2	200	.047
4	10	1.3	200	.050
5	10	1.4	250	.056
6	10	1.4	250	.053
7	10	1.0	160	.039

Data from extension of the experiments on the pentane/ethyl ether-CAB system are given in Table 81. The range of permeate pressure investigated was from 5 to 400 mm. and overlapped the initial data given in Table 73. The charge pressure was held constant at 1 atmosphere. For this film-charge combination the rate again increased with decreasing permeate pressure but the selectivity also improved with lower downstream pressure in contrast to the butanol/ethyl ether binary shown in Tables 74 and 75. There appears to be a maximum separation around 100 mm. permeate pressure.

Table 82 gives data on the pentane/ether-CAB system at constant 300 and 200 mm. downstream pressures with the upstream pressure varied at each level. As predictable from the information presented in Table 81, both the rate and selectivity are better at the lower permeate pressure. Changes in the overpressure on the charge have no effect either on the rate or selectivity at either level of downstream pressure. If a critical permeate pressure exists for operation of an upstream pressure effect in this system, it is below 200 mm.

TABLE 81

ethyl ether:n-pentane; 300g. (49:51 wt.%)
1 mil cellulose acetate butyrate
charge pressure: 760 mm; variable permeate pressure; 20°C

Fraction	Time	Wt. Permeate, g.	Wt.% Ether in Permeate	Permeate Pressure, mm.	Rate $g/hr\text{-}cm^2$	α
1	15 min	0.2	--	400	--	--
2	60	1.1	49	400	.007	1.0
3	15	0.9	68	250	.023	2.2
4	15	0.3	68	300	.009	2.2
5	15	1.0	78	200	.026	3.7
6	15	1.2	84	150	.031	5.5
7	15	1.4	86	100	.038	6.4
8	15	2.3	85	50	.060	5.9
9	10	1.7	84	25	.069	5.5
10	10	2.0	83	5	.077	5.1

TABLE 82

ethyl ether: n-pentane; 600 g. (51:49 wt.%)
1 mil cellulose acetate butyrate
charge and permeate pressures both varied; 20°C

Fraction	Time	Permeate Pressure, mm.	Charge Pressure	Wt. Permeate	Wt.% Ether in Permeate	Rate $g/hr\text{-}cm^2$	α
Forerun	20 min	200	1 atm	6.6	--	--	--
1	7	200	1 atm	1.9	68	.108	2.0
2	5	200	50 psi	1.3	68	.101	2.0
3	5	200	50 psi	1.2	68	.096	2.0
4	5	200	100 psi	1.2	68	.097	2.0
5	5	200	100 psi	1.2	68	.097	2.0
6	5	200	150 psi	1.2	68	.097	2.0
7	5	200	150 psi	1.2	68	.092	2.0
8	5	200	200 psi	1.2	68	.093	2.0
9	15	300	200 psi	3.2	65	.086	1.8
10	5	300	150 psi	0.85	65	.067	1.8
11	5	300	100 psi	0.81	65	.064	1.8
12	5	300	50 psi	0.78	65	.060	1.8
13	5	300	1 atm	0.69	65	.054	1.8
14	5	300	200 psi	0.83	65	.065	1.8

Tables 83 and 84 exhibit data on the effect of permeate pressure (83) and charge pressure (84) on the permeation rate for the pentane/butanol binary through cellulose acetate butyrate. This charge mixture behaves similarly to most of the other binaries examined in that the rate increases with decreasing permeate pressure. Changes in the nitrogen overpressure from one atmosphere to 200 psig did not have any effect on the rate, in contrast to the butanol/ethyl ether binary.

TABLE 83

n-pentane:n-butanol; 300g (∽ 50:50)
1 mil cellulose acetate butyrate
charge pressure: 760 mm; permeate pressure varied; 20°C

Fraction	Time	Permeate Pressure, mm.	Wt. Permeate, g.	Rate $g/hr\text{-}cm^2$
Forerun	15 min	400	--	--
1	60	400	1.9	.012
2	10	300	1.2	.049
3	5	200	0.84	.066
4	5	100	1.0	.079
5	5	50	1.1	.089
6	5	5	1.6	.124

TABLE 84

n-pentane:n-butanol; 300g (~ 50:50)
1 mil cellulose acetate butyrate
charge and permeate pressure both varied; 20°C

Fraction	Time	Charge Pressure	Permeate Pressure, mm.	Wt. Permeate, g.	Rate $g/hr\text{-}cm^2$
Forerun	25 min	1 atm	200	3.6	.056
1	15	1 atm	200	2.2	.057
2	7	50 psi	200	0.95	.054
3	7	100 psi	200	0.96	.054
4	7	150 psi	200	0.97	.054
5	7	200 psi	200	0.95	.053
6	8	200 psi	300	0.93	.052
7	8	150 psi	300	0.79	.039
8	8	100 psi	300	0.79	.039
9	8	50 psi	300	0.73	.036
10	8	1 atm	300	0.65	.032

The final experiments exploring permeate and permeant pressure effects were concerned with the permeation of a pentane/heptane mixture through polypropylene and polyethylene films. The data are shown in Tables 85 and 86. Table 85, fraction 1-6, shows that alpha decreased with permeate pressure and that charge pressure did not influence pentane selectivity through polypropylene (fraction 6-8). As usual, rate increased with decreasing permeate pressure, but was unaffected by increased charge pressure when the downstream pressure was held at 200 mm. Essentially the same thing can be said for the polyethylene run shown in Table 86. No maximum in either selectivity or rate was apparent in either experiment and for the MD polyethylene this was consistent with previous data on that film.

TABLE 85

n-pentane:n-heptane; 600g (50:50 wt.%)

1 mil polyethylene

charge and permeate pressures both varied; 20°C

Fraction	Time	Permeate Pressure, mm.	Charge Pressure	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$	α
Forerun	30 min	400	1 atm	0.54	93	.007	13.3
1	60	400	1 atm	0.48	91	.003	10.1
2	20	300	1 atm	1.9	91	.037	10.1
3	10	200	1 atm	4.2	67	.165	2.0
4	5	100	1 atm	2.5	69	.195	2.1
5	5	5	1 atm	2.2	56	.169	1.3
6	5	200	1 atm	0.85	81	.067	4.3
7	5	200	100 psi	0.91	83	.072	4.9
8	5	200	200 psi	0.99	82	.078	4.6

TABLE 86

n-pentane:n-heptane; 600g (50:50 wt.%)

1 mil polyethylene - medium density

charge and permeate pressure both varied; 18°C

Fraction	Time	Permeate Pressure, mm.	Charge Pressure	Wt. Permeate, g.	Wt.% Pentane in Permeate	Rate $g/hr\text{-}cm^2$	α
Forerun	30 min	400	1 atm	0	--	0	--
1	60	300	1 atm	0.36	93	.002	13.3
2	60	200	1 atm	3.2	88	.021	7.3
3	30	100	1 atm	2.5	81	.033	4.3
4	15	5	1 atm	1.3	60	.035	1.5
5	15	5	100 psi	1.4	54	.037	1.2
6	15	5	200 psi	1.3	57	.034	1.3

4.0 CONCLUSIONS AND RECOMMENDATIONS

While some progress has been made toward the ideal of predicting separation factors, rates, optimum operating conditions, and suitable films for the permeation of a given binary, it is still apparent that each permeation system must be investigated individually in order to determine its permeation properties. Whether changes in permeate pressure will increase or decrease selectivity for a given system, or whether a denser film will improve the permeation results are still questions that must be resolved empirically. A start has been made however, in determining which conditions to change in attempts to improve initially determined rates and selectivity and what operating conditions will create the greatest changes or permit certain film to be employed. A reasonably suitable initial choice can also be made regarding selection of films and operating conditions.

Increasing film density or crystallinity will almost invariably decrease the rate of permeation and will probably enhance the selectivity. These results are attained most consistantly when hydrocarbon binaries are permeated, but may fail for more polar charge mixtures.

Changes in permeate pressure have a marked effect on both selectivity and rate. The rate will decrease with increase in pressure but selectivity has been shown to change in either direction and in some instances to go through a maximum at some intermediate permeate pressure.

Use of correct permeate pressure can allow films which would usually dissolve in the charge mixture to be used as a permeation membrane and have on several occasions exhibited very long life.

Superatmospheric charge pressures increase permeation rates and may affect the perm-selectivity although usually this is not the case. The magnitude of both types of changes induced by charge pressure variations however, is less than that produced by permeate pressure variations. In addition, there appears to be some critical downstream pressure below which no overpressure is effective in changing rates.

Continued investigation is necessary before more general statements can be made about the various factors affecting membrane permeation or a consistent explanation of all the observed results propounded. We believe that further work should be done on permeate and permeant pressure variations to determine, if possible, which classes of binary mixtures are most affected by these changes and in which direction. A closer look at the rate changes induced by permeate pressure variations in the lower pressure ranges also is necessary. Classification of binaries or of film types by the magnitude and direction of the changes produced on them by permeate pressure may be possible.

Further work would also be desirable on rate changes to determine if an optimum rate is attained at some combination of permeate and charge pressures and if some critical permeate pressure actually exists.

Temperature effects are also not yet clearly defined and together with dual film combinations and film conditioning by a "preparative" permeation of a molecule of suitable size or shape present additional possibilities for future investigation.

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