

Hydrocarbons Separation with Polymer Membranes.

I. Butadiene-Isobutene Separation with Nitrile Rubber Membranes

J. P. BRUN, G. BULVESTRE, A. KERGREIS, and M. GUILLOU,
*University of Paris Val de Marne, Laboratoire de Thermodynamique et
D'Electrochimie des Materiaux, 94000 Créteil, France*

Synopsis

The permeation characteristics and the selectivity of four nitrile rubber films with respect to 1,3-butadiene and isobutene were studied as a function of experimental conditions and the nature of membrane material. A specific research apparatus was developed, allowing the determination of both permeation rate and selectivity, at a temperature varying between 0° and 30°C and under a pressure of from 1 to 3 bars. The inverse proportion of permeation rate to membrane thickness was verified for a thickness of from 12 to 500 microns. An increase in temperature promotes liquid permeation and is detrimental to gas permeation, the latter being facilitated by an increase in pressure. The introduction of an inert gas pressure on the liquid did not bring about an increase in the liquid permeation rate. The permeation rate decreases as a result of an increase in the proportion of acrylonitrile in the rubber, which also affects selectivity; the latter reaches a maximum value when said proportion is about 23%. The effect of the composition of the feed mixture was also studied and curves were determined relating, simultaneously, selectivity and permeation rate to the 1,3-butadiene content. Selectivity is maximal with mixtures having a very high 1,3-butadiene content. The solubilities of 1,3-butadiene and of isobutene in the four types of nitrile rubber were measured at 0°C and at 20°C (68°F). Selectivity can be interpreted in terms of the solubilities of the two hydrocarbons.

INTRODUCTION

During the past two decades, much research has been done on the permeation of gases and liquids through polymer films. Relative to such research, an interest has developed in the possibility of applying this permeation process, for separation purposes, to organic compounds as well as to mineral substances.

The different techniques used are gas diffusion, vapor permeation, liquid permeation, and liquid vapor permeation. Their common basis is the generation within the membranes of a free enthalpy gradient, for the diffusing species, on which the migration of elements depends. Migration occurs in three steps: (1) dissolution into the upstream side of the film, (2) diffusion through the polymer, and (3) desorption from the downstream side of the film. The differences in migration speed during these

three steps initiate the compositional changes accompanying the transfer and the resulting selectivity. The latter is defined for a pair (A, B) of diffusing substances by the separation factor $\alpha_{A/B}$ of the membrane, in relation to substance A and with respect to substance B, by

$$\alpha_{A/B} = \frac{y_a/x_a}{y_b/x_b} \quad (1)$$

where x and y are upstream and downstream concentrations, respectively. Permeation rate and selectivity depend not only on experimental conditions (temperature, pressure, composition) but also on the chemical nature and the size factor of migrant molecules, as well as the physicochemical properties of the membrane material.

Imbrication of the various parameters in the diffusion process leads to an a priori distinction between two types of membranes: (1) semipermeable membranes, in which the transfer capacity is a function only of geometrical features of the macromolecular grid and of size factors—size and diffusion section of each diffusing molecule; (2) "specific" membranes, to the extent that a distinct chemical interaction between the polymer and one of the diffusing species occurs in the diffusion process.

The first category includes a certain number of basic polymers,¹⁻¹³ whose utilization is apparently widespread: reverse osmosis, hydrocarbon cracking splitting, separation diffusion of permanent gases. These are polyolefins (polyethylene, polypropylene), polystyrene, nonpolar vinyl substances (acetate, chloride, etc.). These materials show very different permeabilities for molecules with dissimilar steric factors, but they prove to be poorly selective for molecules whose size factors are quite similar.

The term "specific" implies that there is a very close relationship between the membrane material and the diffusing substance. Such a membrane is only specific to a particular substance or chemical function. Polymers may well be the center of important chemical interactions, without possessing such a property. For instance, the fixation of sulfonic groups SO_3H on a macromolecular substratum, makes it permeable to cations but not to anions. It is a selective material for cations but is not specific to either of them. Similarly, a hydrophilic polymer,¹⁴⁻²² such as cellophane or poly(vinyl alcohol), is permeable to polar substances. As far as aqueous mixtures are concerned, interactions are limited to the formation of particularly resistant hydrogen linkings. Selectivity to water, sometimes very high,²⁰ is essentially due to its polarity, which is much greater than that of the other components generally involved. Provided that permeation rates thus obtained are sufficient,¹⁻⁴ these polymers can be usefully applied to concentrated juices, by selective elimination of the water. However, their poor selectivity to molecules which appear to have nearly the same size and same polarity does not enable them to be really specific and to reach a competitiveness suitable for other separation uses.

Specificity requires the existence of active complexing groups within the macromolecular grid. These groups can usually be chemically fixed into

an inert macromolecular substratum by chemical alteration (grafting or copolymerization of a monomer showing said groups). The resulting material allows the separation of two compounds having nearly the same polarity and size appearance,²²⁻²⁵ provided that their capacities to associate with the active group are very different.

In spite of the arbitrary nature of such a division of materials, it is generally acknowledged that specificity is essentially dependent on the strength of the physicochemical affinity between polymer and diffusing substance, in other words, on the capacity of the polymer to create a genuine "resonant macromolecular complex" with the diffusing substance. The resulting selectivity illustrates the fact that it is always the substance with the highest solubility that diffuses fastest.^{4, 18, 22, 26}

A second basic distinction concerns the structure itself of the material and its effect on permeation rate. The latter is closely related to the degree of crystallinity of the polymer, as well as to its glass transition point.

A good permeability requires that the polymer contains a high proportion of amorphous areas. It is preferably,²⁶⁻²⁸ if not exclusively in these areas, that diffusion occurs. It was possible to formulate an empirical relationship^{26, 29} between the activation energy of diffusion and the difference between the glass transition temperature and the temperature at which diffusion occurs:

$$Ed = a - b(T - T_g) \quad (2)$$

where a and b are constants referring to the diffusing substance.

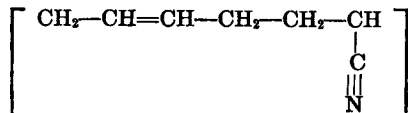
This equation is proved notably in the case of gas diffusion through elastomers. It indicates that during the transfer process, resistance to transfer decreases with an increase in mobility of the chain segments under the effect of temperature; a temperature change of 40°C can thus vary the diffusion rate²⁶ by a factor of 10.

Insofar as the structure of elastomers provides, in the same way, for a greater swelling up to 500% in volume, they should as a rule give rise to permeation rates which are much greater in liquids than those observed in plastics.

Many studies relative to gas diffusion through elastomers²⁶ have been published, but one finds very few which treat permeation.^{12, 30, 31} As far as we know, permeation through elastomers for separation purposes has never really been the subject of extensive research.

We considered this topic too important to overlook. Because of their structural pliability, some elastomers have sufficient mechanical strength and chemical resistance to allow them to be used in the same way as plastics. This study, therefore, is the first part of a series of experiments on the permeability of modified elastomers and their possible applications as specific membranes. Taking the couple butadiene-isobutene as an example we analyzed the effect of experimental conditions (membrane thickness, pressure, temperature) on the separation characteristics obtained with the butadiene acrylonitrile copolymers. The material, selected because of

the particular affinity that nitrile groups show for 1,3-butadiene, can be represented by the following developed equation:



The nitrile groups are intended to entail a specific complexing effect on the butadiene, at the expense of the isobutene, this granting the polymer an increased selectivity as compared to that of the homopolymer. The effect of the proportion of acrylonitrile on permeation characteristics and on selectivity has therefore been the subject of a special study. We also considered it worthwhile to test the effect of the degree of crosslinking in relation to separation.

EXPERIMENTAL

Apparatus

The apparatus used for measuring the permeation rate and selectivity of a membrane consists of the following parts (Figs. 1 and 2): permeation cell, temperature control unit, feed and collecting system, and gas phase chromatographic analysis device.

The permeation cells (A) are made of two Pyrex-glass hemispheres each having a ground flange (E) allowing a classical coupling by means of clamps and bolts. Each hemisphere has a 75-mm diameter and is separated from the other by a membrane M; it also includes a central capillary inlet tube which permits its efficient sweep. The membrane, which has an operational area of 35 cm², rests on a porous support (S), made of sintered glass or metal and whose periphery is coated with an autopolymerizing resin. The imperviousness of the assembly is ensured by two Teflon gaskets (J), one on each side of the membrane sintered support ensemble. The cell is immersed in a standard thermoregulated bath (T).

The liquid feed is stored under pressure away from light in a Pyrex glass container (R) whose capacity is approximately 300 ml. It goes through a pressure-reducing valve (D) so as to reach the upstream compartment at the required pressure. At the outlet of the cell, a valve (V) and a set of capillaries provide for constant and adjustable outflows of evacuated gas (from 1 to 100 cm³/min) which is then collected by condensation in a graduated trap (P) immersed in a bath of carbon dioxide ice-acetone (-80°C). In order to avoid variations of the composition of the feed due to selective diffusion, the outflow of gas is always approximately ten times higher than that of the permeant flow.

The permeant flow is extracted from the downstream compartment which is maintained in a partial vacuum (75 mm Hg) by means of a filter trump. It is collected by condensation in a graduated trap (P₂). Once the vacuum has been created, a valve (V₂) disconnects the filter trump from the down-

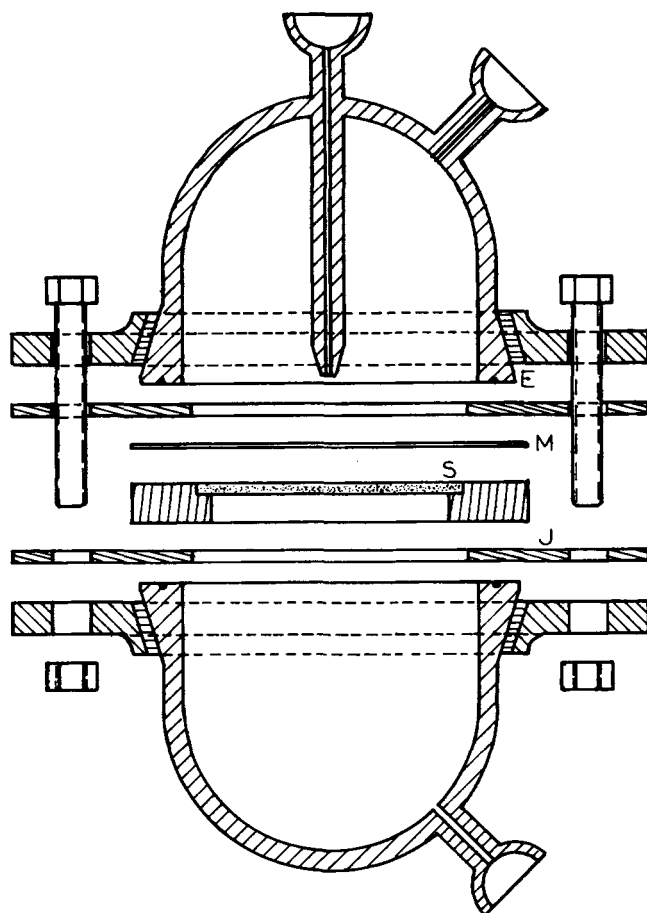


Fig. 1. Permeation cell.

stream circuit, which remains at the preset reduced pressure, as a result of the simple cold-wall phenomenon. Using Rilsan pipes and brass joints ensures a thorough imperviousness. The permeation rates are determined from the variations in the volume of the condensate in relation to time.

The continuous dosage of the evacuated gas and of the permeant can be achieved by chromatography in the gas phase, because of two injection valves set up at the outlet of the cell on the upstream and downstream circuits. The two columns are composed of C_{22} ground bricks containing 30% 2,4-dimethylsulfolane. A flame ionization detector is used.

The device allows the study of separation characteristics for a given membrane as regards a mixture of gas or liquid chemical substances under pressure, in fixed experimental conditions (composition, pressure, temperature). Operational limits are imposed by the physical or thermal resistance of the different parts. The downstream pressure can be fixed arbitrarily between 0 and 1 bar. In such conditions, the maximal permissible

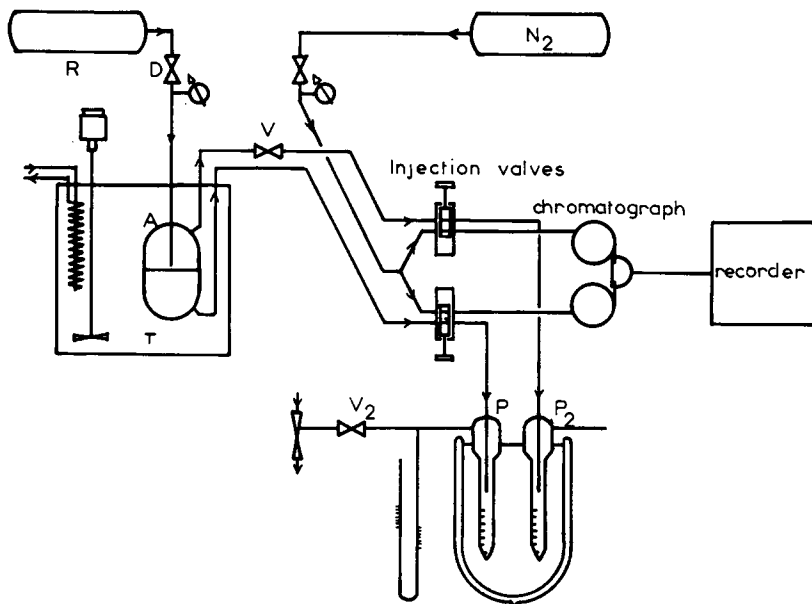


Fig. 2. Schematic of apparatus for measuring permeation rates and selectivities.

upstream pressure is 3 bars, given the mechanical resistance of the porous support and of the cell. When this pressure is not reached (liquid gas permeation), an extra nitrogen pressure can be applied up to the amount of a total pressure of 3 bars. Because of the presence of nonstabilized butadiene in the downstream circuit, we never used a temperature higher than 50°C.

Membranes

Membranes in butadiene-acrylonitrile copolymers are obtained by molding at the Institut Français du Caoutchouc, le Mans, France. The raw polymer is prepared from a mixture containing 100 parts butadiene and x parts acrylonitrile. Different acrylonitrile contents $x/100$ are thus obtained. Crosslinking takes place during molding in 10 min and 165°C by previous incorporation of 0.5% to 2% dicumyl peroxide. The phase thus obtained is a statistical copolymer of butadiene and acrylonitrile. The membranes so obtained are homogeneous and have a constant thickness ranging from 50 to 500 micrometers. Thinner membranes (down to 12 μ) can be obtained by bidirectional stretching of 50 μ latex membranes—a moderate stretching (<200%) which changes only slightly the physico-chemical parameters of these membranes. Research on thinner membranes has not been pursued since the implementation of the films would require very sophisticated technology with respect to the surface conditions. The absence of porosity is proved under a pressure of nitrogen before each test.

TABLE I
Manufacturing Codes of Copolymers

Code	Polymer	Dicumyl peroxide, %
BR 1220	polybutadiene	1,2
BT 105	poly(butadiene 100-acrylonitrile 35)	2
BT 205	poly(butadiene 100-acrylonitrile 51)	2
BT 305	poly(butadiene 100-acrylonitrile 61)	2
BT 308	poly(butadiene 100-acrylonitrile 61)	0,5
BT 405	poly(butadiene 100-acrylonitrile 75)	2
NBR 10	poly(butadiene 100-acrylonitrile 11)	2

The manufacturing codes of the different copolymers (butadiene and acrylonitrile) used are shown in Table I.

Chemicals

Butadiene and isobutene are supplied by Air Liquide, Paris, France, graded N. 20 (purity >99%) and used as delivered. Nitrogen and hydrogen used for chromatography as feed gas and fuel gas, respectively, for the F.I.D. detection are supplied by Air Liquide, graded N. 45 (purity >99.995%). Air supplied by the local compressor is used as a support for the F.I.D. detection after being freed from dust and cold dried.

Operating Procedure and Results

Membrane thickness is determined by weighing, the sample having the shape of a homogeneous disc:

$$l = \frac{4m}{\pi d^2 \rho_r} \quad (3)$$

The permeation outflow φ is determined from the slope of the straight line corresponding to the steady diffusion rate

$$\varphi = \rho \frac{dv}{dt} \text{ g/hr.} \quad (4)$$

The mass or volume of the flux is determined by the following equalities:

$$F_{\text{weight}} = 286\varphi \text{ g/hr} \cdot \text{m}^2 \quad (5)$$

$$F_{\text{volume}} = 119\varphi \text{ l./hr} \cdot \text{m}^2 \text{ gas (standard conditions)} \quad (6)$$

$F \times l$ products are expressed in microns \times liter per hour and square meter; $F \times l$ is thus homogeneous to one diffusion.

$$1\mu \times \text{l./hr} \cdot \text{m}^2 = 2.78 \times 10^{-9} \text{ cm}^2/\text{s gas}$$

$$1\mu \times \text{l./hr} \cdot \text{m}^2 = 9.59 \times 10^{-12} \text{ cm}^2/\text{s liquid}$$

The average diffusion factor \bar{D} can then be established, provided that the volumic fraction σ of permeating substances in the membrane material is known.

$$\bar{D} = \frac{F \times l}{\sigma} \quad (7)$$

Membrane selectivity as regards binary butadiene-isobutene is determined by the weight proportion of the two components in the evacuated feed excess and in the permeant:

$$\alpha = \frac{x'}{1 - x'} \cdot \frac{1 - x}{x}$$

Such a result corresponds to its true definition only to the extent that the composition of the feed mixture can be considered as constant. This proves true when the speed of sweep of the membrane is much higher (about 10 times) than that of the permeant flow.

Swelling

The hypothesis currently recognized in published studies of the isotropic swelling^{12,32} was established as that of preservation of the molar volume of the solvent during dissolution in the polymer. Thus,

$$V \text{ (swollen polymer)} = V_0 \text{ (dry polymer)} + V_1 \text{ (dissolved substances)}$$

so that

$$V_r = 1 - \sigma = \frac{V_0}{V}$$

A parallelepiped band of nitrile rubber (length = $L_0 \simeq 10$ cm, width and thickness $\simeq 2$ mm) is introduced into a Pyrex vessel containing liquid butadiene (-5°C). After closing the vessel and resetting the temperature at 15°C , we measured the sample's new length L , at regular intervals until stabilization. Solubility σ can then be expressed as

$$\sigma = 1 - \left(\frac{L_0}{L}\right)^3$$

The solubility of the four butadiene acrylonitrile copolymers was thus determined at 15°C .

RESULTS AND DISCUSSION

Correlation Between Permeation Rate and Thickness

In practice it is necessary to know the relationship between the permeation rate and the thickness of the membrane; for the results to be compared deal frequently with films of different thickness. Therefore we first verified that the homographic relationship currently accepted as far as gas

TABLE II
Permeation of Butadiene Through a BT 305 Membrane^a

l, μ	$F \times l, \mu \times \text{l./hr} \cdot \text{m}^2$		
	15°C	17°C	20°C
500	4290	3220	2160
420	4370	3320	2370
230	4280	3110	2200
145	4230	2990	2260
α	+0.239	+0.753	-0.017
$t_{0.025} \sigma_a$	0.79	1.29	1.69

^a Upstream pressure 1.70 bar, downstream pressure 0.10 bar.

TABLE III
Liquid-Gas Permeation at 15°C Through a BT 305 Membrane^a

l, μ	$F \times l, \mu \times \text{l./hr} \cdot \text{m}^2$
500	28,000
420	25,000
320	32,000 ^b
145	30,300
68	29,400
12	37,200 ^b
α	-14.4
$t_{0.025} \sigma_a$	20.7

^a Downstream pressure 0.1 bar.

^b Values computed from the dual-curve permeation rate selectivity.

diffusion is concerned,²⁶ was applicable in the case of the permeation of easily condensable vapors.

Our results refer to butadiene gas or liquid permeation through a membrane of butadiene-acrylonitrile copolymer. Products of permeation rate and thickness were measured for dry membranes having a thickness of between 500 and 12 microns (Tables II and III).

The inverse proportion of permeation rate to thickness is proved in each case by statistical computation. The relatively important discrepancy of results obtained in liquid-gas permeation has two origins: (1) variation in the composition of feed mixture; and (2) increase of permeation rates, due to membrane stretching when thin membranes are involved. The phenomenon is slight but already noticeable for 12- μ membranes (200% stretching).

The $F \times l$ product will be considered as the "permeation rate" from now on. This value, in fact, is actually determined by (1) the physicochemical parameters of the diffusing species; (2) the nature of membrane material; and (3) experimental conditions (temperature and pressure).

In case any industrial application should be taken into consideration, it would be possible to extrapolate the result concerning thicker membranes to the range of thin membranes. Though the results have been found only

for BT 305 copolymers, the relationship can be considered valid for all copolymers of this type for any thickness down to 10μ .

Effect of Pressure

The relationship between the permeation rate and the pressure of the diffusing species offers valuable information^{6,8,26} with respect to the diffusion mechanism, particularly the equation

$$\log F \times l = kp \quad (9)$$

where k is a constant, which is graphically accessible and which is a result of a variation in diffusion rate with a concentration that varies according to an experimental law.²⁶ It shows the existence, within the polymer, of a very strong interaction between the diffusion substances and the macromolecular grid.

The passage from gas permeation to liquid-gas permeation gives meaningful information, too: the presence or absence of discontinuity. The permeation rate is directly related to the kinetics of the three phases of the permeation process.

Five different temperatures were used for this research. Permeation rates (Figs. 3 and 4) are recorded as a function of upstream pressure. During all the measurements, the downstream pressure is fixed at 0.1 bar. Although no lower limit is theoretically imposed on the upstream pressure, the necessity to obtain measurable permeation rates led us to use pressures greater than 1.2 bars.

Equation (9) was proved quite adequately for gas permeation within the range of pressure investigated. The straight-line curves so obtained seem to indicate a point of convergence that can be related to a 0 concentration diffusivity²⁶ in the equation

$$D = D_{\sigma=0} \cdot e^{\gamma\sigma} \quad (10)$$

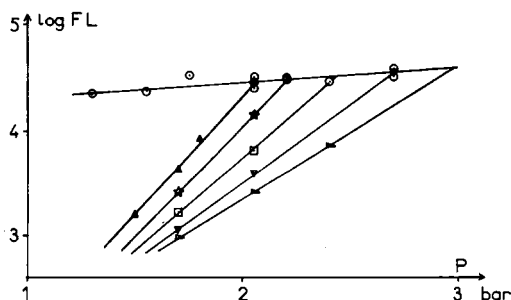


Fig. 3. Effect of pressure on gas and liquid-gas permeation rates of butadiene through a BT 305 membrane: (Δ) gas permeation at 15°C; (\star) gas permeation at 17°C; (\square) gas permeation at 20°C; (∇) gas permeation at 23°C; (\blacktriangleright) gas permeation at 26°C; (\circ) pervaporation between 1.5° and 26°C; $a = +0.124$; $b = 4.22$; $t_{0.025} \sigma_a = 0.081$.

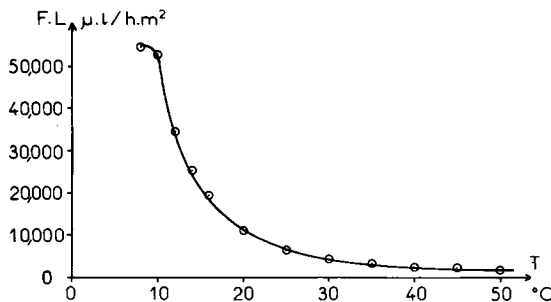


Fig. 4. Effect of temperature on pure butadiene gas permeation. BT 205 membrane. Upstream pressure, 1.80 bar. Downstream pressure, 0.10 bar.

In fact, these "straight lines" curve inward when the upstream pressure decreases, and eq. (9) is really just an approximation which is valid only when the activities of the feed and the permeant differ considerably.

On the upper part of each curve is a limit point which corresponds to the gas liquefaction pressure at each given temperature; all of these points form the liquid-gas permeation curve. There is no particular reason a priori for these curves to be straight lines. However, since the range of measurements is limited, regression can be acknowledged. Thus a comparison of slopes of the straight lines and the two types of diffusion shows the following:

$$\left(\frac{\partial \log (F \times l)}{\partial P} \right)_{\text{gas}} = 1.5 \text{ to } 2$$

$$\left(\frac{\partial \log (F \times l)}{\partial P} \right)_{\text{liquid}} = 0.12.$$

Quantitatively, this result is logical: the free enthalpy variations due to pressure are much less significant for a liquid than for its saturated vapor, near its liquefaction point³³; that of the permeant being the same in each case, the free enthalpy gradient within the membrane increases less in liquid-gas permeation than in gas permeation.

Since there is no discontinuity during passage from gas permeation to liquid-gas permeation, it is evident that there is no fundamental difference between the two diffusion processes. This result also supplies us with information about the kinetics of both absorption and diffusion. If the free enthalpy gradient remains unchanged during the passage of saturated vapor permeation to liquid permeation, the concentration of the diffusing substances near the membrane is much lower in the first case than in the second. Thus, the kinetics of the solubility process of the substance is always slower with a saturated vapor than with a liquid. The fact that this kinetic change has no influence on the permeant flux shows that in this case the speed of dissolution in the polymer is always much greater than the speed of migration.

TABLE IV
Liquid-Gas Permeation Under Extra Nitrogen Pressure^a

Nitrogen pressure	Total pressure	$F \times l$
0	1.20	14,100
1	2.20	14,400
2	3.20	14,000

^a BT 308 membrane. Temperature, 0.5°C. Downstream pressure, 0.1 bar.

Effect of Extra Pressure

According to Paul,¹² application of extra pressure on a liquid feed brings about a marked increase in the liquid-gas permeation rates. The author interprets this phenomenon as the effect of dynamic pressure on benzene upstream and downstream volumetric fractions, in the polymer, which are not those obtained with the polymer-solvent thermodynamic equilibrium.

A nitrogen pressure of up to 2 bars was thus applied (Table IV) on the liquid feed. In these conditions, Paul multiplied his benzene permeation rates by 2.5.

No increase in the permeation rates was observed, and it can be concluded that the free enthalpy of the liquid, a hydrocarbon, was in no way affected by the presence of the nitrogen. The existence of very fast sorption kinetics at the liquid-polymer edge, implying that each side of the film is practically at polymer-solvent thermodynamic equilibrium, does not disprove the results.

For membranes whose thickness is greater than or equal to 10 μ , it is always the migration stage that controls permeation rates. Liquid-gas permeation corresponds to optimal transfer conditions.

Effect of Temperature

Under constant pressure, the solubility of an easily condensable vapor in a polymer greatly decreases when temperature is raised, since the liquefaction point has been passed. A quantitative interpretation of the phenomenon can be demonstrated by an equation of Flory-Huggins.³³ A rapidly decreasing permeation rate is to be expected at least at the beginning.

On the other hand, in liquid-gas permeation, an increase in temperature corresponds to an increase in free enthalpy for the diffusing substance. Much has been admitted^{26,34} about an Arrhenius-type law of evolution in the literature:

$$F \times l = F \times l \times \exp \left[-\left(\frac{E_p}{RT} \right) \right]$$

where E_p represents the activation energy of permeation taking account both solubility and diffusion rate. In these conditions, the function

$$\log F \times l = f \left(\frac{1}{T} \right)$$

TABLE V
Gas Permeation. Butadiene-Isobutene 50/50 Mixture*

$T, ^\circ\text{C}$	$F \times l, \mu \times \text{l./hr} \cdot \text{m}^2$	$T, ^\circ\text{C}$	$F \times l$	$T, ^\circ\text{C}$	$F \times l$
15	21,100	21	8300	32	1850
17	16,700	22	7700	36	860
18.5	12,500	25	5300	40	485
20	8,700	26	3970		

* BT 205 membrane. Upstream pressure, 2.10 bar. Downstream pressure, 0.10 bar.

TABLE VI
Gas Permeation. Butadiene-Isobutene 70/30 Mixture*

$T, ^\circ\text{C}$	$F \times l$	$T, ^\circ\text{C}$	$F \times l$	$T, ^\circ\text{C}$	$F \times l$
14	3260	18	1570	23	515
15.6	1950	19	1210	24	635
16	1790	20	835	30	254

* BT 405 membrane. Upstream pressure, 2.10 bar. Downstream pressure, 0.10 bar.

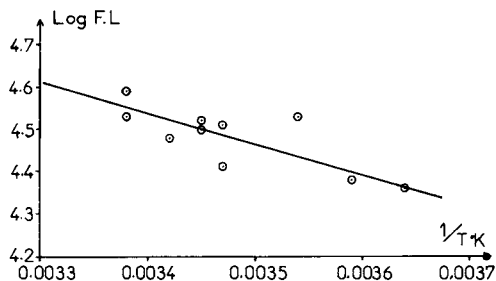


Fig. 5. Effect of temperature on pure butadiene liquid-gas permeation. BT 305 membrane. Downstream pressure, 0.10 bar.

is linear and is represented graphically by a straight line with an angle coefficient equal to $-E_p/R$.

In gas permeation, the pressure is set and the cell temperature is then varied. In liquid-gas permeation, pressure is determined by the temperature. Consequently, the results are the same as those obtained in relation to pressure.

In gas permeation, if pressure is constant, temperature has a considerable effect on permeation rates. A 50% decrease is obtained when temperature is increased by 3°C over the liquid-gas permeation temperature (Fig. 4). There appears to be no significant difference in the shape of the curves obtained for different types of membranes (Tables V and VI).

In liquid-gas permeation, temperature has less of an effect, as can be seen in Figure 5. The function, increasing slightly, has a slope coefficient

$$\frac{\partial \log F \times l}{\partial(1/T)} = 1600.$$

The activation energy E_p for permeation is thus approximately 3200 cal/mole.

This datum can be applied to determine the activation energy E_d in diffusion. It is necessary, then, to know the energy of the solution ΔH_s , which is known to be very close to that of vaporization heat for condensable vapors.²⁶ The heat of the mixture is of less importance. In these conditions,²⁶

$$P = D\sigma \text{ implies } E_p = E_d + \Delta H_s$$

where $\Delta H_s = 5500$ cal/mole for 1,3-butadiene,³³ and consequently

$$E_d = 5500 + 3200 = 8700 \text{ cal/mole.}$$

Effect of Acrylonitrile Content

Certain authors^{6,8,13,35,36,37} have proved the influence of size inherent in branchings on macromolecular chains or on the diffusing elements themselves. Therefore, the proportion of acrylonitrile in the elastomer is likely, a priori, to affect permeation rate, as illustrated by the results shown in Table VII.

These results are given only as indications. A more precise study would have to treat the comparison of polymers which have the same swelling in the diffusing species. This is not the case here. It seems, however, that a high proportion of nitrile groups (BT 405) bring about an appreciable decrease in the permeant's permeation rate. These groups, by altering the

TABLE VII
Gas and Liquid-Gas Permeation of Butadiene Through Nitrile Rubbers

Membrane	Gas permeation $F \times l$ at 23°C under 2.05 bar	Liquid-gas permeation $F \times l$ at 15°C
BR 1220		145,000
BT 205	5780	46,000
BT 305	3970	30,400
BT 308		33,000
BT 405	2080	3,260

TABLE VIII
Liquid-Gas Permeation of Butadiene Through Nitrile Copolymers at 15°C

Membrane	$F \times l$ gas standard conditions	σ	\bar{D} gas standard conditions, cm ² /s	\bar{D} liquid, cm ² /s
BT 205	46,000	0.38	3.37×10^{-4}	11.6×10^{-7}
BT 305	30,400	0.46	1.84×10^{-4}	6.3×10^{-7}
BT 308	33,000	0.56	1.64×10^{-4}	5.9×10^{-7}
BT 405	3,260	0.34	0.27×10^{-4}	0.9×10^{-7}

TABLE IX
Liquid-Gas Permeation Between 1.5° and 15°C^a

$T, ^\circ\text{C}$	Pressure, bars	$F \times l$ (P downstream = 0.1 bar)	$F \times l$ (P downstream = 1 bar)
1.5	1.30	800	670
5	1.50	845	845
10	1.80	850	960
15	2.10	915	920

^a BT 308 membrane. Butadiene-isobutene mixture, 65/35.

oscillation frequency of the macromolecular chains, must hinder the progression of permeant substances.

Table VIII summarizes the permeability and average diffusion rate values in the different copolymers investigated.

Effect of Downstream Pressure

Insofar as permeant pressure differs appreciably from the saturated vapor pressure of diffusing elements, it hardly interferes at all with liquid-gas permeation rate, as can be seen in Table IX.

Effect of Membrane Thickness on Selectivity

As far as permeation rate is concerned, the use of thin membranes offers a definite advantage only if it is assumed that selectivity is not itself affected by a decrease of membrane thickness. No studies illustrating this hypothesis have been published, relevant research generally covering membranes of a fixed thickness. The separation characteristics of these membranes, and especially their selectivity, prove satisfactory down to about 17 microns.²²

Two series of results were obtained, corresponding to the liquid-gas permeation of a 60/40 mixture, at 15°C, under a reduced downstream pressure or equal to one atmosphere.

It was observed (Fig. 6) that selectivity is not dependent on thickness as long as the latter is greater than 100 μ . On the other hand, selectivity is dependent on experimental conditions when the thickness is less than 100 μ . It shows a noticeable decrease when pressure in the downstream compartment is one atmosphere, and it proves practically independent of thickness when a vacuum is maintained in the compartment.

The interpretation of this phenomenon is simple when one considers that an elastomer and especially a latex is composed of very thin grains (0.5 to 5 μ); consequently, highly tortuous micropores are present in the membrane material. When the membrane thickness is much greater than that of the grains, the number of micropores which are regular vectors from one side to the other is extremely limited. The micropore diffusion thus remains negligible as compared to intramembrane transport proper. The phenomenon is mainly perceptible when the size of the thickness is comparable

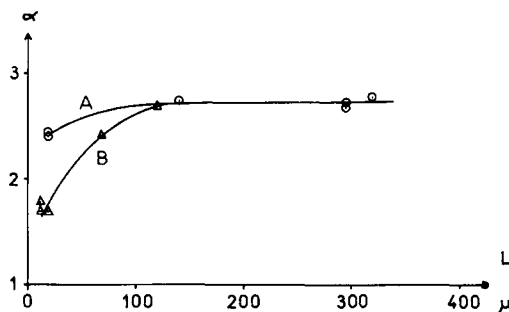


Fig. 6. Effect of membrane thickness on selectivity: curve A, reduced downstream pressure; curve B, one atmosphere downstream pressure.

to that of the grain. Under a high-pressure gradient, the micropores disappear under the influence of the crushing. On the contrary, under a weaker gradient, the micropores are less obstructed and the transport by porous diffusion is no longer negligible.

We shall keep in mind that selectivity depends only slightly on thickness if the pressure gradient is sufficient. It is possible, then, by using thin membranes, to improve permeation rates considerably, while maintaining a good selectivity.

Effect of Physical Condition of the Feed

Liquid-gas permeation has been shown as a membrane swelling which is much greater than that in gas permeation. The hypothesis that an increase in the transfer process would ensue is not to be excluded. The result might well be a decrease in selectivity. But the results obtained with respect to a 50/50 mixture show that there is none. Selectivity in liquid-gas permeation maintaining nearly the same value as in gas permeation (Table X).

Effect of Temperature

Though a reverse evolution has sometimes been noticed,³⁸ it is generally acknowledged that a temperature increase leads to a loss in selectivity.^{26,35}

TABLE X
Liquid-Gas Permeation at 3.0 Bars. Gas Permeation for Lower Pressures*

Upstream pressure, bars	α
3.00	2.57
2.10	2.33
2.10	2.36
1.80	2.45
1.80	2.56
1.00	2.36
α	+0.08
$t_{0.02} \sigma_a$	0.20

* Downstream pressure, 0.1 bar. BT 205 membrane.

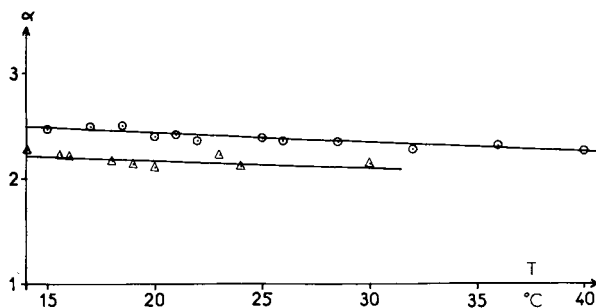


Fig. 7. Effect of temperature on selectivity. Gas permeation, 50/50 mixture. Upstream pressure, 2.10 bars. Downstream pressure, 0.10 bar: (○) BT 405 membrane, a ($^{\circ}\text{C}$) $^{-1}$ = -0.008 , $t_{0.025} \sigma_a = 0.006$; (△) BT 205 membrane, a ($^{\circ}\text{C}$) $^{-1}$ = -0.009 , $t_{0.025} \sigma_a = 0.004$.

Therefore, despite the advantage, as far as permeation rate is concerned, of a high temperature liquid-gas permeation, an optimal temperature allowing a good selectivity is frequently desired. The results corresponding to two types of nitrile rubber are grouped on Figure 7.

It is evident that temperature does not have a marked influence on selectivity. In the least favorable instance, the decrease in selectivity due to 10°C temperature increase is only 0.09. The hypothesis, already proved in the study on pressures, that selectivity is not dependent on the physical conditions of the diffusing substance, is confirmed here.

Effect of Membrane Material

The results obtained with sulfur-vulcanized membranes do not show a satisfactory reproducibility. A premature aging of these membranes, noticed in other respects as well, make impossible any attempt to compare measurements already made. This is probably because of the influence of additives (zinc oxide, N-cyclohexyl-2-benzothiazolesulfenamide) used in this kind of vulcanization. Consequently, our results bear only on butadiene acrylonitrile copolymers vulcanized with dicumyl peroxide (2%).

The nature of the copolymer is thus essentially a function of two parameters: the acrylonitrile proportion and the degree of crosslinking.

The proportion of acrylonitrile limits the permeation rates just as it conditions the permeation rates observed in gas diffusion.²⁶ The existence of marked interactions between butadiene and nitrile groups should logically lead to a close relationship between the acrylonitrile concentration in the polymer and its selectivity as regards the butadiene. Figure 8 shows results covering the four polymers studied.

A close examination of this figure reveals that selectivity is essentially due to the presence of acrylonitrile in the polymer. A polybutadiene membrane has practically no selectivity of its own. The part played by the nitrile group is probably complex, and it is the subject of another study. Probably a resonant type complex between the butadiene and the nitrile

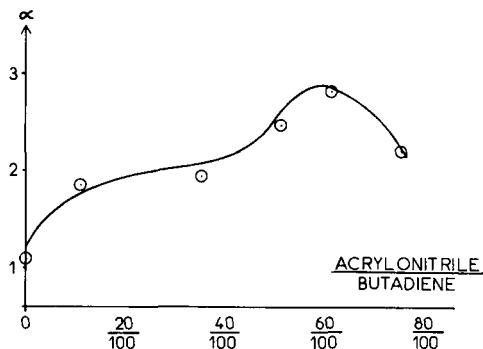


Fig. 8. Effect of membrane composition on selectivity. Liquid-gas permeation Butadiene-isobutene mixture 60/40. Upstream pressure, 2.10 bars. Downstream pressure, 0.10 bar.

group is at the origin of the preferential solubility of a component in the membrane. This solubility conditions selectivity which is very unlikely to be the result of the difference between the diffusion rates of the two molecules since their sizes and shapes are nearly the same.

An optimal proportion exists, beyond which the acrylonitrile rate is unfavorable to selectivity. This proportion corresponds approximately to the BT 305 copolymer. The maximum selectivity observed is thus a function of the crosslinking rate of the polymer. In liquid-gas permeation at 15°C, BT 305 copolymer selectivities for 60/40 mixtures are as follows: BT 305 vulcanized with 2% of dicumyle peroxide, 2.82; BT 305 vulcanized with 4% of dicumyle peroxide, 3.53.

The proportion of vulcanizer, incorporated into the polymer with a view to its crosslinking, thus considerably influences its selectivity.

Effect of Feed Composition on Separation Characteristics

The permeation rates of pure components through a BT 305 polymer membrane were determined in identical conditions: Temperature, 20°C; upstream pressure, 2.10 bars; downstream pressure, 0.10 bars; butadiene, $8700 \mu \times \text{l./hr} \cdot \text{m}^2$, isobutene, $302 \mu \times \text{l./hr} \cdot \text{m}^2$.

The ratio between the permeation rates recorded is approximately 30. A joint variation of permeation rate and selectivity as a function of the feed composition is to be expected. The separation characteristics of two kinds of membranes were determined for mixtures including different butadiene contents. For each membrane, two curves have been plotted (Figs. 9 and 10), indicating, as a function of the permeation rate, the upstream content, on the one hand, and the downstream butadiene content on the other hand. A "dual-curve" is thus obtained showing for each polymer a joint evolution of permeation rate and selectivity, as a function of component mass proportions.

Optimal selectivity values are obtained for mixtures high in butadiene and not for mixtures containing nearly the same proportions as those of the

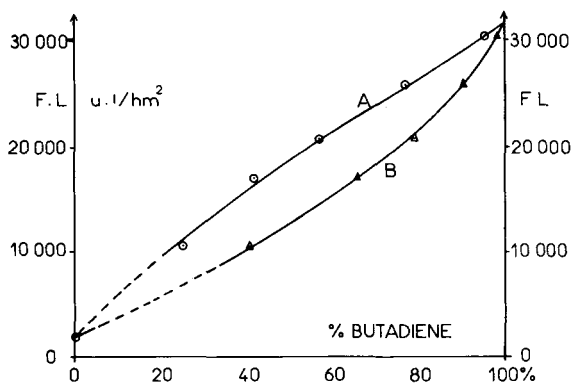


Fig. 9. Effect of the feed composition on separation. Liquid-gas permeation at 14°C. BT 305 membrane; upstream pressure, 2.10 bars: (A) upstream butadiene content; (B) downstream butadiene content.

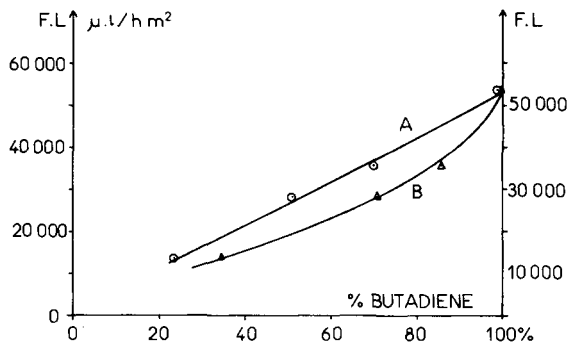


Fig. 10. Effect of the feed composition on separation. Liquid-gas permeation at 14°C. BT 205 membrane. Upstream pressure, 2.10 bars: (A) upstream butadiene content; (B) downstream butadiene content.

two components.⁸ It varies slightly when the butadiene content is between 50% and 100%, it decreases more rapidly when the isobutene content varies from 50% to 100%.

The selectivity value clearly differs from the value derived directly from the ratio of the permeabilities of pure components. The presence of butadiene causes a greater swelling in the polymer and a stretching of the grid which promotes isobutene migration. As proved by some authors with other materials,³⁹⁻⁴¹ the transfer process thus created affects membrane performance, and the higher the isobutene proportion the more the membrane performance is affected.

CONCLUSIONS

The characteristic values (permeation and selectivity) of the permeation of the two hydrocarbons through nitrile rubber clearly differ from those generally observed in gas diffusion. They are rather similar to those ob-

served in liquid-gas permeation. On the other hand, the evolution of these characteristic values, as a function of experimental conditions, seems to be consistent with the scheme taking for valid basis Fick's laws which are generally accepted for gas diffusion.

The elastomer structure of the membrane material substantially improves the permeation rates but has no detrimental effects on selectivity as it has often been observed with natural rubber. The chemical nature of the elastomer may undoubtedly be considered as responsible for the selectivity; more particularly, the proportion of specific groups has a definite influence on selectivity. These groups thus monitor the preferential transfer of the component that has strong complexing capacities with them. Up to now it is rather difficult to have an exhaustive knowledge of the mechanism of this preferential transfer, but classical investigation methods applied to said specific groups are likely to lead to it.

Nomenclature

A	useful surface of membrane (35 cm ²)
D	diffusion rate
\bar{D}	average diffusion factor (cm ² ·s ⁻¹)
F	permeation flow $\begin{cases} \text{l./hr} \cdot \text{m}^2 \text{ gas (standard conditions)} \\ \text{g/hr} \cdot \text{m}^2 \end{cases}$
d	membrane diameter (10.0 cm)
l	membrane thickness (μ)
k	constant
b	0 ordinate
m	membrane mass (g)
M	butadiene molar mass (54 g)
P	pressure (bar)
P_s	saturating vapor pressure (bar)
P	permeability (cm ² ·s ⁻¹)
v	condensate volume (permeant) (cm ³)
V_r	volume fraction of the polymer
V	liquid butadiene molar volume at -80°C (77 cm ³ /mole)
x	butadiene ponderal fraction in the evacuated gas (%)
x'	butadiene ponderal fraction in the permeant (%)
t	time
T	temperature
x/y	mixture composed of $x\%$ of 1,3-butadiene and $y\%$ of isobutene
α	selectivity (dimensionless)
φ	rate of permeation to weight ratio through the membrane
μ	micron
θ	temperature (°C)
ρ	liquid butadiene volume mass at -80°C (0.70 g/cm ³)
ρ_r	polymer volume mass: BT 205, 0.89 g/cm ³ ; BT 305, 0.92 g/cm ³ ; BT 405, 0.96 g/cm ³ ; BT 1220, 0.86 g/cm ³
σ	volume fraction of diffusing species in the polymer (cm ³ /cm ³)

- γ constant
 a angle factor of the least-squares straight line
 $t_{0.025}$ t in Student's law for probability 0.95
 σ_a variant of a

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