Correlation of separation factor versus permeability for polymeric membranes

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Abstract

The separation of gases utilizing polymeric membranes has emerged into a commercially utilized unit operation It has been recognized in the past decade that the separation factor for gas pairs varies inversely with the permeability of the more permeable gas of the specific pair An analysis of the literature data for binary gas mixtures from the list of He, H_2, O_2, N_2, CH_4, and CO_2 reveals an upper bound relationship for these mixtures The upper bound can be represented by a log-log plot of α_{ij} (separation factor $= P_i/P_j$) versus P_i (where $P_i =$ permeability of the more permeable gas) Above the linear upper bound on the log-log plot, virtually no values exist The slope of this line (n) from the relationship $P_i = k\alpha_{ij}^n$ can be related to the difference between the gas molecular diameters Δd_{ji} ($d_j - d_i$) where the gas molecular diameter chosen is the Lennard-Jones kinetic diameter This relationship yields linearity for a plot of $-1/n$ versus Δd_{ji}, and the line passes through $(0,0)$ for the x-y plot thus providing further verification of this analysis These results indicate that the diffusion coefficient governs the separating capabilities of polymers for these gas pairs As the polymer molecular spacing becomes tighter the permeability decreases due to decreasing diffusion coefficients, but the separation characteristics are enhanced

Keywords gas separation, separation factor, permeability, theory data analysis, gas diffusivity

Introduction

Membrane separation of gases has emerged from a technical curiosity in the 1960's, to initial commercialization in the 1970's followed by intense research activity and further commercialization in the 1980's. Probably, the key to this development was the ability to obtain ultra-thin membranes (of the order of 1000 Å) via improvement of asymmetric membrane or thin-film composite fabrication. Another key in this development involved use and/or development of polymers which maximized the permeability of the desired species (P_i) and the separation factor of the gas pair to be separated (α_{ij}) ($\alpha_{ij} = P_i/P_j$). In the past decade it has been noted in many references that increasing P_i generally leads to lower values of α_{ij} [1–5]. In fact these references allude to an "upper bound" relationship for specific gas pairs, generally plotted as α_{ij} versus log P_i

where a linear or curved line denotes the limit of separating ability of polymers for specific gas pairs. In a few cases, the relationship is plotted as log α_{ij} versus log P_i. These correlations of α_{ij} and P_i often present the data as the expected behavior for polymeric systems and utilize the data to show unexpected behavior for the particular polymer under investigation. The data utilized for these correlations are selective as opposed to being comprehensive. Thus a study based on a comprehensive review of literature appears warranted and is the subject of this paper.

In this study, the permeability from over 300 references (including reviews [6–9]) have been compiled and plotted for a series of gas mixtures (O_2/N_2; H_2/CH_4; CO_2/CH_4; H_2/N_2; He/CH_4; He/N_2; He/H_2; He/O_2; H_2/O_2). The data demonstrate the "upper bound" concept for the limits of α_{ij} for specific values of P_i. In essence, a plot of log α_{ij} versus log P_i yields an upper bound (linear line on the log–log plot) above which no data (or at least very limited data) exist. A correlation of the slope of the upper bound lines for the various gas pairs exist with the molecular diameter difference $(d_j - d_i)$ for the gas pairs. The upper bound limits and the resultant correlation would not have been possible a decade ago; however, with the significant increase in the literature on membrane separation, sufficient data exist to yield reasonable upper bound limits for the gas pairs listed for 4 to 5 decades of permeability for the more permeable gas.

The choice of data to be included in this study could not be randomly selected as significant differences in polymeric materials, film preparation, measurement techniques do not allow for sufficient accuracy to utilize P_i and P_j values from different references on a specific polymer. In addition, there are cases of significant errors in the literature, and these, while not specifically noted in each case in this paper, were compared with other literature data or in a few cases experimentally investigated to establish verification. The details on the selection of data chosen for this study are further discussed in this paper.

Background

A number of reviews and books have been published on the subject of polymer permeability [10–16]. In addition several reviews and books exist on the specific subject of gas separation through polymeric membranes [17–24]. This paper will briefly review the characteristics of polymer permeability as it relates to gas separation. The correlation of permeability, solubility, or the diffusion of gases in polymers has been noted in various papers. The correlation of gas pair separation factors to polymer properties or structure, however, has been only briefly attempted in a very qualitative manner. The relationship of gas separation factor with polymer permeability has been noted as will be discussed. The basic permeability equation (for non-concentration dependant Fickian diffusion) is

$$P=DS \tag{1}$$

where P is the permeability coefficient, D is the diffusion coefficient, S is the solubility constant. The diffusion coefficient of common gases in polymers was recognized early as a strong function of the effective molecular diameter of the gas molecule and various correlations existing in the literature will be noted. The solubility constant for the common gases generally follows Henry's law behavior. For several gases utilized in the gas pairs noted in this paper (namely CO_2 and CH_4), dual mode sorption is commonly observed in glassy polymers. The dual mode sorption theory comprises a sorption isotherm consisting of a Henry's law "dissolved" solubility and a Langmuir "hole-fitting" solubility

$$C=kp+\frac{C'_H bp}{1+bp} \tag{2}$$

where k is the Henry's law constant, p is the pressure, C'_H is the Langmuir capacity constant and b is the Langmuir affinity constant. The value of C'_H was shown by Toi et al. [25] to be a linear function of the T_g with an intercept with a value of zero at a temperature equal to the T_g.

The solubility constant of gases in a specific polymer was shown to be related to the boiling point and the critical point of gases by van Amerongen [26]. A simple linear relationship was noted when the log of the solubility constant in natural rubber was plotted versus either of the boiling point or critical temperature of the gas. Stannett [27] compared literature data on gas solubility (benzene and n-heptane) in polyethylene, natural rubber, and Hydropol. A linear relationship between the log of the solubility constant versus the Lennard–Jones force constant (ϵ/k) gave an excellent fit for each system. The slopes for each polymer were equal. Chern et al. [28] noted a similar relationship for the log of the solubility constant versus critical temperatures of the gases for a series of glassy polymers. Van Krevelen [29] compared the solubility of O_2, N_2, CO_2, and H_2 in 23 different polymers and noted the following ranges

Solubility constant [$cm^3(STP)/cm^3$-bar]

	Range	Ratio (high/low)
N_2	0 02 –0 081	4 05
O_2	0 029–0 126	4 34
CO_2	0 19 –1 78	9 37
H_2	0 018–0 047	2 61

Except for CO_2, the highest values for solubility constant were observed in silicone rubber. While there exists a fair range in the solubility constant for these polymers, it must be noted that the solubility constant ratios (which

contribute to the separation factor) generally exhibit a lower range except where CO_2 was involved as noted by the data below:

	Solubility constant ratio range	ratio (high/low)
O_2/N_2	1 21- 3 39	2 80
CO_2/N_2	5 31-63 5	11 9
N_2/H_2	0 87- 1 72	1 98
CO_2/H_2	9 15-83 3	9 10
O_2/H_2	1 12- 4 32	3 86
CO_2/O_2	3 41-27 5	8 06

These data indicate that the solubility constant of CO_2 is more sensitive to polymer structure than the less polar O_2, N_2, and H_2 gas molecules. Van Amerongen [26] noted that a slight dependence of polymer polarity. With increasing polarity (in butadiene/acrylonitrile elastomers), the solubility constant of CO_2 increased slightly whereas decreases were noted for O_2, N_2, and H_2. Koros noted a solubility selectively of CO_2 versus CH_4 in carbonyl containing polymers [30].

As will be shown in this paper, an upper bound appears to exist for α_{ij} (P_i/P_j) versus P_i (i=fast gas). The role of the solubility separation (S_i/S_j) appears to be of minimal significance relative to this observation, and the primary factor is due to the diffusion separation (D_i/D_j) value in the following expression:

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j}\right)\left(\frac{S_i}{S_j}\right) \tag{3}$$

Comparison of S_i/S_j (and later D_i/D_j) will be made with He/N_2 (i/j) as the α_{ij} of this gas pair is quite sensitive to P_i. In Fig. 1, the literature data existing for S_i/S_j is plotted versus $\log P_i$. Generally, the data are clustered in the range of 0.05–0.35. One data point in the literature is off the graph [cellulose nitrate, (S_i/S_j=2.67)]. This point is from the same reference as the ethyl cellulose data point (at S_i/S_j=1.25, P_i=52.7 barrers) [9,31] as shown on the graph. Both points may be suspect. The other point at S_i/S_j=1.25; P_i=0.177 barrers is from Ref. [32] and represents data for Vectra (liquid crystalline polyester). As this system is highly impermeable, the data point implies that the interchain dimensions may be too small to effectively accomodate N_2 molecules.

It has been well recognized that the diffusion coefficient is the primary factor in determining the absolute value of gas permeability in polymers. The diffusivity of gases (in elastomers) was shown by van Amerongen [26] to decrease rapidly as the collision diameter of the gas molecule (determined from gas viscosity data) increases. In comparison of various elastomers, a proportionality (although not ideally linear) was shown to exist for the plot of $\log D$ versus the gas molecule diameter. It was noted that the effective diameters of
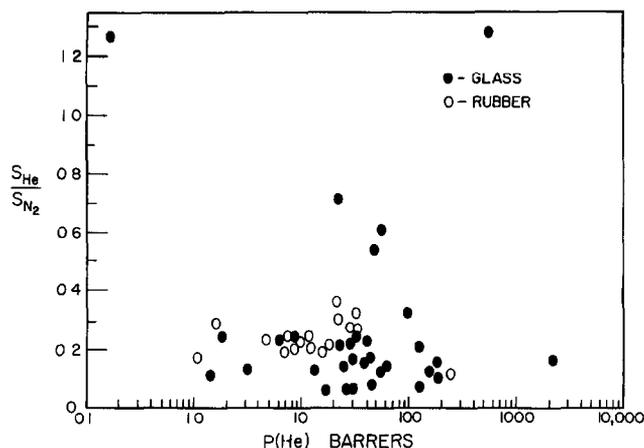
Fig 1 Comparison of the solubility ratio (He/N$_2$) versus He permeability for various polymers

the diffusing molecules were not sufficiently accurate to give an absolute numerical relationship between D and the diameter. Michaels and Bixler [33] showed a linear correlation between the log of a reduced molecular diameter $(d-\phi^{1/2}/2)$ (where $d=$ diameter of gas and $\phi^{1/2}/2$ is the mean unoccupied distance between two chain segments) for a series of gases in natural rubber (with the exception of He and N$_2$). The diffusivities of a wide variety of gases and vapors in poly(vinyl chloride) were reported by Berens and Hopfenberg [34]. A plot of the logarithm of the diffusion coefficient versus the van der Waals molar volume exhibited a systematic progression. The diffusion coefficient changes ten orders of magnitude with an order of magnitude change in the diameter. Other molecular size parameters proposed include molar volume, square root of molecular weight, and kinetic or Lennard–Jones diameter Note that the relationships of these quantities would give different correlation results. A specific example involves CO$_2$ which has a low kinetic diameter but a larger molar volume or molecular weight square root. For glassy polymers, the kinetic diameter has been shown to be correlated with diffusion coefficients better than other noted size related functions [35,36].

In order to compare the diffusion separation characteristics for polymers as a function of the polymer permeability, a plot of log D_i/D_j for He/N$_2$ ($i=$ He) versus log P_i is shown in Fig. 2 It is quite apparent that the observed increase in selectivity (of He/N$_2$) with decreasing He permeability is primarily the result of the diffusion coefficient selectivity as opposed to the solubility constant selectivity.

Generally only the diffusion coefficient has been correlated with gas molecular dimensions, however, Hammon et al. [37] noted that the permeability of glassy polymers followed a linear relationship for the plot of log permeability versus the square of the molecular diameter for nobel gases. For polymers with $T_g < T$, the trend observed was an increasing permeability for molecular diameters argon. This is not unexpected based on other literature, e.g. natural
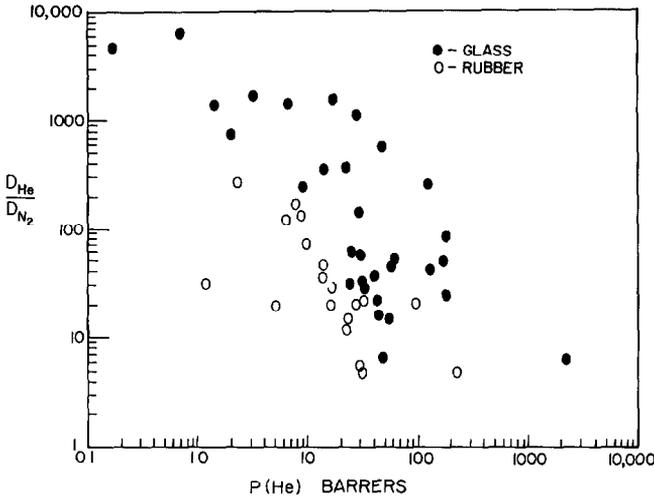
Fig. 2 Comparison of the diffusivity ratio (He/N$_2$) versus He permeability for various polymers

rubber versus PVC in a plot of D versus van der Waals molecular diameter where natural rubber exhibited a much lower dependence on molecular diameter than PVC [33]. As a consequence, this result is the reason that glassy polymers generally exhibit higher separation factors for gas pairs exhibiting molecular diameter differences.

In addition to the correlations of diffusivity and solubility noted above, several other correlations have been mentioned in the literature. Pilato et al. [38] noted a relationship between permeability and polymer density for a series of poly(aryl ethers) and polycarbonates. Chern et al. [29] also noted a similar relationship for the diffusion coefficient and density for a selected number of polymers. Schmidhauser and Longley noted a correlation between oxygen permeability and the reciprocal of specific free volume for polyarylate and polyetherimides [39]. They also noted a trend of higher O$_2$ permeability with increasing T_g for polycarbonates. Puleo et al. [40] noted a correlation of the permeability of substituted polystyrenes with specific free volume. Tanaka et al. [41] observed a correlation of the diffusion coefficients of specific gases with free volume fraction for polymides. O'Brien et al. [42] noted a correlation between the d-spacing of polyimides and the permeability to gases. The d-spacing is obtained from X-ray diffraction data where the d-spacing refers to the amorphous halo dimension characteristic of amorphous polymers. Increasing d-spacing values indicate larger intermolecular spacing and thus increased permeabilities. The relationship for the permeability of copolymers

$$\ln P = \phi_a \ln P_a + \phi_b \ln P_b \qquad (4)$$

(where ϕ_a and ϕ_b are the volume fractions of the monomers) has been noted

by Barnabeo et al. [43]. The utility of Maxwell's equations for relating the permeability of phase separated block copolymers to the permeability of the constituents has been noted by Robeson et al. [44]. The role of antiplasticization additives in decreasing the permeability [45] and increasing the resultant separation factor of gas mixtures [46] has been noted in the literature.

In terms of correlation of the separation factor, Stannett and Swarc [47] and Rogers et al. [48] proposed a relationship for the permeability of gases in polymers and showed a reasonable ratio existed for the separation factor of gas pairs for a wide variety of polymers. The functional relationship for permeability involved a factor relating to the basic permeability of the polymer $[F(\text{polymer } \iota)]$ and a factor relating to the gas $[G(\text{gas } k)]$. Thus, $P_{i,k} = F(\text{polymer } \iota) \cdot G(\text{gas } k) \gamma(i,k)$ and the separation factor is then

$$\frac{P(\iota,k)}{P(\iota,l)} = \frac{G(\text{gas } k) \gamma(\iota,k)}{G(\text{gas } l) \gamma(\iota,l)} \tag{5}$$

As $\gamma(\iota,k) \simeq \gamma(\iota,l) \simeq 1.0$ for simple non-polar gases, the separation factor was predicted to be invariant with polymer choice. The number (and range) of polymers existing at that point in time did not allow for the observation of the increasing $\alpha_{\iota j}$ versus P_{ι} relationship noted in this paper. Another important factor is the recent data on substituted polyacetylenes which help to establish the $\alpha_{\iota j}$ versus P_{ι} relationship at higher values of P_{ι} than previously mentioned in the literature. Poly(trimethylsilylpropyne), for example, exhibits a permeability to common gases an order of magnitude higher than silicone rubber which was for decades the most permeable polymer known.

The correlation of gas permeability and polymer structure was noted by Salame [49]. Although the correlation is noted to be based on a scale of numerical values from the polymer cohesive energy density and fractional free volume, it is, in essence an empirical approach which assigns values based on repeat units of the polymer structure. The values are chosen to give the best overall fit with experimental data. These values, termed Permachor values (π), are based on calculating a polymer value of π where $\pi = \Sigma \pi_i / n$. The π_i's are the individual segment values for the backbone and side groups, and n represents the number of individual units in the backbone repeat unit. This approach yields a reasonable correlation of permeability with structure (for the π_i values available) and does predict an increasing $\alpha(O_2/N_2)$ with decreasing permeability. For O_2 permeability equal to 53 barrers, $\alpha(O_2/N_2) = 2.94$; and for O_2 permeability equal to 0.000725, $\alpha(O_2/N_2) = 7.25$. The upper bound values for $\log \alpha(O_2/N_2)$ versus $\log P(O_2)$ shown later in this paper are considerably above this correlation. The spread of O_2/N_2 data illustrated by Salame is considerably lower than the literature data compiled in this paper.

The overall trend of increasing $\alpha_{\iota j}$ with decreasing P_{ι} ($i =$ the more permeable gas) has only been recently noted in the open literature for specific gas

TABLE 1

Literature correlations for separations factor versus permeability

Gas pair	Plot	Comments	References
O_2/N_2	Linear α versus log P	Increasing α with decreasing P for a series of silicone based polymers	[1]
He/CH_4	Linear α versus log P	Indicates polyetherimide lies above expected "upper bound"	[2]
He/CH_4 and CO_2/CH_4	Linear α versus log P	Indicated specific polyimides are above typical polymers	[3,4]
CO_2/CH_4 and O_2/N_2	Linear α versus log P	Indicates specific polyimides are above correlations for other polymers	[5]
He/CH_4 CO_2/CH_4	log α versus log P Linear α versus log P	Comparative curve showing antiplasticized PPO and PSF versus typical polymer expectation	[46]
O_2/N_2 CO_2/CH_4	Linear α versus log P	Comparative data for substituted polycarbonates versus other polymers	[50]
O_2/N_2	Linear α versus log P	Comparative data of poly (vinylidene cyanide-vinyl acetate) versus typical polymers	[51]
O_2/N_2	Linear α versus log P	Comparative data of polyalkoxysilyl-butadienes versus typical polymers	[52]

pairs, however, no correlation with polymer structure or gas molecule physical parameters (e.g. dimensions) has been presented. The trend is now well recognized by the prominent investigators in this field as noted by the compilation noted in Table 1 Many of the correlations noted have been published from the membrane separations program at the University of Texas. Most of the correlations noted plot linear α_{ij} versus P_i, although for He/CH_4 a plot of log α_{ij} versus log P_i yielded a more linear correlation for typical polymers. In some of these cases, specific polymers (e.g. polyimides) were shown to be above the expected correlation. The expected trend of α_{ij} versus P_i has also been shown for blends of miscible polymers where P_i varies significantly with concentration [53,54].

Permeability data analysis

The data utilized for the upper bound correlation to be presented was obtained from the open literature along with specific patent references. Reviews [6–9] listing tables of permeability data were also included where data was properly referenced. The data utilized for the specific gas pairs came from the same references. If data were utilized from different references for specific data points (α_{ij}, P_i) the scatter would be too great to have any correlation utility Generally, α_{ij} data would be expected to be reasonably correct from a single reference, as calibration errors, film preparation differences, and film compositional differences would not significantly affect the separation factor but on the other hand they could result in major changes in the permeability coefficient for different investigators. Several serious errors were uncovered in the literature and were removed where verification was not possible. Specifically, several cases exist where values were reported to be significantly above the upper bound correlation and either other literature data were available for comparison or the actual results obtained by the author did not allow for verification. A specific case in this respect (widely quoted) involves a reference to cellulose nitrate [9,31] where $P(O_2) = 1.46$ barrers and $\alpha(O_2/N_2) = 16\,8$ was noted. Other literature references on cellulose nitrate (and the author's own unpublished data) indicate $\alpha_{ij}(O_2/N_2)$ to be in the range of 4.0–5.0 with permeabilities in the range of 0.5 to 1.5 barrers.

In plotting the data, it became quite apparent that the typical plots of linear α_{ij} versus log P_i did not yield linearity for the upper bound correlation. Excellent results were however obtained for log α_{ij} versus log P_i over many decades of P_i for all the gas pairs investigated including O_2/N_2; He/N_2; He/CH_4; H_2/N_2; H_2/CH_4; He/H_2; CO_2/CH_4; H_2/O_2; and He/O_2. Phase separated block copolymers and polymer mixtures, composite films, plasma treated films, and surface modified films were not included in this analysis. Values above the upper bound correlation can be obtained from the use of specific composite films (and predicted from the series resistance model). Surface modified films are only a ramnification of a composite film. A composite film consisting of a thin layer of a polymer with low permeability over a highly permeable polymer will yield a composite separation factor similar to the lower permeable polymer but a composite permeability significantly higher than the lower permeable polymer. This has been well documented in the literature [55].

Additionally, values of polymers having facilitated transport containing moieties (e.g. oxygen-binding cobalt complexes) have not been included in this analysis. With enhanced transport polymeric systems noted in the literature [56–58], oxygen selectivity decreases with increasing O_2 partial pressure, and these systems generally exhibit poor selectivity stability with time.
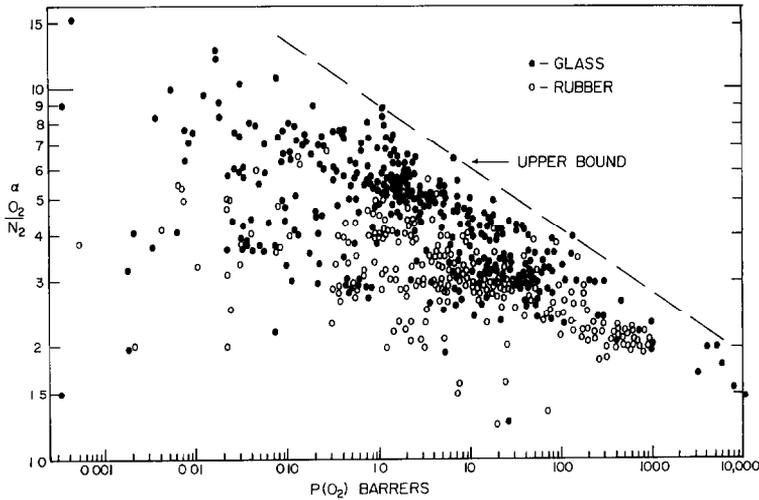
Fig 3 Literature data for O_2/N_2 separation factor versus O_2 permeability

O_2/N_2 separation data correlation

The correlation of the O_2/N_2 separation versus permeability (linear α_{ij} versus log P_i) exists in several literature references (see Table 1). The plot of log α_{ij} versus log P_i for the data compiled for this study is shown in Fig. 3. The results clearly show an upper bound relationship above which virtually no data exist and below which the data are almost continuous. Specific points on or near the upper bound worthy of noting include:

Polymer	$\alpha(O_2/N_2)$	$P(O_2)$ (barrers)	Reference
Poly(trimethylsilylpropyne)	2 0	4000	[59]
Tetrabromo Bis A polycarbonate	7 47	1 36	[60]
Poly(tert-butyl acetylene)	3 0	300	[59]
Vectra polyester	15 3	0 000460	[32]
Poly(triazole)	9 0	1 2	[61]
Polypyrrolone	6 5	7 9	[62]

Note that the log–log correlation fits the literature data better than the linear-log (α_{ij} versus log P_i) relationship. As noted previously, a data point for nitrocellulose widely quoted in the literature [9–31] is believed incorrect and has not been included in this analysis.

H_2/N_2 separation data

No correlation of the H_2/N_2 separation factor with H_2 permeability was found in the literature. The literature data for this pair is given in Fig. 4 and shows a
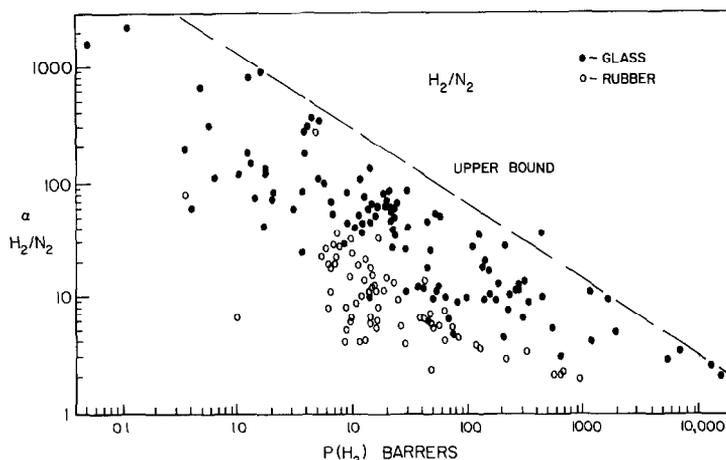
Fig 4 Literature data for H_2/N_2 separation factor versus H_2 permeability

reasonable upper bound when a log–log plot is employed. The values of α_{ij} and P_i on or near the upper bound are listed below:

Polymer	$\alpha(H_2/N_2)$	$P(H_2)$ (barrers)	Reference
Poly(trimethylsilylpropyne)	2 40	16 160	[63]
Poly(tert-butyl acetylene)	11 5	1,150	[59]
Isotactic PMMA	921	1 29	[64]
Atactic PMMA	385	4 5	[64]
Syndiotactic PMMA	362	4 7	[64]
Poly[4-bis (trimethylsilyl-methyl styrene)]	40 0	480	[65]

The various poly(methyl methacrylate)s establish the upper bound at lower H_2 permeability and poly(trimethylsilylpropyne) determines the position at high H_2 permeability. The value for poly[4-bis(trimethylsilylmethylstyrene)] is slightly above the overall relationship. It would be of interest to have further verification of this point

He/N₂ separation data

No He/N_2 separation factor correlation with the He permeability has been noted for a wide range of polymers in the literature. The log–log relationship for α_{ij} and P_i for this gas pair is illustrated in Fig. 5. The slope of the upper bound relationship is steeper than that for H_2/N_2, and the log–log relationship appears to give a reasonable upper bound over 4 decades of He permeability.
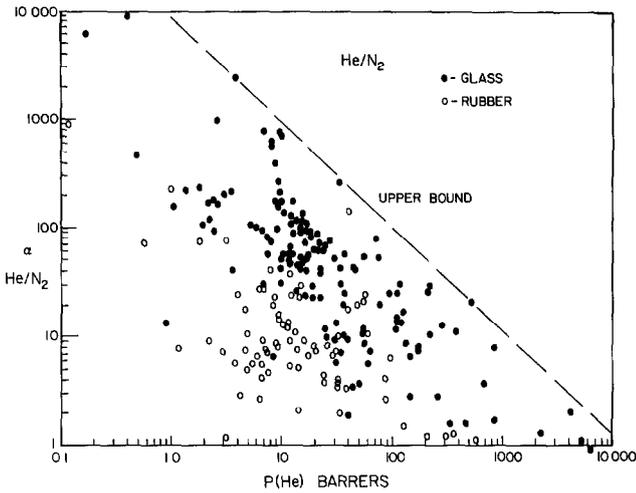
Fig 5 Literature data for He/N$_2$ separation factor versus He permeability

The key points helping to position the upper bound are:

Polymer	α(He/N$_2$)	P(He) (barrers)	Reference
Poly(trimethylsilylpropyne)	2 05	4,100	[59]
Isotactic PMMA	2,679	3 75	[64]
Atactic PMMA	806	9 43	[64]
Syndiotactic PMMA	736	9 57	[64]
6 FDA/tetramethyl PDA polyimide	23 2	530	[66]
Poly(trichloromonochloroethylene)	284	34 1	[67]
PDA = phenylene diamine			

As with H$_2$/N$_2$ data, the various PMMA's establish the upper bound at low H$_2$ permeability and poly(trimethylsilylpropyne) at high permeability.

H$_2$/CH$_4$ separation data

No H$_2$/CH$_4$ separation factor correlation with H$_2$ permeability has been noted in the literature for a wide range of polymers. The log–log relationship for α_{ij} and P_i(i=H$_2$) for this gas pair is illustrated in Fig. 6. The upper bound relationship is linear over 4 decades of H$_2$ permeability. The key points near or at the upper bound line noted are:

Polymer	$\alpha(H_2/CH_4)$	$P(H_2)$ (barrers)	Reference
Poly(trimethylsilylpropyne)	1 01	16,160	[63]
Poly(2,6-dimethylphenylene oxide)	30 2	130	[6]
Poly(tert-butyl acetylene)	7 19	1,150	[59]
Atactic PMMA	818	4 5	[64]
Syndiotactic PMMA	734	4 7	[64]
6 FDA/Trimethyl PDA Polyimide	11 4	433	[66]
6 FDA/4,4' - ODA Polyimide	98 5	52 2	[5]
6 FDA/4,3' - ODA Polyimide	438	14 0	[5]

Again, the poly(methyl methacrylate) variants establish the position of the upper bound at low H_2 permeability and poly(trimethylsilylpropyne) at high H_2 permeability. Various polyimides are at or near upper bound conditions for intermediate H_2 permeabilities.
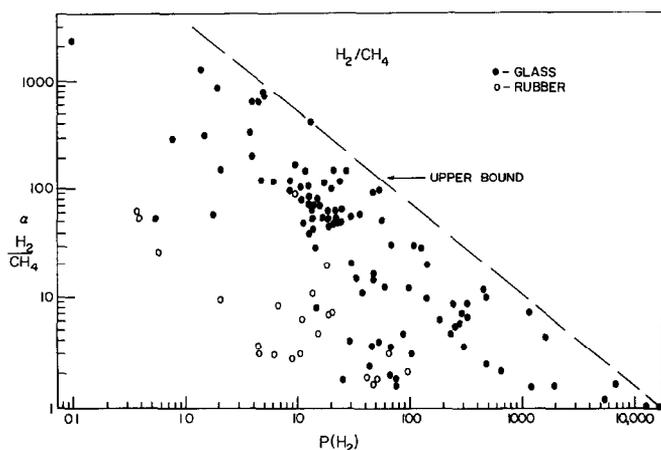
Fig 6 Literature data for H_2/CH_4 separation factor versus H_2 permeability

He/CH₄ separation data

Several references note α_{ij} and P_i relationships for He/CH₄ [2,3,4,46]. References 2, 3, and 4 plot α_{ij} versus log P_i and Ref. [46] plots log α_{ij} versus log P_i. The literature data shown in Fig. 7 demonstrate a linear relationship for the upper bound for a log–log plot over 3 decades of He permeability. The key data for the position of the upper bound for Fig. 7 are:

Polymer	$\alpha(He/CH_4)$	$P(He)$ (barrers)	Reference
Nafion 117	401	40 9	[68]
Poly(trimethylsilylpropyne)	0 98	4,100	[59]
Poly(trichloromonochloroethylene)	406	34 1	[67]
6 FDA-DAF Polyimide	156	98 5	[3]
Syndiotactic PMMA	1,495	9 57	[64]
Atactic PMMA	1,715	9 43	[64]
Tetramethyl bis HF Polycarbonate	43 8	206 (at 10 atm)	[69]
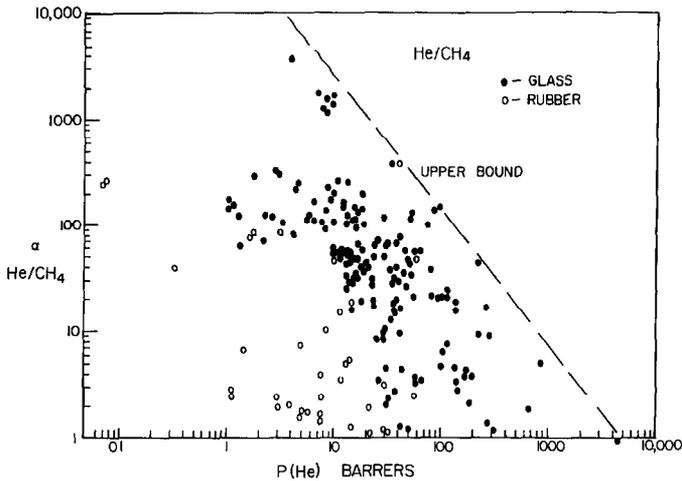
Fig 7 Literature data for He/CH$_4$ separation factor versus He permeability

PMMA variants establish the upper bound position at low He permeability and poly (trimethylsilylpropyne) at high He permeability. Tetramethyl bis HF polycarbonate data was included. However, the data are compared at 10 atm. pressure for pure components. Slightly lower α_{ij}'s might be expected at 1 atm. pressure.

CO$_2$/CH$_4$ separation data

Correlation of the CO$_2$/CH$_4$ separation factor data for glassy polymers has been noted in several references where linear α_{ij} was plotted versus log P_i ($i = O_2$) [3,4,5,6,50]. It was noted [3,4] that specific polyimides were significantly above that characteristic for other glassy polymers. The CO$_2$/CH$_4$ data compiled in this paper, however, show a reasonable upper bound relationship when plotted on a log–log plot as shown in Fig. 8. The key points for the upper bound relationship are:

Polymer	α(CO$_2$/CH$_4$)	P(CO$_2$) (barrers)	Reference
Poly (trimethylsilylpropyne)	4 3	18,000	[59]
Poly (tert-butylacetylene)	8 5	1,360	[59]
Polyimide (6 FDA-ODA) (10 atm)	60 3	23 0	[4]
Polyimide (6 FDA-DAF) (10 atm)	51 0	32 2	[3]
Poly (methyl methacrylate)	130	0 65	[70]
Poly (methyl methacrylate)	140	0 50	[71]
Poly (tetramethyl bis L sulfone)	37 6	65	[38]

The polyimide data noted were obtained at 10 atm. Data in the patent litera-
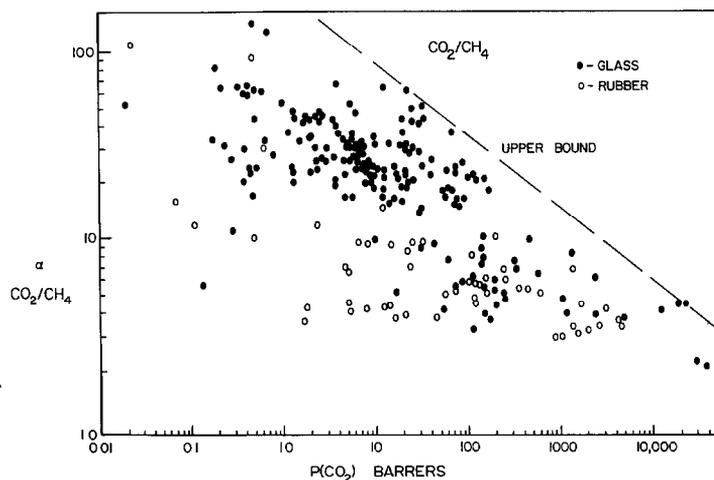
Fig 8 Literature data for CO_2/CH_4 separation factor versus CO_2 permeability

ture were found which gave values slightly above the noted upper bound. They, however, were obtained at 400 psi and thus cannot be compared. Even at 10 atm pressure, it was noted [4] that mixed gas permeability data is slightly lower. The value for poly(tetramethyl bis L sulfone) is interesting, but needs verification. As with all the other gas pairs, poly(trimethylsilylpropyne) determines the position of the curve at high CO_2 permeability.

He/H$_2$ separation data

For most polymers, the separation factor for He/H_2 is around unity. Higher permeable polymers and polymers with low T_g generally have values less than 1.0, and glassy polymers with low to moderate permeability have values slightly greater than 1.0. The literature data are illustrated in Fig. 9. There is a trend in He/H_2 separation factor as a function of He permeability which appears to follow an upper bound log–log plot as with the other gas pairs. The key data points for positioning of the upper bound curve are:

Polymer	$\alpha(He/H_2)$	$P(He)$ (barrers)	Reference
Poly(vinyl alcohol)	10 9	0 0071	[72]
Poly(vinyl alcohol)	7 27	0 052	[73]
Isotactic PMMA	2 91	3 75	[64]
Nafion 117	4 39	40 9	[68]
Polyimide	1 17	396	[74]

The data for Nafion 117 are clearly above the upper bound relationship noted here
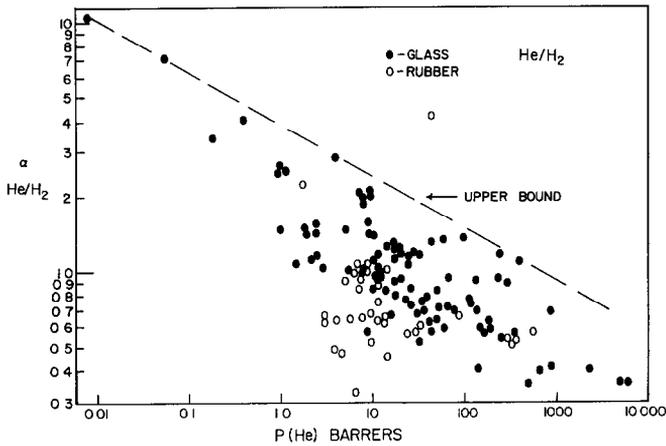
Fig 9 Literature data for He/H₂ separation factor versus He permeability

Analysis of the separation factor versus permeability data

For the analysis of the separation factor versus permeability data plotted as per log–log data, the equation $x = ky^n$ is utilized. Thus:

$$P_\iota = k\alpha_{\iota\jmath}^n \tag{6}$$

The values of k and n calculated for the upper bound linear relationship as noted in the Figures (3)–(9) are listed below.

Gas pair	k (barrers)	n
He/N₂	12,500	−1 0242
H₂/N₂	52,918	−1 5275
He/CH₄	5,002	−0 7857
H₂/CH₄	18,500	−1 2112
O₂/N₂	389,224	−5 800
He/O₂	4,600	−1 295
H₂/O₂	35,760	−2 277
CO₂/CH₄	1,073,700	−2 6264
He/H₂	960	−4 9535

The equation $P_\iota = k\alpha_{\iota\jmath}^n$ can be rearranged to yield

$$\alpha_{\iota\jmath} = k^{-1/n} P_\iota^{1/n} \tag{7}$$

A trend exists between n and the molecular (kinetic) diameter difference $(d_\jmath - d_\iota)$. In fact, a linear relationship is observed between the value of $-1/n$ and $\Delta d_{\jmath\iota} (d_\jmath - d_\iota)$ where $d_\jmath = $ kinetic diameter of the lower permeability gas and $d_\iota = $ kinetic diameter of the higher permeability gas. The kinetic diameters as reported by Breck [72] are listed in Table 2.

TABLE 2

Lennard–Jones kinetic diameters of various gases

Gas	He	H$_2$	CO$_2$	O$_2$	N$_2$	CH$_4$
Kinetic diameter (Å)	2 6	2 89	3 3	3 46	3 64	3 8
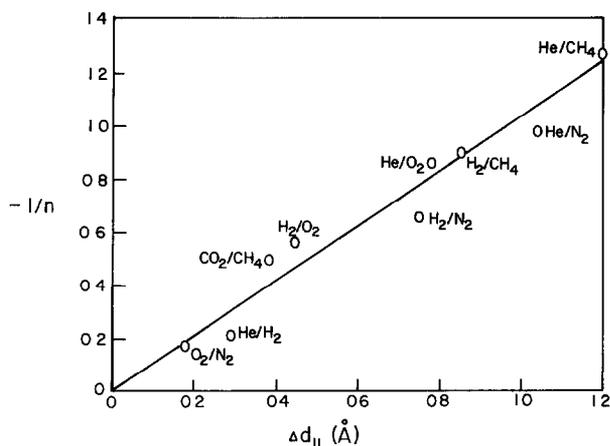
Fig 10 Relationship between upper bound slope (n) and kinetic diameter difference of gas pairs

The kinetic diameter offers a better correlation versus $-1/n$ than the other dimensional relationships previously noted. The plot of $-1/n$ versus Δd_{jt} is shown in Fig. 10. A reasonably linear relationship is observed which passes though the value of $-1/n=0$ at $\Delta d_{jt}=0$. As the data intercept the x and y axis at (0,0), this provides further verification of this analysis.

It should be noted that the exact position of the upper bound was chosen to be a best visual fit of the available data. The potential values of n for each log P_t versus log α_{tj} figure, however, were quite close to the data shown and thus the end result is not an artifact of the chosen procedure It is of interest to note that when this data was first correlated (3 years ago) the upper bounds were all slightly lower. The large amount of recent data has resulted in a slight change in position, but the slope n remained reasonably constant, and the correlation in Fig 10 virtually unchanged If more accurate kinetic diameter (e.g. more significant figures for He, CO$_2$, CH$_4$) data were available, perhaps the correlation presented in Fig. 10 would be improved.

Conclusions

The availability of a significant number of amorphous, high T_g polymers in

the past decade, their resultant permselective characterization in the literature, and the data on poly (trimethylsilylpropyne) yield sufficient data for an analysis of the limits of polymeric gas separation characteristics. When the data in the literature for the gas pairs from the list of He, H_2, O_2, N_2, CH_4, and CO_2 are plotted for α_{ij} versus P_i, a log α_{ij} versus log P_i upper bound relationship is noted A linear upper bound is observed on this log–log plot above which virtually no data exists This relationship holds over 4 to 5 decades of permeability for the more permeable gas. The slope of this line correlates with the molecular diameter difference between the constituents of the gas pair This analysis thus leads to the conclusion that the diffusion coefficient governs the membrane separation capabilities for polymeric systems for the gas pairs noted in this paper Of course, for more polar gases and higher pressure, the solubility characteristics play a more important role in the permselectivity properties. It is of interest to note that several polymers exhibit upper bound characteristics for many of the gas pairs. This tends to imply that the molecular dimensions (e g. free volume spacings) for these polymers are better defined and the distribution of these spacings is narrow and closer to molecular sieve type dimensions. Glassy polymers exhibit a significant advantage over polymers with a T_g lower than the permeability test temperature.

The upper bound relationship noted in this paper represents the present state of the technology. As further structure/property optimization of polymers based on solution/diffusion transport occurs, the upper bound relationship should shift slightly higher. The slope of the line would, however, be expected to remain reasonably constant.

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