Contributions of diffusion and solubility selectivity to the upper bound analysis for glassy gas separation membranes

Lloyd M. Robeson [a,*], Zachary P. Smith [b], Benny D. Freeman [b], Donald R. Paul [b]

[a] Lehigh University, 1801 Mill Creek Road, Macungie, PA 18062, USA
[b] Department of Chemical Engineering, Texas Materials Institute, Center for Energy and Environmental Research, The University of Texas at Austin, 10100 Burnet Road, Bldg. 133, Austin, TX 78758, USA

ABSTRACT

Prior analyses of the upper bound of permselectivity versus permeability, both theoretical and empirical, have assumed that this relationship is a consequence of the dependence of gas diffusion coefficients on the molecular diameter of the gases of interest. The solubility selectivity has been assumed to be invariant with permeability (and free volume). However, a few literature sources note that the solubility coefficient for specific families of glassy polymers correlate with free volume. A large database of permeability, diffusivity and solubility coefficients for glassy polymers was compiled to investigate this hypothesis. A critical analysis of the data demonstrates a modest solubility selectivity contribution to permselectivity as a function of free volume and, thus, permeability. The solubility selectivity (S_i/S_j) generally decreases with increasing permeability (and free volume) when the diameter of gas j is larger than that of gas i. This empirical trend is likely a consequence of larger gas molecules having less access than smaller molecules to sorption sites as the polymer packing density increases and free volume decreases. The diffusion data permit determination of a diffusivity upper bound, which is modestly different from the permeability-based upper bound relationship. The diffusion data analysis allows a determination of a new set of gas diameters more appropriate for gas diffusion in polymers than prior correlations.

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1. Introduction

The separation of gases by polymeric membranes has been an active area of research and industrial use for several decades [1]. In 1979, Monsanto (now Permea, owned by Air Products and Chemicals, Inc.) developed the first commercial asymmetric hollow fiber membrane module for gas separation; the fiber was based on polysulfone, and the first application was for hydrogen recovery (H_2/N_2) in the ammonia synthesis process [2–6]. Polymer membranes have since been commercialized for separating a number of other common gas pairs such as O_2/N_2, CO_2/CH_4, H_2/CH_4, He/air, and for the dehydration of air and natural gas [2]. In general, polymer membrane research focuses on identifying materials with high combinations of permeability and permselectivity. Permselectivity is defined as the ratio of the permeability coefficient of the faster permeating gas, i, to that of the slower permeating gas, j (i.e., P_i/P_j). However, it was recognized that there is a trade-off between P_i/P_j and P_i [7–11]. A large body of experimental evidence empirically suggests an upper bound to this trade-off relationship

having the following mathematical form [12]:

$$P_i = k_{up}\alpha_{ij(u)}^{n_{up}} \text{ where } \alpha_{ij(u)} = P_i/P_j \qquad (1)$$

On a log–log plot of $\alpha_{ij(u)}$ versus P_i, polymers with the highest separation efficiency and highest gas throughput are bounded by a linear relationship given by Eq. (1) that is commonly referred to as the "upper bound". There are virtually no data above this line. This empirical upper bound has been predicted from fundamental principles as will be discussed later [13]. Between 1991 and 2008, as more permeability data became available, modest shifts in the empirical upper bound became apparent for several gas pairs [14]. Correlating permeability data of P_i versus P_j allowed the determination of the kinetic diameters of He, H_2, O_2, N_2, CO_2, and CH_4 [15]. Correlations of P_i versus P_j with free volume [16,17] and activation energies of permeation and diffusion [18] have been noted in the literature. Furthermore, the effect of temperature on the upper bound was recently predicted and showed good agreement with the limited data available [19]. Group contribution approaches have also been employed for predicting gas permeability and permselectivity from information on polymer structure [20–22].

As noted, two somewhat different fundamental approaches have been employed to describe permeability and permselectivity

* Corresponding author. Tel.: +1 610 481 0117.
E-mail address: lesrob2@verizon.net (L.M. Robeson).

behavior. The approach of Freeman [13] combined fundamental principles involving transition state theory for diffusion and thermodynamic relationships for solubility to predict the upper bound values of n_{up} and k_{up}. The approach of Alentiev and Yampolskii [16,17] involved free volume models applied to diffusion and permeability for gas/polymer systems. It is well established that diffusion coefficients are related to free volume, and to a lesser extent solubility coefficients are affected by free volume; as a result, permeability coefficients are strongly related to free volume [20,23–30]. Consequently, although the derived parameters from these two approaches have different physical meanings, the general form of the equations is equivalent.

Correlations showing the separate effects of diffusion and solubility coefficients on the relationship between permselectivity and permeability are more limited. The most significant data in the literature have been summarized by Yampolskii and Alentiev [16,17], who employed an extensive database of P, D, and S values in various polymers for the gases of interest.

In the expression

$$\frac{P_i}{P_j} = \frac{D_i}{D_j}\frac{S_i}{S_j} \tag{2}$$

for a specific gas pair, the permselectivity (i.e., P_i/P_j) has diffusion (i.e., D_i/D_j) and solubility (i.e., S_i/S_j) selectivity components. It is generally assumed that as P_i (and free volume) decreases, the increase in permselectivity is due to increases in diffusion selectivity, and solubility selectivity remains invariant with P_i (and free volume); thus, the permeability upper bound relationship is controlled by diffusion selectivity [12–14]. This assumption is inherent in the upper bound theory, which embodies solubility coefficients in the constant k_{up} in Eq. (1). The determination of gas kinetic diameters from upper bound data [31] and from permeability data [15] assumed no changes in solubility selectivity as P_i varied.

The assumption that solubility is independent of free volume in the upper bound analysis needs to be critically addressed. In most cases, literature data show the diffusion coefficient of CO_2 to be lower than that of O_2 even though the kinetic diameter of CO_2 and O_2 are quite similar from upper bound [31] and permeability correlations [15]. Additionally, the kinetic diameters determined from zeolites [32] show CO_2 to have a smaller diameter than O_2. If the solubility coefficient is a function of free volume, which is consistent with several correlations noted in the literature [27,33–35], an accurate description of k_{up} must be included in this dependency. This paper demonstrates that solubility selectivity (i.e., S_i/S_j) and the solubility coefficients (i.e., S_i) both vary with permeability (and, thus, free volume) leading to a solubility selectivity contribution to permselectivity. The extent of this contribution changes for each gas pair considered. Correlations in the literature for permeability, diffusivity and solubility often employ fractional free volume. In this paper, we refer to free volume and fractional free volume trends as qualitatively equivalent.

2. Correlations of diffusion coefficients

The database for diffusion coefficients used in this analysis only includes glassy polymers and comprises many of the literature references employed for prior permeability [15] and permselectivity [14] correlations, as well as including more recent references. The selection of data follows a similar protocol previously employed; namely, data were selected in the range of 25–35 °C from polymers tested in the same laboratory and for gases tested on the same film. The database also included solubility coefficients along with permeability coefficients. Perfluorinated glassy polymers were not included due to their unique gas solubility relative to other polymers. The vast majority of the data from the literature determined D from time-lag measurements and calculated S from the relationship $P=DS$. In a few cases, S was determined directly from sorption measurements, and D was calculated from $P=DS$. For a given pressure, the effective diffusion coefficients for glassy polymers will have slightly different values depending on whether they were determined from time-lag measurements or from $D=P/S$ [36]. A detailed discussion of these differences for polysulfone and a polymer of intrinsic microporosity (PIM-1) is included in Appendix A of this paper to illustrate the range of possibilities. The database includes over 800 different polymers from over 200 references. The database is not as large as previously noted for the permeability correlations since many papers only report permeability results. Data were compiled for 15 gas pairs involving He, H_2, O_2, N_2, CO_2 and CH_4.

The data are analyzed using the following basic equation:

$$D_j = k_d D_i^{n_d} \tag{3}$$

where i and j are chosen such that $n_d > 1$. The data are presented on log–log plots where D_i (y-axis) and D_j (x-axis) yield the following equation:

$$\log D_i = -\frac{\log k_d}{n_d} + \frac{\log D_j}{n_d} \tag{4}$$

When plotted as D_i (x-axis) and D_j (y-axis), the relevant equation is

$$\log D_j = \log k_d + n_d \log D_i \tag{5}$$

Standard least squares fits to both Eq. (4) and to Eq. (5) were made. If there is limited scatter in the data, similar results would be obtained from both equations; however, these results will differ more significantly when there is more scatter in the data. The previously published permeability correlation [15] had limited scatter in the data, and a visual fit was employed. A review of the visual fit to the permeability data showed that the average of the log k and n values from Eqs. (4) and (5) gave virtually the same results as the reported visual fit to the data. Since there is significantly more scatter in the diffusion data for some gas pairs, a visual fit was not realistic; thus, the analysis protocol employed the average of the values obtained by the two methods.

Glassy polymers exhibit dual-mode sorption behavior, which is characterized by sorption isotherms that are concave to the pressure axis; this curvature is more pronounced for gases with high condensability [37,38]. Therefore, a pressure dependency of D and S arises when the sorption and permeation behavior exhibits dual-mode behavior. The literature values of D and S in our database involve some variation in the pressures used for measurement of P, D or S. While these variations will be expected to yield quantitative differences in our analysis, the qualitative trends are not believed to be significantly affected by dual-mode effects. However, to illustrate the magnitude of the possible effects, an analysis of the pressure dependency on gas sorption and diffusion for polysulfone and PIM-1 is included in Appendix A.

Examples of plots of diffusion coefficient data for several gas pairs are illustrated in Figs. 1,2 and 3. For gas pairs involving He or H_2, the data show considerable scatter. This is partly due to limited data relative to the other gas pairs but primarily due to the larger experimental error involved with accurately determining very short time-lag values [39]. Table 1 includes values of n_d from Eqs. (4) and (5), the average n_d values, the n_p values from the permeability correlation using this database, which employs P instead of D (i.e., $P_j = k_p P_i^{n_p}$), and the n_p values from the previously employed database [15]. The correlation of n_p values from this database agree well with the much larger database used previously. Fig. 4 presents the correlation between n_d from diffusion data and n_p from permeability data. The correlation for gas pairs not containing CO_2