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The upper bound revisited

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ABSTRACT

The empirical upper bound relationship for membrane separation of gases initially published in 1991 has been reviewed with the myriad of data now presently available. The upper bound correlation follows the relationship $P_i = k\alpha_{ij}^n$, where P_i is the permeability of the fast gas, α_{ij} (P_i/P_j) is the separation factor, k is referred to as the "front factor" and n is the slope of the log–log plot of the noted relationship. Below this line on a plot of $\log \alpha_{ij}$ versus $\log P_i$, virtually all the experimental data points exist. In spite of the intense investigation resulting in a much larger dataset than the original correlation, the upper bound position has had only minor shifts in position for many gas pairs. Where more significant shifts are observed, they are almost exclusively due to data now in the literature on a series of perfluorinated polymers and involve many of the gas pairs comprising He. The shift observed is primarily due to a change in the front factor, k, whereas the slope of the resultant upper bound relationship remains similar to the prior data correlations. This indicates a different solubility selectivity relationship for perfluorinated polymers compared to hydrocarbon/aromatic polymers as has been noted in the literature. Two additional upper bound relationships are included in this analysis; CO_2/N_2 and N_2/CH_4. In addition to the perfluorinated polymers resulting in significant upper bound shifts, minor shifts were observed primarily due to polymers exhibiting rigid, glassy structures including ladder-type polymers. The upper bound correlation can be used to qualitatively determine where the permeability process changes from solution-diffusion to Knudsen diffusion.

1. Introduction

The separation of gas mixtures employing polymeric membranes has been commercially utilized since the late 1970s. While the ability to separate gas mixtures was recognized much earlier, the commercial reality generated a significant amount of academic and industrial research activity. Membrane separation offers the advantage of low energy cost but has a high initial capital expense relative to the more established gas separation processes (e.g. adsorption and cryogenic distillation). With the increased cost of energy, membrane separation is reemerging as an economic option for various gas separations. Another area of emerging importance could be the recapture of CO_2 from industrial processes for reuse or sequestration, and the key separation (CO_2/N_2) for this area is included in the upper bound analysis. The key parameters for gas separation are the permeability of a specific component of the gas mixture and the separation factor. It was recognized that these are trade-off parameters as the separation factor generally decreases with increasing permeability of the more permeable gas component. This trade-off relationship was shown to be related to an upper bound relationship where the log of the separation factor versus the log of the higher permeability gas yielded a limit for achieving the desired result of a high separation factor combined with a high permeability [1,2] for polymeric membranes. The upper bound relationship was shown to be valid for a multitude of gas pairs including O_2/N_2, CO_2/CH_4, H_2/N_2, He/N_2, H_2/CH_4, He/CH_4, He/H_2, H_2/CO_2 and He/CO_2. The upper bound relationship is expressed by $P_i = k\alpha_{ij}^n$, where P_i is the permeability of the more permeable gas, α is the separation factor (P_i/P_j) and n is the slope of the log–log limit. It was observed that $-1/n$ versus Δd_{ji} (where Δd_{ji} is the difference between the gas molecular diameters $(d_j - d_i)$) yielded a linear relationship. This observation revealed that the diffusion coefficient governed the upper bound limits. Group contribution methods were noted to predict both permeability and separation factors for aromatic polymers and demonstrated the structure–property relationships to optimize membrane separation [3–5].

The empirical upper bound relationship was shown to be theoretically predicted by Freeman [6] yielding good agreement with the experimental data previously compiled. The value of $-1/n$ was shown to be predicted by activation energy theory to be related to

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the gas molecular diameters by:

$$\frac{-1}{n} = \left(\frac{d_j}{d_i}\right)^2 - 1 = \left[\frac{d_j + d_i}{d_i^2}\right](d_j - d_i) \qquad (1)$$

As the term in the square brackets is reasonably constant, the value of $-1/n$ can be approximated by $(d_j - d_i)$ as demonstrated by the empirical relationship. The value of k was predicted by Freeman to be expressed by:

$$k^{-1/n} = \frac{S_i}{S_j} S_i^{-1/n} \exp\left\{\frac{1}{n}\left[b - f\left(\frac{1-a}{RT}\right)\right]\right\} \qquad (2)$$

where S_i and S_j are the solubility constants, a has a universal value of 0.64, b has a value of 9.2 for rubbery polymers and 11.5 for glassy polymers and f is a constant dependant upon the polymer and chosen to be 12,600 cal/mol to provide the best fit of the upper bound data. The value of k is referred to as the front factor for the upper bound relationship.

The data utilized for the initial upper bound relationship was from studies listing permeability data on various polymers with limited emphasis on membrane separation. Since the publication of the upper bound concept, a significant number of studies have been directed towards achieving and exceeding the upper bound for various gas pairs. The published data on membrane separation since 1991 now well exceeds the data utilized in the initial correlation and thus provides an excellent comparison of the validity of the upper bound concept and progress towards optimizing the structure/property relationships. This paper will tabulate the data since the initial publication and compare these results versus the original empirical upper bound data. As would be expected, the increased emphasis on membrane separation and the improved structure/property understanding from experimental studies and group contribution approaches has resulted in a number of observations equal to and exceeding the original upper bound. The comment in the original paper [1] "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." will be shown to be correct. The upper bound relationship is based on homogeneous polymer films and several approaches involving heterogeneous membranes have been demonstrated to easily exceed the upper bound. Surface modification is one method that clearly exceeds the upper bound limits as would be expected from the series resistance model as noted in an earlier paper [2]. UV surface modification [7], ion beam surface carbonization [8] and surface fluorination [9,10] are among the viable surface modifications yielding such behavior. Another approach initially proposed by Koros and co-workers [11] is typically referred to as a mixed matrix approach where selective molecular sieving structures are incorporated into a polymeric membrane. The mixed matrix approach has been reported in many studies [12–14] with results exceeding upper bound behavior. Another approach involving carbon molecular sieving membranes produced by carbonization of aromatic polymer membranes [15,16] also yields permselective properties well above the upper bound relationships. Molecular sieve membranes with well-defined uniform pore structure would, in essence, be considered to be the true upper bound limit for polymeric membranes. A recent paper on a novel approach to molecular sieving type structures [17] employed a solid-state thermal transformation of a polyimide to a benzooxazole-phenylene structure in the main chain yielding a material with remarkable CO_2/CH_4 separation. The thermal transformation yielded insoluble and infusible polymers with molecular sieving pore dimensions. Achievement of such molecular sieving structures in solution (or melt) processable polymeric membranes is presently not possible and the upper bound correlation is an empirical relationship demonstrating the state-of-the-art for approaching true molecular sieving structures. Heterogeneous membranes, surface modified membranes and molecular sieve membranes are not considered in the same class of polymeric materials employed for establishing the upper bound correlation. It should be noted that several of the polymers comprising points on or near the present empirical upper bound have structural characteristics (e.g. ladder-type polymers) that start approach molecular sieving type structures.

The initial publication on the upper bound allowed for a determination of the state-of-the-art limits for polymeric gas membrane separation. With a specific goal in focus, a large number of studies have resulted with the objective to find polymeric structures which exceeded the empirical upper bound limits. While only modest increases have been observed with some of the gas pairs, there have been gas pairs where important shifts have occurred as discussed in the following data review. The major surprise involves the unique characteristics of a series of perfluorinated commercial polymers relative to He based gas pairs. The importance of ladder-type rigid polymers was at least partly recognized earlier and several examples of these polymers have allowed shifts in the upper bound.

2. Upper bound relationships

The protocol chosen for data selection involved a similar procedure as noted in the original paper [1]. Data were chosen where the polymer data were utilized from the same study with the same experimental film preparation conditions. Generally these involve soluble (or melt) processible polymers. While the vast majority of the data in the literature appears correct, there are situations where errors have been observed. These can include experimental errors, manuscript errors ("typos"), and insufficient significant figures in the permeability value(*s*). In several cases, the potential where such data errors or insufficient significant figures may be present are pointed out for the cases where the data comprise upper bound properties. In a few cases, data were not included where it has been noted by other studies in the literature to not be either correct or not reproducible. One of the specific polymers where extremely large variations have been reported include polyaniline variants. The overall literature is fortunately consistent in the permeability-separation factor data for polyaniline variants and these data were included. The number of papers where the data were obtained approached 300 thus inclusion of all the references is not presented except in the cases where the specific data points were in the range of or comprise the present upper bound. The specific polymeric structures of interest are not presented but rather the designation of the polymer class and relevant description. The interested reader should refer to the references noted for actual structure. Thermal transformation of polymers to yield molecular sieving structures is considered outside this analysis. These procedures will yield separation characteristics well above the upper bound correlation but also yield insoluble and infusible polymeric materials. It is noted that the "upper bound" line is determined empirically ("by eye") as in the original reference [1] with sufficient data to establish a realistic bound over several decades of permeability.

3. O_2/N_2 upper bound relationship

The O_2/N_2 separation remains the most studied gas pair with more data existing in the literature than any of the other pairs. The myriad of data points shows an intensity just below the original