Olefin/Paraffin Separation through Facilitated Transport Membranes in Solid State

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ABSTRACT

A simple mathematical model for facilitated mass transport through a fixed site carrier membrane was derived by assuming an instantaneous, microscopic concentration (activity) fluctuation. The current model demonstrates that the facilitation factor depends on the extent of concentration fluctuation, the time scale ratios of diffusion to chemical reaction and the ratio of the carrier concentration to the solute solubility in matrix. The model was examined against the experimental data on oxygen transport in membranes containing metallo-porphyrin carriers, and the agreement was exceptional (within 10 % error). The basic concept of this approach was applied to separate olefin from olefin/paraffin mixtures. A proprietary carrier, developed here, resulted that the selectivity of propylene over propane was more than 120 and the propylene permeance exceed 40 gpu.

INTRODUCTION

The facilitated transport with fixed site carrier membrane can be unique in providing stability as well as both high permeability and high permselectivity. In the case of normal Fickian diffusion membrane, there has been frequently observed a trade-off between permeability and permselectvity. Therefore, polymeric membranes with fixed site carriers have been the subject of much recent investigation.

MATHEMATICAL MODEL

Only a few mathematical models have been developed to analyze the facilitation phenomena in a fixed site carrier membrane. The dual sorption model has been commonly employed, because the dual sorption phenomenon is conceptually analogous to the mass transport through a facilitated membrane with fixed site carriers. More rigorous analyses were presented by introducing concepts of "the effective diffusion coefficient between fixed site carriers" by Noble [1] and "the limited mobility of chained carriers" by Cussler et al [2]. All theses mathematical models suffer from their unpredictability and no mathematical model has been ever tried to compare with the experimental data.

A new mathematical model to describe mass transport through facilitated transport membranes in solid state was developed by assuming a fluctuated concentration profile at steady state as illustrated in Figure 1 [3,4].

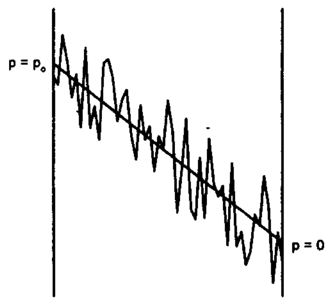

Figure 1. Fluctuated concentration (pressure) profile in fixed site carrier membrane

As a result, the permeability P_f of the facilitated transport membrane can be written as :

$$\frac{P_f}{P} = 1 + \left(\frac{p_d}{p_0}\right)\sqrt{n^2 + \left(\frac{2\pi k_2 L^2 C_B}{P}\frac{\ln(1 + Kp_0)}{p_0}\right)^2} \qquad (1)$$

where P is permeability of matrix polymer. p_0 and p_d are applied pressure and the extent of pressure fluctuation, respectively. n= $N_A C_B(\pi r_s^2 L)$. N_A and r_s are the Avogadro number and the radius of solute gas molecule, respectively. C_B is the carrier concentration and L the membrane thickness. k_2 and K are backward reaction rate constant and equilibrium constant of the reversible reaction of a specific solute and carrier, respectively. According to the current model, P_f depends strongly on p_d and k_2 in addition to C_B as demonstrated in Figure 2 [5]. When P is high, the facilitation factor is not high and *visa versa.*

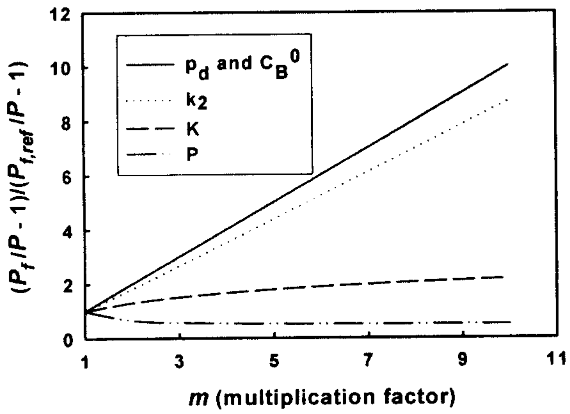

Figure 2. A plot of sensitivity $(P_f/P-1)/(P_{f,ref}/P-1)$ as a function of multiplication factor m.

SEPARATION OF AIR AND OLEFIN/PARAFFIN MIXTURE

This model predicts the oxygen permeability values [6] within 10 % accuracy in the PDMS, PBMA and PMMA membranes containing metalloporphyrin with one adjustable parameter p_d (Figure 3) [3,4].

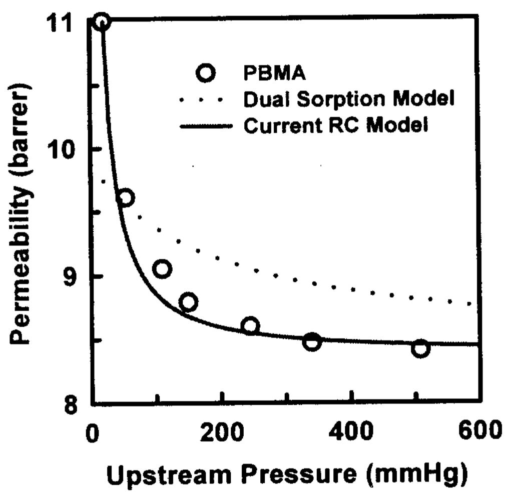

Figure 3. Comparison between the model predictions and experimental data of ref. 6

The facilitated transport phenomena in solid state have been applied to separate olefin from paraffin. A novel proprietary carrier was developed. The resulting facilitated membranes exhibited the propylene selectivity over propane of more than 120 and the propylene permeability of almost 40 gpu as shown in Figure 4. In common facilitated transport membranes, the permeability increases with decreasing pressure and thus the selectivity becomes low at high pressure. This makes the facilitated transport membrane unpractical. However, in our new approach, the selectivity remains very high at high pressures as much as 8 atm. In conclusion, the facilitated transport phenomena can provide an efficient way to overcome the trade-off behavior between permeability and selectivity.

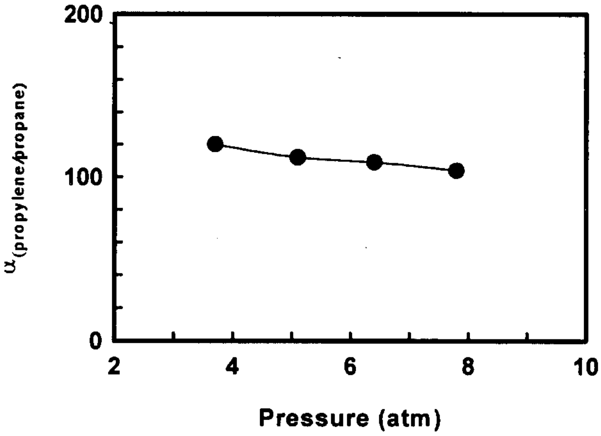

Figure 4. A plot of the α(propylene/propane) as a function of upstream pressure.

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