

Supplementary Information

A High-Performance Hydroxyl-Functionalized Polymer of Intrinsic Microporosity for An Environmentally Attractive Membrane-Based Approach to Decontamination of Sour Natural Gas

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Permeation Modeling. Koros et al. considered two distinct molecular environments (Henry's law and Langmuir) in which penetrants move with different inherent mobilities.¹⁻³ The so-called "partial immobilization" (or dual-mode) model accounts for the fact by expressing Fick's law as:

$$N = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (\text{S1})$$

where N is the total diffusive flux, and D_D and D_H are the local diffusion coefficients in the Henry's law and Langmuir environments, respectively. This model predicts the permeability of a pure gas measured with an upstream fugacity f_2 and negligible downstream fugacity f_1 as follows:

$$P_i = k_{D_i} \cdot D_{D_i} \left(1 + \frac{F_i \cdot K_i}{1 + b_i \cdot f_{2i}} \right) \quad (\text{S2})$$

where

$$K = \frac{c_H \cdot b}{k_D} \quad (\text{S3})$$

$$F = \frac{D_H}{D_D} \quad (S4)$$

The dual-mode model can also be applied to ternary or even more complex mixtures using the following equation:

$$P_i = k_{D_i} \cdot D_{D_i} \left(1 + \frac{F_i \cdot K_i}{1 + \sum_{i=1}^n b_i \cdot f_{2i}} \right) \quad (S5)$$

Hence,

$$\alpha_{A/B} = \frac{k_{D_A} \cdot D_{D_A} \left(1 + \frac{F_A \cdot K_A}{1 + \sum_{i=1}^n b_i \cdot f_{2i}} \right)}{k_{D_B} \cdot D_{D_B} \left(1 + \frac{F_B \cdot K_B}{1 + \sum_{i=1}^n b_i \cdot f_{2i}} \right)} \quad (S6)$$

In the dual-mode model, the derivations for permeability using Fick's law were under the assumption that diffusive flux is the only contributor to overall flux through the membrane, and "frame of reference" complications could be neglected.⁴ This is reasonable when the sorbed concentrations are low and the flux depends only on a Fickian diffusion driven process. However, some examples of non-negligible bulk flux contributions have been observed. In mixed gas permeation, the flux of each component can be quite dependent on the concentrations and fluxes of all the species in the mixture.⁴ Thus, the so-called "frame of reference" model has been developed.^{4,5} In this model, the flux of each component through a membrane is actually the sum of the diffusive flux and the bulk (convective) flux according to the expressions in Eqs. S7-S11 for a ternary mixture of components *A*, *B* and *C* in a polymer, *p*.⁶

$$n_i = n_i^{bulk} + n_i^{diffusive} \quad (S7)$$

$$n_A = (n_A + n_B + n_C + n_p) \cdot \omega_A - \rho \cdot D_{A,m} \cdot \frac{d\omega_A}{dx} \quad (\text{S8})$$

$$n_B = (n_A + n_B + n_C + n_p) \cdot \omega_B - \rho \cdot D_{B,m} \cdot \frac{d\omega_B}{dx} \quad (\text{S9})$$

$$n_C = (n_A + n_B + n_C + n_p) \cdot \omega_C - \rho \cdot D_{C,m} \cdot \frac{d\omega_C}{dx} \quad (\text{S10})$$

$$n_p = (n_A + n_B + n_C + n_p) \cdot \omega_p - \rho \cdot D_{p,m} \cdot \frac{d\omega_p}{dx} \quad (\text{S11})$$

In the equations given above, $D_{i,m}$ is the effective ternary diffusion coefficient for component i in the polymer, ρ is the density of the polymer membrane, and ω_i is the mass fraction of component i in the polymer. Because the membrane is stationary at steady-state, the flux term for the polymer (n_p) is zero. Therefore, the mutually dependent flux for each component can be derived and consequently expressed by Eqs. S12-S15.

$$n_A = \frac{-\rho \cdot D_{D,A} \cdot \frac{d\omega_A}{dx}}{1 - (1 + \frac{1}{r} + \frac{1}{p}) \cdot \omega_A} \quad (\text{S12})$$

$$n_B = \frac{-\rho \cdot D_{D,B} \cdot \frac{d\omega_B}{dx}}{1 - (1 + r + \frac{1}{q}) \cdot \omega_B} \quad (\text{S13})$$

$$n_C = \frac{-\rho \cdot D_{D,C} \cdot \frac{d\omega_C}{dx}}{1 - (1 + p + q) \cdot \omega_C} \quad (\text{S14})$$

$$r = \frac{n_A}{n_B}, p = \frac{n_A}{n_C}, q = \frac{n_B}{n_C}, n_A > n_B > n_C \quad (\text{S15})$$

Component A is assumed to have highest mass flux among all the components, and component B is assumed to have a higher mass flux than component C . Hence, r , p , and q will always be greater than or equal to 1. Note that $q = p/r$, so these are only two independent parameters; but it is more convenient to use the three separate coefficients in actual calculation. The following boundary conditions can be defined below for the mass fractions of each component in the upstream and downstream sections of the membrane. The downstream mass fractions of the penetrants approach zero when the downstream of the membrane is under vacuum.

$$x = 0, \omega_A = \omega_{A,up}, \omega_B = \omega_{B,up}, \omega_C = \omega_{C,up}$$

$$x = l, \omega_A = \omega_{A,down} \approx 0, \omega_B = \omega_{B,down} \approx 0, \omega_C = \omega_{C,down} \approx 0$$

By integrating Eqs. S12-S14 using the above boundary conditions, the following expressions can thus be obtained, accounting for the bulk flow or frame of reference effects:⁴

$$n_A \cdot l = \frac{\rho \cdot D_{D,A} \cdot \ln \left[\frac{1 - \left(1 + \frac{1}{r} + \frac{1}{p}\right) \cdot \omega_{A,down}}{1 - \left(1 + \frac{1}{r} + \frac{1}{p}\right) \cdot \omega_{A,up}} \right]}{\left(1 + \frac{1}{r} + \frac{1}{p}\right)} \approx \frac{\rho \cdot D_{D,A} \cdot \ln \left[\frac{1}{1 - \left(1 + \frac{1}{r} + \frac{1}{p}\right) \cdot \omega_{A,up}} \right]}{\left(1 + \frac{1}{r} + \frac{1}{p}\right)}$$

(S16)

$$n_B \cdot l = \frac{\rho \cdot D_{D,B} \cdot \ln \left[\frac{1 - \left(1 + r + \frac{1}{q}\right) \cdot \omega_{B,down}}{1 - \left(1 + r + \frac{1}{q}\right) \cdot \omega_{B,up}} \right]}{\left(1 + r + \frac{1}{q}\right)} \approx \frac{\rho \cdot D_{D,B} \cdot \ln \left[\frac{1}{1 - \left(1 + r + \frac{1}{q}\right) \cdot \omega_{B,up}} \right]}{\left(1 + r + \frac{1}{q}\right)}$$

(S17)

$$n_C \cdot l = \frac{\rho \cdot D_{D,C} \cdot \ln \left[\frac{1 - (1 + p + q) \cdot \omega_{C,down}}{1 - (1 + p + q) \cdot \omega_{C,up}} \right]}{(1 + p + q)} \approx \frac{\rho \cdot D_{D,C} \cdot \ln \left[\frac{1}{1 - (1 + p + q) \cdot \omega_{C,up}} \right]}{(1 + p + q)}$$

(S18)

In these equations, ω_i is the mobile concentration of the pertinent component, which can be derived from the dual-mode sorption model to give the following expressions:^{4, 7}

$$\omega_A = \omega_A^{mobile} = \frac{k_{D,A} \cdot f_A \cdot M_A}{22400 \cdot \rho} \cdot \left(1 + \frac{F_A \cdot K_A}{1 + b_A \cdot f_A + b_B \cdot f_B + b_C \cdot f_C} \right)$$

(S19)

$$\omega_B = \omega_B^{mobile} = \frac{k_{D,B} \cdot f_B \cdot M_B}{22400 \cdot \rho} \cdot \left(1 + \frac{F_B \cdot K_B}{1 + b_A \cdot f_A + b_B \cdot f_B + b_C \cdot f_C} \right)$$

(S20)

$$\omega_C = \omega_C^{mobile} = \frac{k_{D,C} \cdot f_C \cdot M_C}{22400 \cdot \rho} \cdot \left(1 + \frac{F_C \cdot K_C}{1 + b_A \cdot f_A + b_B \cdot f_B + b_C \cdot f_C} \right)$$

(S21)

where M is the molecular weight of each component. Thus, using Eqs. S16-S18 and the definition of r , p , and q , the flux for each component can be determined iteratively and can be used to predict the permeability, or permeance, of a glassy polymeric membrane with frame of reference effects taken into account using the equation below.

$$P_i = \frac{22400 \cdot n_i \cdot l}{M_i \cdot \Delta f_i} \tag{S22}$$

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