

# Nonlinear Parameter Estimation for Solution-Diffusion Models of Membrane Pervaporation

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**ABSTRACT:** An optimization-based procedure for estimating unknown parameters in solution-diffusion models of membrane pervaporation is presented. Permeation of two components through a polymer membrane is described by distinct solution and diffusion models. The solution model is based on a modified form of Flory-Huggins theory that accounts for interactions between the two penetrants. The diffusion model is derived from Fick's law, where the diffusion coefficients are allowed to depend on the local concentration of each component in the membrane. A phenomenologic relation is used to account for the effect of temperature on the component fluxes. The solution and diffusion models, as well as the temperature-flux relation, contain parameters that are not directly measurable. It is shown that these parameters can be estimated effectively from sorption and flux data by the solution of suitably formulated nonlinear optimization problems. The separation of styrene and ethylbenzene with a polyurethane membrane is used to illustrate the parameter estimation procedure.

**KEYWORDS:** pervaporation; solution-diffusion model; parameter estimation

## INTRODUCTION

Pervaporation is a membrane-based process that has emerged as one of the most promising technologies for the separation of liquid mixtures.<sup>1</sup> A unique feature of pervaporation is that there is a phase change from a liquid on the feed side to a vapor on the permeate side. The separation is achieved by applying a vacuum on the permeate side, such that there is fugacity gradient across the membrane. Because mass transfer is largely independent of the vapor-liquid equilibrium properties, pervaporation is especially well suited for azeotropic and close boiling mixtures that are difficult to separate by distillation.<sup>2</sup> Typical applications include the removal of volatile organic compounds from water<sup>3,4</sup> and the separation of olefin/paraffin mixtures, such as ethylene/ethane or propylene/propane.<sup>1,5</sup>

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Although other types of pervaporation membranes have been developed,<sup>5</sup> polymer membranes remain the most common material for the construction of pervaporation modules. The solution-diffusion model is the accepted mechanism for describing permeation in polymer membranes.<sup>6,7</sup> According to this mechanism, pervaporation involves the following three steps: (1) the liquid species are dissolved into the membrane surface, (2) the species diffuse through the membrane, and (3) the species desorb from the downstream membrane surface in the vapor phase. Quantitative prediction of pervaporation membrane performance requires the development of mathematical models for the sorption of the penetrants into the membrane and the transport of the penetrants through the membrane. This is commonly achieved by the development of separate solution and diffusion models. Flory-Huggins thermodynamics, the UNIQUAC model, and the penetrant solubility model have been used to describe the solution process.<sup>1</sup> Diffusion is typically modeled using free volume theory<sup>1</sup> or a phenomenologic approach.<sup>8</sup>

Regardless of the specific descriptions employed, solution-diffusion models invariably contain parameters that are not available in the literature and that cannot be measured directly. These unknown parameters provide degrees of freedom that allow the model to be fit to experimental data. Manual adjustment of parameters is inefficient and results in solution-diffusion models that are suboptimal with respect to their predictive capability. Despite its obvious importance, the development of automated parameter estimation techniques for solution-diffusion models has received little attention.

In this paper, a parameter estimation procedure based on nonlinear optimization is proposed for solution-diffusion pervaporation models. A specific estimation strategy is developed for a solution model based on Flory-Huggins theory, a diffusion model derived from Fick's law and a phenomenologic relation used to account for the effect of temperature on the component fluxes. The separation of styrene and ethylbenzene with a poly(hexamethylene sebacate) based polyurethane membrane<sup>9,10</sup> is used to illustrate the parameter estimation procedure. It is important to note that optimization-based parameter estimation is not restricted to the particular model forms used here. Similar estimation strategies could be developed for other types of solution-diffusion models.

## ESTIMATION OF SOLUTION MODEL PARAMETERS

### Theory

The component volume fractions sorbed into the membrane are predicted from thermodynamic properties of the liquid-polymer mixture. The solution model is based on Flory-Huggins theory<sup>11</sup> and utilizes the interaction parameter equations proposed by Mulder *et al.*<sup>12</sup> When a polymer film is exposed to a pure liquid, Flory-Huggins theory yields the following relation for the pure component activity  $a^P$ :

$$\ln a^P = \ln(1 - \phi_2) + \left(1 - \frac{V_1}{V_2}\right)\phi_2 + \chi\phi_2^2, \quad (1)$$

where  $\phi_2$  is the volume fraction of the polymer;  $V_1$  and  $V_2$  are the molar volumes of the liquid and polymer, respectively; and  $\chi$  is the Flory-Huggins interaction

parameter. The Gibbs free energy of mixing  $\Delta G_{\text{mix}}$  of a ternary system comprising a binary liquid mixture and a polymer membrane is expressed by

$$\frac{\Delta G_{\text{mix}}}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12} n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3, \quad (2)$$

where the subscripts 1 and 2 denote the liquid components and the subscript 3 denotes the polymer;  $n_i$  and  $\phi_i$  are the mole fraction and volume fraction, respectively, of component  $i$ ;  $\chi_{ij}$  is the interaction parameter between components  $i$  and  $j$ ;  $T$  is the temperature; and  $R$  is the gas constant. The volume fraction  $\phi_i$  is defined by

$$\phi_i = \frac{n_i V_i}{\sum_{i=1}^3 n_i V_i} \quad (3)$$

The interaction parameter  $\chi_{12}$  involving the two liquid components is calculated using excess functions. The following equation holds for binary mixtures:<sup>13</sup>

$$\frac{\Delta G_{\text{mix}}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{G_E}{RT}, \quad (4)$$

where  $G_E$  is the excess Gibbs free energy and  $x_i$  is the mole fraction of component  $i$  in the liquid phase. The free energy of mixing of the binary mixture is calculated using Flory-Huggins theory,<sup>11</sup>

$$\frac{\Delta G_{\text{mix}}}{RT} = x_1 \ln \psi_1 + x_2 \ln \psi_2 + \chi_{12} \psi_1 \psi_2 \left( x_1 + x_2 \frac{V_2}{V_1} \right), \quad (5)$$

where  $\psi_i$  is the volume fraction of component  $i$  in the liquid phase:

$$\psi_1 = \frac{V_1 x_1}{V_1 x_1 + V_2 x_2}, \quad \psi_2 = \frac{V_2 x_2}{V_1 x_1 + V_2 x_2} \quad (6)$$

The excess Gibbs free energy is expressed by

$$\frac{G_E}{RT} = x_1 \ln \gamma_1^L + x_2 \ln \gamma_2^L, \quad (7)$$

where  $\gamma_i^L = a_i^L/x_i$  is the activity coefficient of component  $i$  in the liquid phase and  $a_i^L$  is the activity of component  $i$  in the liquid phase. The liquid phase activities are estimated from vapor-liquid equilibrium data using the two-suffix Margules equation,<sup>13</sup>

$$RT \ln \gamma_1^L = Ax_2^2, \quad RT \ln \gamma_2^L = Ax_1^2. \quad (8)$$

The Margules constant  $A$  is determined from vapor-liquid equilibrium data using the following equation:

$$P^{\text{sat}} = \sum_{i=1}^2 x_i \gamma_i^L P_i^{\text{sat}} = x_1 P_1^{\text{sat}} \exp\left(\frac{A}{RT} x_2^2\right) + x_2 P_2^{\text{sat}} \exp\left(\frac{A}{RT} x_1^2\right), \quad (9)$$

where  $P^{\text{sat}}$  is the vapor pressure of the binary mixture and  $P_i^{\text{sat}}$  is the temperature dependent vapor pressure of pure component  $i$ . The following equation for  $\chi_{12}$  is readily derived by combining Equations (4)–(8):

$$\chi_{12} = \frac{1}{x_1 \psi_2} \left[ x_1 \ln \left( \frac{x_1}{\psi_1} \right) + x_2 \ln \left( \frac{x_2}{\psi_2} \right) + \frac{Ax_1 x_2}{RT} \right]. \quad (10)$$

The interaction parameters  $\chi_{13}$  and  $\chi_{23}$  between the liquid components and the polymer in the ternary mixture can be determined from solubilities of the pure liquids in the polymer. From (1) it follows that the activity of pure component  $i$  in the polymer is

$$\ln a_i^P = \ln(1 - \phi_3^{bi}) + \left( -\frac{V_i}{V_3} \right) \phi_3^{bi} + \chi_{i3}^b (\phi_3^{bi})^2, \quad (11)$$

where the superscript  $b$  denotes a binary property of the ternary mixture and the superscript  $bi$  denotes a binary property between liquid component  $i$  and the polymer in the ternary mixture. Equilibrium between the polymer phase and the pure liquid phase requires that  $a_i^P = a_i^L = 1$ . The following equation for the binary interaction parameter  $\chi_{i3}^b$  is obtained from Equation (11):

$$\chi_{i3}^b = -\frac{\ln(1 - \phi_3^{bi}) + (1 - V_i/V_3) \phi_3^{bi}}{(\phi_3^{bi})^2} \quad (12)$$

The polymer volume fraction  $\phi_3^{bi}$  for a binary mixture of polymer and liquid component  $i$  is calculated as follows:

$$\phi_3^{bi} = \frac{S_i^b}{\frac{S_i^b}{\rho_i} + 1} \quad (13)$$

where  $S_i^b$  is the solubility of pure component  $i$  in the polymer and  $\rho_i$  is the density of component  $i$ . Typically the ternary interaction parameters  $\chi_{i3}$  depend on the component concentrations in the polymer. They are calculated from the binary interaction parameter  $\chi_{i3}^b$  using the relation proposed in Reference 12,

$$\chi_{13} = \chi_{13}^b + a_1 u_2^2 + a_2 u_2 + a_3 (\phi_3 - \phi_3^{b1}), \quad (14)$$

$$\chi_{23} = \chi_{23}^b + b_1 u_1^2 + b_2 u_1 + b_3 (\phi_3 - \phi_3^{b2}), \quad (15)$$

where  $u_i$  is the volume fraction of component  $i$  in the polymer on a polymer free basis, that is

$$u_1 = \frac{\phi_1}{\phi_1 + \phi_2}, \quad u_2 = \frac{\phi_2}{\phi_1 + \phi_2} \quad (16)$$

Relation (1) can be extended to the ternary system that results when a polymer is exposed to a binary liquid mixture:

$$\begin{aligned} \ln a_1^P = & \ln \phi_1 + \phi_2 + \phi_3 - \phi_2 \frac{V_1}{V_2} - \phi_3 \frac{V_1}{V_3} + \chi_{12} \phi_2 (\phi_2 + \phi_3) + \chi_{13} \phi_3 (\phi_2 + \phi_3) \\ & - \chi_{23} \phi_2 \phi_3 \frac{V_1}{V_2} - u_1 u_2 \phi_2 \frac{\partial \chi_{12}}{\partial u_2} - u_1 u_2 \phi_3 \frac{\partial \chi_{13}}{\partial u_2} - \phi_1 \phi_3^2 \frac{\partial \chi_{13}}{\partial \phi_3} \\ & + \frac{V_1 u_2^2 \phi_3}{V_2} \frac{\partial \chi_{23}}{\partial u_1} - \frac{V_1 \phi_2 \phi_3^2}{V_2} \frac{\partial \chi_{23}}{\partial \phi_3} + \frac{V_1 P_3}{M_c} \left( 1 - \frac{2M_c}{M} \right) \left( \phi_3^{1/3} - \frac{1}{2} \phi_3 \right) \end{aligned} \quad (17)$$

$$\begin{aligned} \ln a_2^P = & \ln \phi_2 + \phi_1 + \phi_3 - \phi_1 \frac{V_2}{V_1} - \phi_3 \frac{V_2}{V_3} + \chi_{12} \phi_1 \frac{V_2}{V_1} (\phi_1 + \phi_3) + \chi_{23} \phi_3 (\phi_1 + \phi_3) \\ & - \chi_{13} \phi_1 \phi_3 \frac{V_2}{V_1} - \frac{V_2}{V_1} u_1^2 \phi_2 \frac{\partial \chi_{12}}{\partial u_2} + \frac{V_2}{V_1} u_1^2 \phi_3 \frac{\partial \chi_{13}}{\partial u_2} - \frac{V_2}{V_1} \phi_1 \phi_3^2 \frac{\partial \chi_{13}}{\partial \phi_3} \\ & - u_1 u_2 \phi_3 \frac{\partial \chi_{23}}{\partial u_1} - \phi_2 \phi_3^2 \frac{\partial \chi_{23}}{\partial \phi_3} + \frac{V_2 \rho_3}{M_c} \left( 1 - \frac{2M_c}{M_3} \right) \left( \phi_3^{1/3} - \frac{1}{2} \phi_3 \right), \end{aligned} \quad (18)$$

where  $\rho_3$  is the density of the polymer,  $M_3$  is the molecular weight of the polymer, and  $M_c$  is the molecular weight between two crosslinks of the polymer. Equilibrium between the two phase requires that

$$a_1^L = a_1^P, \quad a_2^L = a_2^P. \quad (19)$$

### Parameter Estimation Strategy

The objective is to solve the solution model for the component volume fractions sorbed into the polymer ( $\phi_1, \phi_2$ ). To this end, the nonlinear algebraic Equations (17) and (18) are written to more clearly illustrate their functional dependencies:

$$f_1(a_1^P, \phi_1, \phi_2, \phi_3, \chi_{12}, \chi_{13}, \chi_{23}) = 0, \quad (20)$$

$$f_2(a_2^P, \phi_1, \phi_2, \phi_3, \chi_{12}, \chi_{13}, \chi_{23}) = 0. \quad (21)$$

Clearly, the three volumes fractions must sum to unity. Thus,

$$\phi_1 + \phi_2 + \phi_3 = 1 \Rightarrow f_3(\phi_1, \phi_2, \phi_3) = 0. \quad (22)$$

The activities  $a_i^P$  are determined explicitly from (8) and (19) as follows:

$$a_1^P = a_1^L = x_1 \gamma_1^L = x_1 \exp\left(\frac{Ax_1^2}{RT}\right), \quad a_2^P = a_2^L = x_2 \gamma_2^L = x_2 \exp\left(\frac{Ax_2^2}{RT}\right). \quad (23)$$

The interaction parameter  $\chi_{12}$  is determined explicitly from (10). The other interaction parameters,  $\chi_{13}$  and  $\chi_{23}$ , are computed using (12)–(15). The five nonlinear algebraic equations, (14), (15), (17), (18), and (22), involving five unknowns ( $\phi_1, \phi_2, \phi_3, \chi_{13}, \chi_{23}$ ) are solved simultaneously to yield the volume fractions  $\phi_1$  and  $\phi_2$ . We use the MATLAB nonlinear equation solver `fsolve` for this purpose.

To use the computation procedure outlined above, it is necessary to generate estimates of the unknown solution model parameters. The unknown parameters are the Margules constant ( $A$ ) and the six constants ( $a_1, a_2, a_3, b_1, b_2, b_3$ ) associated with the ternary interaction parameters in (14) and (15). The Margules parameter is estimated from the nonlinear algebraic Equation (9) using vapor–liquid equilibrium data for the binary liquid mixture. This equation is rewritten

$$g(T, P, x_1, x_2, A) = 0. \quad (24)$$

Given vapor–liquid equilibrium data over a range of conditions, the constant  $A$  is determined by solving the following nonlinear optimization problem:

$$\begin{aligned} \min_A \quad & \sum_{j=1}^N [g(T_j, P_j, x_{1,j}, x_{2,j}, A)]^2 \\ \text{subject to:} \quad & 0 < A \leq A_u \end{aligned} \quad (25)$$

where  $N$  is the number of data points;  $P_j, T_j, x_{1,j}$ , and  $x_{2,j}$  are the pressure, temperature, component 1 mole fraction, and component 2 mole fraction, respectively, for the  $j$ th data point; and  $A_u$  is an upper bound on  $A$ . The problem is solved using the MATLAB constrained optimization routine `fmincon`.

Estimates of the six constants associated with the ternary interaction parameters are generated similarly. The nonlinear algebraic Equations (14) and (15) are rewritten

$$f_4(\chi_{13}, \chi_{13}^b, \phi_3^{b1}, u_2, \phi_3, a_1, a_2, a_3) = 0 \quad (26)$$

$$f_5(\chi_{23}, \chi_{23}^b, \phi_3^{b2}, u_1, \phi_3, b_1, b_2, b_3) = 0. \quad (27)$$

Assume the availability of solubility data in mass of component  $i$  sorbed per unit mass of polymer for the ternary mixture over a range of liquid compositions. Given the densities of the liquid components and the polymer, the binary ( $S_i^b$ ) and the ternary ( $S_i$ ) solubilities of component  $i$  in mass of component  $i$  sorbed per unit volume of polymer are readily computed. The binary polymer volume fractions  $\phi_3^{bi}$  and binary interaction parameters  $\chi_{i3}^b$  are calculated from the binary solubilities using (13) and (12), respectively. The ternary volume fractions  $\phi_i$  are computed from the ternary solubilities using an equation analogous to (13).

The parameter estimation problem involves the least-squares minimization of the difference between the measured values of the ternary volume fractions ( $\phi_i^m$ ) and those predicted by the solution model ( $\phi_i$ ),

$$\min_{a_1, a_2, a_3, b_1, b_2, b_3} \sum_{j=1}^M \sum_{i=1}^3 [(\phi_i^m)_j - (\phi_i)_j]^2, \quad (28)$$

where  $M$  is the number of ternary solubility data points and the subscript  $j$  denotes the data point. The quadratic objective function is minimized subject to equality constraints imposed by the solution model equations and inequality constraints corresponding to bounds on the parameter values (if such information is available). The set of nonlinear algebraic equations that comprise the equality constraints is obtained by combining (26) and (27) with (20), (21), and (22). These five equations have the following vector form representation, where only the unknown variables and parameters are shown explicitly:

$$f(\phi_1, \phi_2, \phi_3, \chi_{13}, \chi_{23}, a_1, a_2, a_3, b_1, b_2, b_3) = 0. \quad (29)$$

The resulting nonlinear optimization problem is solved using the MATLAB routine `fmincon`.

### Application to Styrene/Ethylbenzene Pervaporation Membrane

The estimation procedure for solution model parameters is applied to a poly(hexamethylene sebacate) (PHS) based polyurethane membrane developed for styrene/ethylbenzene separations. FIGURE 1 shows the styrene and ethylbenzene uptake for a membrane of thickness  $50 \mu\text{m}$  as a function of the feed styrene concentration.<sup>9</sup> The styrene uptake increases with increasing feed styrene concentration, whereas the ethylbenzene uptake exhibits a maximum. The sorption mechanism favors styrene permeation. The necessary pure component physical property data are listed in TABLE 1. The Margules constant,  $A$ , was determined by solving the nonlinear optimization problem (25) using the vapor–liquid equilibrium data and the Antoine equations shown in TABLE 2.<sup>14</sup> The estimate obtained was  $A = 163.9 \text{ Pa/molK}$ .

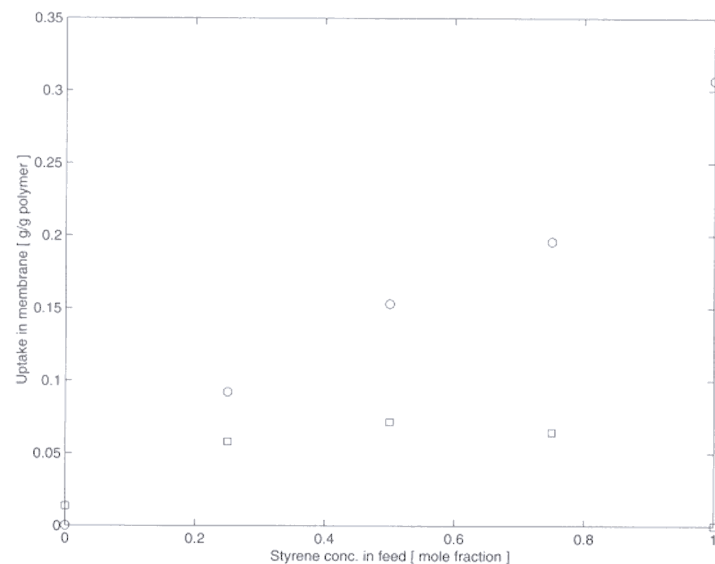


FIGURE 1. Effect of feed concentration on styrene (○) and ethylbenzene (□) uptake in a polyurethane membrane.<sup>9</sup>

The constants  $a_i$  and  $b_j$  were estimated from the data in FIGURE 1, expressed as mass of component  $i$  sorbed per unit mass of polymer. From these estimates the volume fractions  $\phi_i$  of the ternary mixture were computed. In these calculations, the molecular weight between two crosslinks ( $M_c$ ) was taken as the PHS molecular weight and the polymer molecular weight ( $M_3$ ) was assumed to be very large compared to  $M_c$ . Because there are only six data points (styrene and ethylbenzene values at the three intermediate styrene feed concentrations) available to estimate the six unknown parameters, there are no degrees of freedom for optimization. In this case, the nonlinear optimization problem is reduced to solving Equation (29). The resulting expressions for the interaction parameters are

TABLE 1. Pure component physical property data

Property	Styrene	Ethylbenzene	Polyurethane Membrane
Molar volume (cm <sup>3</sup> /mol)	115.0	122.4	—
Density (g/cm <sup>3</sup> )	0.9060	0.8670	0.96
Liquid viscosity (cP)	0.725	0.6428	
Heat capacity (J/g K)	1.6907	1.752	
Heat of vaporization (J/g)	421.7	335.0	
Solubility (g/g polymer)	0.307	0.014	

TABLE 2. Vapor-liquid equilibrium data for styrene/ethylbenzene mixtures at atmospheric pressure

Temperature (°C)		29.15	30.60	31.68	32.40
$x_2$	1.0	0.777	0.651	0.575	0.433
$y_2$	1.0	0.835	0.732	0.663	0.535

Vapor Pressure Equations

$$P_1^{\text{sat}} = 10 \exp\left(7.2788 - \frac{1649.6}{230 + T}\right)$$

$$P_2^{\text{sat}} = 10 \exp\left(6.95366 - \frac{1421.914}{212.931 + T}\right)$$

$$P_i^{\text{sat}} \text{ (mmHg)}, \quad T \text{ (°C)}$$

NOTE: 1, styrene; 2, ethylbenzene.

$$\chi_{13} = 1.142 - 8.951u_2^2 + 5.866u_2 - 5.652(\phi_3 - 0.754) \quad (30)$$

$$\chi_{23} = 3.297 + 13.537u_1^2 - 11.157u_1 + 8.694(\phi_3 - 0.984). \quad (31)$$

The predicted volume fractions obtained with the estimated parameters are shown in FIGURE 2. The model provides very accurate predictions of this, admittedly, limited data set. Note that the model captures the maximum in the ethylbenzene volume fraction. We have found that this effect cannot be captured with interaction parameter equations simpler than (14) and (15).

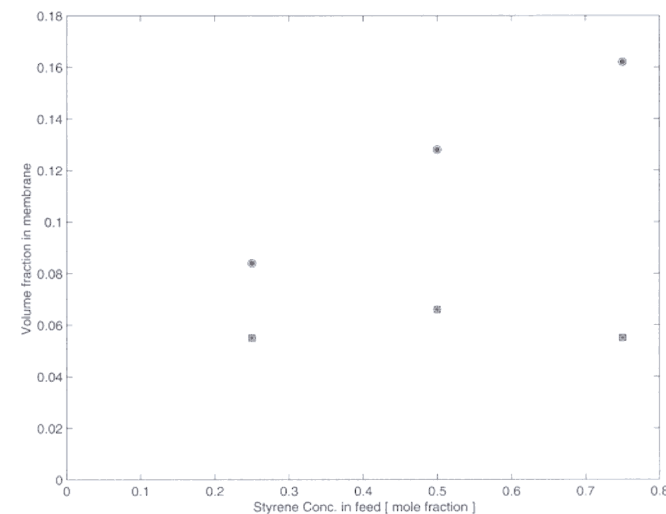


FIGURE 2. Comparison of experimental (● styrene and ★ ethylbenzene) and predicted (○ styrene and □ ethylbenzene) solubilities in a polyurethane membrane.

## ESTIMATION OF DIFFUSION MODEL PARAMETERS

## Theory

The component fluxes through the membrane are predicted with a diffusion model in which the component volume fractions on the feed-side surface of the membrane are obtained from the solution model. The diffusion model is based on Fick's law and uses the six parameter diffusion coefficient equations for binary liquid mixtures proposed by Brun *et al.*<sup>8</sup> Under the assumption of moderate membrane swelling, diffusion of component  $i$  through the polymer membrane is described by the following form of Fick's law:

$$J_i = -\frac{D_i}{1-\phi_i} \frac{dC_i}{dz}, \quad (32)$$

where  $J$  is the mass flux,  $z$  is the flux direction,  $C$  is the mass concentration, and  $\phi$  is the volume fraction.

The component diffusion coefficient  $D_i$  may depend on the concentration of each component in the liquid mixture. To account for this possibility, the identity  $C_i = \rho_i \phi_i$  is used to rewrite (32) as follows:

$$J_i dz = -\frac{\rho_i D_i}{1-\phi_i} d\phi_i, \quad (33)$$

where  $\rho_i$  is the density of component  $i$ . At  $z=0$  the component volume fraction  $\phi_i$  is equal to the sorption value, which is denoted here by  $\phi_i^0$ . The volume fraction on the permeate side of the membrane is approximately zero when the permeate pressure is maintained near vacuum. Under the assumption that  $D_i$  is constant, integration of (33) from  $z=0$  to  $z=l$  yields

$$J_i^* l = \rho_i D_i \ln(1-\phi_i^0), \quad (34)$$

where  $l$  is the membrane thickness and  $J_i^*$  denotes the component flux obtained under permeate vacuum.

Equation (34) suggests that a plot of  $J_i^* l$  versus  $\ln(1-\phi_i^0)$  should be linear. If the relationship is significantly nonlinear, then  $D_i$  is not constant but, rather, is a function of the component concentrations. In this case, the functional form of the concentration dependence can be deduced from the shape of the curve.<sup>15</sup> Although other nonlinear functions could be used, the diffusion coefficients are assumed to depend exponentially on the concentration of each component, as suggested by Brun *et al.*,<sup>8</sup>

$$D_1 = D_1^0 \exp(A_{11} C_1 + A_{12} C_2) \quad (35)$$

$$D_2 = D_2^0 \exp(A_{21} C_1 + A_{22} C_2), \quad (36)$$

where  $D_i^0$  is the diffusion coefficient at infinite dilution for component  $i$  and the  $A_{ij}$  are constant parameters.

## Parameter Estimation Strategy

The diffusion model is solved for the two component fluxes ( $J_1^*$  and  $J_2^*$ ) by using the following procedure. The flux Equation (33) is combined with the diffusion coefficient relations (35) and (36) to yield

$$J_1 dz = -D_1^0 \rho_1 \frac{\exp(A_{11} \phi_1 + A_{12} \phi_2)}{1-\phi_1} d\phi_1 \quad (37)$$

$$J_2 dz = -D_2^0 \rho_2 \frac{\exp(A_{21} \phi_1 + A_{22} \phi_2)}{1-\phi_2} d\phi_2. \quad (38)$$

These equations are integrated from  $z=0$ , where  $\phi_i = \phi_i^0$ , to  $z=l$ , where  $\phi_i = 0$ :

$$J_1^* = -\frac{D_1^0 \rho_1}{l} \int_{\phi_1^0}^0 \frac{\exp(A_{11} \phi_1 + A_{12} \phi_2)}{1-\phi_1} d\phi_1 \quad (39)$$

$$J_2^* = -\frac{D_2^0 \rho_2}{l} \int_{\phi_2^0}^0 \frac{\exp(A_{21} \phi_1 + A_{22} \phi_2)}{1-\phi_2} d\phi_2. \quad (40)$$

Approximating the integrals by Gaussian quadrature<sup>16</sup> yields

$$J_1^* \approx -\frac{D_1^0 \rho_1}{l} \sum_{k=1}^P \frac{\exp(A_{11} \phi_{1,k} + A_{12} \phi_{2,k})}{1-\phi_{1,k}} w_k \quad (41)$$

$$J_2^* \approx -\frac{D_2^0 \rho_2}{l} \sum_{k=1}^P \frac{\exp(A_{21} \phi_{1,k} + A_{22} \phi_{2,k})}{1-\phi_{2,k}} w_k, \quad (42)$$

where  $P$  is the number of quadrature points used,  $w_k$  is the quadrature weight at the quadrature point  $\xi_k$  (the quadrature point  $\xi_k \in [0, 1]$  is obtained as the root of the appropriate Jacobi polynomial), and

$$\phi_{1,k} = (1-\xi_k)\phi_1^0, \quad \phi_{2,k} = (1-\xi_k)\phi_2^0. \quad (43)$$

Equations (41)–(43) allow the component fluxes,  $J_i^*$ , to be computed from the results of the solution model.

To solve the diffusion model, values must be specified for the six empirical constants in the diffusion coefficient Equations (35) and (36). The vector of six unknown parameters is denoted by  $\theta = [D_1^0, D_2^0, A_{11}, A_{12}, A_{21}, A_{22}]^T$ . Assume that  $N$  experiments are performed to obtain the sorption and flux data  $\{J_{1,j}^*, J_{2,j}^*, \phi_{1,j}^0, \phi_{2,j}^0\}$ , where  $j$  denotes the data point. The discretized flux equations, (41) and (42), are written for each data point to yield  $2N$  nonlinear algebraic equations in the six unknown parameters  $\theta$ . Parameter estimates are obtained by solving the following nonlinear least-squares estimation problem:

$$\min_{\theta} \sum_{j=1}^N [J_{j,1}^{*,m} - J_{j,1}^*]^T [J_{j,1}^{*,m} - J_{j,1}^*], \quad (44)$$

where  $J_{j,1}^{*,m} = [J_{1,j}^{*,m}, J_{2,j}^{*,m}]^T$  and  $J_{j,1}^* = [J_{1,j}^*, J_{2,j}^*]^T$  are the measured and predicted values, respectively, of the component flux. The minimization is performed subject to nonlinear equality constraints derived from the  $2N$  component flux equations and inequality constraints on the estimated parameters (e.g.,  $D_i^0 > 0$ ).

### Application to Styrene/Ethylbenzene Pervaporation Membrane

The estimation procedure for diffusion model parameters is applied to the polyurethane membrane considered previously. Component fluxes  $J_i^*$  are obtained from the flux and selectivity data<sup>9</sup> shown in FIGURE 3. Note that the styrene selectivity decreases rapidly as the feed styrene concentration is increased due to a loss of sorption selectivity. First, the assumed form of the diffusion coefficient Equations (35) and (36) are checked using (34), where  $l = 50\mu\text{m}$  and values of  $\phi_i^0$  are obtained from the sorption data in FIGURE 1. The results in FIGURE 4 verify that the styrene diffusion coefficient has an exponential concentration dependence. An appropriate functional form for the concentration dependence of the ethylbenzene diffusion coefficient is less clear. Based on the styrene behavior, we also used the exponential function (36) for ethylbenzene. The diffusion model parameters were estimated from the sorption and flux data in FIGURES 1 and 3, respectively, by solving the constrained nonlinear optimization problem (44). There are a total of ten data points (styrene and ethylbenzene values for five styrene feed concentrations) available to estimate the six unknown parameters. The following relations were obtained:

$$D_1 = 8.78 \times 10^{-12} \exp(19.9C_1 - 0.06C_2) \quad (45)$$

$$D_2 = 8.13 \times 10^{-12} \exp(-13.7C_1 + 58.5C_2), \quad (46)$$

where styrene and ethylbenzene are designated components 1 and 2, respectively. Styrene has a slightly higher diffusion coefficient at infinite dilution than does ethylbenzene. On the other hand, the ethylbenzene diffusion coefficient increases more rapidly with increasing ethylbenzene concentration than does the styrene diffusion

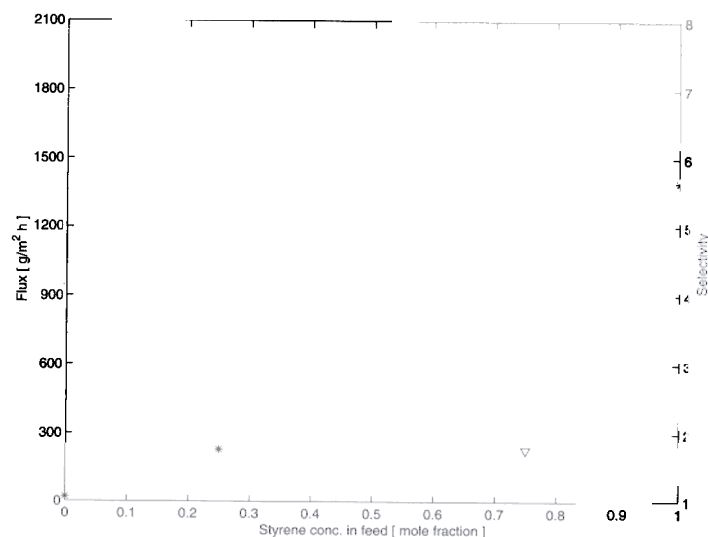


FIGURE 3. Effect of feed concentration on flux (▽) and (★) selectivity of a polyurethane membrane.<sup>9</sup>

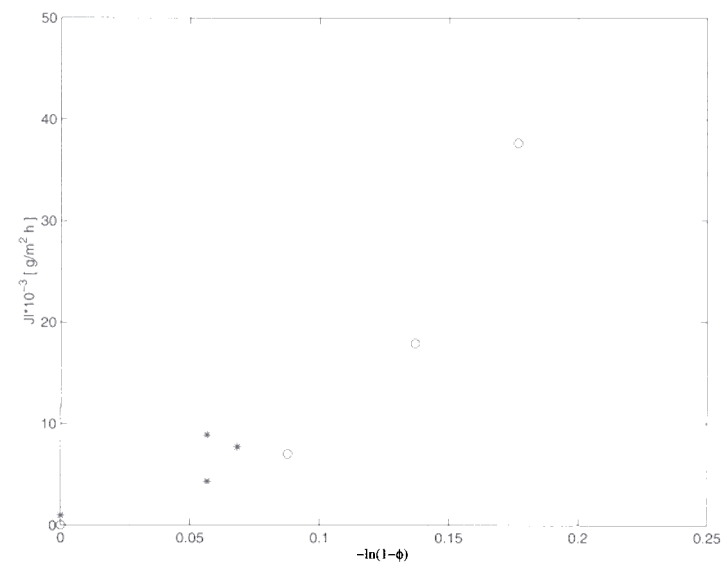


FIGURE 4. Concentration dependence of styrene (○) and ethylbenzene (★) diffusion coefficients.

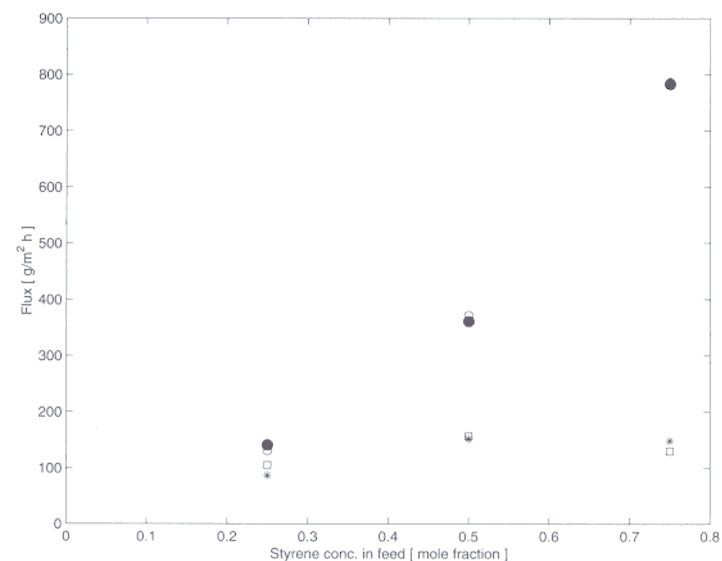


FIGURE 5. Comparison of experimental (○ styrene and □ ethylbenzene) and predicted (● styrene and ★ ethylbenzene) component fluxes in a polyurethane membrane.

coefficient with increasing styrene concentration. The ethylbenzene diffusion coefficient is significantly reduced by increasing styrene concentration, whereas the styrene diffusion coefficient is virtually unaffected by the ethylbenzene concentration. As a result of this behavior, sorption rather than diffusion is the primary mechanism that controls the styrene permselectivity of the polyurethane membrane.<sup>9</sup>

In FIGURE 5, component flux data are compared to calculated fluxes derived from the estimated diffusion coefficient Equations (45) and (46). The diffusion model provides accurate predictions of both fluxes given the diffusion coefficient form used for ethylbenzene and the limited number of data points available. Note that the model is able to predict the maximum in the ethylbenzene flux. We have found that this effect cannot be captured if the coupling terms ( $A_{12}$  and  $A_{21}$ ) are zero.

### ESTIMATION OF TEMPERATURE DEPENDENT FLUX PARAMETERS

The potentially strong effect of temperature on the component fluxes<sup>17</sup> should be included in the solution–diffusion model to ensure accurate predictions of separation performance. Typically there is insufficient data to account for the temperature effect separately in the solution and diffusion models. A simpler and more direct alternative is to correct the fluxes derived from the diffusion model. Let  $T_0$  denote the fixed reference temperature used for estimation of the solution and diffusion model parameters. The following phenomenologic relation<sup>17</sup> is used to account for temperature variations:

$$J_i^*(T) = J_i^*(T_0) \exp \left[ -\frac{E_i}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (47)$$

where  $J_i^*(T_0)$  is the flux of component  $i$  generated by the solution–diffusion model,  $J_i^*(T)$  is the temperature corrected flux of component  $i$ ,  $E_i$  is an activation energy parameter for component  $i$ , and  $R$  is the gas constant.

The parameter estimation problem involves the determination of the unknown parameters  $E_i$  from temperature dependent flux data. Equation (47) shows that a plot of  $\ln J_i^*(T)$  versus  $T^{-1} - T_0^{-1}$  should be linear with slope  $-E_i/R$ . Therefore, nonlinear optimization is not required in this case. FIGURE 6 illustrates the procedure for the polyurethane membrane considered previously. The required temperature dependent flux data were obtained from Reference 9 for a feed styrene mole fraction  $x_f = 0.5$  and reference temperature  $T_0 = 25^\circ\text{C}$ . Both styrene and ethylbenzene exhibit an exponential dependence on temperature. The following activation energy parameters were derived:  $E_1 = 1.343 \times 10^4 \text{ J/mol}$  and  $E_2 = 2.986 \times 10^4 \text{ J/mol}$ , where styrene and ethylbenzene are designated components 1 and 2, respectively. The estimated activation energies demonstrate that the ethylbenzene flux is more strongly affected by temperature than is the styrene flux.

Membrane mass transfer coefficients can be computed directly from the temperature corrected component fluxes. The following calculation is valid if the permeate pressure is negligible, the liquid behavior is ideal, and boundary layer resistances are negligible. Then, the membrane mass transfer coefficient of component  $i$  ( $k_{mi}$ ) is related to the component flux ( $J_i^*$ ) as follows:

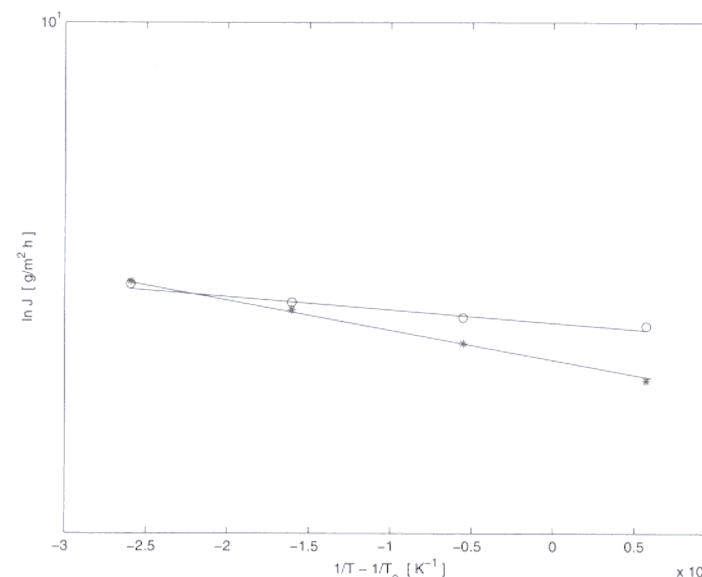


FIGURE 6. Temperature dependence of styrene (○) and ethylbenzene (★) flux.

$$J_i^* = k_{mi} x_i P_i^{\text{sat}}, \quad (48)$$

where  $x_i$  is the liquid composition of component  $i$  and  $P_i^{\text{sat}}$  is the saturation pressure of component  $i$  at temperature  $T$ . This equation is rearranged to yield

$$k_{mi} = \frac{J_i^*}{x_i P_i^{\text{sat}}}. \quad (49)$$

The mass transfer coefficients can be used directly to characterize a dense film membrane, or they can be combined with appropriate expressions for the liquid boundary layer resistance to determine the separation performance of a membrane module.<sup>18</sup>

### SUMMARY AND CONCLUSIONS

An optimization-based procedure for estimating unknown parameters in solution–diffusion models of membrane pervaporation has been developed and evaluated. Although the general methodology is applicable to a wide variety of model types, we have presented a specific estimation strategy for a solution model based on Flory–Huggins theory, a diffusion model derived from Fick's law, and a phenomenologic temperature dependent flux relation. The parameter estimation problem is posed as nonlinear optimization problem in which the unknown parameters are the decision variables and the objective function is the least-squares difference between the measured data and the model predictions. The objective function is minimized subject to equality constraints imposed by nonlinear model equations and inequality constraints

representing known bounds on the parameter values. The resulting nonlinear optimization problems are solved using the MATLAB routine `fmincon`, although other nonlinear programming codes also could be employed. Advantages of the optimization-based procedure as compared to manual parameter adjustment are illustrated by application to the separation of styrene and ethylbenzene with a polyurethane membrane.

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