

Multicomponent Transport in Swollen Networks

John R. Dorgan and Oluwasijibomi Okeowo
Department of Chemical Engineering
Colorado School of Mines
Golden, CO 80401 USA

New membrane materials are developed in an empirical manner without the advantage of a truly scientific *a priori* design procedure. Accordingly, a better theoretical understanding of coupled transport through cross-linked polymers is needed. An analytical formulation of the free energy provides an *a priori* concentration dependence of the diffusion coefficient. The model requires only two independently determinable equilibrium properties – the crosslink density (which is available from mechanical tests) and the thermodynamic interaction parameters (which can be measured in swelling experiments in the pure solvents).

There have been many models developed for transport in pervaporation membranes. Transport through pervaporation membranes has been described by various solution-diffusion models that explicitly consider crosslinking.¹⁻³ There are also many empirical, semi-empirical, and theoretical models used to describe the transport of solute in a membrane. The PI has used the UNIFAQ-FV model and observed reasonable predictions as shown below,⁴ the same UNIQUAC-FV gave good predictions for the sorption of ether and ester in poly urethaneimide. Correlation based on the UNIFAC model does not reflect the effects of crosslinking and fails to account for diffusion effects. A study by Molina et al.⁵ used the thermodynamics of irreversible process to obtain a close fit with experimental data for the pervaporation of ethanolic solutions through a PDMS membrane using different pressures on the permeate side. However, the model does not provide the fundamental understanding required for membrane development. Maxwell-Stefan theory has been applied to pervaporation⁶, and does combine the solution-diffusion model and the effects of coupled diffusion; good agreement between experimental data and theoretical predictions was reported.⁷ The results of a comprehensive review of models for pervaporation by Lipnizki and Tragardh² suggested the need for a new combination of models. That is, the results from this survey suggest that no comprehensive model has appeared; they maintain at least a small number of adjustable parameters that are fit to the data.

In 2003, Barriere and Liebler published a model for the pervaporation performance of crosslinked polymers.³ The model gives analytical expressions in terms of the respective sizes of the two solvents relative to the polymer, interaction parameters, and the viscosity ratio between the two solvents but only for the limiting case of *small swelling* during the pervaporation process. That is, when the interactions are not significantly affected by the presence of the penetrants. It does not include the effects of the concentration dependence of the diffusion coefficients and flux coupling. Our recent work has moved to capture all of these important missing effects.

In the original Flory-Rehner theory,⁸ two contributions to the free energy of a solvent swollen crosslinked elastomer are present. Namely, mixing and deformation terms are written. For favorable energetics, the network wants to swell and this causes the polymer chains to become extended. Extension of polymer chains is entropically unfavorable because it limits the number of conformations between the ends that are fixed by crosslinking – this leads to an entropically

driven restoring force. We have extended this model to include the effects of swelling in the presence of two solvents.

The underlying free energy of the system is written as a combination of two contributions,

$$\Delta G = \Delta G_M + \Delta G_E \quad (1)$$

in which ΔG_M represents the free energy of mixing and ΔG_E represents the elastic term. The distinction from the usual Flory-Rehner argument is that the free energy of mixing is taken as that of a *ternary* system rather than the usual binary one. That is,

$$\Delta G_M = kT[n_A \ln \phi_A + n_B \ln \phi_B + n_M \ln \phi_M + \chi_{AB} n_A \phi_B + \chi_{AM} n_A \phi_M + \chi_{BM} n_B \phi_M] \quad (2)$$

In Equation 2, χ_{ij} is the interaction parameter between species *i* and *j*; subscripts A and B represent the two solvents and M the polymer network. The network is envisioned as homogenous with a volume-averaged value of the interaction parameters of the blend components. The blend creates a mean-field environment for the penetrating solutes. The elastic term assumes the same form as in Flory-Rehner theory,

$$\Delta G_E = (kT \nu_e / 2)(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln \alpha_x^2 \alpha_y^2 \alpha_z^2) \quad (3)$$

Combination of the two terms and appropriate differentiation provides expressions for the chemical potentials. In the solvent phase, the mixture is modeled by the binary variant of Equation 2 for solvents A and B.

The resulting expressions for the chemical potentials of species A and B in the membrane are:

$$\begin{aligned} \Delta \mu_{AM} / RT &= \ln \phi_{AM} + (1 - \phi_{AM}) - \phi_{BM} (V_A / V_B) + \\ &\chi_{AB} \phi_{BM} (1 - \phi_{AM}) + \chi_{AM} (1 - \phi_{AM} - \phi_{BM})(1 - \phi_{AM}) - \chi_{BM} \phi_{BM} (1 - \phi_{AM} - \phi_{BM})(V_A / V_B) + \\ &\nu_e V_A ((1 - \phi_{AM} - \phi_{BM})^{1/3} - \frac{1}{2}(1 - \phi_{AM} - \phi_{BM})) \\ \Delta \mu_{BM} / RT &= \ln \phi_{BM} + (1 - \phi_{BM}) - \phi_{AM} (V_B / V_A) + \phi_{BM} \phi_{AM} (V_B / V_A) + \\ &\chi_{BM} (1 - \phi_{AM} - \phi_{BM})(\phi_{AM} + \phi_{BM}) - \chi_{AM} \phi_{AM} (1 - \phi_{AM} - \phi_{BM})(V_B / V_A) + \\ &\nu_e V_B ((1 - \phi_{AM} - \phi_{BM})^{1/3} - \frac{1}{2}(1 - \phi_{AM} - \phi_{BM})) \end{aligned} \quad (4)$$

In the feed solution, the appropriate forms are,

$$\begin{aligned} \Delta \mu_{AS} / RT &= \ln \phi_{AS} - (1 - \phi_{AS}) + (1 - \phi_{AS})(V_A / V_B) - \chi_{AB} (1 - \phi_{AS})^2 \\ \Delta \mu_{BS} / RT &= \ln (1 - \phi_{AS}) + \phi_{AS} (1 - V_B / V_A) - \chi_{AB} (V_B / V_A) \phi_{AS}^2 \end{aligned} \quad (5)$$

where subscript “m” corresponds to the membrane phase while the subscript “s” corresponds to the solvent feed. Equilibration of the chemical potential expressions for each penetrant allows for solution of the phase equilibrium. Results from the calculations are now presented.

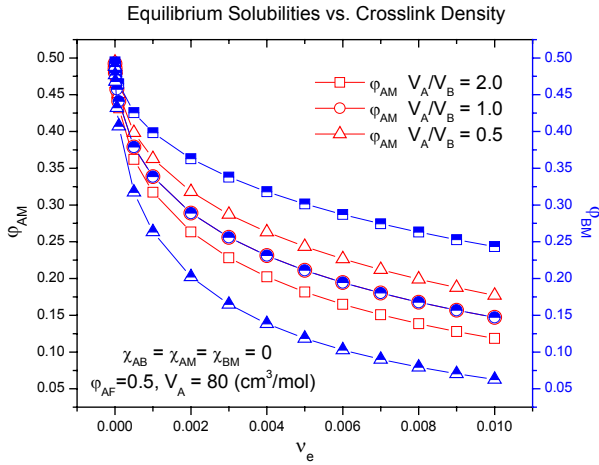


Figure 1. Equilibrium swelling of a two solvent in a membrane system as a function of crosslink density and the ratio of penetrant molar volumes

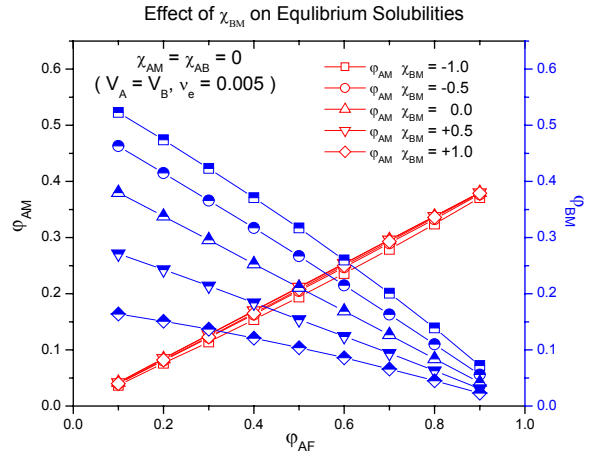


Figure 2. Equilibrium swelling of two solvents as a function of the feed composition.

Figure 1 presents the equilibrium volume fractions of the solvents in the membrane phase for a 50:50 feed mixture in contact with the rubber – in this case, all interaction parameters are set equal to zero. Solubility differences between the two penetrants reflect differences in molar volumes. Figure 1 clearly demonstrates the profound that both molecular size and crosslinking effects are captured by the model.

Figure 2 shows the concentrations of species A and B in the membrane as the single interaction parameter χ_{BM} is varied (all other interaction parameters remain at zero). In the absence of B-interactions ($\chi_{BM} = 0$), the concentration in the membrane is linearly dependent on the feed concentration in accordance with Henry's Law. Under such conditions, strict solubility selectivity is not possible; the component with the greater concentration will have a greater solubility. Increasing values of χ_{BM} leads to less of component B in the membrane

Using the physically realistic free energy outlined above, a theoretically sound approach is to work with the chemical potentials directly as the driving force for diffusion; instead of Equations 13 we adopt,⁹

$$\begin{aligned} -J_A &= \Omega_{AA} \nabla \mu_A + \Omega_{BA} \nabla \mu_B \\ -J_B &= \Omega_{BA} \nabla \mu_A + \Omega_{BB} \nabla \mu_B \end{aligned} \quad (6)$$

where instead of concentration dependent practical diffusion coefficients, the fundamental Onsager coefficients are introduced. In this approach, the Onsager coefficients are taken as symmetric in accord with arguments from non-equilibrium thermodynamics, the symmetry of the coefficients is also adopted (i.e. $\Omega_{12} = \Omega_{21}$). The perceptive reader will ask how non-symmetric coupling (as in the case where one component highly swells the membrane while the other does not) can be captured in a model having symmetric coefficients? The answer to this apparent contradiction can be resolved through application of the chain rule for differentiation applied to Equations 6 in order to use volume fractions as the independent variable.

$$\nabla \mu_1 = \frac{\partial \mu_1}{\partial x_i} = \sum_j \left(\frac{\partial \mu_1}{\partial \varphi_j} \right) \left(\frac{\partial \varphi_j}{\partial x_i} \right) = \sum_j \left(\frac{\partial \mu_1}{\partial \varphi_j} \right) \nabla \varphi_j \quad (7)$$

Substitution of this argument into Equations 6 provides,

$$\begin{aligned} -J_A &= \left\{ \Omega_{AA} \left(\frac{\partial \mu_A}{\partial \varphi_A} \right) + \Omega_{AB} \left(\frac{\partial \mu_B}{\partial \varphi_A} \right) \right\} \nabla \varphi_A + \left\{ \Omega_{AA} \left(\frac{\partial \mu_A}{\partial \varphi_B} \right) + \Omega_{AB} \left(\frac{\partial \mu_B}{\partial \varphi_B} \right) \right\} \nabla \varphi_B \\ -J_B &= \left\{ \Omega_{BA} \left(\frac{\partial \mu_A}{\partial \varphi_A} \right) + \Omega_{BB} \left(\frac{\partial \mu_B}{\partial \varphi_A} \right) \right\} \nabla \varphi_A + \left\{ \Omega_{BA} \left(\frac{\partial \mu_A}{\partial \varphi_B} \right) + \Omega_{BB} \left(\frac{\partial \mu_B}{\partial \varphi_B} \right) \right\} \nabla \varphi_B \end{aligned} \quad (8)$$

Equations 8 are the appropriate framework for understanding coupled transport in swollen rubbery membranes. For readers knowledgeable about non-equilibrium thermodynamics, the so-called “*solvent-fixed*” *frame of reference* has been adopted;¹⁰⁻¹² the polymer membrane is fixed in space and required to have a zero valued flux. This fact avoids the redefinition of driving forces to satisfy constraints of the Gibbs-Duhem equation.

Here we will show that the following Ansatz for the Onsager coefficients,

$$\Omega_{AA} = \frac{kT}{\mu_A R_A} \varphi_A \quad \Omega_{BB} = \frac{kT}{\mu_B R_B} \varphi_B \quad \Omega_{AB} = \Omega_{BA} = \frac{kT}{\mu_{AB} R_{AB}} \varphi_A \varphi_B \quad (9)$$

provides the correct physical response of the system. Equations 9 are simply concentration scaled versions of the Stokes-Einstein relationship that maintain the required symmetry of the Onsager relationship; R_A and R_B are effective radii of the permeants and the subscript AB denotes the geometric average of the pure component values. Adoption of this form for the Onsager coefficients is equivalent to setting the values equal to a concentration scaling pure component **self-diffusivities** (D_{ii}). Self-diffusion coefficients are extensively cataloged and can be estimated by a number of correlations and group contribution methods, accordingly these are fixed known values, not adjustable parameters.¹³ Substitution of Equations 9 into Equations 8 provides the following parameter free model,

$$\begin{aligned} -J_A &= \left\{ D_{AA} \varphi_A \left(\frac{\partial \mu_A}{\partial \varphi_A} \right) + D_{AB} \varphi_A \varphi_B \left(\frac{\partial \mu_B}{\partial \varphi_A} \right) \right\} \nabla \varphi_A + \left\{ D_{AA} \varphi_A \left(\frac{\partial \mu_A}{\partial \varphi_B} \right) + D_{AB} \varphi_A \varphi_B \left(\frac{\partial \mu_B}{\partial \varphi_B} \right) \right\} \nabla \varphi_B \\ -J_B &= \left\{ D_{AB} \varphi_A \varphi_B \left(\frac{\partial \mu_A}{\partial \varphi_A} \right) + D_{BB} \varphi_B \left(\frac{\partial \mu_B}{\partial \varphi_A} \right) \right\} \nabla \varphi_A + \left\{ D_{AB} \varphi_A \varphi_B \left(\frac{\partial \mu_A}{\partial \varphi_B} \right) + D_{BB} \varphi_B \left(\frac{\partial \mu_B}{\partial \varphi_B} \right) \right\} \nabla \varphi_B \end{aligned} \quad (10)$$

Equations 10 are an important new development in understanding cross-coupling transport in multicomponent polymer networks. All of the numerical coefficients, which number only 5 (χ_{AB} , χ_{AM} , χ_{BM} , v_e , D_{AA} , D_{BB}) are *independently* calculable or measurable. Also, comparison of Equations 10 with 5 leads to a form for the **transport diffusion coefficients** that is very similar to one that is often assumed; we obtain,

$$\mathcal{D}_{AA}(\varphi_A, \varphi_B) = \left\{ D_{AA} \varphi_A \left(\frac{\partial \mu_A}{\partial \varphi_A} \right) + D_{AB} \varphi_A \varphi_B \left(\frac{\partial \mu_B}{\partial \varphi_A} \right) \right\} \quad (11)$$

whereas, a commonly assumed form used to capture thermodynamic non-idealities is,

$$\mathcal{D}_{AA}(\varphi_A, \varphi_B) = D_{AA} \varphi_A \left(\frac{\partial \mu_A}{\partial \varphi_A} \right) \quad (12)$$

Our new findings show that the previously assumed form is missing important features including the correct dependence of coupling effects on the cross-derivative of the species chemical potential. Another encouraging result is that the coupling transport diffusivities, \mathcal{D}_{AB} , are calculated to be negative – negative terms are often observed experimentally.¹⁴ Because of page limitations, the concentration dependencies are not plotted, however, they are directly calculable using Equation 11 and its analogues – the only parameters of the model are χ_{AB} , χ_{AM} , χ_{BM} , v_e , D_{AA} , D_{BB} and these are independently determinable. In some instances, the crosslink density dependence of χ_{AM} and χ_{BM} must be included.^{15, 16}

At this juncture, membrane performance can be *calculated*. The only assumptions needed are that the feed and permeate phases are in equilibrium with the membrane and that the permeate concentration is approximately zero on the downstream side. The permeance of each species is directly calculable by integrating the flux, for example,

$$\begin{aligned}
 J_A &= -\mathcal{D}_{AA}(\varphi_A, \varphi_B) \left(\frac{d\varphi_A}{dx} \right) - \mathcal{D}_{AB}(\varphi_A, \varphi_B) \left(\frac{d\varphi_B}{dx} \right) \\
 \int_0^L J_i dx &= - \int_{\varphi_{AM}}^0 \mathcal{D}_{AA}(\varphi_A, \varphi_B) d\varphi_A - \int_{\varphi_{BM}}^0 \mathcal{D}_{AB}(\varphi_A, \varphi_B) d\varphi_B \\
 J_A L &= \int_0^{\varphi_{AM}} \mathcal{D}_{AA}(\varphi_A, \varphi_B) d\varphi_A + \int_0^{\varphi_{BM}} \mathcal{D}_{AB}(\varphi_A, \varphi_B) d\varphi_A
 \end{aligned} \tag{13}$$

So that the *permeate composition may be predicted as a function of the feed composition*,

$$\varphi_{A,p} = \frac{J_A L}{J_A L + J_B L} = \frac{J_A}{J_A + J_B} \tag{14}$$

In addition, the individual contributions to the flux due to coupling can be computed. Because of space limitations, we focus on the membrane performance as evaluated by permeate composition

Figure 3 presents results for the permeate concentration as a function of the ratios of molar volumes for the two species. In the absence of enthalpic interactions, the smaller species is preferentially permeated as expected on physical grounds. Figure 4 shows the permeate composition as a function of the χ_{BM} interaction parameter. The results are again highly gratifying. Decreasing the favorable energetics of component B with the membrane as χ_{BM} changes from -1 , to 0 , to $+1$ yields a permeate increasingly enriched in component 1 as would be expected on physical grounds. It is important to understand that the selectivity presented is greater than the solubility selectivity alone; we have captured the salient features of diffusion selectivity as well as solubility selectivity! Various shapes of the permeate-feed curves corresponding different cases in the literature can be reproduced by the model.

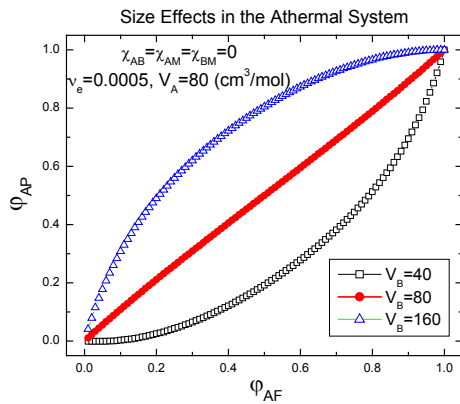


Figure 3. Predicted permeate composition vs. feed composition as a function of molar volume ratio; interaction parameters are zero-valued leading to size selectivity only. Size effects on both solubility and diffusivity are captured.

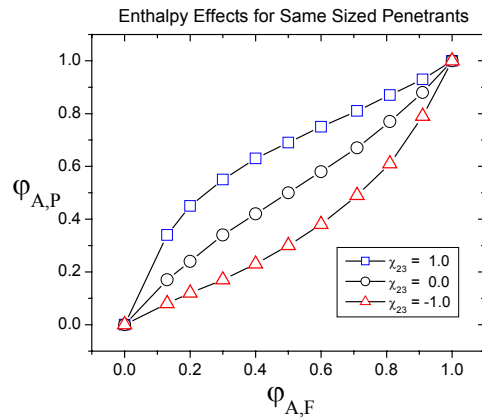


Figure 4. Predicted permeate composition vs. feed composition as a function of χ_{BM} (other interaction parameters are zero) for equal molar volumes; including the effects of diffusion selectivity produces greater than the solubility selectivity alone.

Conclusions

Based on an analytical free energy and rigorous arguments from non-equilibrium thermodynamics a new model for pervaporation is developed which includes an *a priori* prediction for the concentration dependence of the diffusion coefficients. These predictions allow for the prediction of membrane performance in applications. The new model is based on a few independently determinable material properties and resolves long-standing issues regarding coupled penetrant permeation in rubbery materials, a subject that has received considerable experimental attention but relatively little theoretical consideration

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