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Pressure effects in nonporous membranes

J.S. Vrentas*, C.M. Vrentas

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United States

HIGHLIGHTS

- Three models considered for solution-diffusion theory for nonporous membranes.
- Solvent mass flux expressions derived for solvent–polymer membrane systems.
- Solvent flux equations can describe reverse osmosis and negative reverse osmosis.
- Solvent flow driven by pressure diffusion.
- Solvent flow driven by thermodynamic effects.

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ABSTRACT

The solution-diffusion theory for membranes is used as a basis for the formulation and consideration of three models which can describe the mass transfer of solvents through nonporous polymer membranes. Two types of solvent mass transfer processes are considered: the transport of solvent through a membrane immersed in a pure solvent and the osmotic mass transfer of solvent in a solvent–solute-semipermeable membrane system. For the first mass transfer process, the most general of these three mass transfer models (Model III) includes both thermodynamic effects at the solvent–membrane interfaces and pressure diffusion effects inside the membrane. Model I includes only pressure diffusion effects, and Model II includes only thermodynamic effects at the solvent–membrane interfaces. For each model, equations are derived for the solvent mass flux through the membrane and for the mass fraction distribution of solvent inside the membrane. The predictions of each of the models are compared with available mass transfer data for solvent–polymer membrane systems. A similar analysis is used to describe osmotic effects and reverse osmosis. It is concluded that Model III should be the preferred choice for analyzing mass transfer processes for solvents in nonporous polymer membranes.

1. Introduction

It is generally accepted that mass transfer through nonporous membranes can be described by the solution-diffusion theory (Wijmans and Baker, 1995). This theory is based on the assumption that solutes and solvents dissolve in the membrane matrix and subsequently diffuse through the membrane material when concentration and/or pressure gradients are applied across the membrane. When concentration gradients along with negligible pressure gradients are applied to a membrane, the basic theory yields a straightforward mass transfer analysis for the membrane. However, there are at least two different forms of the theory or models which have been proposed to describe the effects of significant pressure gradients on the mass transfer process across a nonporous membrane.

The two models [Model I (Vrentas and Vrentas, 2013) and Model II (Rosenbaum, 1968; Rosenbaum and Cotton, 1969)] can be illustrated by considering the transport of a solute, component 1, and a solvent, component 2, across a polymer membrane material, component 3. In the first model, Model I, it is assumed that there can be gradients of both concentration and pressure and that the diffusion fluxes of both solute and solvent can be generated by the mass fraction gradients as well as by the pressure gradient (Vrentas and Vrentas, 2013, p. 73). This type of behavior is permitted by the equipresence principle of continuum mechanics (Vrentas and Vrentas, 2013, p. 56). In general, the two external phases can be at different pressures, and this model assumes that there is a continuous pressure change across the membrane. Additionally, for thin membranes, it can be assumed that the pressure distribution is linear (Vrentas and Vrentas, 2013, p. 412) so that there is a constant pressure gradient in the membrane. [It is worth noting that it is the pressure gradient dependence of the mass diffusion flux of a particular component that makes it possible to explain phenomena such as equilibrium concentration

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* Corresponding author. Tel.: +1 814 863 4808; fax: +1 814 865 7846.
E-mail addresses: jsv1@psu.edu (J.S. Vrentas), cmv13@psu.edu (C.M. Vrentas).

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distributions in sedimentation (Vrentas and Vrentas, 2013, pp. 511–513) and in ultracentrifuges (Vrentas and Vrentas, 2013, pp. 552–554) for the dilute component in a binary mixture.] For Model I, there are no jumps in pressure at the fluid–membrane interfaces because of the assumption of a continuous pressure change across the membrane. Consequently, it follows that the equilibrium conditions at the two external fluid–membrane interfaces are not thermodynamically affected by the imposition of a pressure difference across the membrane since there are no pressure jumps at these interfaces. Model I has been described elsewhere (Vrentas and Vrentas, 2013, pp. 419–422); however, solutions for the solvent mass flux and for the mass fraction distribution were not presented there and therefore will be included in this paper.

A second model (Model II) has been proposed by Rosenbaum (1968) and Rosenbaum and Cotton (1969). This model supposes that there is a uniform pressure within the membrane equal to the higher fluid pressure value imposed at one of the fluid–membrane interfaces. Consequently, there must be a step change in pressure at the other fluid–membrane interface which has the lower fluid pressure value. At this second fluid–membrane interface, the pressure in the membrane must of course be higher than the pressure in the adjacent fluid phase. Since the membrane phase and fluid phase pressures are different, the required equality of chemical potentials at this boundary must include the effect of the pressure change on the chemical potential relationship there. It can be shown that the presence of a pressure discontinuity will necessarily decrease the activity and thus the concentration of the solvent in the membrane at this fluid–membrane interface. This thermodynamic effect produces a larger concentration difference across the membrane and therefore an additional pressure-induced diffusion flux in the membrane.

It is possible to utilize the above results to propose a third model (Model III) to describe pressure effects in a nonporous membrane. This third model is formulated by using some of the characteristics of both Model I and Model II. For Model III, it is postulated that there is a continuous, linear decrease of pressure from the higher membrane-phase pressure at one fluid–membrane interface to an intermediate membrane-phase pressure at the second fluid–membrane interface that is greater than the lower fluid-phase pressure. There then is a step-change decrease from this intermediate pressure to the lower fluid-phase pressure. Diagrams showing the pressure p distributions for the three models are presented in Fig. 1. All three models have $p_0^s = p_0^m$; this result will be established in Section 2. Note that the superscripts s and m refer to the solvent and membrane phases, respectively, and the subscript here refers to the position in the membrane which extends from $x=0$ to $x=L$. Model I also has $p_L^s = p_L^m$ so that it includes a linear pressure distribution and no step changes in pressure. Model II has $p_0^s = p_0^m = p_L^m$ and a step change from p_L^m to p_L^s at $x=L$. Model III includes a linear pressure distribution from p_0^m to p_L^m and a step change from p_L^m to p_L^s at $x=L$.

The above three models will be used first to analyze the membrane mass transfer process when a membrane is immersed in a pure solvent. The general forms of the predictions of these three models for the solvent flux and for the solvent concentration distribution will then be compared to the general forms of the experimental data collected by Rosenbaum and Cotton (1969) and by Paul and Ebra-Lima (1970). The analysis presented here is carried out at low solvent concentrations in the membrane to facilitate the derivation of analytical results for the mass transfer process in nonporous membranes. Consequently, the following approximations will be used in the mathematical analysis

$$\omega_2^m \ll 1 \tag{1}$$

$$\rho^m \approx \frac{1}{\hat{V}_3^0} \tag{2}$$

where ω_2^m is the solvent mass fraction in the membrane, ρ^m is the total mass density of the membrane, and $\hat{V}_3^0$ is the specific volume of the pure polymer (^ denotes per unit mass and the superscript 0 denotes pure component). In addition, the analysis considered here includes only viscous effects; elastic effects in the membrane are not considered.

It is important to note that the experimental data presented in the two papers listed above (Paul and Ebra-Lima, 1970; Rosenbaum and Cotton, 1969) were obtained at solvent concentrations which are higher than the mass fractions described by Eq. (1). Additionally, the experimental data utilize measurements on crosslinked systems, and hence it is possible that there may be some important elastic effects. It is assumed here that a useful comparison can still be made between the available experimental data and the predictions based on the low mass fraction, purely viscous theory presented in this paper.

In addition to the analysis of solvent mass transfer for a nonporous membrane immersed in a pure solvent, mass transfer results will be obtained for a nonporous membrane immersed in a solvent–solute mixture, thus allowing consideration of reverse osmosis processes. Also, as indicated in the above discussion, the imposition of a pressure difference across a nonporous membrane can produce both a thermodynamic effect and a direct mass transfer effect. The imposed pressure difference can affect the equilibrium mass fractions at the fluid–membrane interfaces, thereby influencing the mass diffusion fluxes through the membrane, and it can lead to a pressure

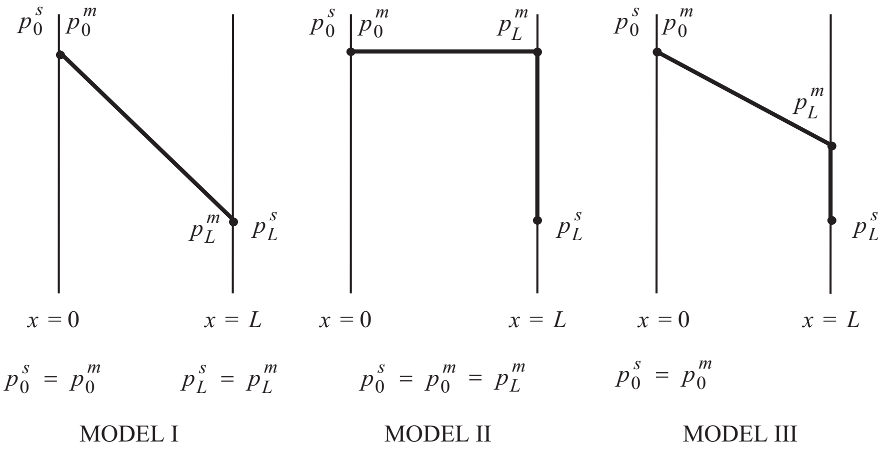

Fig. 1. Description of three models for pressure effects in nonporous membranes.