Journal of Membrane Science 470 (2014) 323–333

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Solution-diffusion with defects model for pressure-assisted forward osmosis

Jintang Duan, Eric Litwiller, Ingo Pinnau*

Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Al-Jazri Bldg. 4, Thuwal 23955-6900, Saudi Arabia

ARTICLE INFO

Article history:
Received 24 March 2014
Received in revised form
3 July 2014
Accepted 11 July 2014
Available online 18 July 2014

Keywords:
Forward osmosis
Solution-diffusion model
Concentration polarization
Pressure
Defects

ABSTRACT

An osmosis transport model is presented that combines the standard internal and external concentration polarization equations in the forward osmosis (FO) field with the selective layer transport equations first proposed by Sherwood in 1967. The Sherwood model describes water flux as the sum of a solute-selective, diffusive component driven by the sum of osmotic pressure and hydraulic pressure differences, and a nonselective, convective component driven by hydraulic pressure difference only. This solution-diffusion with defects (SDWD) model and the solution-diffusion (SD) model were compared against data collected using polyamide thin-film-composite (PA-TFC) and integrally-skinned asymmetric cellulose triacetate (CTA) membranes, evaluated in various configurations. When tested with pure water on the porous support side and 1.5 M (π=72.7 bar) sodium chloride solution on the selective layer side, applying 1.25 bar of hydraulic pressure to the porous support side increased water flux by an order of magnitude for PA-TFC membranes, but had negligible effect on CTA membrane flux. These large flux variations can be explained by the SDWD model, but not the SD model. To confirm the existence of defects, a PA-TFC membrane was coated with a uniform, highly water-permeable, nonselective polymer. After coating to block convection through defects, the influence of hydraulic pressure on water flux through this membrane essentially disappeared. Water flux through these defects is low (< 1% of total water flux for PA-TFC membranes) and of little consequence in practical FO or reverse osmosis (RO) applications. But in pressure-assisted forward osmosis (PAFO) or pressure-retarded osmosis (PRO), convective transport through defects affects the solute concentration difference across the membrane selective layer, increasing or decreasing water flux through defect-free regions. The presence of defects may explain why membrane power density in PRO is lower than that predicted based on FO and RO tests.

1. Introduction

In general, two membrane types are used for industrial desalination: (i) polyamide thin-film composite (PA-TFC) and (ii) integrally-skinned asymmetric cellulose acetate or triacetate (CTA). Though fabricated of different materials by different methods, they share the standard asymmetric membrane morphology, with an ultrathin, solute-selective layer at one surface of a porous support. Both have been used in reverse osmosis (RO) for decades, desalinating water by forcing it through the selective layer under a hydraulic pressure greater than the saline water's osmotic pressure. In recent years interest has grown in potentially using these membrane types for other osmotic processes, including pressure-retarded osmosis (PRO) for power generation and forward osmosis (FO) for desalination. In FO, differences in osmotic pressure provide the driving force for water flux; applied hydraulic pressure differences are generally assumed to be negligible. However, flux in FO may be influenced by superimposing a hydraulic pressure difference onto the osmotic pressure difference – pressure applied inadvertently, as a side-effect of circulating water through membrane modules [1,2], or deliberately, in a process termed pressure-assisted forward osmosis (PAFO) [3–5].

Given an asymmetric membrane, either side may be exposed to a hydraulic pressure p and/or osmotic pressure π. Fig. 1 shows the four possible permutations.

i) Higher p and higher π on selective layer side. If $p > \pi$, this is reverse osmosis; if $p < \pi$, this is pressure-retarded osmosis.
ii) Higher p on selective layer side, higher π on porous support side. This is PAFO (SL-FS) as applied in previous work [3–5].
iii) Higher π on selective layer, higher p on support. This is PAFO (SL-DS) as investigated here. In FO applications, this

* Corresponding author. Tel.: +966 12 808 2406.
E-mail address: ingo.pinnau@kaust.edu.sa (I. Pinnau).

http://dx.doi.org/10.1016/j.memsci.2014.07.018
0376-7388/

configuration may suffer from fouling problems – though a dual-skin membrane [6,7] might improve practicality. As a tool to investigate transport through the selective layer of asymmetric membranes, it has great value.

iv) Higher p and higher π on porous support side. This configuration is impractical because of membrane fouling and mechanical integrity issues.

Water and solute flux through these membranes is described by combining a model for transport through the selective layer with the convection-diffusion equation applied across the porous support and boundary layers adjacent to it. The solution-diffusion (SD) model has become the standard selective layer transport model [8–11], but others have been proposed, including irreversible-thermodynamics models [12,13], pore-flow models [14–16], and modified SD models [17]. For CTA, it is commonly accepted that the Loeb–Sourirajan process can make defect-free asymmetric RO membranes [18], but for PA the evidence is more ambiguous. Defects were detected in RO tests of commercial PA-TFC membranes (BW30 and SW30 from Dow FilmTec) [19], and gas permeation tests demonstrated the presence of selective layer defects in dry samples of commercial RO membranes [20,21]. Such defects may be associated with the PA selective layer's irregular ridge and valley structure [22] and the extremely fast and complex reaction kinetics of the layer formation mechanism [23].

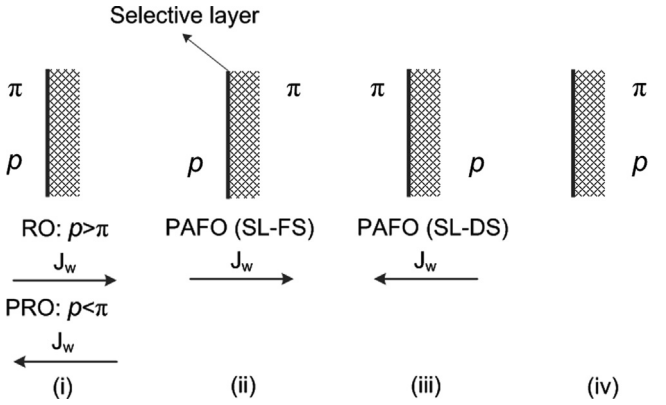

Fig. 1. Schematic of four possible permutations with higher osmotic pressure π and/or higher hydraulic pressure p on either side of an asymmetric membrane (SL-FS means selective layer facing the feed side; SL-DS means selective layer facing the draw side).

Nearly all previous publications in PRO, FO, and PAFO assume that transport through the selective layer occurs by solution-diffusion [2,24,25]. (The only exception is Fang et al. [26] who modeled FO transport using irreversible thermodynamics.) In the SD model, the driving force for water flux J_w is the net pressure difference across the selective layer, $\Delta\pi+\Delta p$, where Δp is approximately zero in FO, negative in PRO and positive in PAFO. The driving force for solute flux through the selective layer is concentration difference across it, proportional to $\Delta\pi$:

$$J_w = A(\Delta\pi + \Delta p) \tag{1}$$

$$-J_s = B(C_{draw,s} - C_{feed,s}) \tag{2}$$

where A is the water permeability coefficient, B is the solute permeability coefficient, and $C_{draw,s}$ and $C_{feed,s}$ are solute concentrations at the selective layer surfaces on the draw solution side and the feed solution side, respectively.

Thus, the SD model predicts that low hydraulic pressure ($\Delta p \ll \Delta\pi$) has little effect on water flux, producing negligible change in concentration polarization and solute flux. However, previous work reported experimental results that conflicted with this model. Coday et al. [2] found that hydraulic pressure had negligible influence on water flux, but measured much lower reverse solute flux under PAFO conditions than under FO conditions; this could not be explained by the SD model. In PRO mode it was reported that solute permeability appears to increase when hydraulic pressure is applied [27–31]. As a practical consequence, membranes operated under actual PRO conditions often produce less power than predicted by permeability coefficients measured under FO conditions [27,30,32]. In the SD model, solute permeability is an intrinsic property of the selective layer material. Why would this property change with pressure? Explanations have been offered that include stretching or deformation of the selective layer, and damage or blocking associated with compression of the membrane porous support against module spacers when hydraulic pressure is applied [2,27–30].

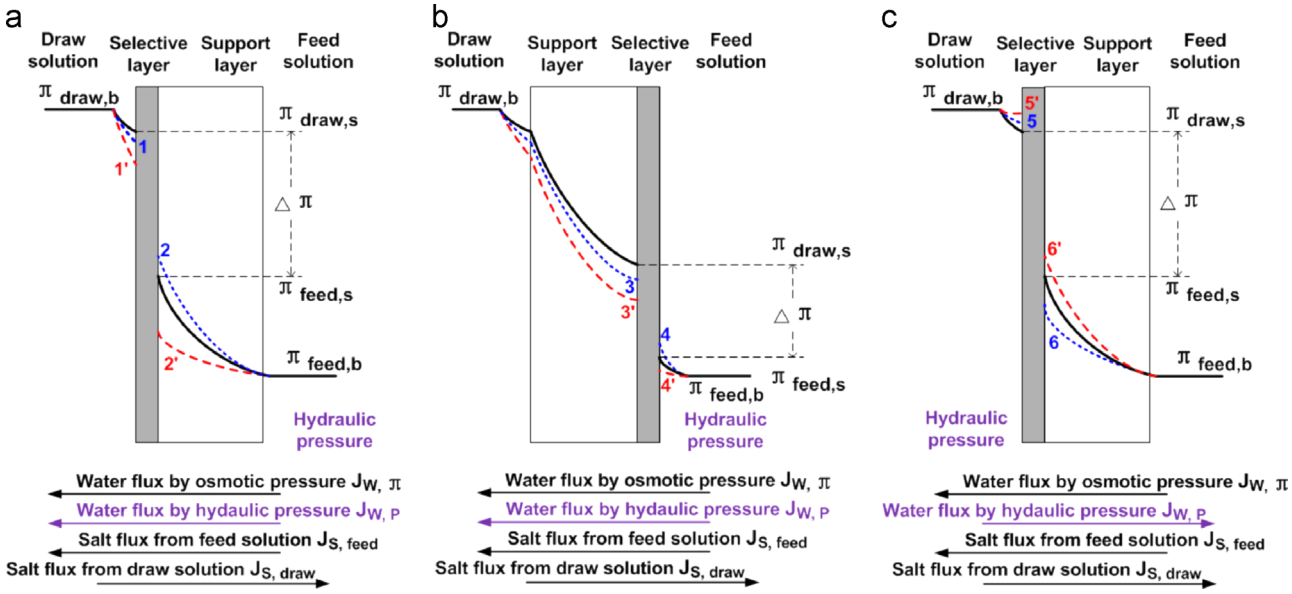

Fig. 2. Schematics of osmotic pressure profiles through thin-film-composite membranes in PAFO and PRO (black solid lines represent the profiles in FO; blue dotted lines 1–6 represent the possible profiles in PAFO and PRO according to the SD model; red dashed lines 1′–6′ represent the possible profiles in PAFO and PRO according to the SDWD model). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)