How can osmosis and solute diffusion be coupled for the simultaneous measurement of the solvent and solute permeabilities of membranes?

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HIGHLIGHTS

- A novel method measures the membrane solvent and solute permeabilities concurrently.
- The method's underlying model is entirely based on osmosis and solute diffusion.
- Osmosis should not be neglected in the calculation of the solute permeability.
- Water and salt permeabilities depend to a large extent on the solution concentration.
- Salt permeabilities thus determined were able to simulate experimental RO rejections.

GRAPHICAL ABSTRACT
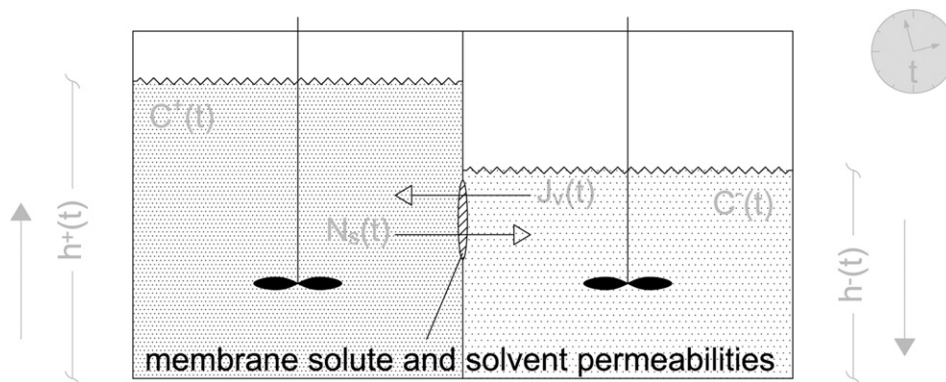
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ABSTRACT

A novel experimental method and its associated model are proposed for the simultaneous determination of membrane solute and solvent permeabilities, which are essential transport parameters of reverse osmosis models used for process simulation. The method utilizes a single bench-scale batch apparatus consisting of two stirred half-cells containing solutions of different concentrations separated by a membrane across which coupled non-steady-state solute diffusion and solvent osmosis take place countercurrently in the absence of transmembrane pressure difference. Results are presented from days-long determinations of the water and sodium chloride permeabilities of Filmtec BW30 and NF270 membrane samples for initial transmembrane salt concentration differences ranging from 1 g L^{-1} to 35 g L^{-1}. When used as input parameters for the simulation of pilot reverse osmosis desalination tests, the osmotic-diffusive salt permeabilities approximated the experimental rejection rates.

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1. Introduction

The development of semipermeable membranes has transformed the way some of the world's most critical issues can be addressed, as for instance water desalination [1–3], water and wastewater treatment [2–5] and sustainable energy generation [6,7]. Several processes based on nonporous osmotic membranes are nowadays viable. These include well-developed industrial processes such as reverse osmosis (RO) [8,

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9] as well as other processes under different stages of development, e.g. forward osmosis (FO) [3] and pressure-retarded osmosis (PRO) [7]. For a given set of operating conditions, the productivity and separation efficiency of these processes are functions of the membrane permeabilities to solutes and solvents essentially.

The membrane solute and solvent permeabilities are key input parameters of membrane separation and process models. Knowing them is thus a prerequisite for process performance simulation. In a previous work [10,11] the authors have developed a numerical model of proven appropriateness for reverse osmosis separations in flat geometries. The model is intended to be a readily usable simulation tool with predictive capabilities, using the fewest and simplest input parameters possible. The membrane solvent and solute permeabilities are two of these input parameters.

Permeability measurements may be fraught with biases. When the determinations are performed during pressure-driven filtrations [3, 7–10,12–25], the concentration polarization (CP) phenomenon [10,11] brings uncertainty to the actual concentration difference between the membrane sides. Indeed, quantifying the unstirred concentration boundary layer of non-permeated solutes on the membrane-liquid interface is not trivial. When the permeability measurements are carried out in a purely diffusive setting (in non-pressurized mode) [9,10,12, 16,17,19,26–38], the main concerns are the propensity for internal concentration polarization (ICP), which entangles the determination of the permeabilities of the selective layer of composite membranes, and the occurrence of a countercurrent transmembrane solvent flux. This flux, which is due to osmosis, affects the estimation of the transmembrane solute flux. As a matter of fact, osmosis is not negligeable unless solutions of very low osmotic pressure are considered. All the more, the permeabilities are pressure-sensitive and concentration-dependent [10,19,20,24,26,39,40] and they are influenced by the membrane conditioning protocol [10,21,39,41]. Despite the fundamental interest and the practical relevance of duly addressing these sources of bias, their discussion is scarce. Here, some of these problems are examined and an experimental alternative to them is put forward.

In this paper, we implemented experimental conditions leading to the more general problem in which countercurrent solute diffusion *and* osmosis coexist. Thus, the membrane solvent and solute permeabilities can be determined simultaneously from a single experiment. The governing equations of a batch system formed by two binary liquid solutions of unequal concentrations separated by a solution–diffusion membrane [8,9,12,26,42] subject to non-steady-state solvent and solute permeation, in the absence of any hydrodynamic flows and of any applied pressure, are presented and solved. Then, a suitable in-house built permeation cell and the associated experimental method are presented. They were applied to the determination of the water and sodium chloride permeabilities of commercial reverse osmosis and nanofiltration membrane samples. The concentration-dependence of the parameters thus measured is evidenced. Finally, the applicability of the permeabilities determined herein as input parameters of a reverse osmosis model was evaluated for the prediction of the overall performance of reverse osmosis pilot desalination tests. The paper's findings are of interest to pressure-driven and osmotically driven processes.

2. Literature review

2.1. Solution-diffusion model

Relying on only two transport parameters, namely the molar solvent and solute permeabilities (A and B respectively), for effectively describing separations by nonporous membranes, the classic solution-diffusion (SD) model is far-reaching in RO, FO and PRO. Accordingly, the solvent and the solute are transferred across the membrane in an uncoupled way. Their relative separation results from their difference of solubility and diffusivity in the membrane material [8,9,12,26,42]. The molar

fluxes (N) of solvent (subscript v) and solute (subscript s) are directly proportional to their driving forces, respectively the net difference between the transmembrane hydrodynamic pressure difference (ΔP) and transmembrane osmotic pressure difference ($\Delta \Pi$), and the solute concentration difference (ΔC) between the membrane feed and filtrate sides:

$$N_v = A(\Delta P - \Delta \Pi) \tag{1}$$

$$N_s = B(\Delta C). \tag{2}$$

Alternatively to Eq. (1), the volumetric transmembrane solvent flux, J_v, can be defined as

$$J_v = I^{-1}(\Delta P - \Delta \Pi) \tag{3}$$

from what, by writing $\hat{V}_v$ for the solvent molar volume,

$$I^{-1} = \hat{V}_v A. \tag{4}$$

The van't Hoff's law is a typical osmotic pressure law in the water desalination field:

$$\Pi = iRTC \tag{5}$$

where i designates the number of dissociated ionic or neutral units per unit of solubilized solute ($i = 2$ for NaCl), R the ideal gas constant and T the temperature of the solution.

In the following, we review the experimental methods applied for the determination of the membrane solute and solvent permeabilities.

2.2. Permeability determination in pressure-driven filtration

2.2.1. Solvent permeability

I^{-1} is generally determined with Eq. (3) from the slope of a plot of J_v as a function of ΔP in the course of a "filtration" of pure solvent, i.e., when $\Pi = 0$ [3,7–10,12–23,39–41]. Such tests are also performed when new membrane samples are conditioned prior to their end-use in order to remove preservatives [41] and to allow for membrane compaction [39,40] and porosity changes [20], which all cause flux and selectivity modifications. However, standardized conditioning procedures are uncommon [39,41]. Moreover, it is difficult to correlate the operating conditions of the conditioning phase (e.g. the maximal applied pressure and the duration) with the operating conditions set for the membrane's end-use.

2.2.2. Solute permeability

The solute permeability is also mostly determined in the course of some pressure-driven crossflow filtration of a feed solution [3,7–10, 13–19,22–25]. For a given set of operating conditions, B may be fitted to linear relations derived from membrane transport models relating it to experimental crossflow filtration data, like the permeate (filtrate) flux and the solute rejection rate, RR. For the SD model [13]:

$$\frac{1}{RR} = \frac{1}{RR_{\Delta P \to \infty}} + \left(\frac{B}{RR_{\Delta P \to \infty}}\right)\frac{1}{J_v} \tag{6}$$

where

$$RR = 1 - \frac{C_l}{C_u} \tag{7}$$

where u and l denote the upstream (feed side) and downstream (permeate side) membrane-liquid interfaces, and $RR_{\Delta P \to \infty}$ is the limiting value attained by RR for very high J_v when $\Delta P \to \infty$. For a perfect SD-membrane, $RR_{\Delta P \to \infty} = 1$. In reality, an asymptotic value in the range 0.9–0.99 for dense membranes (rationalized as σ, the Staverman