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# Analysis of solvent flux through nanofiltration membranes by mechanistic, chemometric and hybrid modelling

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## Abstract

This paper addresses the modelling of the transport of solvents through nanofiltration (NF) membranes. Experimental data generated by the authors and collected from other published studies of 32 different solvent–membrane systems was used for comprehensive model validation. It was found that the most used mechanistic models are not sufficiently general to cover such a wide range of membrane–solvent systems. A set of alternative membrane and solvent descriptors was defined based on published studies, in order to improve the modelling of this system. Since the relationship between the solvent flux and the new selected descriptors is currently not known or poorly known at the mechanistic level, alternative chemometric and hybrid chemometric–mechanistic modelling methodologies were adopted. The main results that can be withdrawn from this study are the following. The analysis of the data by Projection to Latent Structures (PLS) showed that solvent flux through NF membranes could be mainly related to bulk solvent properties such as viscosity and density, and to membrane MWCO. The solvent–membrane systems were classified into clusters of systems with similar properties on the basis of the two most important latent variables. Among the model structures studied, the hybrid solution-diffusion/PLS model was determined to be the best approach for predicting solvent permeability data. For this latter model, the analysis of descriptors contribution showed that the dipole moment, Hildebrand solubility parameter, dielectric constant and ellipsoidal ratio were able to capture up to 40% of variance of the solution-diffusion model residuals. Among these the dipole moment introduced the highest improvement. This model can be further improved by designing new experiments outside the identified membrane–solvent clusters.

*Keywords:* Solvent nanofiltration; Solution-diffusion; Chemometrics; Projection to Latent Structures (PLS); Artificial Neural Networks (ANN); Hybrid modelling

## 1. Introduction

Solvent resistant nanofiltration has been receiving increasing attention due to its potential in dealing with complex separations while allowing for energy and cost savings. Possible applications concern processing of various streams from the petrochemical, fine chemistry and pharmaceutical industries for recovering and recycling of catalysts and organic solvents.

While the fundamentals of water permeation through nanofiltration (NF) membranes are relatively well established, the transport of organic solvents is still not well understood. This situation is due to the use of a wide range of rather distinct membrane–solvent systems with different physical and chemical properties: the membranes used are either hydrophilic or hydrophobic, and their structure and density depend on the degree of cross-linking; additionally, solvent properties such as viscosity, molar volume, and dielectric constant, can vary over a wide range of values.

Three different mechanistic approaches are most frequently applied in describing organic solvent flux through NF membranes: the solution-diffusion approach [1,2], in which the transport of a solvent is assumed directly proportional to its chemical-potential gradient across the membrane; the pore-flow approach [3], in which solvent transport is related to a pressure-driven convective flow through hypothetical membrane pores; and the resistances-in-series approach [4], which assumes that the overall resistance for permeation of solvent molecules through a membrane can be represented by addition of individual resistances.

The general applicability of the pore-flow model to organic solvent nanofiltration has been questioned by some authors [3,5]. Nevertheless, it has been successfully used in specific situa-

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tions, as for example to describe the permeation of alkanes and cyclic compounds through a polydimethylsiloxane (PDMS) NF membrane [6]. The results suggest that in this case the solvent transport could be adequately described by the Hagen-Poiseuille equation.

A resistances-in-series approach was presented by Machado et al. [4], which accounted for viscous transport through the NF and UF (ultrafiltration) membrane layers and for solvent sorption in the membrane top-layer by including a term directly proportional to the surface tension difference between the solvent and the NF membrane top-layer. This approach was shown to adequately describe experimental data (acetone/alcohols and acetone/paraffin binary mixtures) obtained with a hydrophobic MPF-50 solvent-resistant membrane (PDMS-based membrane manufactured by Koch Membrane Systems, USA). However, it could not accurately describe the data obtained for acetone/water binary mixtures.

The solution-diffusion model is currently the most widely used mechanistic formalism for describing organic solvent permeation through NF membranes. Bhanushali et al. [7] suggested the use of a simplified version of the solution-diffusion model for hydrophobic membranes. This approach uses physical properties of the solvent (viscosity and molar volume) as well as membrane descriptors (surface energy and solvent sorption). The model was able to describe with reasonable accuracy experimental data (alcohols and alkanes) obtained with membranes D and DS11AG (GE Osmonics, USA) [7] as well as the data obtained by Machado et al. [4] for the MPF-50 membrane. Stafie et al. [8] applied the solution-diffusion model to the permeation of hexane/sunflower oil and hexane/polyisobutylene binary mixtures through a PAN/PDMS composite membrane. Geens et al. [9] proposed a modification of the model presented by Bhanushali, by introducing surface tension data of both membrane and solvent. This modified model was fitted to experimental data (mostly water/alcohols binary mixtures) obtained for seven different NF membranes (MPF-50, MPF-44, Desal 5DK, Desal 5DL, N30F, NF-PES-10 and SolSep-030505) and the results were compared with those obtained with other modelling approaches, including the pore-flow model and the resistances-in-series approach. Silva et al. [3] compared the applicability of the solution-diffusion and pore-flow methodologies in nanofiltration of ethyl acetate/toluene and methanol/toluene binary mixtures using a SM-122 solvent-resistant NF membrane (W.R. Grace and Co., USA). They concluded that the solution-diffusion model provided the best description for their experimental data.

In spite of the successful application in some particular cases, the currently used mechanistic modelling methodologies are not sufficiently general to cover a wide range of membrane–solvent systems. Possible causes are that relevant properties of solvent mixtures and membranes are not considered by these models.

In the present work, we develop a modelling approach valid for a wide range of solvent–membrane systems. The methodology followed consists of the use of selected physical properties of solvents and membranes, which were considered relevant to determine solvent permeation through NF membranes. Since the mechanisms behind such relationships are not entirely known, chemometric techniques were first used for their identification. Then, the chemometric models were combined with the available mechanistic models in hybrid structures. These structures allowed to investigate which solvent and membrane properties could decisively improve the accuracy of existing mechanistic models. Such results may be valuable for guiding on the formulation of improved mechanistic models for solvent permeation through NF membranes. To fulfil these objectives, experimental data obtained in this study and collected from the literature, have been analysed.

## 2. Mathematical modelling of solvent nanofiltration

### 2.1. Mechanistic models

The predictive capacity of the solution-diffusion model and the pore-flow model was compared using experimental data available in the literature. The solution-diffusion model proved to be more accurate when compared to the pore-flow model (analysis not shown in this work). The resistances-in-series approach was not considered in this study due to physical inconsistencies reported by Machado et al. [4].

#### 2.1.1. Solution-diffusion model

The solution-diffusion model assumes that the pressure inside the membrane polymer is uniform and that the driving force for solvent transport is the chemical potential gradient across the membrane [1,2]. For a binary solvent mixture, the solution-diffusion model can be expressed by:

$$J_1 = \frac{P_{1,\mathrm{m}}}{\rho_1}\left(w_{1,\mathrm{f}} - w_{1,\mathrm{p}} \exp\left(-\frac{\bar{V}_1\,\Delta p}{RT}\right)\right) \tag{1}$$

$$J_2 = \frac{P_{2,\mathrm{m}}}{\rho_2}\left(w_{2,\mathrm{f}} - w_{2,\mathrm{p}} \exp\left(-\frac{\bar{V}_2\,\Delta p}{RT}\right)\right) \tag{2}$$

where $J_i$ is the volumetric flux of component $i$, $\rho_i$ its density $P_{i,\mathrm{m}}$ its mass permeability, $w_i$ its mass fraction in the feed, f, and in the permeate, p, $\bar{V}_i$ its partial molar volume, and $\Delta p$ is the pressure difference between the feed and the permeate compartments.

### 2.2. Chemometric models

Several multivariate chemometric models were employed in this work, namely Projection to Latent Structures (PLS), Artificial Neural Networks (ANN), and a combination of Principal Component Analysis (PCA) with ANN. The goal of using multivariate analysis is twofold: to identify correlations between the properties of interest and to obtain a quantitative relationship between the correlated properties. In the present case, the ultimate goal is to identify and relate independently-determined solvent and membrane descriptors with the membrane permeability regarding a defined solvent or solvent mixture.

#### 2.2.1. Projection to Latent Structures (PLS)

PLS [10–13] is a multivariate linear regression methodology, based on the decomposition of the data into a set of orthogonal