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# The averaged potential gradient approach to model the rejection of electrolyte solutions using nanofiltration: Model development and assessment for highly concentrated feed solutions

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ABSTRACT

Some of the recent publications in nanofiltration modelling converge on the importance of dielectric effects and numerous models have been developed in order to take them into account. However several works reported lately in the literature suggest a screening of image charges effect at high electrolyte concentration and the predominance of the Born effect, due to the change of dielectric constant inside the confined nanopore regarding that of the feed solution. In pursuit of an exhaustive and simple model for nanofiltration, a new approach is developed that account for both dielectric phenomena. Based on the Steric, Electric and Dielectric Exclusion (SEDE), the introduction of an average potential gradient approximation is shown to greatly improve the computational performance of the model without being detrimental to its predictive accuracy. The results obtained with this simplified model (SEDE-APG) are compared to the original SEDE model and an excellent agreement is obtained even in the case of electrolyte mixtures. Ultimately this model is confronted to experimental data of separation obtained for moderately to highly concentrated feed flows and exhibits promising results.



## 1. Introduction

Since 1970s, the field of pressure-driven separation techniques has been push forward by the increasing exigencies of efficiency, prevailing as a cheap, sustainable and reliable solution for separation or concentration operations [1]. The growing need for a technology coupling the high retention rate of reverse osmosis (RO) with the moderate pressure difference used in ultrafiltration (UF) led to the development of nanofiltration (NF), a promising technique which already found applications at industrial scales [2].

The majority of the nanofiltration membranes are polyamide thin-film composite (TFC) [3]. The preparation of those membranes is mainly operated through interfacial polymerisation (IP) on an appropriate microporous support, which is fixed on a woven or non-woven reinforcing layer. The IP is usually realised by in-situ polycondensation on the microporous support [4]. Hence, several factors, inherent to the operating conditions, as well as the choice of the microporous support [5–7], are likely to affect the physic-chemical properties of the active layer. Therefore, the issue of characterisation of the polyamide layer has been addressed in several publications [5,8–11] in order to improve the understanding of the selectivity and permeability processes through this layer.

Even though the rejection of ions can be convincingly modelled by a simple Donnan equilibrium approach in the case monovalent ion solution [12] or for sufficiently large pore [13], the high selectivity regarding multivalent ions, typically observed in the pore range of nanofiltration [14], remains poorly explained by this traditional approach which often relies in inconsistent fitting values for charge densities [15,16] or thickness over porosity ratio [17–19]. A convincing way to address these shortcomings could be to introduce the influence of dielectric effects. The impact of dielectric effect in ion exchange membranes has been firstly stressed by Glueckauf [20] before being roughly considered by Fane et al. [21] and further reviewed and analysed by Yaroshchuk [22], who pointed out its potential importance, as well as the difficulty to quantify its actual contribution. Later, the development of the DSPM&DE model by Vezzani and Bandini [14,23], on the basis of the DSPM model introduced by Bowen and co-workers [16,17,24,25], allowed to take into account the dielectric exclusion resulting from the difference between the dielectric constant of the membrane matrix and the one of the solution – considered as unique in the bulk and inside the confined nanopores. More recently, by developing a steric, electric and dielectric exclusion

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**Notations**

| | |
|---|---|
| $A_k$ | membrane porosity |
| $c_i(0^-)$ | charge of the ion $i$ on the permeate side (mmol $L^{-1}$) |
| $\overline{c_i}(z)$ | concentration profile along the pore (mmol $L^{-1}$) |
| $c_i(\Delta z^+)$ | charge of the ion $i$ on the retentate side (mmol $L^{-1}$) |
| $C_f$ | feed concentration (mmol $L^{-1}$) |
| $d_h$ | hydraulic diameter (m) |
| $D_{i,\infty}$ | bulk diffusion coefficient for the ion $i$ ($m^2$ $s^{-1}$) |
| $q$ | elementary charge (C) |
| $E(z)$ | electric potential inside the pore (V $m^{-1}$) |
| $F$ | Faraday constant (C $mol^{-1}$) |
| $j_i$ | molar flux density of ion $i$ (mol $m^{-2}$ $s^{-1}$) |
| $J_v$ | permeate volumetric flux (m $s^{-1}$) |
| $k_B$ | Boltzmann constant (J $K^{-1}$) |
| $k_m$ | mass transfer coefficient |
| $K_{i,c}$ | convection hindrance factor for the ion $i$ |
| $K_{i,d}$ | diffusion hindrance factor for the ion $i$ |
| $L_p$ | pure water permeability |
| $Pe_i$ | Peclet number for the ion $i$ |
| $r_{i,cav}$ | cavity radius of ion $i$ (m) |
| $R$ | universal gas constant (J $K^{-1}$ $mol^{-1}$) |
| $Re$ | Reynolds number |
| $R_{app}$ | apparent rejection |
| $R_i$ | intrinsic rejection |
| $Sc$ | Schmidt number |
| $S_y$ | least square objective function |
| $T$ | temperature (K) |
| $X(z)$ | charge distribution along the pore (mmol $L^{-1}$) |
| $X_{avg}$ | average charge along the pore (mmol $L^{-1}$) |
| $z$ | axial position along the pore (m) |
| $z_A$ | thickness over porosity ratio (m) |
| $z_i$ | charge of the ion $i$ |

*Greek letters*

| | |
|---|---|
| $\alpha$ | ratio between chloride concentration and sulphate concentration |
| $\alpha_i$ | ratio between the Bjerrum length and the pore size |
| $\gamma_i$ | activity coefficient for the ion $i$ |
| $\eta$ | dynamic viscosity of water |
| $\Lambda_{i,(0^-\|0^+)}$ | partition coefficient at the pore inlet for the ion $i$ |
| $\Lambda_{i,(\Delta z^-\|\Delta z^+)}$ | partition coefficient at the pore outlet for the ion $i$ |
| $\Delta P$ | applied pressure gradient (Pa) |
| $\Delta W'_{i,Born}$ | Born solvation energy barrier for the ion $i$ (scaled on $k_BT$) |
| $\Delta W'_{i,Im(0^-\|0^+)}$ | solvation energy barrier due to image forces for the ion $i$ at the pore inlet (scaled on $k_BT$) |
| $\Delta W'_{i,Im(\Delta z^-\|\Delta z^+)}$ | solvation energy barrier due to image forces for the ion $i$ at the pore outlet (scaled on $k_BT$) |
| $\Delta z$ | pore length (m) |
| $\Delta\pi$ | osmotic pressure difference (Pa) |
| $\Delta\bar{\psi}$ | potential variation inside the pore (V) |
| $\Delta\psi_{D,(\Delta z^-\|\Delta z^+)}$ | normalised Donnan potential at the pore outlet |
| $\Delta\psi_{D,(0^+\|0^-)}$ | normalised Donnan potential at the pore outlet |
| $\Delta\overline{\psi}_N$ | normalised average potential variation inside the pore |
| $\varepsilon_0$ | vacuum permittivity ($J^{-1}$ $C^2$ $m^{-1}$) |
| $\varepsilon_b$ | dielectric constant of the bulk |
| $\varepsilon_m$ | dielectric constant of the membrane matrix |
| $\varepsilon_p$ | dielectric constant inside the pore |
| $\mu$ | effective reciprocal dimensionless screening length |
| $\phi_i$ | steric partition coefficient |
| $\bar{\psi}(z)$ | electric potential along the pore (V) |

(SEDE) model, Szymczyk and Fievet added a stone to the edifice of dielectric effects modelling in nanofiltration processes [26]. It notably includes, in a coherent framework, both the exclusion resulting from the difference of dielectric constant between the bulk and the solution confined in the nanopores – the so-called Born effect, and the one resulting from the difference between the dielectric constant of the membrane matrix and of the electrolyte solution – the so-called image effect.

If the influence of the latter has already been submitted to specific theoretical investigations [22,27], the former, namely Born effect, has recently drawn more attention owing to the simplicity of its computation and its ability to accurately render specific behaviours observed in nanofiltration, and notably the high selectivity regarding multivalent ions. The works of Oatley et al. and, before, that of Bowen & Welfoot have been introducing a two parameter model assuming Born partition to be the only dielectric phenomenon involved at the pore interfaces [16,28–31]. Their approach, involving the study of rejection at the isoelectric point of the membrane and the assumption of screened image forces at high charge densities, has shown to be successful. However this latter assumption is only backed by qualitative considerations, and is all the more questionable as the charge of the membrane is compensated at the point of zero charge.

As a matter of fact, recent computer experiment confirmed the effect of nanoconfinment on the dielectric constant of water and aqueous solutions [32–35]. At the same time, the extensive studies carried out on the theoretical influence of image charges clearly stress their theoretical significance [22,26,27,36] and some experimental results also point towards the importance of taking the low dielectric constant of the membrane matrix into account [37]. Although the overlapping between dielectric and electrostatic effects makes it difficult to accurately assess the share of each in the rejection process, it is herein acknowledge that, *a priori*, the rejection mechanism is a conjunction of steric, electrostatic and dielectric effects.

Recognizing the need for a tool equally simple and exhaustive for NF modelling, this work explores a simplified approach to assess the actual rejection of electrolyte solutions considering the influence of dielectric effects. First, by considering the rejection of electrolytes through homogeneously charged membranes, it is shown, through a study of the electric field along the pore, that it is possible to linearly approximate the potential gradient. Consequently, a simplified model is deduced (SEDE-APG for Averaged Potential Gradient) and compared to the original SEDE model. The results obtained with the former show excellent agreement with those provided by the original model. Moreover it proves to be less resource consuming and faster in terms of computation. Ultimately this simplified model is confronted to experimental data from the literature in order to critically discuss the theoretical contribution of dielectric effects in nanofiltration prediction.

## 2. Theoretical background

NF membrane is assumed to be a matrix of identical pores, characterised by their half-size $r_p$ and their thickness $\Delta z$ as depicted in Fig. 1. The study of concentration polarisation being beyond the scope of this work, the external solution is assumed to be ideal and perfectly stirred, so that this phenomenon can be disregarded throughout the development of the model. The system considered is isothermal at 298 K.