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Experimental and theoretical study of nanofiltration of weak electrolytes: $SO_4^{2-}/HSO_4^{-}/H^{+}$ system

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ABSTRACT

Over recent years, nanofiltration (NF) has been considered as an effective way to improve processing steps in metallurgical and hydrometallurgy applications dealing with mixtures of metal ions in sulphuric-acid-dominated solutions. The principal advantage of NF membranes over reverse osmosis (RO) membranes is their ability to allow for a practically free passage of acid, while metallic species, especially multi-charged species, are efficiently rejected. In general, these sulphuric solutions cover a range from strongly acidic solutions with pH below 1 up to moderately acidic solutions of pH 3. Over this range, changes in the feed acidity influence both the aqueous electrolyte solution speciation ($SO_4^{2-}/HSO_4^{-}/H^{+}$) and the membrane acid–base properties (protonation of carboxylic and amine groups). However, few studies have been published on the trans-membrane transport of inorganic species coupled to changes in their speciation as well as to the properties of the membrane phase.

In this study, experimental data on the sulphuric acid rejection for pH values from 1 to 3 have been obtained with an aromatic poly(piperazine)amide membrane (NF270) at various trans-membrane pressures. The results were modelled by a novel version of the Solution-Electro-Diffusion model taking into account equilibrium reactions, and a general (quasi)analytical solution was obtained for the transport of weak electrolytes of arbitrary valence type. The equilibrium weak acid reaction made the total sulphate (SO_4^{2-}/HSO_4^{-}) rejection decrease strongly as the fraction of single-charged hydrogen sulphate (HSO_4^{-}) in the feed increased. From the modelling procedure, permeances to H^{+}, HSO_4^{-} and SO_4^{2-} over the studied pH range were determined.

1. Introduction

Sulphuric acid is one of the most produced chemicals worldwide. In the past the scale of its production was even used as an indicator of industrial strength. Nowadays, sulphuric acid is still widely used in a large number of applications (e.g. mineral processing, hydrometallurgy and for pH control). In the mining industry, it is used as a leaching agent to dissolve minerals for metal extraction [1]; sulphuric acid is also used in electroplating and acid pickling in the metal-finishing industry [2]. In both cases, a large amount of effluent is generated. However, new environmental legislation promotes sustainability and sulphuric acid recovering technologies. Therefore, as an alternative to neutralisation/precipitation, several techniques, such as electrolytic deposition, ion exchange, diffusion dialysis, electrodialysis, solvent extraction [2–5] and more recently pressure-driven membrane processes, have been applied to treat these effluents. Among them, nanofiltration (NF) offers unique opportunities for acid purification. Typically, NF membranes show low rejection of acids, but high rejection of multivalent ions. As the acid rejection is low, its concentrations on both sides of the membrane are close to each other. Accordingly, the contribution of acid to the differential osmotic pressure is very limited [6]. Then, in comparison with the techniques listed above, it has relatively low energy consumption.

The use of NF for removing metal ions from acidic solutions has been previously studied [7–13]. Nyström et al. [10] separated metal (iron, chromium and nickel) sulphates and nitrates from acidic media achieving high rejections (around 99%) with an NF-45 membrane. González et al. [12] tested several reverse osmosis (RO and NF membranes in the treatment of concentrated phosphoric streams (from 2 to 8 M). NF allowed to obtain higher flows and higher acid permeations than did RO. However, the metal rejection in RO was a little higher than in NF. Skidmore and Hutter [13] patented a process for

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Nomenclature

c_i	Concentration of component i inside the membrane	P_i	Membrane permeability to ion i
c_{ip}	Concentration of component i in permeate side	P_i^*	Membrane permeance to ion i
j_i	Ion flux	pK_a	Acidity constant
J_v	Trans-membrane volume flow	x	Dimensionless position in the membrane
L	Membrane thickness	z_i	Ion charge
		α	Equilibrium dissociation constant
		φ	Dimensionless electric potential in the membrane

purification of phosphoric acid by NF. High rejections of multivalent ions (Al(III), Fe(III), Mg(II)) were observed. Thus, the typically high ion concentration of strongly acidic solutions, which may restrict the use of other membrane techniques, can be overcome with nanofiltration.

Modelling of ion rejection in NF is useful for the process optimisation and scale-up. Ion transport through NF membranes has been widely described by either non-equilibrium thermodynamic models [14–17] or extended Nernst–Planck equations [18–21]. Among various approaches, Yaroshchuk et al. [22] demonstrated that, for single salts, the Solution-Diffusion-Film (SDF) model is applicable, and later it was extended to electrolyte mixtures by including the coupling between the electro-diffusion fluxes of various ions via the electric field of the membrane potential [23–25]. Taking this into account, a good description of ion rejection dependence on the trans-membrane volume flow was achieved for a number of electrolyte mixtures consisting of one dominant salt and trace ions [24,25]. This approach also accounts for the existence of a concentration-polarisation layer where the ion transfer occurs via electro-diffusion and convection. This description of trans-membrane mass transfer by the so-called Solution-Electro-Diffusion-Film (SEDF) model allows for efficient determination of membrane permeances to single ions from experimental data. However, to date only limited attempts have been reported to describe membrane transport of solutes being in chemical equilibrium with other solutes (e.g. anions with acid/base properties, or ions with complexing properties) [7,26]. This is the case with the sulphuric acid solutions where, at pH values close to the pK, HSO_4^- and SO_4^{2-} species are present in commeasurable concentrations. In order to model these results, the equilibrium reaction must be accounted for in the model. By using the solution–diffusion model, Nir. et al. [27,28] considered proton and hydroxyl ions as traces in RO, taking into account the chemical equilibrium between them. Niewersch et al. [29,30] modelled numerically the trans-membrane ion fluxes under high-acidity conditions in NF. In this paper we present a novel quasi-analytical approach to the modelling of NF transport in a system of three components, coupled by an equilibrium chemical reaction. For simplicity, in this study we neglected the concentration polarisation phenomena in the first approximation.

Another objective of this work is to extending the validation of the Solution-Electro-Diffusion model towards the transport of reacting species via comparison with experiment. A wide pH range was used in order to explore the effect of changes in the acid–base equilibrium of the membrane functional groups, and to evaluate the effect of incomplete acid dissociation. The experiments were carried out using an NF270 membrane in a cross-flow experimental set-up. The results of these measurements have been interpreted in terms of ionic permeances of the membrane to HSO_4^-, SO_4^{2-} and H^+.

2. Reactive transport of ions in nanofiltration membranes: model formulation

The ion fluxes are described according to the Solution-Electro-Diffusion model. One of the assumptions of this model is that there is no coupling between solute and solvent flows inside the membrane or, in other words, reflection coefficients are assumed to be equal to one for all species. The model uses 'virtual' concentrations, which are defined as those in a solution that could be in thermodynamic equilibrium with an infinitely small volume inside the membrane. 'Virtual' concentrations satisfy the chemical-equilibrium condition with the bulk association constant. The partitioning coefficients, which quantify the ratios between the real and virtual species concentrations in the membrane (and possible changes of association constant there) are included in the ion permeances [24]. The ion transport is described by Eq. (1).

$$j_i = -P_i \cdot c_i \cdot \left(\frac{dlnc_i}{dx} + z_i \cdot \frac{d\varphi}{dx}\right) \tag{1}$$

where j_i (mol/m^2 s) is the trans-membrane volume flow of component i; P_i is the membrane permeability to ion i; c_i and z_i stand for its virtual concentration and its charge, respectively; ϕ is the dimensionless virtual electrostatic potential and x is the position across the membrane.

The transport of ions is:

- Subjected to the zero-current condition defined by Eq. (2).

$$\sum_i z_i \cdot j_i = 0 \tag{2}$$

- Subjected to the electro-neutrality condition in the virtual solution defined by Eq. (3):

$$\sum_i z_i \cdot c_i = 0 \tag{3}$$

- Virtual ion concentrations are not independent but related by a chemical equilibrium condition at a given constant temperature and ionic strength ($\alpha = 10^{pK_a}$), where pK_a is the acidity constant, defined by Eq. (4):

$$c_3 = \alpha \cdot c_1 \cdot c_2 \tag{4}$$

It should be stressed that the chemical reaction is subjected to charge conservation ($z_3 = z_1 + z_2$).

By using Eqs. (1) and (2) for a system of three ions (e.g. H^+, HSO_4^-, SO_4^{2-}) an expression for the gradient of electrostatic potential in virtual solution can be derived (Eq. (5)):

$$\frac{d\varphi}{dx} = -\sum_i \left(\frac{t_i}{z_i}\right) \cdot \frac{dlnc_i}{dx} \tag{5}$$

where t_i is the transport number of ion 'i' defined by Eq. (6):

$$t_i = \frac{z_i^2 \cdot P_i \cdot c_i}{\sum_j z_j^2 \cdot P_j \cdot c_j} \tag{6}$$

From the chemical equilibrium condition, a relationship can be obtained between the derivatives of logarithms of concentrations of the species described by Eq. (7):

$$\frac{dlnc_3}{dx} = \frac{dlnc_1}{dx} + \frac{dlnc_2}{dx} \tag{7}$$

By combining the chemical equilibrium and electro-neutrality conditions (in the virtual solution) this could be obtained:

$$\frac{dlnc_2}{dx} = \frac{1}{1+\alpha \cdot \left(1+\frac{z_1}{z_2}\right) \cdot c_1} \cdot \frac{dlnc_1}{dx} \tag{8}$$

Due to the chemical reaction, the trans-membrane ion fluxes of all three components are not conservative (they change across the membrane). However, owing to the reaction stoichiometry, exactly the same