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Modelling non-stationary ion transfer in neutralization dialysis

A. Kozmai[c], M. Chérif[a,b], L. Dammak[a], M. Bdiri[a], C. Larchet[a], V. Nikonenko[c,*]

[a] Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182 CNRS – Université Paris-Est Créteil, 2 Rue Henri Dunant, 94320 Thiais, France
[b] Laboratoire de Sciences des Matériaux et de l'Environnement (MESLAB), Université de Sfax pour le Sud, Route de la Soukra km 4 – BP no. 802, 3038 Sfax, Tunisia
[c] Membrane Institute, Kuban State University, 149 Stavropolskaya Street, 350040 Krasnodar, Russia

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ABSTRACT

A non-steady state theoretical model is developed using the Nernst-Planck equations in order to study ion transport kinetics through Ion-Exchange Membranes (IEMs) during water desalination by Neutralization Dialysis (ND) in batch mode. The ND cell under study involves three compartments (acid, saline, and alkali) separated by two membranes (a cation-exchange and an anion-exchange ones) assumed ideally permselective and homogeneous. The presence of Diffusion Boundary Layers (DBLs) at the membrane-solution interface is taken into account in the saline compartment. The results of numerical simulation are compared with known experimental data. A good agreement is obtained between experimental and theoretical values representing the pH and the conductivity of the saline circulating solution as functions of time. These experimental results are also compared with the calculations made using the quasi-steady state model developed by Denisov et al. [10]. It is shown that the quasi-steady state approach is not applicable at the beginning of the ND process, during a few tens of minutes, where the concentration profiles in the membranes are far from linear. Within this stage, a few pH fluctuations are possible, while only one or two pH fluctuations occurs in the quasi-steady stage. The mechanism of these fluctuations, which are determined by the periodical change of the "leadership" between the cation-exchange and the anion-exchange membranes, delivering the H^+ and the OH^- ions into the saline solution, respectively, is discussed.

1. Introduction

The Neutralization Dialysis (ND) process was first suggested by Igawa et al. [1] for water desalination. It is based on the simultaneous use of two Donnan dialysis operations: one using acidic solution and a cation-exchange membrane (CEM) and the other one using alkaline solution and an anion-exchange membrane (AEM). The H^+ ions penetrate across the CEM and the OH^- ions penetrate across the AEM into the desalination compartment in exchange for the mineral ions initially present there, thus allowing the demineralization of the feed solution.

This method has certain advantages over existing methods such as Distillation [2], Nanofiltration [3], Reverse Osmosis [4] and Electrodialysis [5]. ND is not technically sophisticated, it demands low investment costs, it is characterized by low energy consumptions; its implantation is easy for isolated locations. Thus, ND can be considered as a promising membrane process convenient mainly to the developing countries, which suffer from the water lack but have access to ground and surface brackish waters [6].

Moreover, many studies [7–9] reveal the efficiency of ND process for desalination of solutions containing organic substances (mono- and oligosaccharides, polysaccharides, proteins). Different applications were considered such as separation of weak acids and bases [8], transport of glycine [9] and desalination of aqueous solutions of carbohydrates and milk whey [7].

However, this process is poorly studied both experimentally and theoretically. It is particularly difficult to maintain a predetermined value of pH of the product, while the applications require a specified value of pH [10–13]. Namely, for drinking water, the pH must be close to 7; for organic solutions, the desired value of pH depends on the form of the resulting product to be obtained. Moreover, low or high pH reduces the ion-exchange rate of desalination [13].

Apart from ND there are a number of other diffusion based membrane processes, such as diffusion dialysis, Donnan dialysis or reverse electrodialysis, which attract more and more attention. Besides, in electrodialysis (ED) concentration when the concentration gradients are significant, ion diffusion transport through the membrane must be taken into account. In the pulsed electric field mode of electrodialysis, during the pauses when the current does not flow, diffusion remains the only transport mechanism. In the great part of the mentioned above processes, transient diffusion is important. However, most of the known

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* Corresponding author.
E-mail addresses: dammak@u-pec.fr (L. Dammak), v_nikonenko@mail.ru (V. Nikonenko).

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theoretical models describing diffusion processes in membrane systems consider only steady or quasi-steady state diffusion. In particular, Denisov et al. [10] have proposed quasi-steady-state models for batch mode of ND; similar models for continuous and batch modes of ND were developed by Sato et al. [11]. The main quasi-steady state assumption is that the rates of the concentration profile formation in the solution and membranes are substantially greater than the rate of change in the inlet concentration.

In the present study, we propose a more comprehensive non-steady state mathematical model. This allows describing desalination process in conditions where the quasi-steady state assumption is not valid, especially in the beginning of the process (the first 10 or 15 min). In particular, we examine the impact of the initial state of membranes on the exchange rate. We show that in the conditions of the experiment carried out earlier [13], this initial state was important, and the correct description of its effect allowed us to obtain a good agreement between the theoretical and experimental results.

2. Theoretical

2.1. System under study

A system, consisted of three compartments filled with different solutions (HCl, NaOH and NaCl) separated by a cation- and an anion-exchange membranes, is studied (Fig. 1).

V^A, V^B and V^D are the volumes of acid, alkali (base) and saline (under desalination) solutions, respectively, circulating through the corresponding compartments and intermediate tanks. Upper indexes *A*, *B* and *D* correspond to acid, base and desalination compartments, respectively. δ is the diffusion boundary layer (DBL) thickness assumed the same near the CEM and AEM. CEM (of thickness d^c) and AEM (of thickness d^a) are supposed to be ideally selective (the co-ion transport is neglected), which is justified in relatively diluted solutions as used in this study. Indeed, the evaluation below shows that the co-ion flux under experimental conditions is about two orders of magnitude smaller than the counterion flux. The evaluation is carried out for the limiting case, where the membrane separates a 0.1 M NaCl solution and water. In this case, as it is known from literature [14,15], the diffusion permeability, *P*, of Neosepta AMX and CMX membranes is less than 10^{-8} cm^2 s^{-1}. The maximum value of the co-ion flux in the steady state through a CMX or AMX membrane in these conditions calculated using equation $J = P\Delta c/d$ [14,16] is about 5×10^{-8} mmol cm^{-2} s^{-1} (here Δc is the difference in the electrolyte concentration on both sides of the membrane, *d* is the membrane thickness). Even if we assume that in the case of HCl (CMX) and NaOH (AMX) the diffusion permeability would be one order of magnitude higher than in NaCl solution, the co-ion flux (5×10^{-7} mmol cm^{-2} s^{-1}) should be nearly 100 times lower than the counterion flux (which has the order of 10^{-5} mmol cm^{-2} s^{-1}, Fig. 2c).

Convective transport within the diffusion layers is neglected; it is taken into account implicitly by adjusting the DBL thickness. Longitudinal concentration changes along the channel are not taken into account. It is assumed that the ion concentrations in the bulk of compartment *D* and in the corresponding intermediate tank are the same. In conditions of the experiment described by Cherif et al. [13], these assumptions are justified by a short length of the cell (10 cm) and the pipes (60 cm) used in the hydraulic circuit, as well as a high velocity of solution flowing. Indeed, the time of solution passage through the *D* compartment (about 5 s) as well as that through the overall circuit (about 40 s) are small compared with the time of one experimental run. During 40 s, the concentration of NaCl in the circuit can change only by 0.4%, which is small compared to the concentration measurement error. Hence, the material balance equations are applied to the circulating solution of volume V^D as a whole.

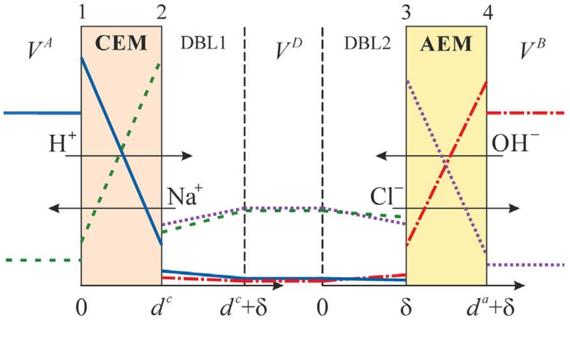

Fig. 1. Scheme of the system under study. Concentration profiles are shown schematically for H^+ (solid line), Na^+ (dashed line), OH^- (dash-dot line) and Cl^- (points) ions.

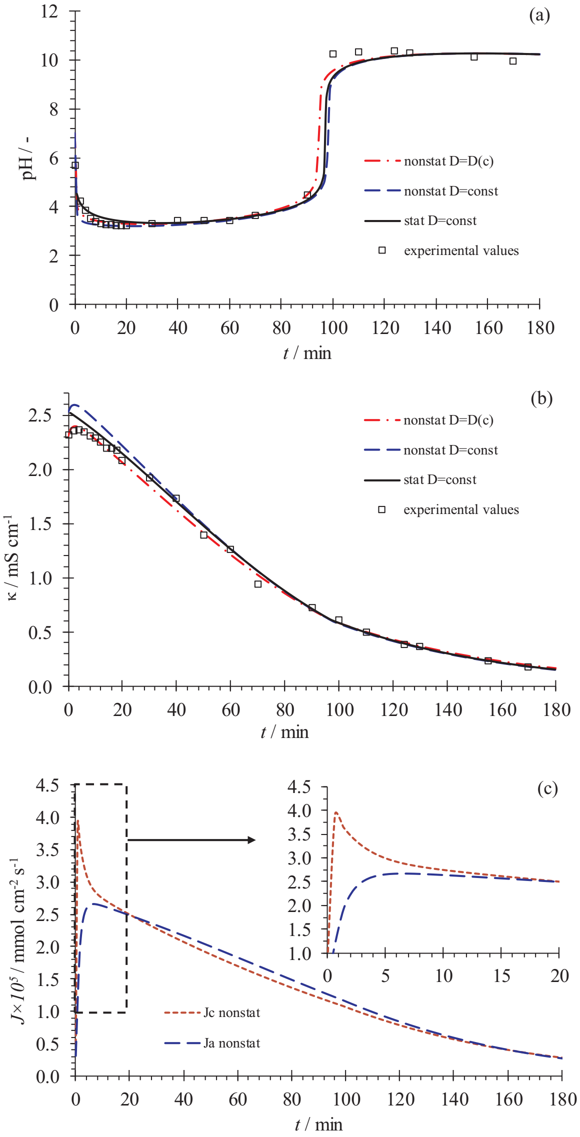

Fig. 2. Calculated (using non-steady state ("nonstat") and quasi-steady state ("stat") models) and experimental time-dependences of the saline solution pH (a) and conductivity (b) in the desalination compartment as well as flux densities (c) across the CEM (J^c) and AEM (J^a). The values of parameters used in both models are the same and listed in Table A3 of Annex 3. The prehistory of the membranes (see Section 3) were taken into account.

In the states close to the quasi-stationary one, ion fluxes across a membrane and two adjacent DBLs are close. As a consequence, concentration gradients as well as absolute variation of concentration in both DBLs adjoining the membrane should be close. In these conditions, the relative variation of concentration in the *A* or *B* compartments