



Batch electro dialysis of ammonium nitrate and sulfate solutions



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ARTICLE INFO

Article history:

Received 6 July 2015

Received in revised form

28 August 2015

Accepted 30 August 2015

Available online 3 September 2015

Keywords:

Batch electro dialysis

Ammonium nitrate

Ammonium sulfate

Current efficiency

Extended Nernst-Planck equation

ABSTRACT

Batch electro dialysis of ammonium nitrate and sulfate solutions at potentiostatic conditions was investigated using the PC SA and SK membranes. The influence of the initial concentration (0.3–1.5 M) and applied voltage (15, 20 V) on the current efficiency, CE, and minimal diluate concentration was investigated. It was found that for both salts the average CE was comparable and was in the range 67–80%, depending on the conditions. For the concentrate concentration not exceeding 0.8 M, the lowest diluate concentration was below 0.002, 0.005 M for sulfate, nitrate, respectively. In the final stage of electro-dialytic process, the correlation between the time dependence of the instantaneous CE and the changes of electric current and of potential drop on the membrane stack was analyzed. It was found that by estimating inflection point of these dependencies it is possible to find the moment of process when CE decreases and the energy consumption increases approximately twice. The concentration changes were fitted using the model based on the extended Nernst-Planck equation and ideal Donnan equilibrium. The results of each experiment were fitted with a very good accuracy, however, it was not possible to fit all the experimental results with one set of the model parameter values. The volume changes were satisfactorily approximated by a two parametric equation relating volume flux with electric current density and concentration difference. The effective electroosmotic coefficient referring to a membrane pair corresponds to ca. 6–8 mol of water per 1 F of electric charge passed through the membrane stack.

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1. Introduction

Electro dialysis (ED) is a membrane process driven by the electric force in which anion-and cation-exchange membranes alternately arranged and placed between two electrodes are used. With this technique one can decrease/increase ion concentration in solutions. Numerous applications of this technique can be found in [1–4].

The problem of utilizing wastewaters containing ammonium salts by the ED method has been investigated only by some authors [5–9]. The electro-electro dialysis process in which ammonium salt was splitted into acid and base was discussed in [5,6]. Gain et al. [5] treated the waters containing ammonium nitrate, produced in the nuclear fuel cycle, using the electro-electro dialysis and ED techniques. In the ED experiment, using the membranes CMV and AMV (Asahi Glass Co.), they obtained average current efficiency ca. 95%. During the process ammonium nitrate concentration in the diluate was reduced from 1 M to 0.0035 M, whereas the concentrate concentration increased from ca. 1 to 2.3 M. Lee et al. [7] investigated the removal of ammonium sulfate from lysine fermentation waste using NEOSEPTA membranes

(CMB, CM-1, AM-1, Tokuyama Corp.). The initial solution contained ca. 1 M NH_4^+ , 0.74 M sulfate, 0.3 M Cl^- , 0.2 M K^+ , and some amounts of Mg and Ca. Using CMB and AM-1 the authors removed ammonium down to 0.24 M with the current efficiency $CE=73\%$, whereas sulfates – to 0.15 M with $CE=83\%$. Siminiceanu and Cotet [8] performed ED of dilute ammonium sulfate solutions (ca. 0.09 M) at constant voltage using CMS and AMX Neosepta membranes. They conducted the process only ca. 0.5 h, therefore no significant decrease in sulfate concentration was obtained (≥ 0.03 M). No electric current was recorded and no estimation of the current efficiency was given. Yang et al. [9] treated ammonium sulfate solutions of rather low initial concentration (0.023–0.077 M) using CEM-2 and AEM-2 membranes of unknown origin. They investigated the influence of voltage, initial concentration, flow rate, and temperature on desalination performance, however there also no current efficiency was presented.

In this work we present the results on the electro dialytic (batch mode) desalination/ concentration of ammonium nitrate and sulfate solutions using the PC SA and SK membranes (PCA GmbH, Germany). We focus on the determination of the changes of instantaneous current efficiency, CE, during the ED process and the correlation with the changes of electric current and potential drop on the membrane stack. The influence of the initial concentration of solutions and applied voltage on CE is also shown.

The second aim of the paper is the quantitative description of

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the investigated process. There are numerous papers dealing with modeling of the ED process. One can mention the works by Tanaka [10–12], Kraaijeveld et al. [13], Fidaleo and Moresi [14–16], Gong et al. [17], Ortiz et al. [18], Kaláb and Palatý [19]. Different equations to model the membrane transport were used. The most demanding approach is that based on the Maxwell-Stefan equations [13], because the number of the Maxwell-Stefan diffusivities, which should be known, is large; e.g. for the system NH_4NO_3 -water-membrane it would be 6. Apart of the assumption that ion-exchange membranes are perfectly selective [20], the simplest approach is that based on the two-parameter Eq. (1) which is applied for the description of fluxes of solute and water or volume, J_i , referring to the ED cell pair [21,15,16]:

$$J_i = \frac{t_{i,\text{eff}}}{F} j - L_{i,\text{eff}} \Delta C_s \quad i = \text{solute, water, volume} \quad (1)$$

In Eq. (1), j is the electric current density, ΔC_s – concentration difference between concentrate and diluate, $t_{i,\text{eff}}$ – effective or overall transport number of a species i referring to the pair of cation- and anion-exchange membranes, $L_{i,\text{eff}}$ – effective permeability; the definition of both coefficients, $t_{i,\text{eff}}$ and $L_{i,\text{eff}}$, depends on the kind of flux J_i . Eq. (1) is justified by the linear equations of nonequilibrium thermodynamics [22]. Eq. (1) was extended by Tanaka [10] who added the terms representing the leakage of ions or solution arising from pinholes in the membranes and a pressure difference across the membranes. In modeling the ED of tartaric acid, Kaláb and Palatý [19] added a linear term with a diluate concentration; all the transport coefficients were determined experimentally. The model calculations become more complex when the changes of concentration and current density along the membrane surface (ED channel) [23,24] are incorporated into the model.

In our approach we will draw attention only to membrane transport described by the extended Nernst-Planck equation and Donnan equilibrium, similarly as in our previous works (e.g. [25,26]). The main goal of this modeling is examination to what extent the model parameters are influenced by the experimental conditions, like the initial solution concentrations, applied voltage, kind of electrolyte. To simplify the model calculations the average (observed) electric current and the concentrations on the outlet from the ED module will be used.

2. Membrane transport model

Taking into account the ED cell pair, the flux of ion i into the concentrate compartment is equal to:

$$J_i = J_i^{\text{CM}} - J_i^{\text{AM}} \quad z_i = 1, 2 \quad (2)$$

and the flux of salt $A_{\nu_1}B_{\nu_2}$ is given by:

$$J_s = (J_1^{\text{CM}} - J_1^{\text{AM}})/\nu_1 = (J_2^{\text{CM}} - J_2^{\text{AM}})/\nu_2 \quad (3)$$

where J_i^{AM} , J_i^{CM} are fluxes of i th ion through anion-, cation-exchange membrane, respectively, ν_i is the number of i th ions formed from 1 salt molecule. Using the equation relating the current density, j , to the ion fluxes:

$$j/F = z_1 J_1^\alpha + z_2 J_2^\alpha \quad \alpha = \text{AM, CM} \quad (4)$$

we can rearrange Eq. (3) and express J_s in terms of the counterions fluxes:

$$J_s = J_1^{\text{CM}}/\nu_1 - J_2^{\text{AM}}/\nu_2 - j/(Fz_1\nu_1) \quad (5)$$

where z_i is charge number of i th ions. The direction of J_2^{AM} is negative in our system. As it results from Eq. (3) or (5), it is not

possible to distinguish in J_s the contributions J_i^{CM} and J_i^{AM} . Therefore to model the membrane transport, only one set of parameters referring to a hypothetical membrane being a resultant of the cation- and anion-exchange membranes will be used. Choosing the hypothetical membrane to be e.g. anion-exchange one we can substitute J_1^{CM}/ν_1 by $(-J_2^{\text{AM}}/\nu_2)$ in Eq. (5) and model the transport through that membrane. For the description of the ion transport inside the membrane we choose the extended Nernst-Planck equation written in the form [25]:

$$J_i = -k_{m,i} D_i \left(\frac{d\bar{c}_i}{dx} + z_i \bar{c}_i \frac{F}{RT} \frac{d\bar{\phi}}{dx} \right) + \bar{c}_i J_v \quad i = 1, \dots, 4 \quad (6)$$

In Eq. (6), J_i and J_v are the ion, volume fluxes, respectively, referred to the unit membrane area, x is dimensionless coordinate, $x = \bar{x}/(\theta l_m)$, \bar{x} – coordinate associated with a pore, θ – pore tortuosity, equal to the pore length divided by the membrane thickness, l_m , D_i – reference diffusion coefficient of i -th ion, $\bar{\phi}$ – electric potential in the pore solution, F and R are Faraday and gas constant, respectively, T – absolute temperature, $k_{m,i}$ – combination of basic membrane parameters and the ion diffusivity ratio:

$$k_{m,i} \equiv \frac{1}{l_m} \frac{V_p \bar{D}_i}{\theta^2 D_i} \quad (7)$$

where \bar{D}_i is diffusion coefficient of i -th ion in a pore solution, V_p – volume fraction of pores. Next we assume that $\bar{D}_1/D_1 = \bar{D}_2/D_2$ and, consequently, $k_{m,1} = k_{m,2} = k_m$. Replacing $d\bar{\phi}/dx$ in Eq. (6) with the current density, j , using the relation $j = F(z_1 J_1 + z_2 J_2)$, we can transform Eq. (6) into:

$$\frac{d\bar{c}_2}{dx} = \frac{a_0 + \bar{c}_2(a_1 + \bar{c}_2 J_v)}{a_2 + a_3 \bar{c}_2} \quad (8)$$

where:

$$a_0 = -J_2 t_1 X_m / z_2$$

$$a_1 = (1 - t_1) j / (z_2 F) + X_m J_v / z_2 - J_2$$

$$a_2 = k_m D_s X_m z_1 / (z_1 z_2 - z_2^2)$$

$$a_3 = k_m D_s$$

$$D_s = D_1 D_2 (z_1 - z_2) / (D_1 z_1 - D_2 z_2)$$

$$t_1 = z_1 D_1 / (z_1 D_1 - z_2 D_2) \quad (9a-g)$$

In the derivation of Eq. (8) the electroneutrality condition, $z_1 \bar{c}_1 + z_2 \bar{c}_2 + X_m = 0$, was used, where $X_m = z_m \bar{c}_m$; z_m and \bar{c}_m denote the charge number and concentration of fixed charges, respectively. Although the ED experiments were performed at constant voltage, we assume that at a given moment the current is constant. Thus, in Eq. (8) it is possible to separate variables \bar{c}_2 and x and perform integration which yields:

$$\frac{a_3}{2J_v} \ln(a_0 + \bar{c}_2(a_1 + \bar{c}_2 J_v)) + \frac{(a_1 a_3 - 2a_2 J_v)}{\sqrt{a_1^2 - 4a_0 J_v}} \ln \left(\frac{1 + f(\bar{c}_2)}{1 - f(\bar{c}_2)} \right) \Bigg|_{\bar{c}_2 = \bar{c}_{2,d}}^{\bar{c}_2 = \bar{c}_{2,c}} = 1 \quad (10)$$

where $f(\bar{c}_2) = (a_1 + 2J_v \bar{c}_2) / \sqrt{a_1^2 - 4a_0 J_v}$. The concentrations $\bar{c}_{2,d}$ and $\bar{c}_{2,c}$ are connected to the external concentrations at the membrane surface, $c_{s,d}^{(m)}$ and $c_{s,c}^{(m)}$, by the ideal Donnan equation:

$$\bar{c}_1^{\nu_1} \bar{c}_2^{\nu_2} = \nu_1^{\nu_1} \nu_2^{\nu_2} c_s^{\nu_1 + \nu_2} \quad (11)$$

Because of the concentration polarization at the membrane surfaces, $c_{s,d}^{(m)}$ and $c_{s,c}^{(m)}$ are related to the bulk concentrations, $c_{s,d}$

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