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# Transport of nitric acid through anion-exchange membrane in the presence of sodium nitrate

Zdeněk Palatý*, Helena Bendová

*Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

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ABSTRACT

Simultaneous transport of nitric acid and sodium nitrate has been investigated in a batch cell with an anion-exchange membrane Neosepta-AFN. The transport of the individual components has been quantified by four phenomenological coefficients, which have been determined by the numerical integration of basic differential equations describing the time dependences of acid and salt concentrations in the low concentration compartment. This integration has been followed by an optimizing procedure. Using all the experimental data obtained at various initial concentrations of both components it has been found that the phenomenological coefficients are strongly dependent upon the concentrations of both components in the membrane.

## 1. Introduction

Dialysis and diffusion dialysis, which serve to separate liquid mixtures, are mostly studied in a two-compartment cell with stirrers. During the measurements at unsteady state, it is possible to obtain a series of experimental points, from which various transport characteristic of the membrane/solution system, such as the overall dialysis coefficient, the permeability of the membrane, the membrane mass transfer coefficient and diffusivity of the component, can be determined.

The investigation of the dialysis process in a batch cell was an object of a series communications [1–10]. Several anion-exchange membranes were examined by Narebska and Warszawski [1] to highlight the relationship between the membrane composition and the ability to separate acid and salt mixtures by diffusion dialysis. The competitive transport between sulphuric acid and sodium and zinc sulphates was an object of the communication [2]. Therein, it was found that the high difference in diffusivities between acid and salts in the membrane can be explained by the stronger affinity of sulphuric acid and the higher mobility of protons in the membrane with respect to sodium and zinc cations. Reference [3] presents the results of the separation of lactic acid from sodium lactate by diffusion dialysis. For this purpose, Neosepta-AFN and Selemion-DSV membranes were used. It was reported that the separation factor for lactic acid/sodium lactate was approx. 20 and 30 for the Neosepta-AFN and Selemion-DSV membrane, respectively. Ersöz et al. [4] studied diffusion dialysis of sulphuric and hydrochloric acids using a polyether-sulfone anion-exchange membrane. Water was used as a stripping agent. The transport of both acids was quantified by diffusion and membrane mass transfer coefficients. It was observed that the membrane mass transfer coefficients are slightly affected by the initial acid concentration in the compartment initially filled with acid. Kang et al. [5] developed a lumped-parameter model to predict the performance of diffusion dialysis using an anion-exchange membrane Neosepta-AFN for the hydrochloric acid recovery. The diffusion coefficient of acid in the membrane, which was needed in the calculation of the membrane mass transfer coefficient introduced in the model, was determined from batch dialysis experiments. Xu and Yang dealt with the sulphuric acid recovery from titanium white (pigment) waste liquor [6] using diffusion dialysis with a new series of anion-exchange membranes. The membranes were prepared from poly(2,6-dimethyl-1,4-phenylene oxide) by bromination in both benzyl and aryl positions and following amination and functionalization. An extensive study on the recovery of formic acid from pickling solution in the leather industry, which consists of sodium chloride, formic acid, sulphuric acid and organic dirt, was presented by Akgemci et al. [7]. For this purpose, diffusion dialysis and electro-electrodialysis were used. The aim was to find optimum operating conditions for both the processes using four commercial anion-exchange membranes - Neosepta-AFN, -ACM, -AMH and Polysulfone SB-6407. Alexandrova and Iordanov [8] investigated the transport of cadmium and iron through a poly(vinyl chloride)/poly(methyl methacrylate-

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* Corresponding author. Tel.: +420 466 037 360; fax: +420 466 037 068.
*E-mail address:* Zdenek.Palaty@upce.cz (Z. Palatý).

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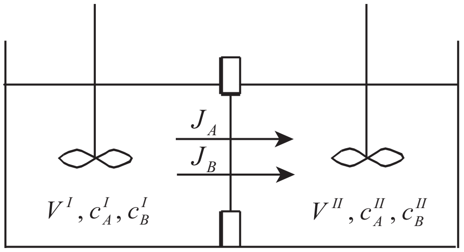

**Fig. 1.** Scheme of dialysis cell.

co-divinyl benzene) carboxylic ion-exchange membrane from an HCl + $CdCl_2$ or HCl + $FeCl_3$ mixture. The experiments showed that the transport of both cations was dependent upon the concentration of hydrogen ions in the stripping solution and the transport rate of $Cd^{2+}$ ions was about 35% higher than that of $Fe^{3+}$ ions. The anion-exchange membrane Neosepta-AFN and Selemion DSV were used in the separation of acetic acid + sodium acetate and propionic acid + sodium propionate mixtures by Narebska and Staniszewski [9]. The sorption equilibria established for acetic acid, propionic acid and the sodium salts of both acids revealed a high sorption of acids in both the membranes and the rejection of carboxylates. Luo et al. [10] prepared poly (2,6-dimethyl-1,4-phenylene oxide) (PPO)-$SiO_2$ hybrid membranes, which were successfully applied for the recovery of hydrochloric acid from the mixture containing hydrochloric acid and ferrous chloride. The results showed that the hybrid membranes exhibit a better separation performance under higher temperatures. The separation factor of the hybrid membranes was much higher than that of a commercial polymeric membrane DF-120.

Beside the studies of mass transfer using a batch dialysis cell, attention has also been paid to mathematical modeling [11–16] and investigation of dialysis in a continuous dialyzer [17–20].

From the short review given above it follows that majority of studies was focused on systems, which consist of hydrochloric or sulphuric acid and their salts. A low attention is paid to dialysis of mixtures containing nitric acid and its salts. For this reason, the aim of this paper is the quantitative description of dialysis of an $HNO_3$ + $NaNO_3$ mixture as this system can be an object of a practical interest.

## 2. Theory

Fig. 1 schematically depicts a two-compartment dialysis cell with a membrane, which separates two solutions containing nitric acid (component A), sodium nitrate (component B) and water as a solvent. If the concentrations of both these components in compartment I are higher than those in compartment II, then the transport of both these component through the membrane exists (from compartment I to compartment II). The fluxes, $J_{iM}$ ($i$ = A, B), can be expressed by the following equations

$$J_{\mathrm{AM}} = -D_{\mathrm{AA}}\frac{dc_{\mathrm{AM}}}{dx} - D_{\mathrm{AB}}\frac{dc_{\mathrm{BM}}}{dx} \tag{1}$$

$$J_{\mathrm{BM}} = -D_{\mathrm{BA}}\frac{dc_{\mathrm{AM}}}{dx} - D_{\mathrm{BB}}\frac{dc_{\mathrm{BM}}}{dx} \tag{2}$$

where $c_i$ ($i$ = A, B) is the molar concentration of the component, $D_{ij}$ ($i$ = A, B; $j$ = A, B) are the phenomenological coefficients and $x$ is the length coordinate. Subscript M means the membrane.

Supposing the pseudo-steady state ($J_{iM}$ = const. ($i$ = A, B)), Eqs. (1) and (2) can be rewritten into the forms

$$J_{\mathrm{AM}} = -\frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{AM}}}^{c^{\mathrm{II}}_{\mathrm{AM}}} D_{\mathrm{AA}}dc_{\mathrm{AM}} - \frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{BM}}}^{c^{\mathrm{II}}_{\mathrm{BM}}} D_{\mathrm{AB}}dc_{\mathrm{BM}} \tag{3}$$

$$J_{\mathrm{BM}} = -\frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{AM}}}^{c^{\mathrm{II}}_{\mathrm{AM}}} D_{\mathrm{BA}}dc_{\mathrm{AM}} - \frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{BM}}}^{c^{\mathrm{II}}_{\mathrm{BM}}} D_{\mathrm{BB}}dc_{\mathrm{BM}} \tag{4}$$

where $\delta_{\mathrm{M}}$ is the membrane thickness and $c^j_{i\mathrm{M}}$ ($i$ = A, B; $j$ = A, B) are the component concentrations at the solution/membrane interfaces in the membrane.

The fluxes of components A and B can also be expressed on the basis of volume and concentration changes in compartment II with time.

$$J_{i\mathrm{M}} = \frac{1}{A}\frac{dn^{\mathrm{II}}_i}{d\tau} = \frac{V^{\mathrm{II}}}{A}\frac{dc_i}{d\tau} + \frac{c^{\mathrm{II}}_i}{A}\frac{dV^{\mathrm{II}}}{d\tau} \quad i = \mathrm{A,B} \tag{5}$$

where $A$ is the membrane area, $n_i$ ($i$ = A, B) is the amount of the component, $V$ is the liquid volume and $\tau$ is time. Superscript II denotes compartment II.

A combination of Eqs. (3)–(5) and further rearrangement lead to the set of equations describing the time dependences of components A and B in compartment II

$$\frac{dc^{\mathrm{II}}_{\mathrm{A}}}{d\tau} = -\frac{A}{V^{\mathrm{II}}}\frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{AM}}}^{c^{\mathrm{II}}_{\mathrm{AM}}} D_{\mathrm{AA}}dc_{\mathrm{AM}} - \frac{A}{V^{\mathrm{II}}}\frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{BM}}}^{c^{\mathrm{II}}_{\mathrm{BM}}} D_{\mathrm{AB}}dc_{\mathrm{BM}} - \frac{c^{\mathrm{II}}_{\mathrm{A}}}{V^{\mathrm{II}}}\frac{dV^{\mathrm{II}}}{d\tau} \tag{6}$$

$$\frac{dc^{\mathrm{II}}_{\mathrm{B}}}{d\tau} = -\frac{A}{V^{\mathrm{II}}}\frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{AM}}}^{c^{\mathrm{II}}_{\mathrm{AM}}} D_{\mathrm{BA}}dc_{\mathrm{AM}} - \frac{A}{V^{\mathrm{II}}}\frac{1}{\delta_{\mathrm{M}}}\int_{c^{\mathrm{I}}_{\mathrm{BM}}}^{c^{\mathrm{II}}_{\mathrm{BM}}} D_{\mathrm{BB}}dc_{\mathrm{BM}} - \frac{c^{\mathrm{II}}_{\mathrm{B}}}{V^{\mathrm{II}}}\frac{dV^{\mathrm{II}}}{d\tau} \tag{7}$$

Using the substitution $dc_{i\mathrm{M}} = \frac{dc_{i\mathrm{M}}}{dx}dx$ ($i$ = A, B), it is possible to rewrite Eqs. (6) and (7) into the final forms

$$\frac{dc^{\mathrm{II}}_{\mathrm{A}}}{d\tau} = -\frac{A}{V^{\mathrm{II}}}\frac{1}{\delta_{\mathrm{M}}}\int_{0}^{\delta_{\mathrm{M}}}\left[D_{\mathrm{AA}}\frac{dc_{\mathrm{AM}}}{dx} + D_{\mathrm{AB}}\frac{dc_{\mathrm{BM}}}{dx}\right]dx - \frac{c^{\mathrm{II}}_{\mathrm{A}}}{V^{\mathrm{II}}}\frac{dV^{\mathrm{II}}}{d\tau} \tag{8}$$

$$\frac{dc^{\mathrm{II}}_{\mathrm{B}}}{d\tau} = -\frac{A}{V^{\mathrm{II}}}\frac{1}{\delta_{\mathrm{M}}}\int_{0}^{\delta_{\mathrm{M}}}\left[D_{\mathrm{BA}}\frac{dc_{\mathrm{AM}}}{dx} + D_{\mathrm{BB}}\frac{dc_{\mathrm{BM}}}{dx}\right]dx - \frac{c^{\mathrm{II}}_{\mathrm{B}}}{V^{\mathrm{II}}}\frac{dV^{\mathrm{II}}}{d\tau} \tag{9}$$

The initial conditions for Eqs. (8) and (9) are

$$\tau = 0, \quad c^{\mathrm{II}}_i = c^{\mathrm{II}}_{i,0} = 0 \quad i = \mathrm{A,B} \tag{10}$$

The equilibrium relations (11) must be added to Eqs. (8) and (9) to fully describe mass transfer in the membrane

$$c^j_{i\mathrm{M}} = \Psi^j_i c^j_{if} \quad i = \mathrm{A,B}; \quad j = \mathrm{I,II} \tag{11}$$

In Eq. (11) $\Psi_i$ ($i$ = A, B) is the partition coefficient and $c_{if}$ ($i$ = A, B) is the component concentration in liquid at the solution/membrane interface.

Generally, the phenomenological coefficients $D_{ij}$ ($i$ = A, B; $j$ = A, B) are dependent upon the concentrations of both the components in the membrane. For simplicity, suppose that these dependences can be approximated by the second order polynomials of the form

$$D_{ij} = D_{ij,0}(1 + A_{ij,1}c_{\mathrm{AM}} + A_{ij,2}c^2_{\mathrm{AM}} + A_{ij,3}c_{\mathrm{BM}} + A_{ij,4}c^2_{\mathrm{BM}})$$
$$i = \mathrm{A,B}; \quad j = \mathrm{A,B} \tag{12}$$