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Mass transfer characterization of Donnan dialysis in a bi-ionic chloride–nitrate system

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Abstract

The ion transfer through an anion exchange membrane during Donnan dialysis was studied theoretically and experimentally by applying the Nernst–Planck equation in the membrane and in the liquid film in the feed-side of the membrane. An equation was derived for the mass transfer in Donnan dialysis. The theoretically derived equation representing dialysis time according to NO_3^- equivalent ionic fraction in the feed was fitted to the experimental results. It was shown that the mass transfer coefficient is relatively constant whatever the concentration of the strip. Thus, for very dilute solutions, it is the liquid film in the feed, which controls the mass transfer during dialysis.

Keywords: Ion exchange membrane; Donnan dialysis; Nitrate; Mass transfer modelling

1. Introduction

Ion exchange membranes have been used extensively because they allow particular ions to be separated continuously without changing the phase. Among membrane processes, Donnan dialysis is important because it does not need an electric current. Donnan dialysis [1–3] is applied to such problems as enrichment of trace levels of ions, metal separations, and water softening. The Donnan dialysis is based on Donnan equilibrium. The critical factor for this equilibrium is the transfer of ions in the membrane. To compute Donnan dialysis processes, numerous mass transfer equations have been used [4–8]. In our previous publications, we studied the choice of the suitable membrane for the nitrate ion extraction, the equilibrium [9] and the diffusion coefficient [10].

In this study, we applied the Nernst–Planck theory to the transfer of ions in the anion exchange membrane during Donnan dialysis in which feed and strip ions were of equal valence. We have developed a model based on the Nernst–Planck equation: an equation representing the dialysis time related to the equivalent ionic fraction of feed is derived. The mass transfer coefficient is determined using this equation and experimental results fitting.

2. Theoretical treatment

A schematic diagram of Donnan dialysis with an ion exchange membrane is shown in Fig. 1. In this system, the concentration of the driving ions (chloride or species 2) in the strip solution is much larger than the concentration of nitrate ions (species 1) in the feed. Therefore, the species 2 diffuse through the membrane from strip-side (b) to feed-side (a) of the membrane generating a driving force by which the feed ions are pumped up from one side of the membrane (feed-side) and concentrated to another (strip-side).

Assuming that the mass transfer resistance in the strip solution can be neglected (as chloride ion concentration is very important), the Nernst–Planck equations for the counter ions 1 and 2 are represented in the ion exchange membrane by expressions that follow:

$$J_1 = -\bar{D}_1 \left(\frac{\mathrm{d}\bar{c}_1}{\mathrm{d}z} + \frac{F\bar{c}_1 Z_1}{RT} \frac{\mathrm{d}E}{\mathrm{d}z} \right) \quad (1)$$

$$J_2 = -\bar{D}_2 \left(\frac{\mathrm{d}\bar{c}_2}{\mathrm{d}z} + \frac{F\bar{c}_2 Z_2}{RT} \frac{\mathrm{d}E}{\mathrm{d}z} \right) \quad (2)$$

Let us consider a particular case in which counter ions are monovalent ($Z_1 = Z_2 = -1$), and pose the following assumptions.

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Nomenclature

c	concentration in the solution (mol m^{-3})
$\bar{c}$	concentration in the membrane (mol m^{-3})
D	diffusion coefficient in the solution (m^2 s^{-1})
$\bar{D}$	diffusion coefficient in the membrane (m^2 s^{-1})
E	Donnan potential
F	Faraday constant (cb)
J	molar flux (mol m^{-2} s^{-1})
$k_{\mathrm{l,a}}$	film mass transfer coefficient (m s^{-1})
k_{m}	membrane mass transfer coefficient (m s^{-1})
r_{h}	hydraulic radius of the dialysis cell (m)
R	ideal gas constant (kJ kmol^{-1} K^{-1})
Re	Reynolds number (−)
S	membrane area (m^2)
Sc	Schmidt number (−)
Sh	Sherwood number (−)
T	absolute temperature (K)
V	volume (m^3)
y	equivalent ionic fraction in the solution (−)
$\bar{y}$	equivalent ionic fraction in the membrane (−)
z	geometrical cordoning
z_{e}	membrane thickness (m)
$z_{\mathrm{l,a}}$	film thickness (m)
Z	valence (eq. mol^{-1})

Greek symbols

α_1^2	selectivity coefficient (−)
$\bar{\beta}$	$\bar{\beta} = \bar{D}_1/\bar{D}_2$ (−)

Subscripts

a	feed solution
b	strip solution
1	nitrate ion
2	chloride ion
4	fixed ionic groups in the membrane
5	co-ion

2.1. First assumption

Co-ions (species 5) are totally excluded from the ion exchange membrane. In this case the electroneutrality in the membrane can be written as

$$\bar{c}_4 - \bar{c}_1 - \bar{c}_2 = 0 \tag{3}$$

where $\bar{c}_4$ is the concentration of fixed ionic groups in the membrane. The condition of no electric current is

$$J_1 + J_2 = 0 \tag{4}$$

If one supposes that diffusion coefficients are constant and that there is no concentration polarisation, then the integration in the strip-side and that in the feed-side of the membrane gives the following relation obtained by Helfferich [11]:

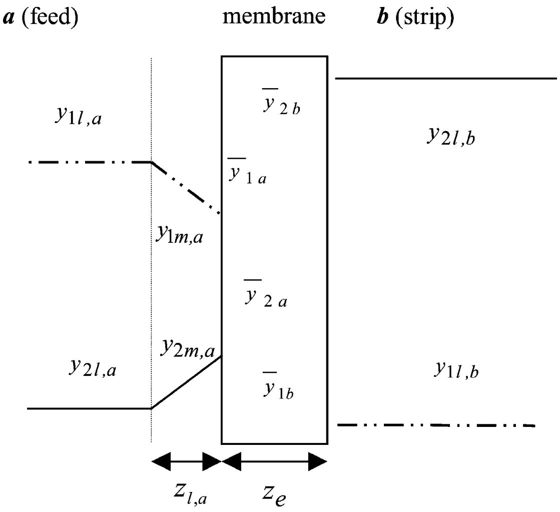

Fig. 1. Donnan dialysis with concentration polarisation in the feed-side of the membrane.

$$J_1 = \frac{\bar{D}_1\bar{c}_4}{z_{\mathrm{e}}((\bar{D}_1/\bar{D}_2)-1)} \ln\left[\frac{1+\bar{y}_{1,\mathrm{a}}((\bar{D}_1/\bar{D}_2)-1)}{1+\bar{y}_{1,\mathrm{b}}((\bar{D}_1/\bar{D}_2)-1)}\right] \tag{5}$$

where z_{e} is the membrane thickness, $\bar{y}_{1,\mathrm{a}}$, $\bar{y}_{1,\mathrm{b}}$ the equivalent ionic fractions of ions 1 and 2 in a- and b-side of the membrane and $\bar{D}_1$, $\bar{D}_2$ are the diffusion coefficients in membrane.

Let us define a coefficient $\bar{\beta} = \bar{D}_1/\bar{D}_2$, Eq. (5) becomes

$$J_1 = \frac{\bar{D}_1\bar{c}_4}{z_{\mathrm{e}}(\bar{\beta}-1)} \ln\left[\frac{1+\bar{y}_{1,\mathrm{a}}(\bar{\beta}-1)}{1+\bar{y}_{1,\mathrm{b}}(\bar{\beta}-1)}\right] \tag{6}$$

At equilibrium, the selectivity coefficient is defined by the following relation:

$$\alpha_1^2 = \frac{\bar{y}_{1,\mathrm{a}}/(1-\bar{y}_{1,\mathrm{a}})}{y_{1\mathrm{m,a}}/(1-y_{1\mathrm{m,a}})} = \frac{\bar{y}_{1,\mathrm{b}}/(1-\bar{y}_{1,\mathrm{b}})}{y_{1\mathrm{m,b}}/(1-y_{1\mathrm{m,b}})} \tag{7}$$

and consequently, the interfacial equilibrium is defined by the following relation [11]:

$$\bar{y}_{1,\mathrm{a}} = \frac{\alpha_1^2 y_{1\mathrm{m,a}}}{(\alpha_1^2-1)y_{1\mathrm{m,a}}+1} \tag{8}$$

Finally, the flux of ion 1 can be written as follows:

$$J_1 = k_{\mathrm{m}}\bar{c}_4 \ln\left[\frac{y_{1\mathrm{l,b}}(\alpha_1^2\bar{\beta}-1)+1}{y_{1\mathrm{l,b}}(\alpha_1^2-1)+1}\,\frac{y_{1\mathrm{m,a}}(\alpha_1^2-1)+1}{y_{1\mathrm{m,a}}(\alpha_1^2\bar{\beta}-1)+1}\right] \tag{9}$$

where $k_{\mathrm{m}} = \bar{D}_1/z_{\mathrm{e}}(\bar{\beta}-1)$.

Mass transfer equation written here assumes considering that the mass transfer resistance in the strip solution is neglected. This corresponds to a high concentration of ions (chloride or species 2) in the strip solution.

2.2. Second assumption

Diffusion coefficients of species 1 and 2 in the liquid are close. In this case, the mass transfer equation in the film (a-side) can be written as follows:

$$J_1 = \frac{D_1 c_{5l,a}}{z_{l,a}}(y_{1l,a} - y_{1m,a}) \tag{10}$$

where the film mass transfer coefficient is $k_{1l,a} = D_1/z_{l,a}$.

2.3. Third assumption

The equivalent ionic fraction of species 1 in the strip-side of the membrane is nil ($y_{1l,b} = 0$). In other words, the chloride ion concentration in the strip solution is many times higher than the nitrate ion concentration. According to this assumption, Eq. (9) becomes

$$y_{1l,a} = \frac{J_1}{k_{l,a}c_{5l,a}} + \frac{1-\exp(J_1/k_m\bar{c}_4)}{(\alpha_1^2\bar{\beta}-1)\exp(J_1/k_m\bar{c}_4) + (\alpha_1^2-1)} \tag{11}$$

This equation allows us to calculate the dialysis flux when the concentration of the feed is known.

2.4. Fourth assumption

The ratio $J_1/k_m\bar{c}_4 \ll 1$. In this case, we can use the first order Taylor formula for the function $\exp(J_1/k_m\bar{c}_4)$, which becomes

$$\exp\left(\frac{J_1}{k_m\bar{c}_4}\right) = 1 + \frac{J_1}{k_m\bar{c}_4} \tag{12}$$

Eq. (11) can then be written as follows:

$$J_1 = \frac{y_{1l,a}}{(1/k_{l,a}c_{5l,a}) + (1/\alpha_1^2(1-\bar{\beta})k_m\bar{c}_4) + (((\alpha_1^2\bar{\beta}-1)/\alpha_1^2(1-\bar{\beta})k_m\bar{c}_4)\, y_{1l,a})} \tag{13}$$

In order to treat experimental results of batch dialysis let us write the exhaustion equation of species 1:

$$\frac{\mathrm{d}y_{1l,a}}{\mathrm{d}t} = \frac{J_1 S}{Vc_{5l,a}} \tag{14}$$

By equalizing both expression of J_1 (Eqs. (13) and (14)), we obtain

$$J_1 = \frac{y_{1l,a}}{(1/k_{l,a}c_{5l,a}) + (1/\alpha_1^2(1-\bar{\beta})k_m\bar{c}_4) + (((\alpha_1^2\bar{\beta}-1)/\alpha_1^2(1-\bar{\beta})k_m\bar{c}_4)\, y_{1l,a})} = -\frac{Vc_{5l,a}}{S}\frac{\mathrm{d}y_{1l,a}}{\mathrm{d}t} \tag{15}$$

Integrating Eq. (15) we obtained the following expression, which correspond to the expression of the dialysis time related to the equivalent ionic fraction of nitrate ions in the feed. This expression enables us to calculate the mass transfer coefficient with parameter setting of the curves representing the equivalent ionic fraction of species 1 in the feed according to time.

$$t = -\frac{Vc_{5l,a}}{S}\left[\left(\frac{1}{k_{l,a}c_{5l,a}} + \frac{1}{\alpha_1^2(1-\bar{\beta})k_m\bar{c}_4}\right)\ln y_{1l,a} + \frac{\alpha_1^2\bar{\beta}-1}{\alpha_1^2(1-\bar{\beta})k_m\bar{c}_4}(y_{1l,a}-1)\right] \tag{16}$$

2.5. Fifth assumption

The Lévêque correlation [12] can be used to compute the mass transfer coefficient in the liquid at small Reynolds number:

$$Sh = 1.85\left[Re\, Sc\frac{4r_h}{L}\right]^{13} \tag{17}$$

where L is the length of the membrane, r_h the hydraulic radius of the cell, Re the Reynolds number (in our experimental conditions $Re \approx 390$), Sc the Schmidt number and Sh is the Sherwood number.

3. Experimental

During the denitrifying process, we exchanged the nitrate ions from a diluted $NaNO_3$ feed solution against chloride ions from a concentrated NaCl strip solution. The solutions were obtained by sodium nitrate or sodium chloride (Sigma–Aldrich, p.a.) dissolution in deionized water. Anion analyses were carried out by capillary ion analyser. A series of dialysis were carried out with an initial load of 100 ppm nitrate. The strip solution had a variable concentration of NaCl (0.2–1 M) and the volume was the same as the feed

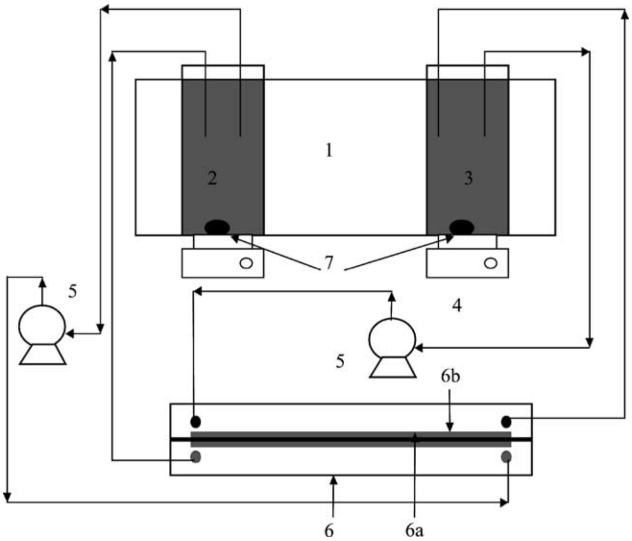

Fig. 2. Experimental setup: (1) thermostatic bath 25 °C; (2) strip solution; (3) feed solution; (4) magnetic stirrers; (5) pumps; (6) dialysis cell; (6a) membrane; (6b) spacer; (7) spinners.

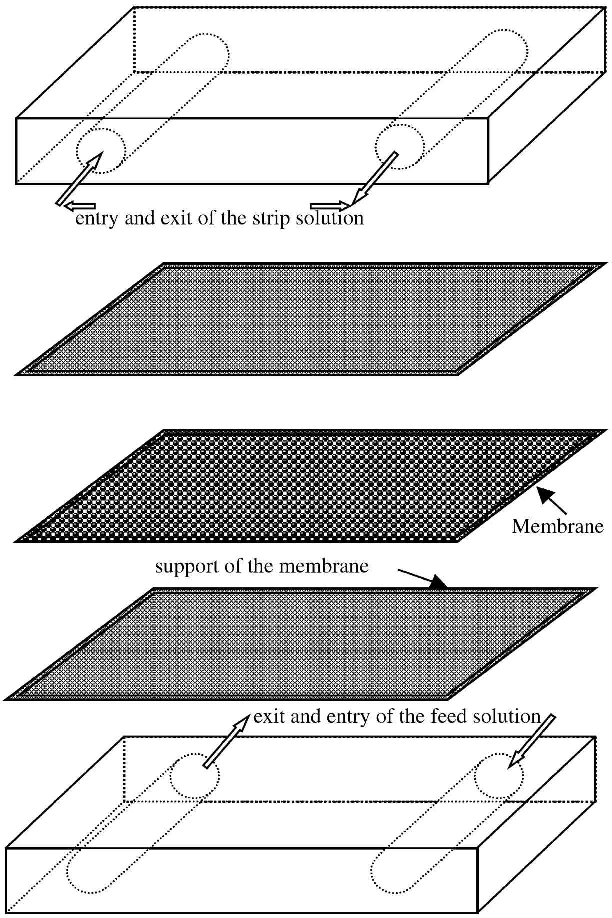

Fig. 3. Dialysis cell.

Table 1
Mass transfer coefficient in the liquid film ($k_{l,a}$) during dialysis ($[NO_3^-]_a = 100$ ppm and $[NaCl]_b = 0.2$–1 M)

Strip solution NaCl (mol l^{-1})	$k_{l,a}$ ($\times 10^{-5}$ m s^{-1})	Error ($\times 10^{-5}$)
0.2	2.49	0.09
0.3	2.43	0.10
0.4	2.47	0.06
0.5	2.47	0.08
0.6	2.29	0.06
0.7	2.42	0.09
1	2.57	0.09

(1 l). The membrane was an ACS (Tokuyama Soda) ion exchange membrane and the temperature of experimentations was 25 °C. The schematic diagram of the experimental setup is represented in Fig. 2.

All dialysis experiments were carried out, on a plane Plexiglass® dialysis cell (Fig. 3). The surface of the membrane was 188.18 cm^2. The membrane was supported by a braided stainless steel grid “316” in each compartment. The solutions penetrate by a slit (2 mm × 73.6 mm). The construction of the cell allowed a perfect sealing between the compartments and outside.

The two solutions (the feed and the strip) circulated countercurrently on both sides of the membrane using two centrifugal pumps. The feed and strip flow rates (Q_V) were 70 l h^{-1}. For all experiments, the feed and the strip solutions were placed in a thermostatic bath at 25 °C. The solutions were maintained homogeneous, using two magnetic stirrers.

3.1. Ion exchange equilibrium

The ion exchange equilibrium was obtained after 48 h in 200 ml flasks with a nitrate and sodium chloride solution of different concentrations. During the equilibrium procedures, the flasks were immersed in a thermostatic bath at 25.0 °C. The concentration of the fixed ionic groups ($\bar{c}_4$) in the membrane and the selectivity coefficient (α_1^2) obtained are assumed constant [9,10]:

$$\bar{c}_4 = 1.07 \pm 0.01\,\text{mol}\,\text{l}^{-1}$$

$$\alpha_1^2 = 1.85$$

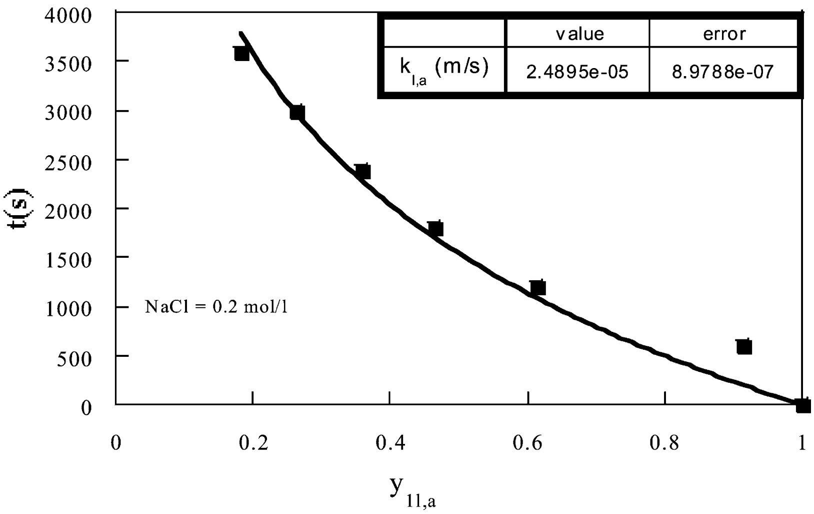

Fig. 4. Experimental data fitting with Eq. (16) for the calculation of the film mass transfer coefficient in the feed (■): experimental data, Eq. (16).

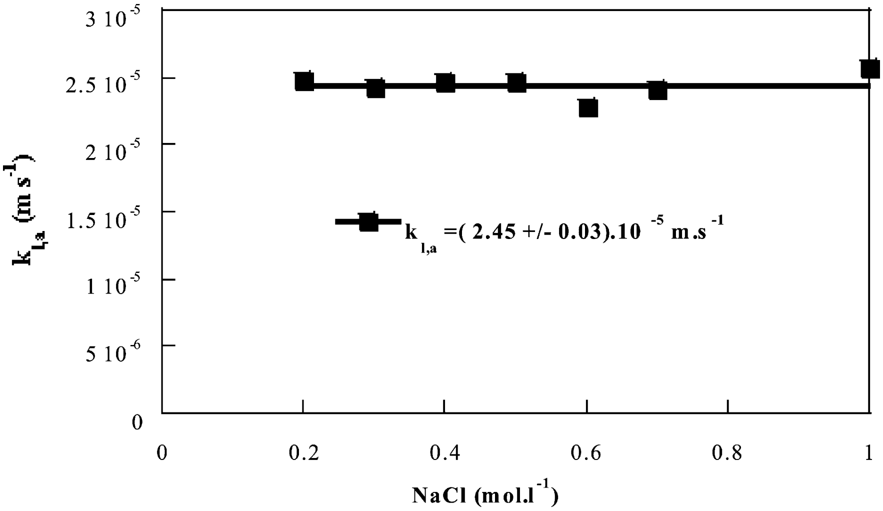

Fig. 5. The average value of the film mass transfer coefficient $k_{1,a}$ for variable strip solution concentrations.

3.2. Electrical conductivity measurement

The electrical conductivity measurements were performed at 25 °C in a jacketed reactor. The diffusion coefficients in the membrane were obtained using a model based on a Nernst–Planck equation [10]:

$$\bar{D}_1 = 6.4308 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$$

$$\bar{D}_2 = 9.6761 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$$

Using the expression $k_m = \bar{D}_1/z_e(1-\bar{\beta})$ it is easy to obtain the value of the mass transfer coefficient k_m: $k_m = 8.31 \times 10^{-4}\,\mathrm{m\,s^{-1}}$.

4. Results and discussion

According to Fig. 4, after the experimental data fitting with Eq. (16), the film mass transfer coefficient ($k_{1,a}$) in the feed is $k_{1,a} = 2.49 \times 10^{-5}\,\mathrm{m\,s^{-1}}$. This procedure has been repeated for all the measurements taken with different concentrations of the strip solution. Table 1 and Fig. 5 show that the film mass transfer coefficient in the feed is constant, when the speed of the fluid is constant. Then, the mass transfer does not depend on the concentration of the strip solution. The polarization of concentration of the strip solution is thus negligible. The average value of the film mass transfer coefficient in the experimental conditions, is according to Fig. 5: $k_{1,a} = 2.45 \times 10^{-5}\,\mathrm{m\,s^{-1}}$. The Reynolds number calculated at the experimental solutions flows rate is $Re = 517$. Let us now check the assumptions carried out during the establishment of mass transfer equations.

4.1. Assumptions verification

4.1.1. Assumption 1

Co-ions (species 5) are totally excluded from the ion exchange membrane. In Fig. 6, we traced the variation of the

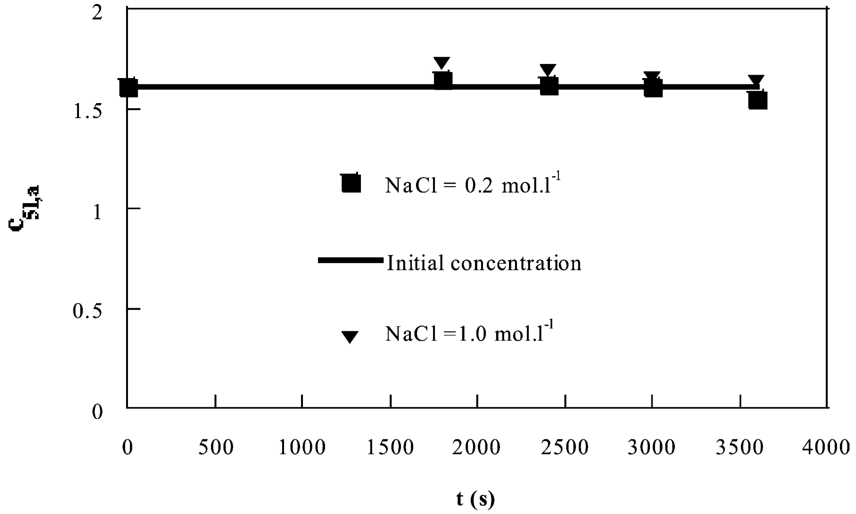

Fig. 6. Total molarity of the anions (chloride + nitrate) vs. dialysis time for two concentrations of the strip solution.

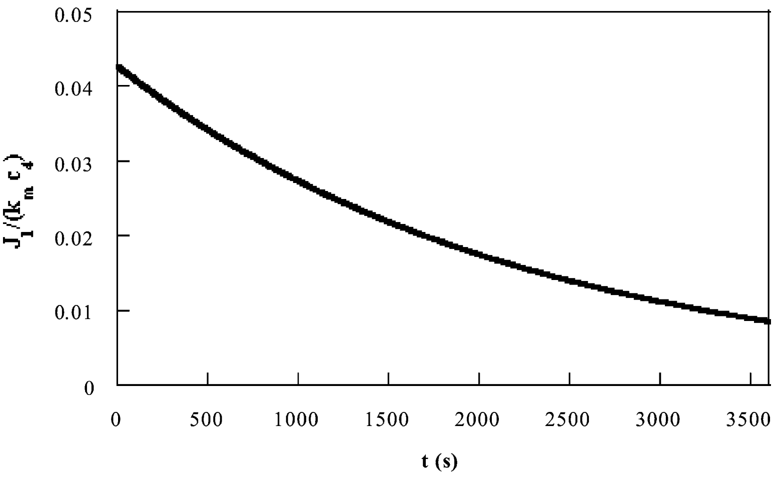

Fig. 7. Ratio $J_1/k_m\bar{c}_4$ vs. time during dialysis.

total molarity of the anions (chloride + nitrate) in the feed according to dialysis time. We can notice that even for a significant strip solution concentration (1 M of NaCl), the total anion concentration remains constant. Thus, we can conclude that, under the experimental conditions, the membrane is permselective.

4.1.2. Assumption 2

Diffusion coefficients of the two species in the liquid phase are close. It have been shown [13] that diffusion coefficients of nitrate and chloride in water at 25 °C are $D_1 = 1.90 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ and $D_2 = 2.03 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$. By assuming the fact that the diffusion coefficients of both ions are equal, the relative error done is 6.41%. In order to attenuate this error, we have used the average value of these diffusion coefficients. In this case, the relative error is 3.2%.

We can now calculate the film thickness in the feed solution with the following formula:

$$k_{1,\mathrm{a}} = \frac{D}{z_{1,\mathrm{a}}} = 2.45 \times 10^{-5}\,\mathrm{m\,s^{-1}}$$

The diffusion coefficients average value of the two ionic species in water at 25 °C is

$$D_1 = D_2 = D = 1.965 \times 10^{-9}\mathrm{m^2\,s^{-1}}$$

For $D = D_1 = D_2$ film thickness in the feed solution is $z_{1,\mathrm{a}} = 80\,\mu\mathrm{m}$.

4.1.3. Assumption 3

$y_{1\mathrm{l,a}} = 0$, the third assumption relates to the nullity of the equivalent ionic fraction of species 1 in the strip solution. At the end of the dialysis experiment, the nitrate concentration in the strip would be equal to 100 ppm in the most unfavourable case one's can have. Then for a strip solution of 0.2 M NaCl we obtained:

$$y_{1\mathrm{l,b}} = 0.008, \qquad y_{2\mathrm{l,b}} = 0.992$$

This calculation thus validates our assumption. Moreover, we have assumed that the concentration polarization in the strip solution is negligible. This assumption is highlighted

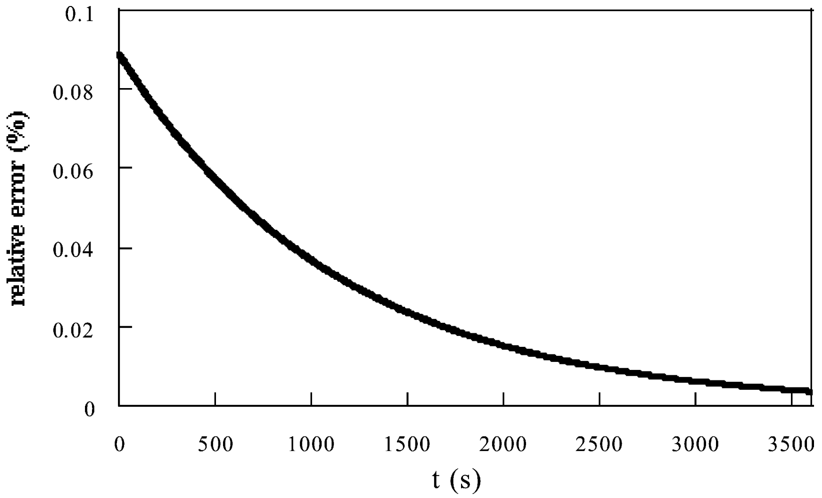

Fig. 8. Relative error done when the expression $\exp[J_1(k_m\bar{c}_4)^{-1}]$ is replaced by $1 + J_1(k_m\bar{c}_4)^{-1}$.

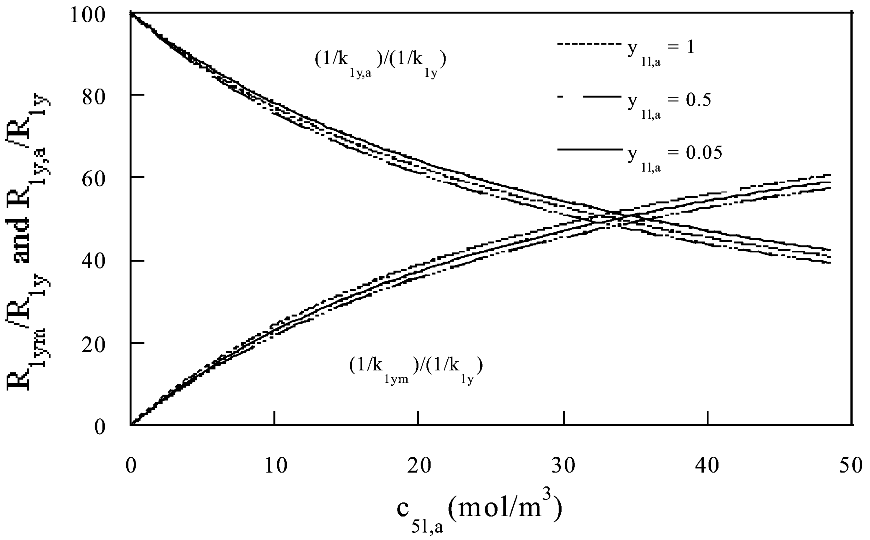

Fig. 9. Ratios (membrane resistance/total resistance) and (film resistance/total resistance) at variable feed solution concentrations.

by the fact that the mass transfer is independent of the concentration of the strip solution.

4.1.4. Assumption 4

The ratio $J_1/k_m\bar{c}_4 \ll 1$. If the ratio $J_1(k_m\bar{c}_4)^{-1}$ is close to zero, $\exp[J_1(k_m\bar{c}_4)^{-1}]$ can be compared to, $1 + J_1(k_m\bar{c}_4)^{-1}$ during dialysis. We have calculate $J_1(k_m\bar{c}_4)^{-1}$ according to the dialysis time (Fig. 7) with the mass transfer coefficients determined previously. We noted that this ratio is always lower than 0.043. Under these conditions, by comparing the exponential to the first term of the limiting development, the error made is always lower than 0.09% during the dialysis (Fig. 8). This error is thus acceptable.

5. Conclusion

We tried here to understand and to describe the mechanisms of dialysis. We integrated the equations of diffusion in the membrane and films: for our experiments, the concentration of the strip solution being very high, the film resistance in the strip can be considered negligible.

We integrated the equation of Nernst–Planck in the film (feed-side of the membrane) and by considering the relation of balance to interfaces, we obtained an expression of flux as function of the concentration of the nitrate ions in the feed for a perfectly permselective membrane. For diffusion coefficients of the two ions in the solution very close, we obtained an algebraic equation, which enables us to determine the film coefficient during batch dialysis.

For low Reynolds number some conclusions concerning the mass transfer mechanism in dialysis can be made:

1. The total mass transfer resistance can be assumed to be equal to the sum of the resistance of film on the feed-side and the resistance of the membrane itself:

$$\frac{1}{k_{1c}c_{51,a}} = \frac{1}{k_{l,a}c_{51,a}} + \frac{1 + (\alpha_1^2\bar{\beta} - 1)y_{11,a}}{\alpha_1^2(1 - \bar{\beta})k_m\bar{c}_4} \tag{18}$$

In this equation

$$\frac{1}{k_{1c}c_{51,a}} = R_{1y} = \frac{1}{k_{1y}}$$ is the total resistance

$$\frac{1}{k_{l,a}c_{51,a}} = R_{1y,a} = \frac{1}{k_{1y,a}}$$
is the film resistance in the feed

$$\frac{1 + (\alpha_1^2\bar{\beta} - 1)y_{11,a}}{\alpha_1^2(1 - \bar{\beta})k_m\bar{c}_4} = R_{1y,m} = \frac{1}{k_{1y,m}}$$
is the membrane resistance

2. At low feed concentration, the liquid film in the feed controls the mass transfer process (Fig. 9).
3. Resistances of the film and the membrane are equal when the concentration of the co-ion in the feed is about 33 mol m^{-3} (Fig. 9).
4. For higher feed concentrations, the mass transfer is controlled by the liquid film and the membrane: the control is a mixed control (Fig. 9).

The mass transfer results obtained in this study depends on the geometry of the cell, the hydrodynamics in the vicinity of the membrane (laminar flow in this study) and the concentration (>1 mol m^{-3}) of the feed. Even for a diluted feed solutions there is a non-negligible membrane resistance (e.g. at 5 mol m^{-3}, the membrane resistance contribution to the total resistance is about of 13%) and it is preferable to take account of this resistance in the modelling of the mass transfer.

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