

Determination of diffusivity from mass transfer measurements in a batch dialyzer: numerical analysis of pseudo-steady state approximation

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The presented paper deals with the numerical analysis of pseudo-steady state conditions used in the modelling of the batch dialysis process. First, under specified conditions, time dependences of component concentrations and liquid volumes in both compartments were generated using a rigorous model based on Fick's second law. From these data, the diffusion coefficient of the component in the membrane was calculated using a simplified model based on Fick's first law. The specified coefficient was then compared with the calculated one. Numerical analysis revealed that in case of not too thick membranes, sufficiently high values of the diffusion coefficient, high intensity of mixing and considering the concentration and volume data in compartments I and II, the pseudo-steady state conditions can be considered as a good approximation of the real state.

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Introduction

Dialysis and diffusion dialysis are membrane processes, which serve for the separation of compounds in liquid mixtures. In order to quantify them, several transport characteristics can be used, e.g., the overall dialysis coefficient, permeability coefficient of the membrane, membrane mass transfer coefficient, and the diffusion coefficient of a component. All these characteristics can easily be determined from dialysis experiments using a two-compartment cell (Elmidaoui et al., 1995; Ersoz et al., 2001; Kang et al., 2001; Xu & Yang, 2001; Akgemci et al., 2005; Alexandrova & Iordanov, 2005; Narębska & Staniszewski, 2008; Luo et al., 2010; Kaczmarek et al., 2008; Wu et al., 2012; Hao et al., 2013a, 2013b). Determination of the last transport characteristic, i.e., the diffusion coefficient, is mostly based on Fick's first law (Sudoh et al., 1987; Audinos & Pichelin, 1988; Allen et al., 1989; Suhara et al., 1989; Narębska & Warszawski, 1992; Heintz & Illenberger, 1996;

Narębska & Staniszewski, 1997; Palatý & Žáková, 2000).

Sudoh et al. (1987) studied the concentration of cupric ions by the Donnan dialysis using a strongly acidic cation-exchange membrane Neosepta C66-5T. The diffusion coefficient, needed in the mathematical modelling of the process, was determined from the experiments in a two-compartment cell. Audinos and Pichelin (1988) used a two-compartment cell to determine the diffusion coefficient of KCl in an agar-agar membrane. Poly[bis(trifluoroethoxy)phosphazene] membranes were synthesised and used in diffusion dialysis experiments to separate Cr^{3+} ions from Co^{2+} and Mn^{2+} ions (Allen et al., 1989). Solutions of Cr^{3+} , Co^{2+} , and Mn^{2+} nitrates were used as feed solutions. In connection with the measurement of the transport numbers, Suhara et al. (1989) experimentally measured the diffusion coefficient of NaOH in a perfluorocarboxylate cation-exchange membrane Flemion. Permeability of several anion-exchange membranes (Neosepta-AFN, -AM1, -AM2, -CM1, -CM2) and dif-

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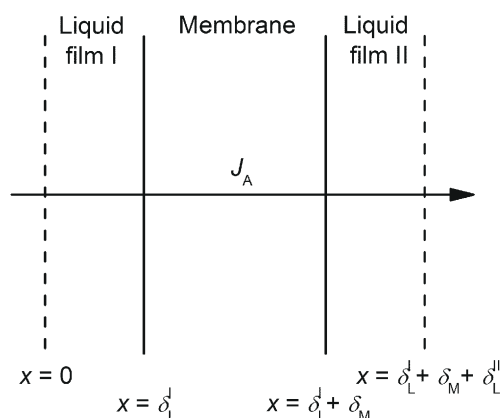


Fig. 1. Membrane with liquid films.

fusion coefficients of hydrochloric acid and sodium chloride were determined from batch dialysis experiments (Narębska & Warszawski, 1992). Heintz and Il-lenberger (1996) reported the measurement of molecular bromine diffusivity in a cation-exchange membrane Selemion CMV. The diffusion coefficient was of the order of $10^{-12} \text{ m}^2 \text{ s}^{-1}$ and its calculation was based on the time dependence of the Br_2 concentration in the receiving compartment. Narębska and Staniszewski (1997) determined the diffusion coefficients of lactic acid and sodium lactate in Neosepta-AFN and Selemion DSV membranes. Palatý and Žáková (2000) used a two-compartment cell to determine diffusivities of inorganic acids (HCl , H_2SO_4 , HNO_3 , H_3PO_4 , HF) in a Neosepta-AFN membrane as functions of the acid concentration.

In a batch cell, dialysis is an unsteady state mass transfer process governed by Fick's second law. To determine the diffusion coefficient of a component in the membrane, the procedure based on Fick's first law is often used. The application of Fick's first law, which is simpler than that of Fick's second law, implicitly assumes a pseudo-steady state. If the real state is far from the pseudo-steady state, this simplification can lead to incorrect results. For this reason, the aim of this communication is to find conditions under which the application of the Fick's first law provides acceptable results.

Theoretical

Consider a dialysis membrane with liquid films on both its sides, which is oriented perpendicularly to the component flux, J_A . The membrane separates two solutions containing component A. This situation is schematically depicted in Fig. 1. Thickness of the membrane is expressed as δ_M , whereas those of liquid films are expressed as δ_L^I and δ_L^{II} . When the concentration of component A in compartment I is higher than that in compartment II, unsteady mass transfer in the direction of axis x occurs. The concentration field of

component A in the membrane and the liquid films is described by the Fick's law.

$$\frac{\partial c_A^I}{\partial \tau} = D_A^I \frac{\partial^2 c_A^I}{\partial x^2} \quad (1)$$

$$\frac{\partial c_{AM}}{\partial \tau} = D_{AM} \frac{\partial^2 c_{AM}}{\partial x^2} \quad (2)$$

$$\frac{\partial c_A^{II}}{\partial \tau} = D_A^{II} \frac{\partial^2 c_A^{II}}{\partial x^2} \quad (3)$$

where c_A is the molar concentration of component A, τ is time, and D_A is diffusivity. Subscript M represents the membrane, while superscripts I and II represent compartments I and II, respectively.

Initial and boundary conditions for Eqs. (1)–(3) are

$$c_A^I = c_{Ab0}^I \quad \text{for } \tau = 0, \quad x \in \langle 0, \delta_L^I \rangle \quad (4)$$

$$c_{AM} = 0 \quad \text{for } \tau = 0, \quad x \in \langle \delta_L^I, \delta_L^I + \delta_M \rangle \quad (5)$$

$$c_A^{II} = 0 \quad \text{for } \tau = 0, \quad x \in \langle \delta_L^I + \delta_M, \delta_L^I + \delta_M + \delta_L^{II} \rangle \quad (6)$$

$$c_A^I|_{x=0} = c_{Ab}^I \quad \text{for } \tau > 0 \quad (7)$$

$$c_A^I|_{x=\delta_L^I + \delta_M + \delta_L^{II}} = c_{Ab}^{II} \quad \text{for } \tau > 0 \quad (8)$$

In Eqs. (4), (7), and (8), subscripts 0 and b represent the initial values and bulk.

If no accumulation of component A occurs at the solution/membrane interfaces, then

$$-AD_A^I \frac{\partial c_A^I}{\partial x} \Big|_{x \rightarrow (\delta_L^I)^-} = -AD_{AM} \frac{\partial c_{AM}}{\partial x} \Big|_{x \rightarrow (\delta_L^I)^+} \quad (9)$$

$$-AD_{AM} \frac{\partial c_{AM}}{\partial x} \Big|_{x \rightarrow (\delta_L^I + \delta_M)^-} = -AD_A^{II} \frac{\partial c_A^{II}}{\partial x} \Big|_{x \rightarrow (\delta_L^I + \delta_M)^+} \quad (10)$$

where A is the membrane area.

Furthermore, conditions of the solution/membrane equilibrium on both sides of the membrane must be considered, i.e.,

$$c_{AM}|_{x \rightarrow (\delta_L^I)^+} = \Psi_A^I c_A^I|_{x \rightarrow (\delta_L^I)^-} \quad (11)$$

$$c_{AM}|_{x \rightarrow (\delta_L^I + \delta_M)^-} = \Psi_A^{II} c_A^{II}|_{x \rightarrow (\delta_L^I + \delta_M)^+} \quad (12)$$

In Eqs. (11) and (12), Ψ_A^j ($j = \text{I, II}$) are the partition coefficients.

Finally, the balance of component A and the mass balance over the liquid volume in compartments I and II must be added to the mathematical model

$$-\frac{1}{A} \frac{d(V^I c_{Ab}^I)}{d\tau} = -D_A^I \frac{\partial c_A^I}{\partial x} \Big|_{x \rightarrow 0^+} \quad (13)$$

$$-\frac{1}{A} \frac{d(V^I \rho^I)}{d\tau} = -D_A^I M_A \frac{\partial c_A^I}{\partial x} \Big|_{x \rightarrow 0^+} \quad (14)$$

$$\frac{1}{A} \frac{d(V^{II} c_{Ab}^{II})}{d\tau} = -D_A^{II} \frac{\partial c_A^{II}}{\partial x} \Big|_{x \rightarrow (\delta_L^I + \delta_M + \delta_L^{II})^-} \quad (15)$$

$$\frac{1}{A} \frac{d(V^{II} \rho^{II})}{d\tau} = -D_A^{II} M_A \frac{\partial c_A^{II}}{\partial x} \Big|_{x \rightarrow (\delta_L^I + \delta_M + \delta_L^{II})^-} \quad (16)$$

where V is the liquid volume, ρ is density, and M is the molar mass.

A combination of Eqs. (13) and (14) using the substitution

$$\frac{d\rho^I}{d\tau} = \frac{d\rho^I}{dc_{Ab}^I} \frac{dc_{Ab}^I}{d\tau} \quad (17)$$

leads to the following differential equations

$$\frac{dc_{Ab}^I}{d\tau} = \frac{A}{V^I} \frac{D_A^I \left(1 - \frac{M_A}{\rho^I} c_{Ab}^I\right)}{1 - \frac{c_{Ab}^I}{\rho^I} \frac{d\rho^I}{dc_{Ab}^I}} \frac{\partial c_A^I}{\partial x} \Big|_{x \rightarrow 0^+} \quad (18)$$

$$\frac{dV^I}{d\tau} = \frac{A}{\rho^I} \frac{D_A^I \left(M_A - \frac{d\rho^I}{dc_{Ab}^I}\right)}{1 - \frac{c_{Ab}^I}{\rho^I} \frac{d\rho^I}{dc_{Ab}^I}} \frac{\partial c_A^I}{\partial x} \Big|_{x \rightarrow 0^+} \quad (19)$$

A similar combination of Eqs. (15) and (16) gives

$$\frac{dc_{Ab}^{II}}{d\tau} = -\frac{A}{V^{II}} \frac{D_A^{II} \left(1 - \frac{M_A}{\rho^{II}} c_{Ab}^{II}\right)}{1 - \frac{c_{Ab}^{II}}{\rho^{II}} \frac{d\rho^{II}}{dc_{Ab}^{II}}} \frac{\partial c_A^{II}}{\partial x} \Big|_{x \rightarrow (\delta_L^I + \delta_M + \delta_L^{II})^-} \quad (20)$$

$$\frac{dV^{II}}{d\tau} = -\frac{A}{\rho^{II}} \frac{D_A^{II} \left(M_A - \frac{d\rho^{II}}{dc_{Ab}^{II}}\right)}{1 - \frac{c_{Ab}^{II}}{\rho^{II}} \frac{d\rho^{II}}{dc_{Ab}^{II}}} \frac{\partial c_A^{II}}{\partial x} \Big|_{x \rightarrow (\delta_L^I + \delta_M + \delta_L^{II})^-} \quad (21)$$

Solving the sets of Eqs. (1)–(12) and (18)–(21), dependences of the component concentrations and liquid volumes in both compartments on time are obtained. Then, these data can be used in the numerical analysis of the pseudo-steady state approximation.

In the mathematical model given above, a constant diffusion coefficient and zero flux of solvent were considered.

Experimental

Generation of component concentrations and liquid volumes in both compartments as functions of time

Partial differential equations Eqs. (1)–(3) with the initial and boundary conditions defined by Eqs. (4)–(8) and other conditions defined by Eqs. (9)–(12) and (18)–(21) were solved by the finite-difference method. For this purpose, the membrane and both liquid films were divided into a grid with the integration steps h^I , h_M , and h^{II} (in the x direction – index i) and k (in the τ direction – index j). The number of grid points in the x direction in the membrane and both liquid films was constant and equal to 100 ($n_M = 100$) and 50 ($n^I = n^{II} = 50$), respectively. The integration step in the τ direction was also constant (3.6 s). The simple and implicit finite-difference method was used to ensure the stability of the solution.

Using a simulation program written in Object Pascal programming language implemented in a Borland Delphi™ Professional (Version 6), the model developed was treated numerically with variables listed in Table 1. In this work, laboratory data were not treated. Values of the individual variables and their ranges are based not only on experience in the field of mass transport through membranes but also on the data from literature. Membrane area, liquid volumes, and initial component concentrations in compartments I and II were the same as those in a real batch dialyzer, see e.g. Palatý and Žáková (2000) and Palatý et al. (2007, 2010). In case of other variables, the aim was to investigate their effect within the variable ranges which can be met in the practice. In all calculations, a fictive component and solvent, with basic characteristics summarised in Table 1, were considered. In the papers cited above, the effect of liquid films on both sides of the membrane was neglected, i.e., $k_L^I = k_L^{II} = k_L \rightarrow \infty$. However, the effect of the mass transfer coefficients on the overall transport through the membrane was investigated. Thus, the so-called generated values of component concentrations in both compartments, $c_{Ab,gener}^I$ and $c_{Ab,gener}^{II}$, were calculated. Moreover, liquid volumes in compartments I and II were also calculated. For illustration, these quantities are plotted against time in Figs. 2 and 3.

Pseudo-steady state approximation

Transport of component A through the membrane and liquid films is described by the following equations

$$J_A^I = -D_A^I \frac{dc_A^I}{dx} \quad x \in \langle 0, \delta_L^I \rangle \quad (22)$$

$$J_{AM} = -D_{AM} \frac{dc_{AM}}{dx} \quad x \in \langle \delta_L^I, \delta_L^I + \delta_M \rangle \quad (23)$$

Table 1. List of specified variables

Variable	Value or range	Reference ^a
A/m^2	62.2×10^{-4}	
$c_{Ab0}^I/(kmol\ m^{-3})$	1.0	Audinos and Pichelin (1988), Narebska and Warszawski (1992), Narebska and Staniszewski (1997)
$c_{Ab0}^{II}/(kmol\ m^{-3})$	0.0	
$D_A^I/(m^2\ s^{-1})$	1.0×10^{-9}	
$D_{AM}/(m^2\ s^{-1})$	1.0×10^{-12} – 5.0×10^{-10}	Narebska and Warszawski (1992), Heintz and Illenberger (1996), Narebska and Staniszewski (1997)
$D_A^{II}/(m^2\ s^{-1})$	1.0×10^{-9}	
$k_L^I/(m\ s^{-1})$	1.0×10^{-6} – 1.0×10^{-3}	
$k_L^{II}/(m\ s^{-1})$	1.0×10^{-6} – 1.0×10^{-3}	
$M_A/(kg\ kmol^{-1})$	72	
V_0^I/m^3	1.0×10^{-3}	
V_0^{II}/m^3	1.0×10^{-3}	
δ_M/m	50×10^{-6} – 500×10^{-6}	Suhara et al. (1989), Narebska and Warszawski (1992), Heintz and Illenberger (1996), Narebska and Staniszewski (1997)
$\rho/(kg\ m^{-3})$	$\rho = \rho_w + 2c_A + c_A^2$	
$\rho_w/(kg\ m^{-3})$	1000.0	
Ψ_A^I	0.1–10.0	Audinos and Pichelin (1988), Suhara et al. (1989), Narebska and Warszawski (1992), Heintz and Illenberger (1996), Narebska and Staniszewski (1997)
Ψ_A^{II}	0.1–10.0	Audinos and Pichelin (1988), Suhara et al. (1989), Narebska and Warszawski (1992), Heintz and Illenberger (1996), Narebska and Staniszewski (1997)

a) Variable falls into the range specified.

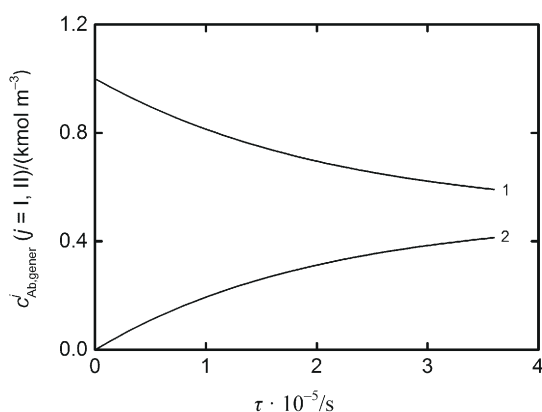


Fig. 2. Dependence of component concentration in compartments I (1) and II (2) on time at $k_L^I = k_L^{II} = 1.0 \times 10^{-6}\ m\ s^{-1}$, $\Psi_A^I = \Psi_A^{II} = 1$, $\delta_M = 50 \times 10^{-6}\ m$ and $D_{AM} = 1.0 \times 10^{-10}\ m^2\ s^{-1}$.

$$J_A^{II} = -D_A^{II} \frac{dc_A^{II}}{dx} \quad x \in \langle \delta_L^I + \delta_M, \delta_L^I + \delta_M + \delta_L^I \rangle \quad (24)$$

Assuming the pseudo-steady state ($J_A^I = J_{AM} = J_A^{II} = J_A$) and constant diffusivity in the membrane and liquid films, Eqs. (22)–(24) can be integrated and rewritten into the forms

$$J_A = k_L^I (c_{Ab}^I - c_{Ai}^I) \quad (25)$$

$$J_A = \frac{D_{AM}}{\delta_M} (c_{AM}^I - c_{AM}^{II}) \quad (26)$$

$$J_A = k_L^{II} (c_{Ai}^{II} - c_{Ab}^{II}) \quad (27)$$

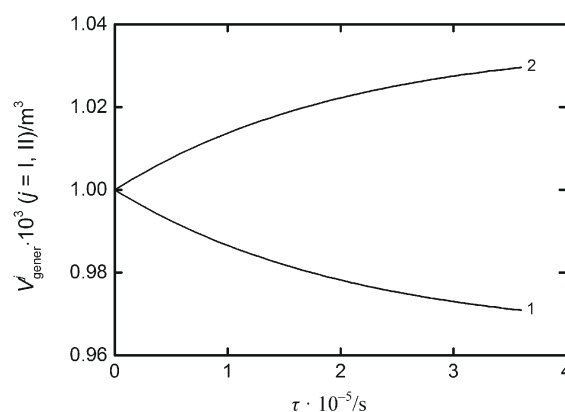


Fig. 3. Dependence of liquid volume in compartments I (1) and II (2) on time. For experimental conditions, see Fig. 1.

where $k_L^j \left(= \frac{D_A^j}{\delta_L^j} \right)$ ($j = I, II$) are the liquid mass transfer coefficients and c_{Ai}^j ($j = I, II$) are the component concentrations in liquid at the solution/membrane interfaces.

The flux of component A can easily be determined from the concentration and volume changes in compartments I or II, i.e.,

$$J_A = -\frac{1}{A} \frac{d(V^I c_{Ab}^I)}{d\tau} = \frac{1}{A} \frac{d(V^{II} c_{Ab}^{II})}{d\tau} \quad (28)$$

A combination of Eqs. (26) and (28) leads to the

differential equations in Eqs. (29) and (30) which describe the dependences of the component concentrations in both compartments on time

$$\frac{dc_{Ab}^I}{d\tau} = -\frac{A}{V^I} \frac{D_{AM}}{\delta_M} (c_{AM}^I - c_{AM}^{II}) - \frac{c_{Ab}^I}{V^I} \frac{dV^I}{d\tau}$$

$$\tau = 0, c_{Ab}^I = c_{Ab0}^I \quad (29)$$

$$\frac{dc_{Ab}^{II}}{d\tau} = \frac{A}{V^{II}} \frac{D_{AM}}{\delta_M} (c_{AM}^I - c_{AM}^{II}) - \frac{c_{Ab}^{II}}{V^{II}} \frac{dV^{II}}{d\tau}$$

$$\tau = 0, c_{Ab}^{II} = c_{Ab0}^{II} = 0 \quad (30)$$

Concentrations of component A in the membrane on both its boundaries, c_{AM}^I and c_{AM}^{II} , can be calculated from the set of Eqs. (25)–(27), to which equilibrium relations are added

$$c_{AM}^j = \Psi_A^j c_{Ai}^j \quad j = I, II \quad (31)$$

When the changes of the liquid volumes and the component concentrations in both compartments are known, it is possible to determine the diffusivity of the component in the membrane. For this purpose, numerical integration, Eqs. (29) and (30), followed by an optimisation procedure to determine the minimum of a suitable objective function can be used. Thus calculated diffusion coefficient can then be compared with that for which the dependences $c_{Ab}^j = f(\tau)$ and $V^j = f(\tau)$ ($j = I, II$) were generated by the rigorous procedure.

Results and discussion

The procedure for the calculation of component A diffusivity in the membrane from data generated consisted of the following steps:

1. Calculation of derivatives $\frac{dV^j}{d\tau}$ ($j = I, II$) from dependences $V^j = f(\tau)$ ($j = I, II$) approximated by second order polynomials.

2. Initial estimation of diffusivity.

3. Numerical integration of basic differential equations (Eqs. (29) and (30)). In this step, calculated values of the component concentrations in both compartments can be obtained at the same time as generated, i.e., $c_{Ab,calc}^I$ and $c_{Ab,calc}^{II}$. For this purpose, the fourth-order Runge–Kutta method with an integration step of 3.6 s was used.

4. Calculation of the objective function

$$F(D_{AM,calc}) = \sum_{i=1}^m \left[\left(c_{Ab,gener}^{I,i} - c_{Ab,calc}^{I,i} \right)^2 + \left(c_{Ab,gener}^{II,i} - c_{Ab,calc}^{II,i} \right)^2 \right] \quad (32)$$

where m is the number of data generated in one time series.

5. Realisation of a one step optimisation procedure. For this purpose, the golden section search was used and corrected value of calculated diffusivity was obtained.

6. Steps 2 to 5 were repeated until a minimum of the objective function Eq. (27) was reached.

Relative error, E , was used to quantify the effect of the simplification due to the pseudo-steady state approximation on the diffusivity determination

$$E = \frac{D_{AM,calc} - D_{AM}}{D_{AM}} \times 100 \% \quad (33)$$

Considering that the determination of the diffusion coefficient can be based on the concentration and volume data in both compartments or on the data concerning compartment II, the relative errors of the diffusion coefficient, E^{I+II} and E^{II} , were calculated. (Note: In case of E^{II} , the objective function in Eq. (32) was based only on the concentrations in compartment II.)

Relative errors of the diffusion coefficient are dependent on the variables included in the following equation

$$E^j = f(D_{AM}, \delta_M, \Psi_A, k_L, c_{A0}^I, k_V, k_A) \quad j = I + II, II \quad (34)$$

where k_V is the ratio of the initial liquid volume in compartment I to that in compartment II ($k_V = V_0^I/V_0^{II}$), k_A is the ratio of the membrane area to the initial liquid volume in compartment I ($k_A = A/V_0^I$). In Eq. (29), the effect of D_{AM} , δ_M , Ψ_A , and k_L was analysed at the constant values of $c_{A0}^I = 1.0 \text{ kmol m}^{-3}$, $k_V = 1.0$, and $k_A = 6.22 \text{ m}^{-1}$.

Results of the numerical analysis are presented graphically as dependences of the relative error on the diffusivity of the component in the membrane. In all cases, the membrane thickness is a parameter of individual dependences. Figs. 4–7 present the cases characterised by very high intensity of liquid mixing in both compartments, $k_L^I = k_L^{II} = k_L = 1 \times 10^{-3} \text{ m s}^{-1}$. An opposite situation, i.e., where very low intensity of liquid mixing was used, is depicted in Figs. (8)–(13) ($k_L^I = k_L^{II} = k_L = 1 \times 10^{-6} \text{ m s}^{-1}$).

From Fig. 4, where E^{I+II} is plotted against D_{AM} , it follows that with thick membranes, low values of D_{AM} , and low values of the partition coefficients the relative error of the diffusion coefficient is on an acceptable level, i.e., $E^{I+II} < 5 \%$. An increase in the partition coefficient increases the relative error, which sharply decreases with an increasing value of D_{AM} (see Fig. 5). A further increase in the partition coefficient has practically no effect on the dependences presented in Fig. 5. A quite different situation occurs when determining the diffusion coefficient from the concentration and volume data in compartment II (see Figs. 6 and 7) as the diffusion coefficients are underestimated and the relative error is almost 20 %. The relative

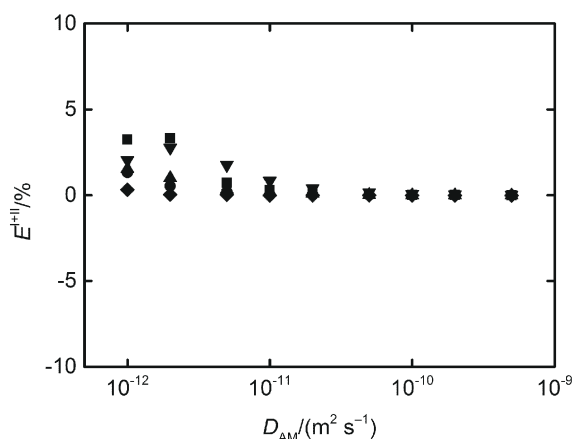


Fig. 4. Dependence of relative error, E^{I+II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-3} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 0.1$: $\delta_M \cdot 10^{-6}/\text{m}$: 50 (\blacklozenge), 150 (\bullet), 250 (\blacktriangle), 350 (\blacksquare), and 500 (\blacktriangledown).

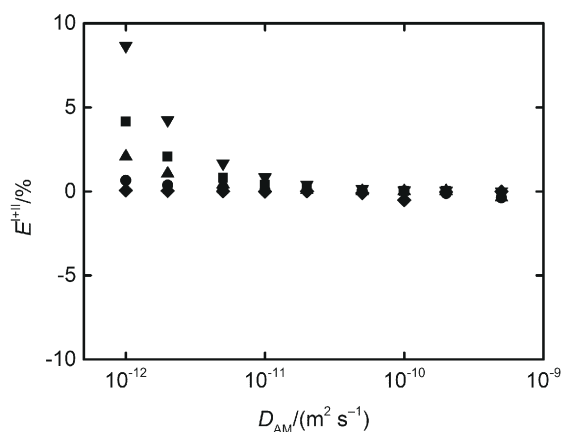


Fig. 5. Dependence of relative error, E^{I+II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-3} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 1.0$. For meaning of symbols, see Fig. 4.

error sharply decreases with an increase in the diffusion coefficient, so that at $D_{AM} > 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, the relative error is below 2 %. These conclusions are valid if the values of the partition coefficient are not too high, i.e., $\Psi_A < 1$. Moreover, under these conditions, an increase in the partition coefficient from 0.1 to 1.0 has practically no effect on the relative error. At high values of the partition coefficients ($\Psi_A = 10$) the relative error is high also for $D_{AM} > 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

As can be seen in Fig. 8, relative error of the diffusion coefficient is very low ($< 2\%$), when also the partition coefficients and the intensity of liquid mixing are very low ($k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$). At medium values of Ψ_A (Fig. 9), increased relative errors can be found on both boundaries of the dependence $E^{I+II} = f(D_{AM})$. In the studied range of D_{AM} , the relative error is below 10 %. In case of thick mem-

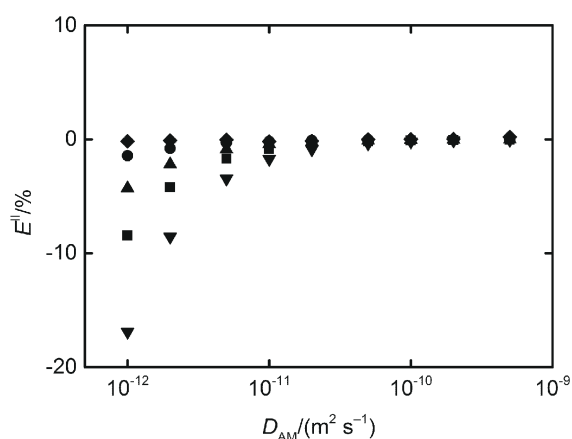


Fig. 6. Dependence of relative error, E^{II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-3} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 10.1$. For meaning of symbols, see Fig. 4.

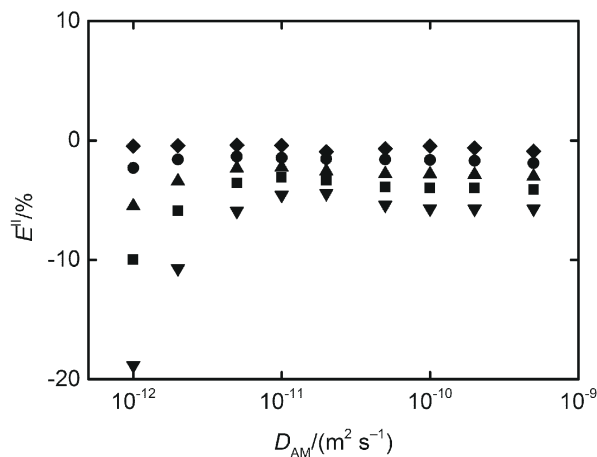


Fig. 7. Dependence of relative error, E^{II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-3} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 10.0$. For meaning of symbols, see Fig. 4.

branes and low values of D_{AM} , it is difficult to meet the pseudo-steady state conditions. In case of thin membranes and high values of D_{AM} , the unfavourable effect of the mass transport governed by the liquid films on both sides of the membrane is pronounced: e.g., if $D_{AM} = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $\delta_M = 50 \mu\text{m}$ then $k_{AM} = D_{AM}/\delta_M = 1 \times 10^{-5} \text{ m s}^{-1}$, whereas $k_L = 1 \times 10^{-6} \text{ m s}^{-1}$. At very high values of the partition coefficients ($\Psi_A = 10$), the relative error can reach almost 40 % (see Fig. 10). When the intensity of mixing is very low and the diffusion coefficient is based on the concentration and volume data in compartment II, the diffusion coefficient is underestimated (see Figs. 11–13). At low and medium values of Ψ_A (Figs. 11 and 12), the relative error can reach almost 20 %, whereas at high values of Ψ_A , the relative error is very high (see Fig. 13).

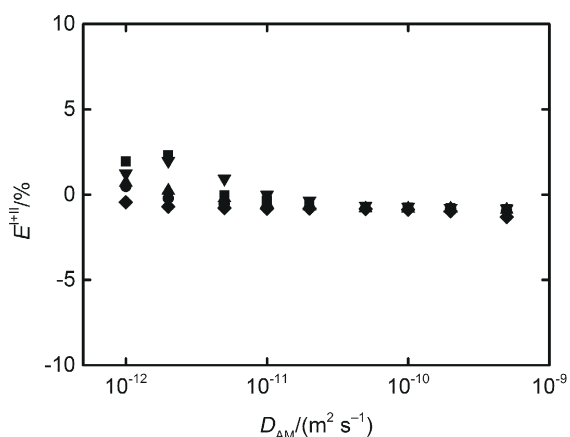


Fig. 8. Dependence of relative error, E^{I+II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 0.1$. For meaning of symbols, see Fig. 4.

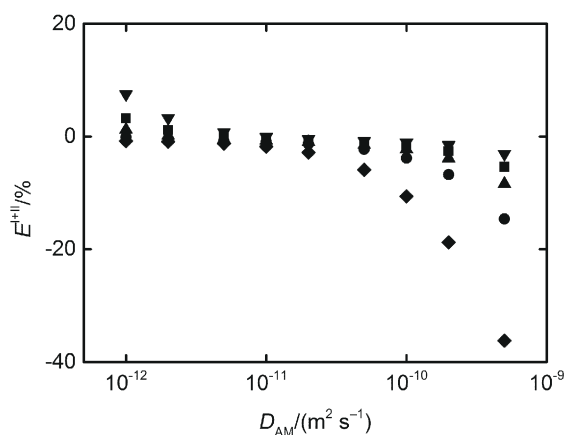


Fig. 10. Dependence of relative error, E^{I+II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 10.0$. For meaning of symbols, see Fig. 4.

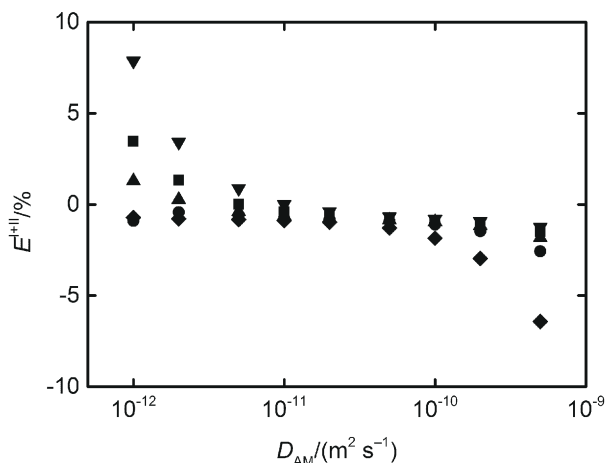


Fig. 9. Dependence of relative error, E^{I+II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 1.0$. For meaning of symbols, see Fig. 4.

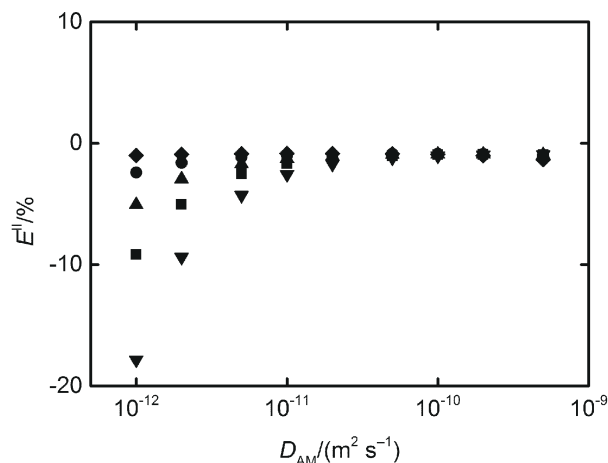


Fig. 11. Dependence of relative error, E^{II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 0.1$. For meaning of symbols, see Fig. 4.

A limited number of calculations were done to determine the effect of physico-chemical properties of the studied liquid. Calculations where $M_A = 100 \text{ kmol kg}^{-1}$ and $\rho = 1000 + 30c_A + c_A^2$ led to the same conclusions as those discussed above.

Conclusions

The pseudo-steady state conditions in the mass transport description in a two-compartment dialysis cell was analysed numerically. The procedure used consisted of two steps: i) under the specified conditions, i.e., the initial concentration of the component (c_{A0}^I), initial volumes of liquid (V_0^I, V_0^{II}), mass transfer coefficients ($k_L^I = k_L^{II} = k_L$), partition coefficients ($\Psi_A^I = \Psi_A^{II} = \Psi_A$), membrane thickness (δ_M), and diffusion coefficient (D_{AM}) dependences of the compo-

nent concentrations and liquid volumes in both compartments were generated using the rigorous model; ii) the diffusion coefficient of the component in the membrane was determined from the concentration and volume data generated using a simplified mathematical model. The thus calculated diffusion coefficient was compared with the specified one. The numerical analysis proved that:

- when the diffusion coefficient is calculated considering the concentration and volume data in both compartments under intensive liquid mixing, then, in case of not too thick membranes and sufficiently high values of the diffusion coefficient, the pseudo-steady state conditions represent a good approximation of a real state;
- value of the diffusion coefficient determined based on the concentration and volume data in the com-

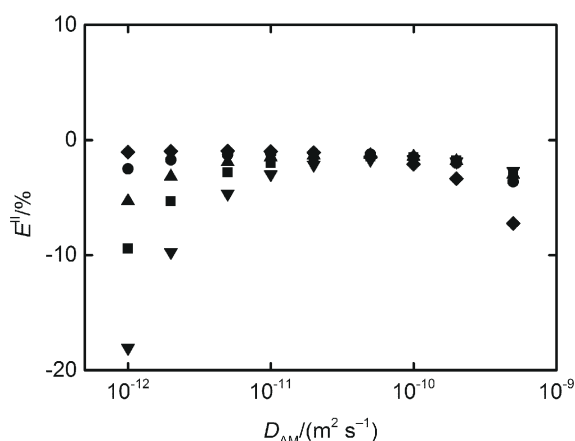


Fig. 12. Dependence of relative error, E^I , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 1.0$. For meaning of symbols, see Fig. 4.

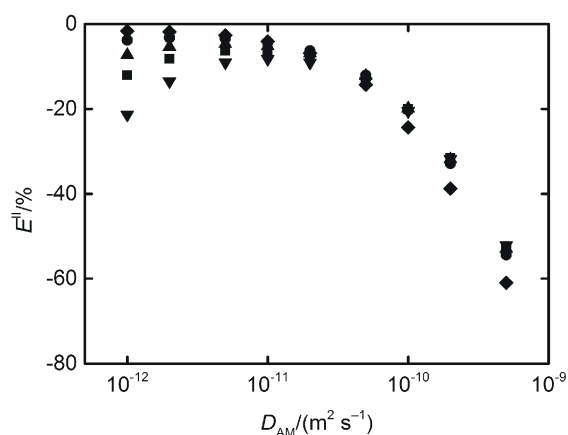


Fig. 13. Dependence of relative error, E^{II} , on the diffusion coefficient of a component in a membrane for $k_L^I = k_L^{II} = 1.0 \times 10^{-6} \text{ m s}^{-1}$ and $\Psi_A^I = \Psi_A^{II} = 10.0$. For meaning of symbols, see Fig. 4.

partment initially filled with pure solvent is underestimated;

– in case of very low intensity of mixing, relative errors of the diffusion coefficient determination are acceptable for low and medium values of the partition coefficients at the D_{AM} determination based on the concentration and volume data in both compartments.

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Symbols

A	membrane area	m^2
c	molar concentration	kmol m^{-3}
D	diffusion coefficient	$\text{m}^2 \text{ s}^{-1}$
E	relative error of diffusion coefficient	

F	objective function	$\text{kmol}^2 \text{ m}^{-6}$
f	general function	
h	integration step in x direction	m
J	flux	$\text{kmol m}^{-2} \text{ s}^{-1}$
k	integration step in τ direction	s
k_A	ratio of membrane area to initial liquid volume in compartment I	m^{-1}
k_L	liquid mass transfer coefficient	m s^{-1}
k_V	ratio of initial liquid volume in compartments I and II	
M	molar mass	kg kmol^{-1}
m	number of data generated	
n	number of grid points	
V	volume	m^3
x	length coordinate	m
δ	thickness	m
ρ	density	kg m^{-3}
τ	time	s
Ψ	partition coefficient	

Superscripts and subscripts

A	referred to component A
b	referred to bulk solution
calc	calculated
gener	generated
i	referred to solution/membrane interface
L	referred to liquid
M	referred to membrane
w	referred to solvent
I	referred to compartment I
II	referred to compartment II
0	initial

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