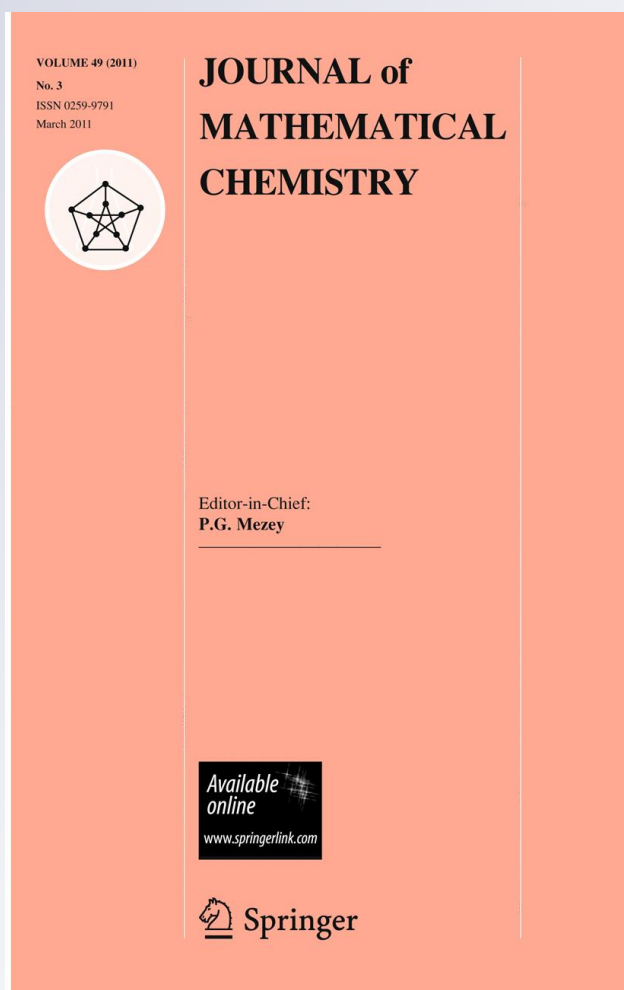


Mathematical modelling of low-frequency oscillations in solute transport by diffusion through a membrane

**Journal of Mathematical
Chemistry**

ISSN 0259-9791
Volume 49
Number 3

J Math Chem (2011)
49:629-642
DOI 10.1007/
s10910-010-9758-3



Your article is protected by copyright and all rights are held exclusively by Springer Science+Business Media, LLC. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your work, please use the accepted author's version for posting to your own website or your institution's repository. You may further deposit the accepted author's version on a funder's repository at a funder's request, provided it is not made publicly available until 12 months after publication.

Mathematical modelling of low-frequency oscillations in solute transport by diffusion through a membrane

N. A. Tikhonov · M. G. Tokmachev

Received: 31 May 2010 / Accepted: 12 October 2010 / Published online: 7 January 2011
© Springer Science+Business Media, LLC 2011

Abstract Low-frequency oscillations of concentration could occur in the case of substance diffusion through a membrane under stable external conditions. This phenomenon had been experimentally observed. A theoretical explanation of the phenomenon was given and the results of mathematical modelling were presented in the present paper. Models considering dependence of local conductivity of a membrane on concentration of a solution were studied. Emergence of positive feedback between fluctuations of flows and concentrations was shown. This determines an appearance of oscillations in the process of substance diffusion.

Keywords Mathematical modeling · Low-frequency oscillations · Diffusion · Membrane

Nomenclature

C [mol/L]	Component concentration in the inner tube (in the left chamber)
C_0 [mol/L]	Component concentration injected at inlet point
D [m ² /sec]	Coefficient of longitudinal convective diffusion of the component in the tube
I_0 [m ³ /sec]	Constant water flow entered into the inner tube
j [m ³ /sec]	Total water flow through the membrane

N. A. Tikhonov · M. G. Tokmachev (✉)
Department of Mathematics, Faculty of Physics, Moscow State Lomonosov University,
Moscow 119992, Russia
e-mail: mike_tokm@yahoo.com

N. A. Tikhonov
e-mail: niktandr@yandex.ru

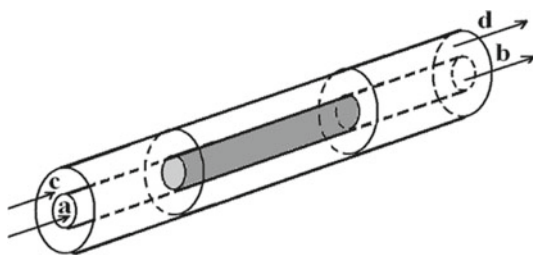
$j_1[\text{m}^3/\text{sec}]$	Flow of water through small channels, where molecules of the component dissolved could not pass (non-conductive channels)
$j_2[\text{m}^3/\text{sec}]$	Flow of water through large channels, which are pervious to the component (conductive channels)
$J[\text{mol}/(\text{m}^2 \cdot \text{sec})]$	Flow of the component through the membrane
$J^{eq}[\text{mol}/(\text{m}^2 \cdot \text{sec})]$	Flow of the component in the equilibrium state through the membrane
$h[\text{m}^2/\text{sec}]$	Effective diffusion coefficient
$H[\text{m}^2/\text{sec}]$	Effective coefficient of component diffusion
$L[\text{m}]$	Membrane width
$m[-]$	Dimensionless coefficient
$P_0[\text{kg}/(\text{m} \cdot \text{sec}^2)]$	Pressure difference fixed in the experiment between the membrane sides
$r[\text{m}]$	Radius of the inner tube
$S[\text{m}^2]$	Square of the membrane surface area
$S_2[\text{m}^2]$	Total square of the conductive channels at $x = 0$
$t[\text{sec}]$	Time
$V[\text{m}^3]$	Volume of the inner tube (of the left chamber)
$w[\text{sec}^{-1}]$	Frequency of concentration oscillations
$x[\text{m}]$	Space coordinate inside the membrane
$y[\text{mol}/\text{L}]$	Component concentration in the membrane
$z[\text{m}]$	Space coordinate along the tube
$z_0[\text{m}]$	The coordinate of the outlet of the tube
$\alpha[-]$	Dimensionless coefficient
$\beta[\text{sec}]$	Variable, which characterizes time of water redistribution between the channels
$\delta[\text{mol}/\text{L}]$	Amplitude of concentration oscillations
$\lambda[\text{L}/\text{mol}]$	Coefficient
$\rho[\text{m}/\text{sec}]$	Linear velocity of the water flow through the membrane
$\phi[\text{m}^6/(\text{sec} \cdot \text{kg})]$	Local conductivity of a membrane
$\psi[-]$	Fraction of flow in the membrane transporting the component

Introduction

The paper [1] presents unusual and interesting experimental results associated with diffusion and substance transfer through a membrane. Shortly, the experiment consisted in the following.

The solution containing component of interest was passed through the tube having walls as a membrane (see the way (*ab*) in Fig. 1). There were several experiments with vitamins Methionine, B₂ or B₁₂. Concentration of the component was kept constant at the inlet point (point *a*) and measured at the outlet point (point *b*). A flow of the solution was forced by supply and suction pumps. Their stable operating mode and absence of pulsations were controlled. Some part of the solution moved out after

Fig. 1 Scheme of the experiment. The tube segment having a membrane wall is highlighted in grey



filtration through a membrane by a high flow of clean water (see the way (*cd*) in Fig. 1).

Instead of a constant concentration of the component at the outlet point, the curves shown in Fig. 2 were observed in the experiment [1].

Unfortunately, there is no full explanation of the results given in [1]. The authors only supposed that oscillations result out convection phenomena arising due to filtration of the solution through a membrane.

High-frequency oscillations and noise in the ion exchange membranes, which come out by extremely high electric current, are well-known and studied [2,3]. These oscillations could be explained by fluctuations in the solution [4]. However, stable low-frequency oscillations could hardly be explained by fluctuations.

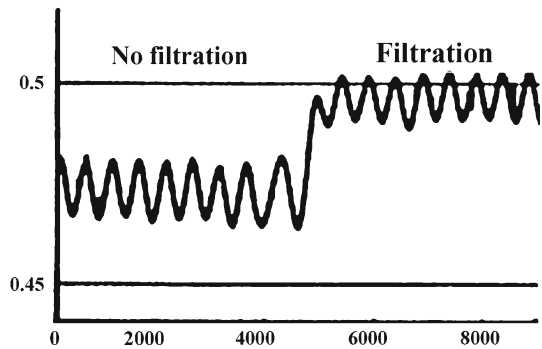
Low-frequency oscillations in case of diffusion and transfer of ions through a membrane under external electric field are also well-known and described in literature. For the first time such oscillations under stable external conditions were discovered by T.Teorell in 1959 [5]. Later low-frequency oscillations with the period from several minutes to several dozens of minutes were experimentally observed many times [6,7]. In contrast to the experiments described in [1] oscillations appear because of diffusion of molecules without influence of an external electric field.

Abnormal kinetics of amino acid sorption onto ionite granules was observed in [8,9]. In these experiments oscillations were detected instead of a standard monotonous change of sorbed amino acid quantity. The sorption process was accompanied by noticeable changes of a granule size, which periodically recurs. An explanation of this phenomenon was given in [10]. The explanation was based on a change in ionite granule volume, when changing concentration in the internal solution of granules. There were however two essential points: the sorbed substance is amino acid and sorption goes onto ionite granules.

Thus, in contrast to the cases shown in [2–7], low-frequency oscillations described in [1] were observed in the process of substance diffusion through a membrane for the extremely simple object, i.e. the process went in the absence of an electric field and the ion exchange process was not the driving force for diffusion of neutral molecules. Therefore the results are of high interest and their theoretical explanation is important.

In the present paper the processes described in [1] are investigated on the basis of mathematical modelling. Two models considering a change of membrane conductivity given a change of solution concentration due to effects resulted from forces of osmotic pressure have been developed and studied. It is shown that oscillations could

Fig. 2 Experimental curves measured at the outlet point. The vertical axis represents a value, which is proportional to concentration of the component of interest. The horizontal axis represents time in s



be explained by positive feedback between changes of solution concentration and a flow through the membrane.

1 Model (I) of the process in case of intensive mixing of the solution

1.1 Model description

Let us consider a membrane which separates two chambers. It is depicted by a dark strip in Fig. 3.

The solution with component concentration C_0 and flow I_0 is injected at inlet point (a) into the left chamber, which volume is V . Some part of the solution penetrates through the membrane; the rest of the solution leaves the chamber at the outlet point (b). Let us consider the simplest case when length of the left chamber is short and mixing in the chamber is sufficiently intensive. Although component concentration C could change over time in this case, its concentration is assumed to be equal all over the chamber at any time point, i.e. $C = C(t)$. Therefore we have a mathematical task, when concentration of the component inside the membrane depends on time and the only space coordinate x . There are two assumptions behind the model. Firstly, the

Fig. 3 Scheme of the simplest process in question

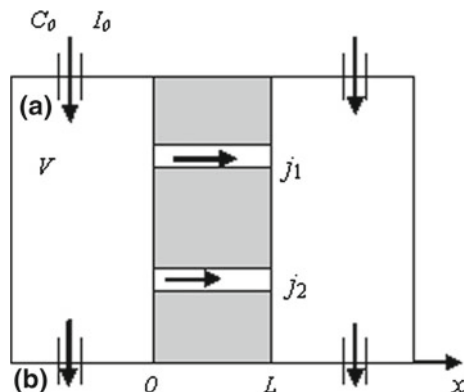
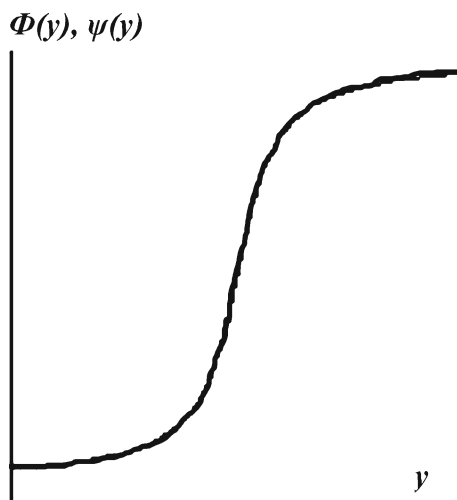


Fig. 4 Shape of functions $\Phi(y)$ and $\psi(y)$



flow of clean water pouring through the right chamber is quite intensive. Secondly, a pressure difference between the chambers is constant.

The membrane is a set of pores and channels between substance threads, which are a skeleton of the membrane. Due to a pressure difference between the chambers clean water with the component dissolved penetrates through the membrane using a set of channels. However, large molecules of the component surrounded by water shell could penetrate only via relatively large channels, while pure water flows through any channel. Let us denote j_1 —flow of water through small channels, where molecules of the component dissolved could not pass (non-conductive channels); j_2 —flow of water through large channels, which are pervious to the component (conductive channels).

We denote average concentration of the component at the layer x as $y(x, t)$. If there was no component in the conductive channels and later it has appeared there then some part of water from pores and channels, where component is unavailable, goes in the conductive channels due to forces of partial pressure. This leads to enlargement of the conductive channels so that they will be able to pass a higher flow j_2 . The non-conductive channels, hence, shrink due to water outflow from them. Thus, both local conductivity of a membrane Φ for water and a fraction of flow transporting the component depend on concentration y . Let $\psi = j_2/j$, where $j = j_1 + j_2$. In the equilibrium state a flow of the component is $J = y \cdot j_2 = y \cdot j \cdot \psi(y)$. Let us consider that an approximate shape of $\Phi(y)$ and $\psi(y)$ in equilibrium corresponds to a curve shown in Fig. 4. (These functions have similar qualitative shapes but different, indeed).

Pores and channels used to transport the solution interlace within the membrane in a complicated way. Difference of the local velocity of the solution, which runs through different micro-ways, results in smearing of y and J . It could be accounted in an effective form by adding small diffusion terms in equations of the model. In addition, if y value changes, flows of water and component become equal to $\psi(y)$ and $J(y)$ only after some time needed for water redistribution between the conductive and non-conductive channels. Therefore we can consider:

$$J^{eq} = yj\psi(y) \quad (1)$$

$$\beta \cdot \partial J / \partial t = J^{eq} - J + h \cdot \partial^2 J / \partial x^2, \quad (2)$$

where J^{eq} - flow of the component in the equilibrium state, h – effective diffusion coefficient, β - variable, which characterizes time of water redistribution between the channels.

Flow of the solution is equal to $(I_0 - j)$ at outlet of the left chamber (point b). At the inlet point of the membrane $y|_{x=0} = \frac{S_2}{S}C$, where S – square of the membrane surface area, S_2 - total square of the conductive channels at $x = 0$. The simplest approximation is: $\frac{S_2}{S} = \frac{1}{S} \left(S_2(0) + \frac{\partial S_2}{\partial y}(0) \cdot y \right)$.

Hence

$$y|_{x=0} = \frac{\alpha C}{1 - \lambda C} \quad (3)$$

where $\alpha = \frac{S_2(0)}{S}$, and $\lambda = \frac{1}{S} \frac{\partial S_2(0)}{\partial y}$.

Flow of the component, which penetrates from the left chamber to the membrane, is equal to $j\psi(y)y|_{x=0}$. Therefore mass balance in the left chamber and conductive channels could be described as following:

$$V \partial C / \partial t = I_0 C_0 - (I_0 - j)C - j\psi(y)y|_{x=0} \quad (4)$$

$$\partial y / \partial t + \partial J / \partial x = H \cdot \partial^2 y / \partial x^2 \quad (5)$$

$$j = P_0 \left[\int_0^L \Phi^{-1}(y) dx \right]^{-1}, \quad (6)$$

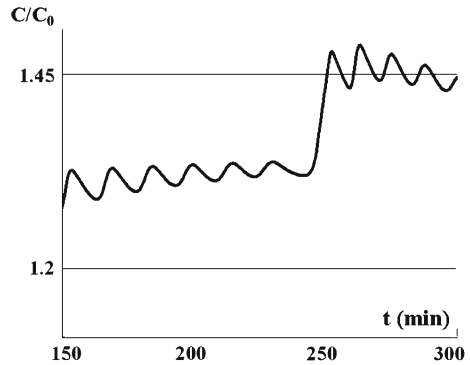
where P_0 —pressure difference fixed in the experiment between the membrane sides; H —effective coefficient of component diffusion.

Equations 1–6 and initial conditions for concentrations C (in the solution) and y (in the membrane) compose a model of the process. We will designate this model as the model (I) for short.

1.2 Results of model (I) quantification

According to the model (I) a computer program was developed and calculations were performed. It was found that oscillations could be observed only in some ranges of coefficients. All figures below show oscillation cases. For instance, we can see dependence of concentration C on time in Fig. 5. The plot corresponds to the following values of parameters: $L = 1$ mm, $V = 1.5$ cm³, $\alpha = 0.2$, $\lambda = 0.14$ L/mmol, $I_0 = 0.025$ cm³/min, $j/I_0 \approx 5 \cdot 10^{-2}$, $\beta = 20$ sec, $H = h = 3 \cdot 10^{-4}$ cm²/min. Parameters of functions $\psi(y)$ and $\phi(y)$ will be clarified below (see explanation for Eq. 10).

Fig. 5 Time dependence of component concentration in the left chamber (see Fig. 3) according to the model (I)



We can see qualitative conformity between estimated and experimental results presented in Fig. 2.

1.3 Explanation of results obtained

It is necessary to answer the following questions:

- why do low-frequency oscillations appear?
- why does shift of value C occur from one average level to another one in Figs. 2 and 5?

We will answer these questions consequently. Model (I) is non-linear and quite complicated. That is the reason why we will consider its separate parts describing different factors in order to take them into the simplest form and give on this basis qualitative explanations, which clarify the physical meaning of the process.

1.3.1 Appearance of oscillations in the membrane results from a delay of the substance flow in comparison with a change of concentration

The equilibrium value J^{eq} of the component flow J depends on concentration y . If y changes, flow J tends to J^{eq} with some delay. The delay is defined by degree of dependence of some parameters on pore size. These parameters are a water flow and a fraction of the total amount of the component in the conductive channels. If y changes then size of the pores also changes after the time, which is necessary for redistribution of water (due to forces of osmotic pressure) between the conductive and non-conductive channels.

Let us consider the simplest case when $h = D = 0$, and $J^{eq}(y) = \rho y$. Then (2) and (5) are transformed into:

$$\begin{aligned} \partial y / \partial t + \partial J / \partial x &= 0 \\ \beta \cdot \partial J / \partial t &= \rho y - J \end{aligned} \quad (7)$$

Let us exclude J from these equations:

$$\rho \cdot \partial y / \partial x + \partial y / \partial t = -\beta \cdot \partial^2 y / \partial t^2 \quad (8)$$

The Eq. 8 is similar to the equation of thermal conductivity with transfer, where places of variables x and t were swapped and the sign in front of the second derivative was negative. Therefore, we have to observe effect of solution transfer and effect, which is opposite to smoothing. Actually, if a small oscillation has appeared at $x = 0$: $y|_{x=0} = y_0 + \delta \cdot e^{i\omega t}$; then (8) gives us a solution: $y = y_0 + \delta \cdot e^{i\omega(t-x/\rho)} \cdot e^{2\omega\beta x/\rho}$. Thus, an amplitude of oscillations increases deep into the membrane that is determined by a delay of changing flow J in comparison with changing concentration y .

1.3.2 Oscillations do not appear at high frequencies

Let us take into consideration the presence of the second derivatives in Eqs. 2 and 5. In order to get an analytical result we will accept H , h , and β as small quantities and $J(y) = \rho y$. Thus:

$$\begin{aligned} \partial y / \partial t + \partial J / \partial x &= H \partial^2 y / \partial x^2 \\ \beta \cdot \partial J / \partial t &= \rho y - J + h \cdot \partial^2 J / \partial x^2 \end{aligned} \quad (9)$$

Looking for a solution to the system (9) as $y = e^{i\omega t} \cdot e^{kx}$ we put the desired solution in (9), and get a dispersion equation, which links ω and k :

$$i\omega + \frac{k\rho}{1 + i\omega\beta - hk^2} = Hk^2.$$

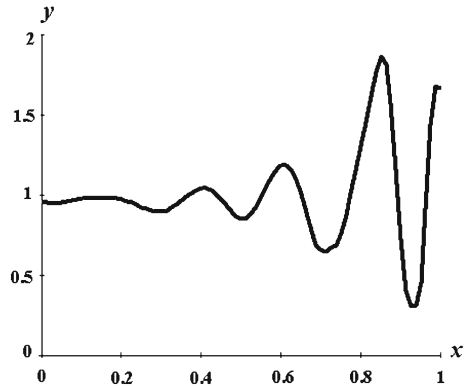
Assuming k as an independent variable we can solve the equation by the method of successive approximations. Because of infinitesimality of H , h and β we may consider them equal to zero. Hence the initial approximation is $k = -i\omega/\rho$. Substituting $k^2 = -\omega^2/\rho^2$ we can get the next approximation in the dispersion equation:

$$k\rho = \omega^2 \left(\beta - H/\rho^2 \right) - \omega^4 \frac{Hh}{\rho^4} - i\omega \left(1 + \frac{\omega^2}{\rho^2} (h + \beta H) \right) \quad (10)$$

Equation 10 yields that if an oscillation with frequency ω has appeared at the membrane boundary then it propagates deep into the membrane (the imaginary part of the right side of Eq. 1 is negative). Therefore, the oscillation amplitude changes along the x axis according to the exponential law with the power $\frac{\omega^2}{\rho} \left((\beta - H/\rho^2) - \omega^2 \frac{Hh}{\rho^4} \right)$. Thus, we can draw two conclusions. Firstly, for raising of the oscillation amplitude it is necessary to satisfy $\beta > H/\rho^2$. Secondly, raising is maximal at the frequency $\omega^2 = \frac{(\beta - H/\rho^2)\rho^4}{2Hh}$ and unavailable at high frequencies.

We have considered the linear system of Eq. 9. Calculations show that if t is fixed dependence of y on x represents a shape presented in Fig. 6.

Fig. 6 Typical shape of dependence of y (normalized to $y|_{x=0}$) on x (normalized to L) if t is fixed. The curve presents calculation results



1.3.3 Oscillations of flows in the membrane result in oscillations of concentration in the chamber

The oscillations of variable y result in a change in a local conductivity Φ . The water flow j through the membrane depends on the conductivity Φ according to (6). A periodic change of j defines a periodic change of the component flow J going into the membrane from the left chamber (see Fig. 3) according to (4): $J|_{x=0} = m \cdot C \cdot j \cdot \psi(m \cdot C)$, where $m = \frac{\alpha}{1-\lambda C}$. As a result, oscillations of concentration y at $x = 0$ take place and feedback appears which is positive at some frequencies. According to (10) oscillations are impossible at high frequencies. In addition, Eq. 6 shows that the higher oscillation frequency, the less change of j and, therefore, feedback. Therefore the main oscillation mode seems to be low-frequency oscillations at such a frequency which is associated with positive feedback.

1.3.4 Explanation of the fact that there are two stable equilibrium states

Let us consider possible steady-state values C and y , i.e. solutions (I), which are time-independent. All functions relating to this case will be marked by bar. The following expression can be concluded from (3) and (4):

$$I_0(\bar{C} - C_0) = \bar{C} \frac{P_0}{L} (1 - \bar{m}\bar{\psi})\bar{\phi}, \quad (11)$$

where $\bar{m} = \frac{\alpha}{1-\lambda\bar{C}}$, $\bar{\psi} = \psi(\bar{m}\bar{C})$, $\bar{\phi} = \Phi(\bar{m}\bar{C})$. At the same time $\bar{y} = \bar{m}\bar{C}$.

Considering that dependencies $\psi(y)$ and $\phi(y)$ have the shapes represented in Fig. 4 one can conclude that the right and left members of Eq. 11 are described by the curves plotted in Fig. 7.

The number of roots of Eq. 11 depends on values of parameters. For the case presented in Fig. 7a there are three roots: C_1 , C_2 and C_3 . Two of them (C_1 and C_3) are stable, and C_2 is unstable. Indeed, quantity $\frac{P_0}{L} (1 - \bar{m}\bar{\psi})\bar{\phi}$ in the right member of Eq. 11 determines the water flow through the non-conductive channels, i.e. bleeding of fresh water from the left chamber. The right side of Eq. 11 represents the flow of

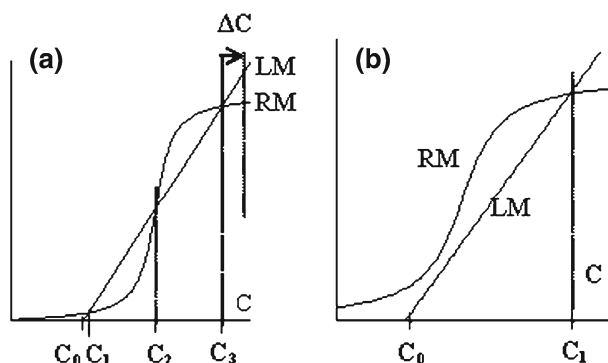


Fig. 7 Dependence of the right (RM) and left members (LM) of Eq. 11 on C

the component $J^{filter}(C)$, which has not been able to leave the chamber with the solution during its filtration through the membrane. The component is captured, goes back to the chamber and increases concentration in it. The right member of Eq. 11 describes an increment of concentration in the chamber in comparison with incoming concentration.

Let us study the point C_3 in Fig. 7a. If C has randomly increased by ΔC then the amount $J^{filter}(C + \Delta C)$ captured during the filtration process would be less than the amount $I_0(C + \Delta C - C_0)$ needed to increase concentration in the incoming flow (see Fig. 7a). Therefore the amount of the component entered into the chamber is insufficient to maintain concentration $(C + \Delta C)$ in the chamber and concentration decreases to C_3 . Similarly, C_1 is a stable point. The opposite situation is in the neighbourhood of the point C_2 . If concentration deviates from C_2 then a change of J^{filter} exceeds a change of $I_0(C - C_0)$. Therefore, the process goes far from the equilibrium value C_2 .

Thus, there are two stable values C of the steady-flow process for the case presented in Fig. 7a. If concentration in the system $C < C_2$ and there are no oscillations then system evolves to the state $C = C_1$; if concentration in the system $C > C_2$ then the system evolves to the state C_3 .

Now we will consider an unstable process. At the beginning of the process $C = 0$. Following the entry of the solution with concentration C_0 to the left chamber (see Fig. 3), the concentration C in the chamber tends to the nearest stable value C_1 . Therefore, oscillations of the concentration and flow of the solution through the membrane appear in the system due to the causes mentioned in Sects. 1.3.1 and 1.3.3. We will denote the mean value of an arbitrary function g by an oscillation period as $\bar{g}$. Let some oscillations δy appear around a time-independent solution $\bar{y}$ and $\delta \bar{y} = 0$. Let y vary in the range, where the second derivative $d^2\Phi/dy^2 > 0$ (see Fig. 4). Under the conditions mentioned in the paragraph $\Phi(\bar{y} + \delta y)$ is more than $\Phi(\bar{y})$. In accordance with Eq. 6, both conductivity of the membrane and flow j increase. This is accompanied by increasing of the value C and the mean value of $\bar{C}$ by the oscillation period (see Eq. 3). When $\bar{C}$ becomes more than C_2 the system comes to the domain of influence of the stable root C_3 .

For calculations, which results are shown in Fig. 5, functions $\psi(y)$ and $\phi(y)$ have been chosen in the shape presented in Fig. 4 so that Eq. 16 should have three roots. The calculation results depicted in Fig. 5 fit the experimental data demonstrated in Fig. 2a in a qualitative manner. Thus, the model (I) explains both the appearance of oscillations and a leap from a lower level of the concentration C to a higher one.

2 Model (II) considering changes of the concentration along the tube

2.1 Model description

The model (I) considered in the previous section is valid for the case when mixing the solution in the left chamber is intensive enough (see Fig. 3) so that $C = C(t)$ and $y = y(t, x)$. This is the simplest, one-dimensional spatial case.

The model (II) is the development of the model (I). Its main assumptions are addressed below. In the facility drawn in Fig. 1 the solution flows inside a thin tube, which is a membrane, and partially leaks through it. The inner part of the tube plays a role of the left chamber presented in Fig. 3; however the chamber is supposed to be long and narrow. Evidently, in this case the component concentration changes along the tube and we have to consider solutions, which depend on two spatial variables. Now we put the axis z along the tube considering $z = 0$ at the inlet and $z = z_0$ at the outlet of the tube. The concentration inside the tube is defined as $C = C(t, z)$. Let x be a coordinate, which is orthogonal to the membrane surface, $x = 0$ corresponds to the inner surface and $x = L$ corresponds to the outer surface of the tube. Considering a local segment of the tube we will neglect its curvature for simplification because thickness of the tube walls is much less than its diameter. Inside the membrane $y = y(t, x, z)$.

According to the laws of conservation of the component and water in the tube we can write the following expressions:

$$\pi r^2 \frac{\partial C}{\partial t} + \frac{\partial(IC)}{\partial z} = \pi r^2 D \frac{\partial^2 C}{\partial z^2} - 2\pi r J(t, 0, x) \quad (12)$$

$$\frac{\partial I}{\partial z} = -2\pi r j, \quad I(0, t) = I_0 \quad (13)$$

where r – radius of the tube, I_0 – constant water flow entered into the tube, $I(t, z)$ – water flow along the tube in the cross-section z , $j(t, z)$ and $J(t, x, z)$ – density of the water flow and density of the component leaving the tube through the membrane, correspondingly; D – coefficient of longitudinal convective diffusion of the component in the tube.

Equations 1–2 and 4–6 are valid inside the membrane.

The diffusion process also takes place in the inlet tube. Let the concentration of the solution be fixed and equal C_0 in some point (a) (see Fig. 1), where the solution comes from. In this case the diffusion flow moved from left to right though the cross-section $z = 0$ causes a deviation between the concentration value C and C_0 in this cross-section. The boundary conditions yield:

$$\left(I_0(C - C_0) = \pi r^2 D \frac{\partial C}{\partial z} \right) \Big|_{z=0} \quad (14)$$

We will put the condition of a free solution leakage at the outlet point of the tube:

$$\left(\frac{\partial C}{\partial z} \right) \Big|_{z=z_0} = 0 \quad (15)$$

The system of Eqs. 1–3, 5–6, 12–15 and initial conditions for C and y are a complete mathematical model describing the process, which scheme is presented in Fig. 1.

The processes inside the membrane are described by similar equations for the models (II) and (I) and go identically. Similar to the model (I), the flow J inside the membrane delays as compared with changing the concentration y . That is the reason why casual or systematic disturbances of the concentration C around the time-independent solution and therefore disturbances of $y|_{x=0}$ result in disturbances of y , which propagate along the x line with a raising amplitude. In turn, the last change causes changes of the water flow j through the membrane and the flow of the component $J|_{x=0}$. This leads to a new change in the concentration C inside the tube.

However, the model (II) differs from model (I) for the processes inside the tube. There are two extreme cases. The first one occurs when the diffusion coefficient is equal to zero: $D = 0$. In this case Eqs. (17)–(20) yield:

$$\pi r^2 \frac{\partial C}{\partial t} + \left\{ I_0 - \int_0^z j dz \right\} \frac{\partial C}{\partial z} = 2\pi r C j \left(1 - \psi \frac{\alpha}{1 - \lambda C} \right), \quad C|_{z=0} = C_0 \quad (16)$$

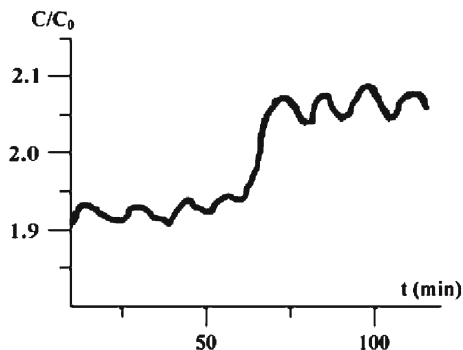
The time-independent solution $\bar{C}(z)$ satisfies the following conditions:

$$\frac{\partial \bar{C}}{\partial z} = \bar{C} \cdot 2\pi r \frac{\phi(m\bar{C}) (1 - m\psi(m\bar{C}))}{L I_0 / P_0 - \int_0^z \phi(m\bar{C}) dz}, \quad m = \frac{\alpha}{1 - \lambda \bar{C}}, \quad \bar{C}|_{z=0} = C_0 \quad (17)$$

As we can see from (17) $\bar{C}$ is a monotonically increasing function (if z is an independent variable). Equation 16 is a non-linear transfer equation. Any disturbance of C in the point z is passed away by the flow of the solution along the tube in the line of increasing values of z and does not influence the concentration C at smaller values of z . Therefore, positive feedback does not appear and only casual fluctuations around the time-independent solution are potentially possible. Systematic seed oscillations of $y|_{x=0}$ are not generated.

Another extreme case should be considered when D tends to infinity. For this particular case the model (II) is similar to the model (I), which features are addressed in Sect. 1. Intensive diffusion (high value of D) results in the same change of C in every point z . Oscillations appearing in some part of the membrane propagate through the boundary $x = 0$ by oscillation of C . Hence, the stable oscillation process, which is

Fig. 8 Component concentration at the outlet of the membrane tube obtained from calculations using the model (II)



synchronous in every point z , can appear. In addition, there can be two stable states, around which oscillations happen in the same way as it was shown in Sect. 1.

In the intermediate case, when the diffusion coefficient is finite and positive, we can observe some features of both extreme cases. The flow of the solution transfers disturbances of C along z , therefore, oscillations inside the membrane can be asynchronous with a phase delay being equal to time of the solution transfer along the tube. On the other hand, if the flow rate I is low then oscillations of C at some z influence value C at smaller values z because of diffusion of the substance inside the tube. Thus, if the oscillation process has started in some part of the tube then seed changes $y|_{x=0}$ appear in all the parts of the tube caused by diffusion. Certain sets of values of physical parameters make it possible to create positive feedback at some frequencies. The mechanism described in the paragraph can be observed by numerical modelling using the model (II).

2.2 Results of calculations on the model (II)

A computer program was developed and quantification was performed using the model (II). As an example, the result is presented in Fig. 8 for the following input data: $z_0 = 12$ cm, $L = 0.03$ mm, $r = 2$ mm, $\alpha = 0.7$, $\lambda = 0.15$ L/mm, $I_0/\pi r^2 = 2$ cm/min, $\beta = 20$ s, $H = h = 10^{-3}$ cm²/min, $D = 5 \cdot 10^{-4}$ cm²/min.

3 Conclusion

The main results presented in the paper are as follows:

- local oscillations inside the membrane should appear if following a change in the component concentration the solution flow changes. The flow change is determined by changing the cross-section of conductive channels under osmotic pressure;
- positive feedback between the component flow through the membrane and the concentration of the component in the tube may appear at certain frequencies because of effects of diffusion inside the tube and changing of the incoming flow under varying filtration through the membrane. There will be steady oscillations of the concentration in the whole system in this case;

- two steady-state modes of substance diffusion through the membrane can exist under certain characteristics of the membrane material. This allows explaining a leap of the concentration from one level to another observed in the experiments;
- all the findings mentioned above are supported by calculations within the framework of the mathematical models considered.

References

1. T. Kanamori, T. Ohmori, T. Yamagushi, T. Shiubo, Oscillations with a long periodical time observed in solute transport by diffusion combined with convection through a single hollow-fiber membrane. *J. Membr. Sci.* **184**, 287 (2001)
2. M. Yafuso, M.E. Green, Noise spectra associated with hydrochloric acid transport through some cation exchange membrane. *J. Phys. Chem.* **75**, 654 (1971)
3. S.H. Stern, M.E. Green, Noise generated during sodium and hydrogen ion transport across a cation exchange membrane. *J. Phys. Chem.* **77**, 1567 (1973)
4. I. Rubinshtein, B. Zaltzman, J. Pretz, C. Linder, Experimental verification of the electroosmotic mechanism of overlimiting conductance through a cation exchange electrodialysis membrane. *Russ. J. Electrochem.* **38**(8), 853 (2002)
5. T. Teorell, Electrokinetic membrane processes in relation to properties of excitable tissues: Experiments in oscillating transport phenomena in artificial membranes. *J. Gen. Physiol.* **42**, 831 (1959)
6. C. Forgacs, Deviations from the steady-state in ion transfer through permselective membranes. *Nature* **190**, 339 (1961)
7. S.R. Kaplan, D.S. Mikulevsky, in *Ion exchange*, ed by Y. Marinsky, *Mir*, Transfer processes in membranes. (1968, in Russian), p. 420
8. S.I. Karpov, M.V. Matveeva, V.F. Selemenev, Kinetics of sorption of amino acids by helium cation exchanger KU-2-8. *Russ. J. Phys. Chem.* **75**(2), 266 (2001)
9. S.I. Karpov, M.V. Matveeva, V.F. Selemenev, in *Condensed mediums and interphase borders*, Self-oscillating sorption of aromatic amino acids at ion exchangers, **5**(2), 198 (2003), (in Russian)
10. N.A. Tikhonov, Oscillations of the concentration and size of ion exchanger grains during sorption of amino acids. *Russ. J. Phys. Chem.* **81**(8), 1292 (2007)