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Study of a Low-Frequency Oscillation Phenomena Associated with a Diffusion Process via a Hollow-Fiber Membrane

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Abstract—Experimental data related to low-frequency oscillations of substance concentration are under consideration. The phenomenon has been mathematically modeled for stationary external conditions. The model developed here considers the dependence of local membrane conductivity on solution concentration. The calculation results fit the experimental data well. A theoretical explanation of the phenomenon is presented. It has been demonstrated that a positive feedback between changes in flows and concentrations in a membrane occurs in the process that determines the appearance of oscillations in the process of diffusion of the substance.

Keywords: mathematical modeling, low-frequency oscillations, diffusion.

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INTRODUCTION

Passage of fluid through a membrane is usually accompanied by the phenomenon of diffusion, which results in a monotonic change in the concentration of the component under constant external conditions. However, fluctuations in concentration over time have been observed in several experiments.

High-frequency vibrations and noise in ion-exchange membranes resulting in high values of transmitted current were studied in [1, 2]. They were explained by fluctuations arising in the solution [3].

The effect of the emergence of low-frequency oscillations in the diffusion and transport of ions through a membrane under an external electric field was first described by Teorell in 1959 [4]. Low-frequency periodic oscillations with a period of several minutes or 10 min have been subsequently observed experimentally many times [5, 6].

Stationary low-frequency oscillations of the concentration of vitamins in a solution flowing through a membrane in the absence of an external electric field were obtained experimentally in [7]. As well as these oscillations, an abrupt change in the equilibrium position was also observed, with respect to which the concentration was varied.

In the experiment described in [7], a solution containing observed components (the vitamins Methionine, B_2, and B_{12}) was pumped through a tube whose walls were composed of a membrane (path *ab* in Fig. 1, the walls of the inner cylinder are composed of membrane). Part of the solution after filtration through the membrane was carried away on the path *cd* by the flow of clean water at a large expense. The concentration of the component was held constant at the entrance (at point *a*) and the output measured (at point *b*).

A constant flow of solution is provided at the entrance to the tube. However, the pulsating change of the component concentration, which has the shape shown in Fig. 2, was recorded in the output.

Thus, low-frequency oscillations in the process of diffusion of substances through the membrane for the case when the process took place without the influence of an external electric field and in the absence of ion-exchange processes were obtained in [7], unlike the cases described in [1–6]. This makes the results particularly interesting and their theoretical explanation is important.

The theoretical study of the effect was first studied in [8], where a mathematical model was proposed and an explanation of the effect is given. However, some factors influencing the dynamics of the process were not taken into consideration in it. This determines the

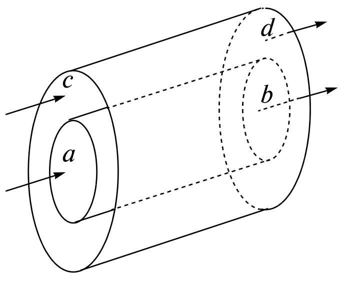

Fig. 1. Schematic diagram of an experiment to determine the low-frequency oscillations of substance concentration in the membrane

need for further study of the process. In this paper, a more complete mathematical model is considered for the case of one-dimensional spatial coordinates, an analytical study of the simplest cases is given, and numerical simulation results are obtained.

1. THE MATHEMATICAL PROCESS MODEL

The scheme of the process is shown in Fig. 3, where the membrane that separates the two cameras is represented by the darkened strip.

The left compartment has volume V and a solution with concentration C_0 of the component under observation enters it at point a. The flow of the incoming solution is I_0. Some of the solution passes through the membrane, but the remaining part exits from the compartment at point b. A significant flow of pure water is passed through the right compartment and this water carries off everything that passes through the membrane. Thus, a constant pressure difference is maintained between the compartments.

A membrane is a collection of pores and channels between the fibers of the substance forming the skeleton of the membrane. Pure water with a component dissolved in it passes through it under the influence of the pressure difference between compartments. However, large component molecules surrounded by a hydration shell can cross the membrane only through relatively large channels, but water passes through a large number of them. Let j_1 be the flow of water through these channels, which do not allow the passage of component molecules (we will term these channels nonconducting), and let j_2 be the flow of water through channels that do transport the component (through conducting channels).

First, in terms of the greatest simplicity, let us examine the modeling case when the length of the left compartment is small and stirring in the compartment is sufficiently strong, such that it can be assumed that the concentration C changes with time in this compartment, but is the same throughout the volume at any instant of time, i.e., $C = C(t)$. In this case, we obtain a problem in which the concentration of the component under consideration inside the membrane depends on time and only one spatial variable, x. Let us specify the amount of the component in the conducting channels in the layer with the coordinate x as $y(x, t)$. If there was no component in the conducting channels, but it subsequently appeared in them, then some of the water from the pores and channels containing no component would pass into the conducting channels under the influence of osmotic pressure. As a result, these conducting channels expand and are able to carry a large flow, j_2. Consequently, the nonconducting channels contract because of the outflow from them. Therefore, both the local conductivity of the membrane material for water Φ and the portion of the flow that transports the component depend on y. Let $\psi = j_2/j$, where $j = j_1 + j_2$. At equilibrium, the flow of the component is $J = yj_2 = yj\psi(y)$. We will assume that approximate form $\Phi(y)$ and $\psi(y)$ at equilibrium corresponds to Fig. 4. (These functions are qualitatively similar, but certainly not identical.)

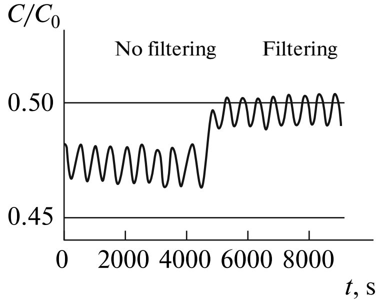

Fig. 2. The concentration curve is taken at the exit of the tube. The quantity proportional to the concentration of the component is plotted on the vertical axis.

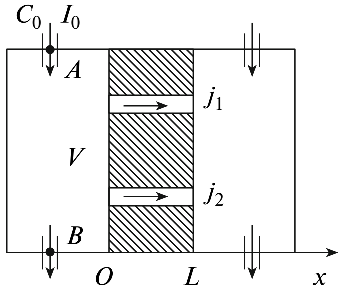

Fig. 3. Schematic diagram of the process.

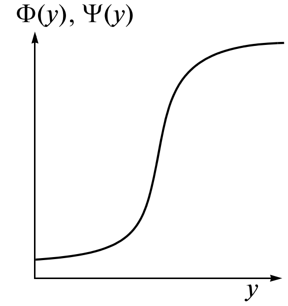

Fig. 4. Qualitative form of the dependencies $\Phi(y)$ and $\psi(y)$.

The membrane channels and pores through which the solution moves are intertwined in a complex pattern. Therefore, what happens at a given point influences the surrounding neighborhood. As a result of differences in local rates of solution movement through the different microroutes, y and J become "smeared out." In the equations of the model, this can effectively be included, leading to small diffusion terms. Furthermore, as the magnitude of y changes, values of the water and component flow become equal to $\psi(y)$ and $J(y)$ only after the time necessary for water

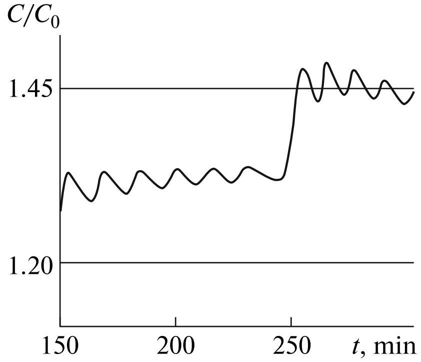

Fig. 5. The concentration curve $C(t)/C_0$ is taken at the exit of the tube.

to be redistributed between the conducting and nonconducting channels. Therefore, we assume that

$$J^{\mathrm{eq}} = yj\psi(y), \tag{1}$$

$$\beta\partial J/\partial t = J^{\mathrm{eq}} - J + h\partial^2 J/\partial x^2, \tag{2}$$

where J^{eq} is the component flow at equilibrium; h is the effective diffusion coefficient; and β is a parameter that characterizes the time for water redistribution between channels.

At the exit from the left compartment (point b), the solution flow is equal to $I_0 - j$. At the entrance into the membrane, i.e., on the border of the left chamber and the membrane, the concentration of component is $y|_{x=0} = \frac{S_2}{S}C$, where S is the surface area of the membrane and S_2 is the total area of the conducting channels in the cross section $x = 0$. In the simplest approximation this is $\frac{S_2}{S} = \frac{1}{S}\left(S_2(0) + \frac{\partial S_2}{\partial y}(0)y\right)$. Hence

$$y|_{x=0} = \frac{\alpha C}{1-\lambda C}, \tag{3}$$

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

The component flow, which moves from the left chamber into the membrane, is equal to $j\psi(y)(y|_{x=0})$. Therefore, the mass balance in the left chamber and the conducting channels is described by the following equations:

$$VdC/dt = I_0C_0 - (I_0 - j)C - j\psi(y)y|_{x=0}, \tag{4}$$

$$\partial y/\partial t + \partial J/\partial x = H\partial^2 y/\partial x^2, \tag{5}$$

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

where P_0 is the pressure difference across the membrane, a fixed quantity in the experiment, and H is the effective diffusion coefficient of the component. Together with the initial conditions for the concentration C in the solution and in the membrane, Eqs. (1)–(6) constitute the model for the process.

2. RESULTS OF NUMERICAL SIMULATION

A computer program was developed and calculations carried out for a mathematical model. Numerical simulation results show that oscillations were observed in some intervals of coefficient values, but not in others. Since we are interested in the former case, we will hereafter give examples in which oscillations were observed. For example, the dynamics of the change in concentration C with time for the following parameters are shown in Fig. 5: $L = 1$ mm, $V = 1.5$ cm^3, $\alpha = 0.2$, $\lambda = 0.14$ l/mol, $I_0 = 0.025$ cm^3/min, $P_0 \approx 0.06$, $\beta = 20$ s, $H = h = 3 \times 10^{-4}$ cm^2/min. The properties of the $\psi(y)$ and $\phi(y)$ functions will be detailed below when discussing the solution of Eq. (10). The results of the calculations presented in Fig. 5 show qualitative correspondence with the experimental observations shown in Fig. 2, in which low-frequency fluctuations and the jump in the equilibrium concentration values on which they occur are displayed.

2.1. Mechanism for the Appearance of Low-Frequency Oscillations

This model is nonlinear and rather complex. Therefore, we will separate its individual units, which take into account one factor or another, and give qualitative explanations illustrating the physical sense of the process on the basis of these simple units.

2.1.1. The appearance of flow oscillations through the membrane. Equilibrium value J^{eq} of the component flow J depends on the concentration y. Component flow J tends to J^{eq} with some lagging. This delay is determined by the fact that both the magnitude of water flow in the conducting channels and the proportion of the total number of components in them depend on the size of these pores. Time is required for the redistribution of water (under the influence of osmotic pressure) between the conducting and nonconducting pores, which is required to vary the pore sizes with changes in y.

Let us examine the simplest modeling case where h and H are equal to zero, and $J^{\mathrm{eq}}(y) = \rho y$. Then from Eqs. (2) and (5), we have the following system of equations:

$$\partial y/\partial t + \partial J/\partial x = 0, \tag{7}$$

$$\beta\partial J/\partial t = \rho y - J. \tag{8}$$

Eliminating the quantity J from Eqs. (7) and (8), we obtain:

$$\rho\partial y/\partial x + \partial y/\partial t = -\beta\partial^2 y/\partial t^2. \tag{9}$$

This is an equation for the type of thermal conductivity with transfer, where the variables x and t have switched places and the sign of the term with the second derivative has changed. Consequently, the effect of transfer in the mathematical solution and the reverse effect to smoothing should be observed. In fact, suppose that a small oscillation occurred at $x = 0$: $y|_{x=0} = y_0 + \delta e^{i\omega t}$. Then it follows from Eq. (9) that $y = y_0 + \delta e^{i\omega(t - x/\rho)} e^{2\omega\beta x/\rho}$. The amplitude of the oscillations increases deep in the membrane. Numerical calculations show that the dependence of y on x at fixed t has the form given in Fig. 6.

Thus, the amplitude of the oscillations increases in proportion to its passage deep into the membrane and this is determined by the time lag of the change in the flow J relative to the change in concentration y.

2.2.2. Absence of oscillations at high frequencies. We take into account the existence of second derivatives in Eqs. (2) and (5). To obtain analytical results we assume H, h, and β are small and $J(y) = \rho y$. We have

$$\partial y/\partial t + \partial J/\partial x = H\partial^2 y/\partial x^2, \tag{10}$$

$$\beta\partial J/\partial t = \rho y - J + h\partial^2 J/\partial x^2. \tag{11}$$

We seek the solution of this system in the form $y = e^{i\omega t}e^{kx}$. Inserting the desired form of the solution in (10) and (11), we obtain the dispersion equation relating ω and k:

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

We view this relationship as an equation in the k.

The dispersion equation is solved by the method of successive approximations. Given the smallness of H, h, and β we put them equal to zero. The initial approximation $k = -i\omega/\rho$ is obtained. Substituting this approximation in the quadratic k terms to the dispersion equation, and solving it, we find

$$k\rho = \omega^2(\beta - H/\rho^2) - \omega^4\frac{Hh}{\rho^4} - i\omega\left(1 + \frac{\omega^2}{\rho^2}(h + \beta h)\right). \tag{12}$$

Equation (12) implies that a harmonic disturbance that arose at the border of the membrane at the frequency ω is propagated inside the membrane (the imaginary part of the right-hand side of Eq. (12) is negative) and the perturbation amplitude varies with respect to x exponentially with the exponent

$$\frac{\omega^2}{\rho}\left((\beta - H/\rho^2) - \omega^2\frac{Hh}{\rho^4}\right).$$

Thus, firstly, to increase the amplitude of perturbation $\beta > H/\rho^2$ must be satisfied; secondly, the increase is maximal at the frequency $\omega^2 = \dfrac{(\beta - H/\rho^2)\rho^4}{2Hh}$ but not at high frequencies.

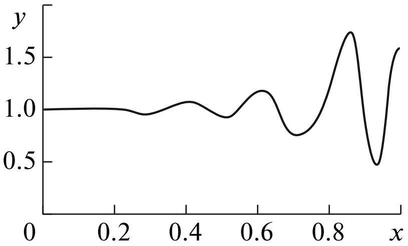

Fig. 6. Characteristic species of the dependence of y (normalized to $y|_{x=0}$) on x (normalized to L) at fixed t obtained by numerical simulation

We have considered a linear system of Eqs. (10)–(11). A similar effect occurs for the considered mathematical model (1)–(6).

2.2.3. Appearance of concentration oscillations in the chamber. In fact, the oscillations of the quantity y considered above lead to a decrease in the local conductivity Φ. The flow of water j through the membrane depends on the conductivity Φ in accord with Eq. (6). The periodic change in j according to Eq. (4) determines the periodic change in the component flow J, which exits from the left compartment (Fig. 3) into the membrane: $J|_{x=0} = mCj\psi(mC)$, where $m = \dfrac{\alpha}{1 - \lambda C}$. Because of this, oscillations of the concentration occur in the left compartment and oscillations of y occur at $x = 0$. Feedback, which will be positive at some frequencies, develops. Oscillations are not possible at high frequencies as follows from Eq. (12). Furthermore, it is seen from Eq. (6) that the higher the frequency of oscillation, the weaker the change in j and, consequently, the feedback. Therefore, the basic oscillation mode will be low-frequency oscillations at the frequency where there is positive feedback. Thus, oscillations of the flow in the membrane lead to oscillations of concentration in the chamber.

2.2. Interpretation of An Abrupt Change in the Equilibrium Position

Let us examine possible steady–state values of C and y, i.e., solutions that do not depend on time. We will label all functions of the corresponding steady-state case with a bar over them. From Eqs. (3) and (4) we have

$$I_0(\bar{C} - C_0) = \bar{C}\frac{P_0}{L}(1 - \bar{m}\bar{\psi})\bar{\phi}, \tag{13}$$

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

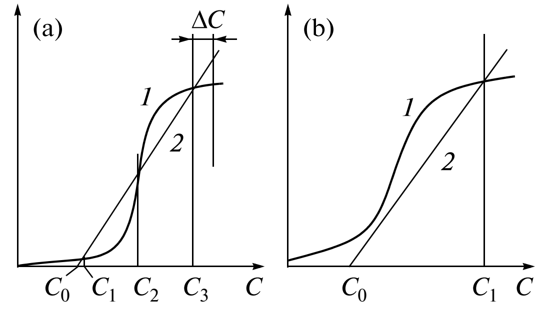

Fig. 7. Dependence of the right side (curve *1*) and left side (curve *2*) of Eq. (13) on the concentration of C for the two cases.

Assuming that the dependence of $\psi(y)$ and $\phi(y)$ have the form shown in Fig. 4, we find that the right hand and left hand sides of Eq. (13) are represented by the curves in Fig. 7.

Depending on the values of the parameters, different numbers of roots of Eq. (13) are possible. For the case depicted in Fig. 7a, there are three roots: C_1, C_2, and C_3. Two of them, C_1 and C_3, are stable, but C_2 is not. In fact, on the right hand side of Eq. (13), the quantity $\frac{P_0}{L}(1-\bar{m}\bar{\psi})\bar{\phi}$ is the flow of water through nonconducting channels, i.e., the fresh water withdrawn from the left compartment. The whole right hand side of Eq. (13) is the amount of the component $J^{\text{filt}}(C)$ that “was not able to exit” with the water from the compartment during filtration. It lags, comes back to the chamber and increases the concentration in it. The right hand side of Eq. (13) describes the increase in concentration in the compartment in comparison to that entering. As an example, let us consider the point C_3 in Fig. 7a. Let the value of C happen to increase by ΔC. Then the amount of component $J^{\text{filt}}(C + \Delta C)$ “held back” in the filtration, as seen from Fig. 7a, will be less than that necessary to raise the concentration in the incoming flow, namely, $I_0(C + \Delta C - C_0)$. Since less of the component enters the compartment than is needed to maintain the level $(C + \Delta C)$ in it, the concentration falls and returns to the level C_3. Point C_1 is stable in the same way. The opposite situation occurs in the neighborhood of point C_2. As the concentration deviates from C_2, the change in the J^{filt} exceeds the change in the value of $I_0(C - C_0)$, and the process departs from the equilibrium position C_2.

Thus, for the case depicted in Fig. 7a, there are two stable values of C in the steady–state process. If the system is in the state that $C < C_2$, then it will shift to the state $C = C_1$ in the absence of oscillations. If $C > C_2$, then the system will shift to the state C_3.

Now let us examine the non-steady-state process, at the start of which $C = 0$. After that, as the flow of solution with concentration C_0 begins to enter the left chamber (Fig. 3), the concentration value C in the compartment closely approaches the steady-state level C_1. Concentration oscillations and solution flow through the membrane begin to occur in the system for the reasons given above. We will designate the average value of the arbitrary function g for the oscillation period as $\bar{\bar{g}}$. Assume that the oscillations $\bar{y}$ developed against the background of the steady–state solution δy such that $\overline{\overline{\delta y}} = 0$. Also assume that the second derivative $d^2\Phi/dy^2 > 0$ over the interval in which the quantity y changes (Fig. 4). Then $\overline{\overline{\Phi(\bar{y} + \delta y)}}$ is more than $\mathrm{F}(\bar{\bar{y}})$. In accord with Eq. (6), the membrane conductivity and the flow j increase. In this case, according to Eq. (3), the value of C and the average level $\bar{\bar{C}}$ (in terms of the oscillation period) increase. When $\bar{\bar{C}}$ becomes larger than C_2, the system shifts to the region of influence around the stable root C_3.

In the calculations, whose results are shown in Fig. 5, the functions $\psi(y)$ and $\phi(y)$ were chosen as shown in Fig. 4 so that Eq. (13) has three roots. The result of the calculations in Fig. 5 agrees qualitatively with the experimentally observed results showed in Fig. 2. Thus, this mathematical model explains both the formation of the oscillations and the transition from the lower average concentration level C to a higher one.

If we chose in the calculations the functions $\psi(y)$ and $\varphi(y)$ in the form presented in Fig. 4, but thus that Eq. (13) has only one root (Fig. 7b), this root is stable. This process just after beginning goes to the oscillation mode around the average level $C \approx C_1$.

CONCLUSIONS

In this paper, an analytical study of simple cases and numerical simulation of the experimental phenomena of low-frequency oscillations in the membrane concentration of the substance was carried out. The following main results within the considered mathematical model were obtained:

—The oscillations inside the membrane can occur if the local changes in component concentration lead to a change in the flow solution with a certain lagging. This may occur due to changes in the cross section of the conducting channels under the influence of osmotic pressure;

—The existence of two steady-state regimes of diffusion of a substance is possible with some characteristics of the membrane material determining the dependence of conductivity on concentration. This explains the phenomenon of concentration of the transition from one level to another, as observed experimentally.

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