

Oscillations of the concentration during sorption of amino acids on ion exchanger grains

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Abstract Low frequency oscillations of the concentration can arise in the process of diffusion and sorption of amino acids under the stationary external conditions. This phenomenon has been observed in some experimental works. In the present paper it is studied by means of modelling. The physical factors responsible for a positive feedback between variations of solution flow and changes in the concentration are found. These factors give rise to instability of the process and oscillations of the concentration. The theoretical explanation of the phenomenon and the results of calculations are presented in this paper.

Keywords Self-oscillations · Diffusion · Ion exchange · Amino acids

List of symbols

Sorption in a plane plate

t	Time (s)
x	Coordinate on the axis perpendicular to the surface of the sorbent layer (m)
$X(t)$	Coordinate of the ion exchange front (m)
$C(x, t)$	Concentration of the amino acid in the internal solution of the sorbent (mol/m ³)
C_0	Concentration of the amino acid in the external solution (mol/m ³)
ν	Specific (per unity of x change) volume of the internal solution in the layer $0 < x < X$ (dimensionless)
ν_0	Value of ν at $C=0$; (dimensionless)

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$w(C)$	Specific volume of the internal solution in equilibrium state (dimensionless)
α	Coefficient that is used in the case when the function $w(C)$ is linear ($w(C) = v_0 + \alpha C$) (mol ³ /mol)
J	Flow of the solution in the sorbent per unit of sorbent surface (m/s)
β	Coefficient of relation between solution flow J and pressure gradient (m ² /s)
a_Σ	Exchange capacity (mol/m ³)
D_{in}	Diffusivity of amino acid in the sorbent (m ² /s)
\widehat{D}_{in}	Coefficient of diffusion between internal and external solutions (m ² /s)
\widehat{C}	Concentration of C at the point $x = X/2$ (mol/m ³)

Sorption in a spherical grain

R	Radius of the grain (m)
$\rho(t)$	Radius of the central zone of the grain that is in the H form (m)
\widehat{C}	Concentration of C at a point separated by $(R + \rho)/2$ from the centre of the grain (mol/m ³)
$\tau = t\beta/R^2$, $r(t) = \rho/R$,	Auxiliary values that are introduced to
$d = D/\beta$, $\chi = \frac{d_{in}}{a_\Sigma}$, $m = \frac{1-r}{1+r}$,	simplify equations
$M = \frac{(1-r^3)m}{3}$	

Comparison of the modelling and the experimental results

$f(t)$	Function describing the amount of the substance sorbed by one grain that was found by simulation
$\delta f(t)$	Separate peak of the function $f(t)$
μ_i	Scaling coefficient of time for i -th grain
N	Number of grains
$n(\mu)$	Number of grains with the scale factor equal to μ
σ	Variance of $n(\mu)$ distribution multiplied by $\sqrt{2}$
h	Height of a separate peak of the function $f(t)$
Δt	Half-width of the peak
t_1	Instant of time when of the peak maximum is reached
f_{mid}	Mean value on the curve $f(t)$ at the interval including the peak
Φ	Error integral. $\Phi(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-x^2} dx$

1 Introduction

The processes, where oscillations appear under stationary exterior conditions are of great interest for chemistry and physical chemistry. Such processes are observed in different fields of investigations. Oscillatory regimes were found both in catalysis processes and in chemical kinetics [1]. Advances in nonlequilibrium pattern formation

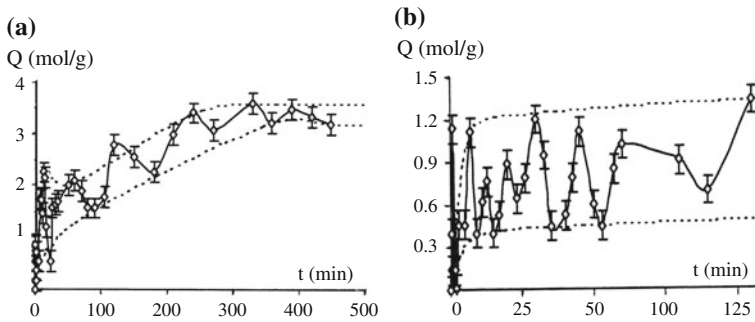


Fig. 1 Sorption of Trp on the cation exchanger KU-2-8 in the H form: **a** from the solution with $\text{pH}=2$; **b** from the solution with $\text{pH}=\text{pI}$

in reaction-diffusion systems are considered in [2]. Oscillations were examined in the processes of substances filtration through a membrane under the action of electric field [3]. T. Teorel was the first who obtained low-frequency oscillations in membranes [4]. The similar oscillations with a period about several minutes or dozen minutes were observed later [5,6]. Well known and investigated are the high-frequency oscillations that appear at “out-of-limit” values of passing current [7,8]. The low-frequency oscillations of a substance flow through a membrane were observed under action of stationary pressure difference in the lack of electric field [9].

The anomalous kinetics of amino acids sorption on grains of ion exchanger was investigated in [10,11]. The low-frequency oscillations of substance concentration were studied. Such phenomenon is unusual for sorption processes because the dependence of substances concentration on time has a monotonic character as a rule. The aim of the present publication is to explain obtained effect.

The experiments involved immersing grains of the cation exchanger KU-2-8 (in the H form) or anionite AB-17-8 (in the Cl form) into solutions of the amino acids Phe or Trp with the concentration of 0.01 mol/L. The time dependence of the amount of sorbed amino acid was measured. Instead of the expected monotonic dependence the experimenters observed oscillations. To illustrate, the experimental data from [10] are shown in Fig. 1.

The sorption was accompanied by noticeable changes in the grain sizes, the changes also being oscillatory in character.

Later S.S. Kovaleva and N.B. Ferapontov (Moscow State University) tested experimentally and confirmed the presence of grain size oscillations in the process of sorption of amino acids from solutions. Using a microscope, they observed fixed sorbent grains. Figure 2 displays one of their results for the grain of cation exchanger KU-2-8, with the concentration of the amino acid being 0.1 mol/L.

In the present paper we show that oscillations can be explained if one considers the dependence of the grain volume on the concentration of the internal solution. If the grain volume increases as a result of the diffusion of the amino acid inside the grain, positive feedback appears between changes in the solution fluxes entering the grain and changes in the concentration inside the grain. It is the factor that causes instability in the process of diffusion. In this work, we theoretically explain the phenomenon

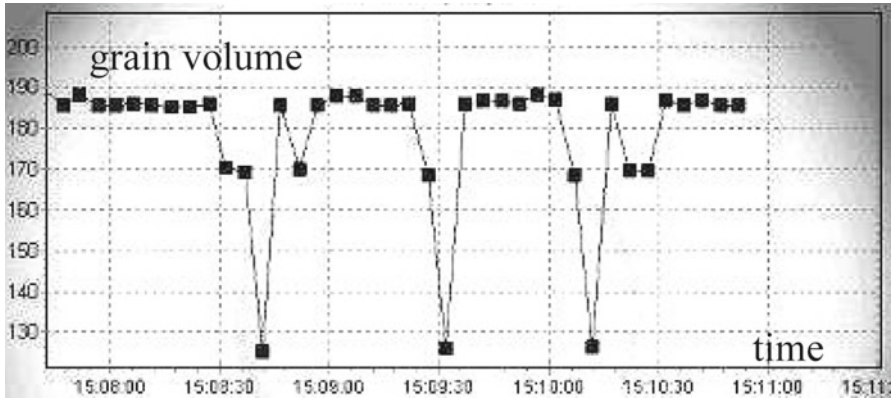


Fig. 2 Time dependence of the grain volume in the process of sorption

and present the results of mathematical modelling which allow the validity of our explanation to be tested.

2 Model of the process

To make the consideration more simple we shall at first examine sorption not in a spherical grain but in a plane plate $2R$ thick.

Let axis x be normal to the plate surface. As it was mentioned above, the noticeable change in the ion exchanger volume was observed in the experiments. For this reason, let the coordinate x be fixed at sorbent particles; that is, let it be a Lagrange coordinate. By virtue of axial symmetry it is sufficient to consider the process in an ion exchanger bed in the range of $0 < x < R$. At $x = 0$ the sorbent is contiguous to the amino acid solution with the concentration C_0 . For definiteness, let this amino acid be Trp and the sorbent be the cation exchanger KU-2-8. Initially, at $t = 0$, the cation exchanger is in the H^+ form. The sorbent used in the experiments was selective with respect to Trp^+ ions. The sorption isotherm has the form close to rectangular, so the process of ion exchange H^+ for Trp^+ occurs in a comparatively thin layer that gradually moves into the sorbent. The coordinate of this layer is denoted by $X(t)$. Thus at $X < x < R$ the ionite is still in the H^+ form and at $0 < x < X$ it is already in the Trp^+ form. At $0 < x < X$ the ion exchanger is weakly acid. That determines comparatively free penetration of the Trp molecules from the external solution into the internal solution in this region.

The amino acid can exist in the form of neutral Trp molecules or in the form of Trp^+ ions, as a result of the $Trp-H^+$ binding. The predominant form of the amino acid depends on the concentration of H^+ ions. The concentration of the amino acid in an internal solution of the sorbent can be denoted as $C(x, t)$. Near the ion exchange front, at $x \approx X$, where H^+ ions pass from the sorbed state into the internal solution, their concentration is high. Hence, in this part of the internal solution the amino acid is in the form Trp^+ . Since the ion exchanger is selective with respect to Trp^+ ions and the ion exchange equilibrium coefficient for Trp^+ in the law of mass action is high,

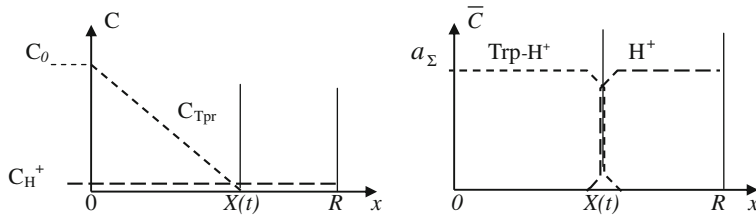


Fig. 3 Approximate dependences of C_{Tpr} (dotted line) and C_H (dot-and-dash line) concentrations on the coordinate. The left-hand graph shows the concentrations in the solution and in the right-hand graph the corresponding dependences in the sorbed phase are demonstrated

the concentration of the amino acid at the ion exchange front is much lower than that of H^+ ions. Therefore, $C_{|x=X} \approx 0$.

At $x \approx X$ the exchange of H^+ for Trp^+ takes place on the cation exchanger functional groups. The Trp^+ ion is formed in association of the Trp molecule with H^+ ion. Therefore, from the viewpoint of the substance balance, such ion exchange is equivalent to the extraction of a neutral Trp molecule from solution and its “deposition” onto a functional group included in the Trp^+ ion. As a result, the process taking place at $x \approx X$ does not change the total amount of hydrogen and extracts Trp from the solution in such a way that $C_{|x=X} \approx 0$. In the absence of oscillations the dependence of the total amino acid concentration and the concentration of hydrogen on x should be approximately such as in the left-hand graph in Fig. 3.

Let’s designate the specific (per unit of x change) volume of the internal solution in the layer $0 < x < X$ as v . The experiments [10] showed that the grain volume changes noticeably in the process of sorption of amino acids. Therefore we should consider v as a variable depending on the concentration C . There are some factors capable of enlarging the volume of the internal solution as C increases. Namely, the amino acid in an internal solution can weaken the bonds between sorbent threads, which therefore start moving apart. In addition [12, 13], amino acid sorption can be accompanied by formation of the chains of molecules of substantial sizes, which push sorbent threads apart. Besides, another factor is changing the osmotic pressure due to variations of C . In fact, the surface layer of a sorbent can be considered as a semi-permeable membrane: the water molecules pass easily through it but the large Trp molecules in water shells penetrate these membranes with difficulties. At the moment the grains are submerged the Trp concentration in the solution outside the grains is C_0 and inside the grains it is equal to zero. The difference in the concentrations causes the osmotic pressure to appear. Under the action of the osmotic pressure some portion of water leaves the grain. In this state the remaining internal volume is v_0 . At this moment the diffusion of the amino acid in the grain begins. A subsequent increase in the concentration C in the internal solution results in a decrease in the osmotic pressure, the solution enters the grain and the grain “straightens out”. The dependence of the size of sorbent grains on the Trp concentration has not been studied by direct experimental methods. Taking into account the above considerations we assume that in the stationary state the volume of the internal solution is $w(C)$, where w is a monotonically increasing function. It reaches “saturation” at high values of C and $w(0) = v_0$.

If the volume of internal solution becomes different from $w(C)$, elastic forces tend to restore the $w(C)$ value of the volume. The forces are described by the Hooke law. The excess pressure Δp in the internal solution is proportional to $[v - w(C)]$. This pressure causes the solution flow J to get into (or out of) the grain. J is proportional to the gradient of pressure: $J = -\beta \frac{\partial [v - w(C)]}{\partial x}$. The solution flow exists until pressures inside and outside become equal.

The amino acid molecules are transferred inside the grains together with solution inflow. If the solution flow is directed into the sorbent, it transfers the amount of Trp equal to $J \cdot C_0$. If the flow is directed outward, the outgoing amount of the amino acid depends on the concentration inside and is equal to $J \cdot C$.

The amino acid flow into the layer $x \approx X$ alters the position of the ion exchange front. $a_\Sigma \frac{\partial X}{\partial t} = -D_{in} \frac{\partial C}{\partial x} |_{x=X}$, where a_Σ is the exchange capacity and D_{in} is the diffusivity of amino acid inside the sorbent.

In order to construct a model containing only ordinary differential equations we have to approximate partial derivatives with respect to x by difference quotients. For this purpose the concentration C at the point $x = X/2$ will be denoted by \widehat{C} , thus, $\frac{\partial C}{\partial x} |_{x=X} \approx \frac{\widehat{C} - 0}{X/2} = \frac{\widehat{C}}{X/2}$. In the approximation applied the diffusion flow of amino acids directed inward the grain is proportional to $(C_0 - \widehat{C})$. The constant of proportionality depends on the diffusion coefficient in the external solution, on the Trp molecules being able to pass through the surface inside the grain, and on the coefficient of internal diffusion D_{in} . The inward diffusion flow is described by the expression $D_{ex} \frac{C_0 - \widehat{C}}{X/2}$, where D_{ex} is an effective coefficient. Apparently, $D_{ex} < D_{in}$.

Thus, we obtain the model of the process for the case of a flat plate in the form of a system of equations that describe the balance of water and the amino acid:

$$\begin{aligned} (Xv\widehat{C})' &= D_{ex} \frac{C_0 - \widehat{C}}{X/2} - D_{in} \frac{\widehat{C}}{X/2} + J_+ \cdot C_0 + J_- \cdot \widehat{C}, & \widehat{C}|_{t=0} &= 0 \\ (Xv)' &= J, & v|_{t=0} &= v_0 \\ X' \cdot a_\Sigma &= D_{in} \frac{\widehat{C}}{X/2}, & X|_{t=0} &= 0 \\ J &= \frac{\beta(w(\widehat{C}) - v)}{X/2}, \end{aligned} \quad (1)$$

where $J_+ = \begin{cases} J, & \text{if } J > 0 \\ 0, & \text{if } J < 0 \end{cases}$, $J_- = \begin{cases} 0, & \text{if } J > 0 \\ J, & \text{if } J < 0 \end{cases}$ and the prime indicates time derivatives.

In model (1) the presence of positive feedback between perturbations of the flow J and the concentration \widehat{C} is traced. Let us consider the simple case when w is the linear function $w(C) = v_0 + \alpha C$ and $\widehat{C}v/a_\Sigma \ll D_{ex}/D_{in}$. After performing simple transformations of Eq. (1), we get:

$$\frac{Xv}{2\alpha\beta} J' = J \{C_0 - \widehat{C} - v/\alpha\} + \frac{2}{X} \left[D_{ex}(C_0 - \widehat{C}) - D_{in}\widehat{C}(1 - v^2/\alpha a_\Sigma) \right] \quad (2)$$

Suppose the system at some instant t_1 is in equilibrium, that means $J' = 0$, $\widehat{C}' = 0$, $v' = 0$, $J > 0$, $X' > 0$. Under the accepted assumptions $\{C_0 - \widehat{C} - v_0/\alpha\} \approx C_0 \frac{d_{in} - d_{ex}}{d_{ex} + d_{in}} - v_0/\alpha$. Let this value be positive. Then the expression in square brackets in

(2) is negative because the whole right-hand part of (2) is equal to zero. As X increases with time, the right-hand part of Eq. (2) at $t > t_1$ becomes positive and J begins to increase. It follows from (1) and (2) that the increase is exponential in the beginning. Hence, for the equilibrium state to be unstable, the condition $C_0 > \frac{v_0}{\alpha} \cdot \frac{d_{in} + d_{ex}}{d_{in} - d_{ex}}$ should be fulfilled. This condition determines the existence of some minimum threshold of the concentration C_0 at which oscillations can be excited.

An avalanche increase in the inward flow can “physically” be explained as follows. In the equilibrium state, because of the absorption of Trp on the ion exchange surface, the concentration of Trp in the internal solution is lower than that in the external one, $\widehat{C} < C_0$. The larger the D_{in}/D_{ex} ratio, the smaller the equilibrium value \widehat{C} . The incoming solution has the concentration C_0 . If the flow of this solution increases it imports an additional amount of Trp exceeding the average in the internal solution. Therefore, the concentration \widehat{C} increases as well as the volume of the internal solution v . If the expression in braces in (2) is positive, an increase in the amount of solution v lags behind an increase in the equilibrium volume $w(C)$. Due to the faster growth of \widehat{C} , the pressure inside the sorbent decreases. This results in a further increase of the inward flow.

The expression in braces in (2) decreases and that in the square brackets increases, as \widehat{C} and v are enhanced. For this reason, the derivative of the flow J vanishes when a certain value \widehat{C} is reached. At this instant, J is maximum. The \widehat{C} and v values, however, continue to increase according to the first two equations of system (1). As a result, the derivative of J becomes negative, the flow into the grain weakens and rapidly decreases to zero. After this, J_+ in the first equation of system (1) is equal to zero, and this equation takes the form $v \cdot \widehat{C}' = \frac{2}{X^2} [D_{ex}(C_0 - \widehat{C}) - D_{in}\widehat{C}]$. The concentration comparatively slowly decreases to its equilibrium value. Physically, the process at this stage can be described as follows: a solution goes out of the grain, removes a proportional amount of Trp, and reduces the volume v . For this reason, the solution outflow from the grain does not change the Trp concentration inside the grain. The concentration changes because of external solution diffusion and diffusion to the ion exchange surface. The system reaches its equilibrium state corresponding to the new X value and the process is repeated as described above. Numerical modelling allows us to study all the process stages, to check and to substantiate the reasoning given above.

Further let us consider the case of a spherical grain with the radius R . An analog of Eq. (1) can easily be written for this case. One can see the changes in the expressions for the volume and the area of the surface layer (X in thickness) in the first two equations, and for the surface area of ion exchange in the third equation of system (1). There appear multipliers describing the distribution of concentration over a spherical layer.

The following notations will be used: $\rho(t)$ is radius of the central zone of the grain that is in the H form; $r(t) = \rho(t)/R$; $m = \frac{1-r}{1+r}$; $M = \frac{(1-r^3)m}{3}$; $\tau = t\beta/R^2$ is the dimensionless time; $d = D/\beta j = \frac{JRm}{\beta}$; $\chi = \frac{d_{in}}{a_{\Sigma}}$; \widehat{C} is the concentration C at the point separated by $(R + \rho)/2$ from the centre of the grain, in the middle of the layer where the ion exchanger is in the Trp form. Having made appropriate transformations, we obtain the model of the process for the case of a spherical grain:

$$\begin{aligned}
 Mv \cdot \widehat{C}' &= (d_{ex} + j^+)(C_0 - \widehat{C}) - rd_{in}\widehat{C}, & \widehat{C}|_{\tau=0} &= 0 \\
 M \cdot v' &= j - \chi \widehat{C}vr, & v|_{\tau=0} &= v_0 \\
 m \cdot r' &= -\chi \frac{\widehat{C}}{r}, & r|_{\tau=0} &= 1 \\
 j &= w(\widehat{C}) - v, & j^+ &= \begin{cases} j, & \text{if } j > 0 \\ 0, & \text{if } j < 0 \end{cases}
 \end{aligned} \tag{3}$$

In Eq. (3) the primes indicate derivatives with respect to τ .

The transition to the spherical case results in the recalculation of the parameters and in the deformation of the process time scale. The main qualitative distinction of the spherical case in comparison with the flat plate consists in a decrease of the surface area of ion exchange with time. Therefore, the withdrawal of Trp from the internal solution on this surface weakens with time as well.

3 Results of numerical modelling

As a result of modelling we get time dependences for a separate grain. To compare results of simulation and experiments one should take into account that in experiments the sorption was performed on a large number of grains simultaneously. As the physical properties of grains, for instance, their sizes, vary, the oscillations in the grains differ in phases. In Fig. 1 the aggregate result of oscillations for many grains is presented.

Now, the problem is formulated as follows. Suppose that the amount of the substance sorbed by one grain is described by the $f(t)$ function which can be calculated by modelling. Let $f(t)$ have the form of a set of positive and negative peaks against the background of a slowly changing mean value. Suppose the forms of oscillations in different grains are identical but the time scales depending on grain sizes are different. The contribution of the i -th grain to the overall process is then $f(\mu_i t)$, where μ_i is the coefficient that determines the time scale for the grain. The total number of grains is N (N is a large number) and the characteristics of grains are distributed according to the normal law: the number $n(\mu)$ of grains with the scale factor equal to μ is $n(\mu) = \frac{N}{k(\sigma)} e^{-\frac{(\mu-1)^2}{\sigma^2}}$, where $k(\sigma)$ is the normalizing coefficient such that $\int_0^\infty n(\mu) d\mu = N$. The problem is to find the simplest way to modify the $f(t)$ function in order to describe the total effect $\frac{1}{N} \sum_{i=1}^N f(\mu_i t)$ obtained for N grains.

Let's consider a separate peak δf of the function $f(t)$ that rises above the horizontal mean level f_{mid} . For simplicity suppose the peak has the form $\delta f(t) = h \cdot e^{-\left(\frac{t-t_1}{\Delta t}\right)^2}$, where h is the height of the peak, Δt is its half-width, and t_1 is the time when the maximum is reached. At the instant $t = t_1$ the value of an appropriate peak of the function $f(\mu t)$ is equal to $\delta f(\mu t_1) = h \cdot e^{-\left(\frac{\mu t_1 - t_1}{\Delta t}\right)^2}$. Hence, the overall effect of the summation of the δf functions for all grains on the formation of the common peak is expressed as:

$$F(t_1) = \int_0^\infty n(\mu) \cdot \delta f(\mu t_1) d\mu = Nh \frac{1 + \Phi\left(\frac{1}{\sigma} \sqrt{1 + \left(\frac{t_1 \sigma}{\Delta t}\right)^2}\right)}{\left(1 + \Phi\left(\frac{1}{\sigma}\right)\right) \sqrt{1 + \left(\frac{t_1 \sigma}{\Delta t}\right)^2}},$$

where Φ is the error integral. The fraction in the above expression shows the degree to which the height of the peak decreases compared to synchronous oscillations of all grains.

Hence, to compare the experimental and simulation results we should transform the calculated curve $f(t)$ using the formula:

$$f_{com}(t) = (f(t) - f_{mid}) F(t) + f_{mid} \quad (4)$$

Here f_{mid} is the mean value of the curve $f(t)$ over the region including the peak. The values Δt and f_{mid} are estimated from the calculated $f(t)$ curve. The value of σ is determined by the spread of grain sizes. It is the curve $f_{com}(t)$ that should be compared with the experimental one.

Formula (4) provides only an approximate description of the transition to a large number of grains. We got (4) assuming that peaks have simple shapes. Models (1) or (3), however, describe only the effects of the most relevant factors. For this reason, processing the obtained calculation results according to models (1), (3) and (4) is likely to be a correct approach.

It should be pointed out that the curves shown in Fig. 1 differ essentially in character from each other. The total Trp concentrations of solutions in both cases are the same, but the pH values are different. The amount of Trp^+ ions depends on pH of the solution. In the case represented at the left in Fig. 1 the amount of neutral Trp molecules is much less than in the case shown at the right.

In modelling we may take into account a change in pH of the solution in different ways. It is possible for the equations describing redistribution of H^+ ions and their associations with Trp molecules to be included in the model. But we can also get the desired result in a simpler way. As mentioned above, from the viewpoint of substance equilibrium, the ion exchange of H^+ to $\text{Trp}-\text{H}^+$ amounts to “extracting” neutral molecules Trp from the solution followed by “depositing” them in the form of ions upon sorbent functional groups. The approach of neutral molecules Trp to the layer $x \approx X$ determines the rate at which the ion exchange front is propagated in the grain. For this reason, in the model the influence of the solution pH was accounted for by taking C to equal the concentration of Trp in the molecular form only. In calculations, different values of the C_0 concentration depending on the solution pH should then be put in correspondence with the constant total amount of the amino acid.

Numerical calculations were performed for both the plane layer and the spherical grain. Figure 4 shows the results of several calculations performed according to model (3) and processed according to formula (4). The curves exhibit the change of the V/V_0 ratio with time, where V is the volume of internal solution and V_0 is the initial value of V . The curves in Fig. 4 were obtained for the following values of the parameters:

Figure 4a $C_0 = 0.004 \text{ mol/L}$, $D_{in} = 1.6 \cdot 10^{-10} \text{ m}^2/\text{s}$, $D_{ex} = 2.4 \cdot 10^{-11} \text{ m}^2/\text{s}$, $\beta = 4 \cdot 10^{-10} \text{ m}^2/\text{s}$, $a_{\Sigma} = 1 \text{ mol/L}$, $\sigma = 0.1$, the function $w(C)$ was linear, $\alpha = 3.4 \cdot 10^3 \text{ l/mol}$.

Figure 4b $C_0 = 0.01 \text{ mol/L}$, other parameters were the same as in the previous case.

The case shown in Fig. 4a differs from that in Fig. 4b only by a smaller value of C_0 . These cases simulate sorption from two solutions with the same total concentration

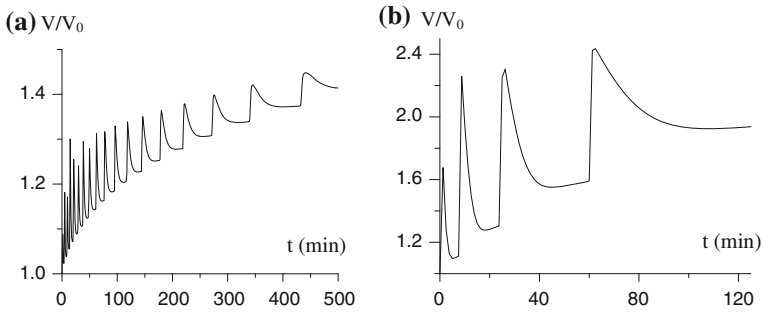
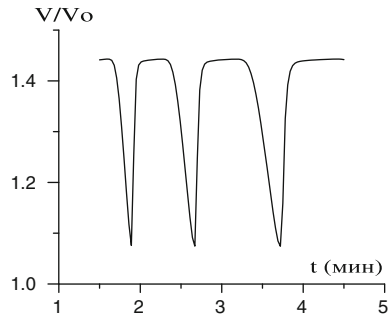


Fig. 4 Calculated time dependences of the volume of internal solution normalized by the initial value

Fig. 5 Calculated time dependence in the case when $w(C)$ reaches “saturation”



of Trp, equal to 0.01 mol/L, but for a different pH. Figure 4a corresponds to the lower concentration of Trp in the molecular form in accordance with a greater value of pH in the solution. In this sense Fig. 4a simulates the situation shown in Figs. 1a and 4b—the case presented in Fig. 1b. One can see close correlation between the curves in Figs. 1 and 4, both in the general character of the curves and in their time scales.

Figure 4 corresponds to the linear dependence $w(C)$. That is reasonable at small C . In the case of high values of C the dependence $w(C)$ reaches “saturation”. In the latter case the modelling yields the result shown in Fig. 5. The frequency of oscillations increases and their shapes are changed. Since the function $w(C)$ at some values of C no longer increases, the peaks are “cut-off” on the curve of time dependence of the grain size. This curve shape corresponds to the experimental result shown in Fig. 2.

In conclusion it is possible to point out that the description and explanation of the unusual experimental results can be made by a fairly simple model. The presented model accounts for the fact that due to osmotic pressure the positive feedback is established between changes in the concentration of the internal solution of the grains and their volume. This factor is responsible for instability of the diffusion process and leads to oscillations in sorption of amino acids.

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