

Low-frequency oscillations in the direct osmotic process in a membrane with nanosized pores

G I Lapushkin, V Yu Stozhkov

DOI: <https://doi.org/10.3367/UFNe.2023.06.039365>

Contents

1. Introduction	931
2. Specific features of the oscillation mechanism	932
3. Experimental technique	932
4. Theoretical description	932
5. Scientific significance of the observed oscillations in a direct osmotic process	933
6. Relevance of the problem, direction of further studies	934
References	935

Abstract. The existence of low-frequency oscillations (1–10 Hz) in some modes of membrane processes (reverse osmosis, electroosmosis, bioosmotic phenomena, and fuel cells) has long been known. Although oscillations are only an accompanying effect of osmotic processes in membranes, many researchers noted such phenomena in their studies. We were the first to discover pressure fluctuations in an osmotic cell during direct osmosis. In the above osmotic processes, there is a significant impact of external factors (e.g., a superimposed external electric field)—but there are no such factors in the process of direct osmosis, allowing us to assert that oscillations are a consequence of the intrinsic properties of the membrane and the transport of water into the cell that occurs in it, which will allow a better understanding of the mechanisms of the processes in the membrane.

Keywords: osmosis, osmotic oscillations, membrane transport

1. Introduction

Low frequency oscillations of pressure and concentration in osmotic processes are described in many publications. Initially, they were noticed in electroosmotic processes as oscillations of the flowing current [1–9]. Similar phenomena were also reported on biological membranes [10, 11] and on membranes of fuel cells [12].

In later papers, not only was the presence of low frequency oscillations in reverse osmotic processes observed, but it was also hypothesized that such processes can have two steady-

state modes of substance diffusion, on which the low frequency oscillations are superimposed [6, 7]. In all papers, the typical frequency value amounts to 0.1–2 Hz, seldom a little greater, but the frequency of 0.01 Hz has also been observed. The oscillations have various shapes and sometimes demonstrate asymmetric jumps. Figure 1 demonstrates an example of such a process; as can be seen, a significant change in the current can completely stop the oscillatory process, i.e., the oscillations do not always occur.

Publications [2–5, 8, 13, 14] offer various mathematical models of the processes describing oscillations that resemble the experimentally discovered ones qualitatively as well as by order of magnitude. Analysis of the models shows that such oscillations arise only at a certain combination of parameters rather than in all regimes of the osmotic process. These oscillations are limited in amplitude, frequency, and region of occurrence, which simplifies the search for causes and comparisons of the experiment with the model.

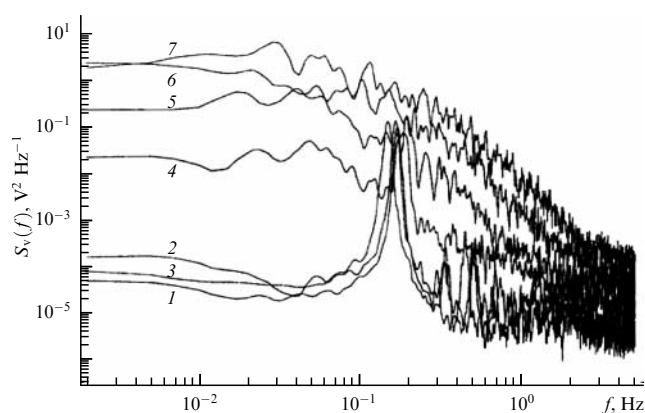


Figure 1. Power spectra of potential fluctuations measured in a solution of NaCl (50 mM) with the addition of 6% glycerol at different current densities: 1—1.3 mA cm⁻², 2—2.5 mA cm⁻², 3—5.0 mA cm⁻², 4—7.5 mA cm⁻², 5—10.0 mA cm⁻², 6—12.5 mA cm⁻², 7—15.0 mA cm⁻². It is clearly seen that for weak currents there are oscillations with a frequency of about 0.1 Hz and a large amplitude, but with an increase in current only noise is left [5].

G I Lapushkin^(*), V Yu Stozhkov

Moscow Institute of Physics and Technology

(National Research University),

Institutskii per. 9, 141701 Dolgoprudny, Moscow region,

Russian Federation

E-mail: ^(*)Lapushkin.GI@mipt.ru

Received 12 June 2022, revised 7 May 2023

Uspekhi Fizicheskikh Nauk 193 (9) 989–993 (2023)

Translated by V L Derbov

A detailed review of oscillatory processes is presented in Ref. [15].

2. Specific features of the oscillation mechanism

A variety of features are believed to cause oscillations, including the different conductance of membrane pores for small solvent molecules and large hydrated molecules of the dissolved substance, which causes instability in solvent transport through the pore (for large pores). Such effects can also arise in the presence of a small number of large-scale membrane pores, comparable in size to hydrated ions.

As to biological membranes, it is difficult to select any single mechanism in them because of the extreme complexity of the studied objects and processes that occur in them [16].

In turn, the pore size can be either small, comparable to the size of an individual molecule, or very large. Although oscillations were observed in both cases, it is difficult to expect that the mechanisms responsible for the occurrence of oscillations will be the same under such a difference in initial conditions.

Even in the presence of conditions for oscillations (e.g., a bistable state of the flow through the pore), the synchronization conditions for micro-oscillations in different pores should hold to provide the noticeable macro-oscillations observed in experiment. This mechanism is far from apparent; in Refs [4, 5], it is supposed that the interaction of micro-oscillations giving rise to macro-oscillations is caused by the microscopic inhomogeneities of the solution flows along the membrane surface. This mechanism was checked experimentally by measuring currents at 16 points of a membrane, which allowed a convincing demonstration of the presence of inhomogeneities, which moved over the membrane surface (Fig. 2).

3. Experimental technique

The setup for measuring osmotic pressure comprises a LOIP LT-300 thermostat filled with distilled water, inside which is a cubic osmotic cell filled with the solution studied. The

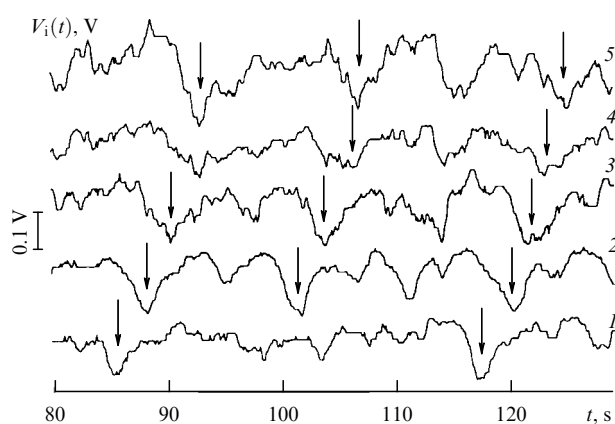


Figure 2. Sections of time series for the same solution as in Fig. 1, recorded from electrodes located at different heights above the lower boundary of a membrane: 1—5.5 mm, 2—6.5 mm, 3—7.5 mm, 4—8.5 mm. Characteristic features are marked by arrows. These features are seen to move in the liquid, which can evidence in favor of a correlation between microstates of the membrane pores via the adjacent liquid layers [5].

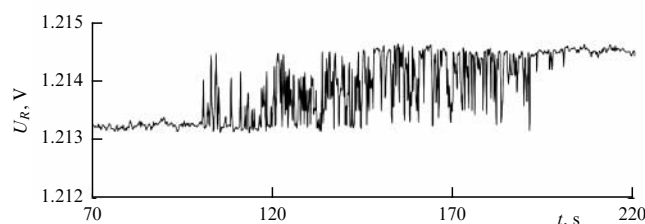


Figure 3. Time dependence of voltage on a 100-Ω resistor upon connecting a 4–20 mA OWEN PDI-100 (model 121) pressure transducer in the current loop mode, measuring the pressure in a hermetic osmotic cell. Stabilized supply voltage of the transducer is 24 V [17].

thermostat allows keeping the temperature in the bath and the cell with an accuracy of up to 0.2 °C.

TW30 1812-50 (FilmTec Corporation, USA) polyamide membranes with a pore size of 1–3 Å used in domestic reverse-osmosis filters were located at vertical open faces of the cube. Metallic grids with holes 2 mm in diameter clamp the membranes. The thickness of the selective polymer layer of the membrane is of the order of 0.2 μm. The total area of the membranes is about 100 cm².

A PD100I-DVO, 1-121-0.25 pressure sensor and a resistance Pt-100 thermometer (OOO PO OWEN, Russia) are built in the upper face of the cubic cell. Data from the sensor are transferred to a computer. The setup allows interrogating the sensors and processing the information with a period of up to 1 ms.

To create an excess hydrostatic pressure of up to 1 atm in the cell, the cell filling unit comprises a solution injector based on a peristaltic pump HA1B06TY (Shenzhen, China) with a DC collector motor. The rate of injecting an osmoticum into the cell is set by smooth variation of the pump supply voltage by means of a voltage regulator on a metal-oxide-semiconductor-field-effect transistor (MOSFET).

Thus, the setup allows setting various pressure levels in the osmotic cell, making it possible to record kinetic curves in different operating ranges, including different temperatures (to 80 °C). Washing the cell and supplying a fresh solution are performed automatically by means of a pump.

In the course of direct osmotic phenomena measurements in solutions of potassium hexacyanoferrat (II) [17], we observed oscillations near the equilibrium pressure value of $\Delta P \approx 200$ Pa (Fig. 3).

4. Theoretical description

The model we propose to describe osmotic process oscillations is based on the hypothesis that a solvent molecule overcomes obstacles in a microscopic pore similarly to a quantum particle passing over a barrier.

This model is applicable only to materials with very small pore sizes (in our case, exactly such membranes were used). It should be noted that the concepts developed in some other models [13] are inapplicable under our conditions because of the very small pores in the membranes used by us.

Since, in the case of water molecules penetrating through the pores of such a membrane, we are dealing with a system whose geometric dimensions are comparable to the de Broglie wavelength λ_{dB} of the penetrating particle (for a water molecule at room temperature, $\lambda_{dB} \sim h/\sqrt{m_{H_2O}k_B T} \approx 0.6$ Å, where k_B is the Boltzmann constant), it is quite reasonable to consider the wave properties of the particles moving through the barrier.

Since the variation in the medium parameters in an osmotic process is quite slow compared to the time of a particle passing through the membrane (the total pressure accumulation takes more than a day), the process can be described by a steady-state Schrödinger equation. The transport of water molecules through the membrane is considered to pass over a potential barrier whose height is assumed to be equal to the difference between the chemical potentials of gaseous and liquid water $\Delta\mu = \mu_{\text{vap}} - \mu_{\text{liq}} \approx 0.5$ eV. This estimate is based on the fact that the molecules in liquid water exist in the form of multiparticle dynamic clusters [18], in which hydrogen bonds are rapidly formed and destroyed. Due to their significant size, associates cannot take part in the transport through membranes with such small cells; therefore, we believe that the transport occurs due to single molecules with sufficiently high energy.

Hence, the energy diagram has three regions: the solvent region with the chemical potential μ_0 equal to that of liquid water, the region of the barrier with thickness d , where the chemical potential is higher by $\Delta\mu$, and the cell region containing the solution, where the chemical potential depends on the concentration of the dissolved substance and the pressure in the cell. Since the concentration of the solution in the cell changes very weakly during a direct osmotic process, the main contribution to increasing the chemical potential is due to the growth of pressure in the cell. From the definition of chemical potential, it follows that in isothermal processes $d\mu = v dP$, where v is the molecular volume of water, from which for the chemical potential μ_{sol} of the solution in the cell we obtain $\mu_{\text{sol}}(t) = \mu_{\text{sol}}(0) + vP(t)$ or $\mu_{\text{sol}}(t) = \mu_0 - v(P_{\text{osm}} - P(t)) = \mu_0 - v\Delta P(t)$.

The processes of transmission above a barrier are thoroughly studied in quantum mechanics, so for a barrier of our type it is possible to adopt a ready solution, e.g., from [19]. Taking into account that μ_0 and $\mu_{\text{sol}}(t)$ are close in value (since the oscillations arise near the equilibrium point), it is possible to express the transmission coefficient D according to [19] as

$$D = \frac{1}{1 + [(k_1^2 + k_2^2)^2 / (4k_1^2 k_2^2)] \sin^2(k_2 d)}.$$

Here, the notations

$$k_1 = \frac{\sqrt{2m\Delta\mu}}{\hbar}, \quad k_2 = \frac{\sqrt{2mv(P_{\text{osm}} - P(t))}}{\hbar}$$

are introduced. After simple transformations, we arrive at the final formula,

$$D = \frac{1}{1 + \Delta\mu / (4\Delta P(t)) \sin^2(k_2 d)}.$$

Since $\Delta\mu \gg \Delta P$ near the equilibrium point, the transmission coefficient is nonzero only when the sine is equal to zero. It follows that

$$\frac{2mv\Delta P d^2}{\hbar^2} = \pi^2 n^2,$$

where n is an integer. To find the oscillation period, it is possible to differentiate this equation with respect to time, then a derivative of the mean pressure appears on its left-hand side (without oscillations taken into account), and the right-hand side contains the product $n dn/dt$. In the latter

expression, the quantity n can be obtained from the previous formula, and the time derivative of n has the meaning of the oscillation frequency. Then, the final expression for the period of oscillations takes the form

$$T = \frac{\pi\hbar}{d dP/dt} \sqrt{\frac{2\Delta P}{mv}}. \quad (1)$$

The oscillations are observed near the equilibrium position; therefore, it is possible to accept the mean value of $\Delta P \approx 2000$ dyn cm⁻² in the region where the oscillations are found. The mean rate of pressure growth in the domain of oscillation existence was approximately $dP/dt \approx 50$ dyn cm⁻² s⁻¹ in experiments; this rate is practically constant over the domain of oscillations. Hence, the estimate of the oscillation period yields the value of 0.7 s, close to the observed one.

It is important to note that the oscillations are observed only in a narrow range of external parameters. Since it is hard to expect a substantial change in the pore conductance and its internal structure under a small change in the external parameters, the emergence or absence of oscillations is most likely related to the phase matching of micro-oscillations in different pores. In a system of microscopic oscillators, macroscopic oscillations are possible only if there are cooperative phenomena, when a jump-like change in the state of one element triggers a change in the state of the nearest neighbors. That is, even in the presence of bistable pore conductance, a resonance in the macroscopic membrane conductance may not always occur. The osmotic process can merely average the differences in the conductance of individual pores without any noticeable macroscopic oscillations, as is likely to happen most frequently.

According to the above considerations, any model of macroscopic osmotic oscillations has to include mechanisms of phase locking of the microscopic oscillations in pores, which is of particular importance in the case of relatively large dimensions.

In particular, in the further development of the model proposed by us, it is desirable to consider mechanisms of cooperative interaction, which support a narrow band of frequencies. For example, as in Refs [4, 5], it is possible to consider macro-oscillations along the membrane surface, so that the oscillations could occur only upon coincidence of the frequency characteristics of the pore conductance and the acceptable frequencies of near-surface vortices.

5. Scientific significance of the observed oscillations in a direct osmotic process

Based on a variety of membrane processes, it could be difficult to expect a priori a universal oscillation mechanism in various types of osmotic processes.

We first discovered a phenomenon of small low frequency oscillations of pressure with an amplitude of 50–80 Pa (see Fig. 3) in direct (forward) osmotic processes [17]. The oscillations were observed in a narrow range of pressures near equilibrium in solutions of sodium hexacyanoferrate (II) at concentrations within 1.5–4.0 g l⁻¹.

This observation is of high importance, since, earlier, the oscillations were reported in electroosmosis, reverse osmosis of fuel cells, ultrafiltration membranes, and biological membranes. These processes are much more complex than mere osmosis, judging by the number of involved factors

(electric current, external applied pressure, and — in the case of biological membranes — a much more complex structure of both the membrane itself and the associated multichannel biochemical processes).

We managed to observe oscillations for the first time in direct (forward) osmosis, a process which is determined only by the properties of the membrane in the absence of any external factors, except the difference between chemical potentials on different sides of the membrane.

If we suppose that there is a universal mechanism for oscillations in different membrane processes, then, within this hypothesis, the oscillations would be due to the properties of the membrane itself and the osmotic processes occurring in it. Then, the external impacts on various osmotic processes are to be considered to be additional, affecting the oscillation parameters.

The assumption about the existence of a universal base for the mechanism of oscillations in various membrane processes can be based on the fact that oscillations for different processes have a noticeable similarity. They occur in a narrow range of parameters, they have frequencies of the order of 1 Hz, and the shape of the oscillations is clearly not sinusoidal, but rather similar to sharp jumps in the presence of a bistable state.

The result obtained by us allows supposing that the phenomenon of low frequency macro-oscillations can be considered inherent to processes in the membrane itself within (rather narrow) intervals of concentration and pressure.

As follows from Eqn (1), when approaching the equilibrium ($\Delta P \rightarrow 0$), the oscillation period should decrease. From our calculations, it is difficult to obtain an exact value of the frequency, but it is possible to roughly estimate the experimentally observed decrease in the period by nearly 1.3 times from the moment of the onset of oscillations to their disappearance (Fig. 4). The estimation is complicated by the fact that the oscillations are not always periodic, especially just before their disappearance. In fact, to obtain the time dependence of the oscillation period, it turned out to be impossible to choose a simple algorithm for extracting the period value from experimental data. Therefore, regions, where a few regular enough oscillations could be observed were selected manually and then their average period was

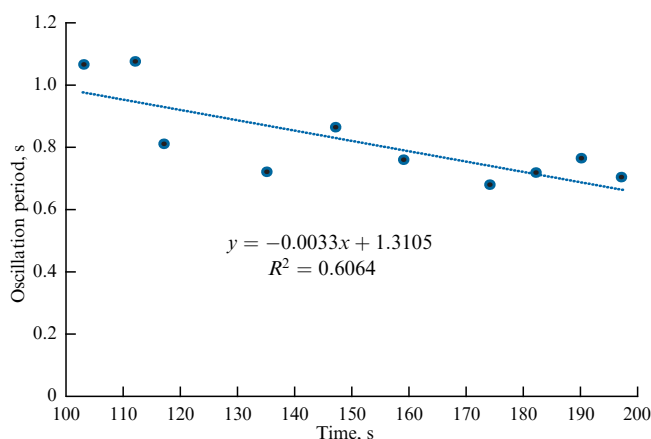


Figure 4. Time dependence of the oscillation period; time scale of the abscissa axis corresponds to time in Fig. 3. Trend line is obtained by the least squares method; trend equation and value of determination coefficient are shown in the figure.

determined: this is how the plot in Fig. 4 was obtained. To apply the numerical Fourier analysis, more initial data are necessary.

From the plot in Fig. 4, it is impossible to extract reliable numerical data, but the decrease in the oscillation period value is quite noticeable, thus indirectly confirming the applicability of our model.

The formulated assumption of a unified base mechanism for oscillations in osmotic processes can be inapplicable to oscillations on biological membranes, since the frequencies in this case are usually 100–1000 times lower, and the mechanisms can be different. According to the data in Ref. [6], for a biological membrane, there is a strong dependence of the oscillation frequency on the flow bulk velocity. Unfortunately, from the data in Ref. [6], it is hard to understand whether such a dependence corresponds to our model or, on the contrary, contradicts it. The conclusion depends on the experimental details, which are lacking in the publication.

6. Relevance of the problem, direction of further studies

The dependence of the oscillation amplitude and frequency on some parameters (pressure, concentration, temperature, composition) can also provide important information about the internal mechanism of membrane processes. To date, as seen from the literature data, this dependence has been poorly studied. Nevertheless, there are papers in which the dependence of oscillations on various parameters is studied in electroosmosis [4, 5]. From the obtained data, it can be concluded that, for electroosmosis, the oscillations are not only current-dependent but can be completely absent when the current is strong enough, manifesting themselves, for example, as flicker-noise effects. In the same papers, the spectral composition of the harmonics of such oscillations and the dependence of the oscillation spectrum on the membrane shape are reported.

There is extremely little literature data about the dependence of the oscillation frequency on the parameters of the osmotic system (difference in pressures, pressure growth rate, and temperature). However, such data can provide a key to the model of such oscillations, so we plan to obtain such data in our setup.

From the practical point of view, the study of osmotic oscillations can provide us with a fine and sensitive tool for studying membrane properties. It can be expected that low frequency oscillations in pressure can, in turn, affect the membrane conductance. In the literature, many successful attempts are described to affect membrane properties by ultrasound [20] and alternating current [21, 22], but no attempts have been made yet to use low frequency oscillations to affect direct osmosis processes. Oscillatory systems, as usual, strongly respond to frequencies close to their own resonance; therefore, it is reasonable to check this hypothesis experimentally.

There are papers on the application of low frequency oscillations (about 10 Hz) for separation on membranes [23]; however, since the membrane pore size is 2–20 μm , here we are now dealing with ultrafiltration rather than with osmotic processes. Successful experiments were also conducted to study the impact of low frequency oscillations on reverse osmotic processes [22, 24, 25] and, therefore, there are reasons to expect that low frequency oscillations may affect direct osmosis as well.

References

1. Teorell T *J. Gen. Physiol.* **42** 831 (1959)
2. Langer P, Page K R, Weidner G *Biophys. J.* **36** 93 (1981)
3. Gedalin K *Physica D* **110** 154 (1997)
4. Budnikov E Yu et al. *Russ. J. Phys. Chem.* **73** 147 (1999); *Zh. Fiz. Khim.* **73** 198 (1999)
5. Budnikov E Yu et al. *Russ. J. Electrochem.* **37** 80 (2001); *Elektrokhimiya* **37** 95 (2001)
6. Kanamori T et al. *J. Membrane Sci.* **184** 287 (2001)
7. Tikhonov N A, Tokmachev M G *Moscow Univ. Phys. Bull.* **65** 460 (2010); *Vestn. Mosk. Univ. Ser. 3. Fiz. Astron.* (6) 33 (2010)
8. Li H, Jian Y *Int. J. Heat Mass Transfer* **115** 703 (2017)
9. Ito T et al. *J. Membrane Sci.* **448** 231 (2013)
10. Saraiva G F R, Souza G M *Procedia Environment. Sci.* **29** 55 (2015)
11. Oglecka K et al. *eLIFE* **3** e03695 (2014)
12. Sanchez D G et al. *J. Electroanal. Chem.* **649** 219 (2010)
13. Tikhonov N A *Russ. J. Phys. Chem. A* **84** 1369 (2010); *Zh. Fiz. Khim.* **84** 1506 (2010)
14. Jin Z-H *Microvascular Res.* **133** 104097 (2021)
15. Rastogi R P, Srivastava R C *Adv. Colloid Interface Sci.* **93** 1 (2001)
16. Shakhidzhanov S S et al. *Phys. Usp.* **62** 660 (2019); *Usp. Fiz. Nauk* **189** 703 (2019)
17. Tropinina A D et al., in *Trudy 63-i Vserossiiskoi Nauchnoi Konf. MFTI 23–29 Noyabrya 2020. Fundamental'naya i Prikladnaya Fizika* (Proc. of the 63rd All-Russian Scientific Conf. MIPT November 23–29, 2020. Fundamental and Applied Physics) (Moscow: MFTI, 2020) p. 233, Section of General Physics
18. Wang L et al. *Sci. Adv.* **9** eadf8488 (2023)
19. Dragunov V P, Neizvestnyi I G, Gridchin V A *Osnovy Nanoelektroniki* (Fundamentals of Nanoelectronics) (Novosibirsk: Izd. NGTU, 2000) p. 18
20. Goula A M, Kokolaki M, Daftsiou E *Food Bioproducts Process.* **105** 157 (2017)
21. Misra J C, Chandra S, Herwig H *J. Hydrodyn.* **27** 350 (2015)
22. Sadek S H, Pinho F T *J. Non-Newtonian Fluid Mech.* **266** 46 (2019)
23. Ullah A et al. *Desalination* **491** 114428 (2020)
24. Horie T et al. *J. Membrane Sci.* **554** 134 (2018)
25. Li N et al. *J. Mater. Chem. A* **11** 297 (2023)