

Osmosis: Membranes Impermeable and Permeable for Solutes, Mechanism of Osmosis across Porous Membranes

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Summary

A mathematical description is presented of osmotic flows across both ideally semipermeable membranes and membranes permeable not only for the solvent but also for the solute. The principles of thermodynamics of irreversible processes used for the description are given and illustrated on the example of electroosmosis. Modern ideas about the physical basis of osmotic pressure on porous membranes are discussed and an experiment is described that models the processes of osmosis on a macroscopic level.

Key words

Osmotic pressure • Mechanism of osmosis • Solute-permeable membranes

Osmotic flows across ideally semipermeable membranes and membranes also permeable for the solute

The volume flow J_v across a membrane may be expressed, e.g. in $\text{ml cm}^{-2} \text{s}^{-1}$, i.e. $\text{cm}^3 \text{cm}^{-2} \text{s}^{-1} = \text{cm s}^{-1}$ and has the dimension of velocity. When the flow proceeds across an ideally semipermeable membrane, i.e. membrane permeable only for solvents but impermeable for solutes, it is equal to the volume flow of the solvent only, and may be expressed as

$$J_v = L_p (\Delta p - \Delta \pi) \quad (1)$$

where L_p is called the hydraulic conductivity of the membrane, Δp is the difference between the hydrostatic pressures on the two sides of the membrane and $\Delta \pi$ is the difference of osmotic pressure between the two solutions. The osmotic pressure π may be calculated according to the formulas thoroughly discussed in the first overview

(Janáček and Sigler 1996), notably by the approximation known as van't Hoff's formula

$$\pi = RTc_s \quad (2)$$

where c_s is the concentration of the impermeable solute in mol/l. (Eq. 1 is sometimes termed the Starling hypothesis; it was developed to describe the volume flow between the blood in capillaries and interstitial fluid. Here, the difference between osmotic pressures is caused by the presence of proteins in blood plasma to which the capillary wall is normally impermeable. It is called colloid osmotic pressure, while the difference in hydrostatic pressure is the capillary pressure resulting from the pumping action of the heart minus the tissue pressure).

When a membrane is permeable not only for the solvent but also for the solute, the simple Eq. 1 does not

hold any more. There are two reasons for this: the volume flow J_v is then no longer equal to the volume flow of the solvent alone, but rather to the difference between it and the volume flow of solute taking place in the opposite direction. Another factor may be still more important: when the solute and the solvent penetrate the membrane by a common pathway, the two flows interact and part of the solvent flow is driven back by the flow of the solute. It should be noted that this factor need not always be present; for instance, a lipophilic solute can penetrate across the lipid bilayer of the cell membrane while water penetrates through specific aquaporin pores. Then there is no interaction of the flows in the membrane.

Interactions of this kind are best described by the thermodynamics of irreversible processes, also called the thermodynamics of the steady state. The basic assumption of this theory is that in various systems each flow may be linearly dependent not only on its conjugate force but also on other forces operating in the system. Thus, apart from diffusion governed by Fick's law, thermodiffusion (thermal diffusion, Soret effect) may proceed in some systems. Phenomenological equations of the thermodynamics of irreversible processes can be written as

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{22}X_2 + L_{21}X_1 \end{aligned} \quad (3)$$

L_{ij} are straight coefficients relating the generalized flows J_i to their conjugate forces X_i , and L_{ij} ($i \neq j$) are cross coefficients relating them to nonconjugate forces. Flows and forces have to be properly chosen; the sum of flows multiplied by their conjugate forces has to give the production of entropy in the system, $d_i S/dt$, or, in isothermal systems, usually the so-called dissipation function $Td_i S/dt$. The two express the tendency of irreversible processes to proceed.

When properly chosen flows satisfy the linear relations such as (3), Onsager's law

$$L_{ij} = L_{ji} \quad (4)$$

holds.

The usefulness of Onsager's law may be illustrated on the description of electrokinetic phenomena, electroosmosis and streaming potentials. Flow of water across a membrane, which separates two salt solutions and is more permeable for either cations or anions, caused by an electric current, is called electroosmosis. The flow of volume J_v and the electric current j interact; the two are linearly related to both the

difference of the hydrostatic (hydraulic) pressure Δp and the difference of the electrical potential ΔE :

$$J_v = L_p \Delta p + L_{pE} \Delta E \quad (5)$$

$$j = L_E \Delta E + L_{Ep} \Delta p \quad (6)$$

Coefficient L_p is the hydraulic conductivity of the membrane and L_E its electric conductivity.

When the electroosmotic volume flow across the membrane is measured by a shift of menisci in calibrated capillaries joined to chambers separated by the membrane, the hydrostatic pressure difference Δp is zero. Then, on dividing (5) by (6), we obtain

$$(J_v/j)_{\Delta p=0} = L_{pE}/L_E \quad (7)$$

When, on the other hand, the fluid is driven across the membrane by the hydrostatic pressure difference Δp and the electric current across the membrane is zero (the so-called streaming potential is measured by a millivoltmeter with a high input resistance), $j = 0$ and Eq. (6) gives

$$(\Delta E/\Delta p)_{j=0} = -L_{Ep}/L_E \quad (8)$$

Since Onsager's law is valid, the right-hand sides of equations (7) and (8) are, except for the minus sign, equal. On measuring just the electroosmotic volume flow we can readily calculate the value of the expected streaming potential in the system, and *vice versa*. This is important: the aim of science is not only to describe but also to predict.

Interactions between the solvent and the solute flows were treated by the above method by Kedem and Katchalsky (1958).

The flow of solvent J_w and that of solute J_s may be described by the following equations:

$$J_w = L_{ww} \Delta \mu_w + L_{ws} \Delta \mu_s \quad (9)$$

$$J_s = L_{ss} \Delta \mu_s + L_{sw} \Delta \mu_w \quad (10)$$

(see, e.g. Kotyk and Janáček 1977).

$\Delta \mu_w$ and $\Delta \mu_s$ are the differences of chemical potential of water and solute across the membrane, respectively, and Onsager's law

$$L_{ws} = L_{sw} \quad (11)$$

is satisfied.

To develop equations (9) and (10) in terms of directly measurable quantities, differences of solute concentrations Δc_s and of hydrostatic pressure Δp , the following formulas can first be used:

$$\Delta\mu_w = V_w \Delta p + RT \Delta \ln x_w \quad (12)$$

$$\Delta\mu_s = V_s \Delta p + RT \Delta \ln x_s \quad (13)$$

Expressing mole fractions as

$$x_w = \frac{c_w}{c_w + c_s} \quad \text{and} \quad x_s = \frac{c_s}{c_w + c_s} \quad (14)$$

the following approximations can be used:

$$\Delta \ln x_w = \Delta \ln \frac{c_w}{c_w + c_s} \approx -\Delta \ln \frac{c_w + c_s}{c_w} = -\Delta \ln \left(1 + \frac{c_s}{c_w}\right) \approx \Delta \frac{c_s}{c_w} = \frac{\Delta c_s}{C_w} \quad (15)$$

where C_w is the mean concentration of water in the two solutions and the approximation $\ln(1+x) \approx x$, valid for small x was used.

$$\Delta \ln x_s = \Delta \ln \frac{c_s}{c_w + c_s} \approx \Delta \ln \frac{c_s}{c_w} = \Delta (\ln c_s - \ln c_w) \approx \Delta \ln c_s = \frac{\Delta c_s}{C_s} \quad (16)$$

(C_s is the mean concentration of the solute, $c_w + c_s \approx c_w$, since $c_w \gg c_s$ and $\Delta \ln c_w \approx 0$).

Equations (12) and (13) may thus be rewritten as

$$\Delta\mu_w = V_w \Delta p - \frac{RT\Delta c_s}{C_w} \quad (17)$$

$$\Delta\mu_s = V_s \Delta p - \frac{RT\Delta c_s}{C_s} \quad (18)$$

The dissipation function (production of entropy in the system, which is a measure of the tendency of irreversible processes to proceed, multiplied by the temperature in Kelvins) may then be rewritten in the new expressions for the differences of chemical potentials

$$\frac{d_i S}{dt} T = J_w \Delta\mu_w + J_s \Delta\mu_s = J_w (V_w \Delta p - \frac{RT\Delta c_s}{C_w}) + J_s (V_s \Delta p - \frac{RT\Delta c_s}{C_s}) \quad (19)$$

On rearranging the terms on the right-hand side of Eq. (19), we obtain

$$\frac{d_i S}{dt} T = (J_w V_w + J_s V_s) \Delta p + \left(\frac{J_s}{C_s} - \frac{J_w}{C_w}\right) RT\Delta c_s = J_v \Delta p + J_D RT\Delta c_s \quad (20)$$

and two new fluxes are thus defined together with their conjugate forces. The first of them, J_v , will interest us

because it is the volume flow across a membrane that may be permeable for both the solvent and the solute. (The other one, J_D , the exchange flow corresponding to the velocity of solute relative to water in the membrane, was discussed, e.g. by Kotyk and Janáček 1977).

We can now write the phenomenological equations in terms of new flows and forces:

$$\begin{aligned} J_v &= L_p \Delta p + L_{pD} RT \Delta c_s \\ J_D &= L_D RT \Delta c_s + L_{Dp} \Delta p \end{aligned} \quad (21)$$

The cross coefficient $L_{Dp} = L_{pD}$ shows how large is the volume flow brought about by a difference of osmotic pressure and how large is the ultrafiltration on the same membrane caused by the difference in hydraulic pressure Δp .

When we measure the osmotic pressure under the condition of zero osmotic flow, $J_v = 0$,

$$\Delta p = \frac{-L_{pD}}{L_p} RT \Delta c_s \quad \text{or} \quad \Delta p = \sigma TR \Delta c_s \quad (22)$$

expresses how the effective osmotic pressure differs from the theoretical one; σ is called the reflection coefficient and it is simply the ratio of the osmotic pressure developed on a membrane permeable for both the solute and the solvent (and measured as Δp) to the pressure which would be measured on an ideally semipermeable membrane. Our equation of osmosis is now

$$J_v = L_p \Delta p - \sigma RT \Delta c_s \quad (23)$$

With a permeable solute the reflection coefficient σ is in general less than unity. One of the reasons is the difference between the volume flow of water and the volume flow of the solvent, which may be shown (cf. Kotyk and Janáček 1977) to reduce the reflection coefficient as follows

$$\sigma = \frac{\Delta p}{RT \Delta c_s} = 1 - \frac{V_s \omega}{L_p} \quad (24)$$

where the coefficient ω , introduced by Kedem and Katchalsky (1958) in the form $RT\omega$ as the permeability coefficient of a nonelectrolyte, is in our terms

$$\omega = \frac{L_p L_D - L_{pD}^2}{L_p} C_s \quad (25)$$

When the reflection coefficient is still lower,

$$\sigma < 1 - \frac{V_s \omega}{L_p} \quad (26)$$

there are probably frictional interactions between the water and the solute flows on a common pathway, in water-filled pores. Such interactions between diffusing ions and the water flow may be so strong that the coefficient σ becomes negative (Katchalsky 1961) and the volume flow proceeds from the more concentrated solution to the dilute one.

Mechanism of osmosis across porous membranes

As shown in a preceding paper (Janáček and Sigler 1996), the volume flow across an ideally semipermeable membrane is related to its driving force by the same hydraulic conductance coefficient L_p , whether the driving force is a hydrostatic pressure difference Δp or an osmotic pressure difference $RT\Delta c_s$. The L_p is also the same irrespective of whether the membrane contains water-filled pores or not. However, the hydraulic flow encounters less resistance (and hence the membrane displays a higher L_p coefficient) than a diffusional flow of molecules moving separately. Accordingly, the osmosis across membrane pores is bound to proceed not by diffusion, but by the same mechanism as that brought about by hydrostatic pressure and the difference of solute concentration has somehow to produce an equivalent hydrostatic pressure drop.

Various hypotheses have been developed to explain how this happens. According to the rather attractive hypothesis called the solvent tension theory (Hammel and Scholander 1976), the solvent in a solution is always under tension, i.e. under negative hydrostatic pressure. The total pressure of any solution is, according to this theory, composed of positive partial pressure of the solute and negative partial pressure of the solvent. The latter is transmitted by Pascal's law to the membrane and pulls water through it. The theory was discussed in depth by several authors (Hammel 1979a, Hildebrand 1979, Mauro 1979, Soodak and Iberall 1979, Hammel 1979b) and although it has its merits it should be discarded (cf. Janáček 1984). The concept of partial pressures it uses is obviously valid only for ideal gases in which intermolecular forces are negligible.

Soodak and Iberall (1978) suggested that "The water in the semi-permeable membrane is stretched by the outward diffusion drive acting on the membrane water at the solution interface". A molecular picture of

this situation based on the kinetic theory of liquids had previously been given by Dainty (1965). A qualitative description of this theory is as follows: Jumps of water molecules from the higher concentration in the pores are more frequent than in the opposite direction and hence leave behind more vacancies. As a result of this the density of water, and hence also its hydrostatic pressure, is lower in this part of the pore than in the surroundings. This pressure drop counteracts the concentration fall of water at the pore opening and, at the same time, it brings about a mass flow from the other end of the pore, i.e. osmosis. Dainty's theory provides the right order of magnitude of the hydrostatic pressure drop.

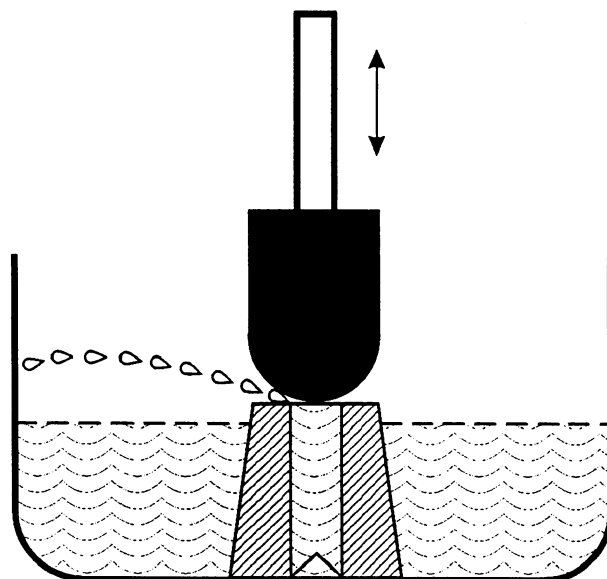


Fig. 1. *Experimental device for macroscopic modeling of osmosis across a membrane pore.*

Another theory of the molecular-dynamic basis of osmosis was given by Ferrier (1984) and described by Dainty and Ferrier (1989) as follows: "... a truly molecular theory would have to consider the intermolecular forces involved in the behavior of the solute and solvent molecules in or near an aqueous pore. Let us consider how often a solute molecule would be at the mouth of a pore. In solution containing 0.1 mol/l solute, only about 1 in 550 molecules is a solute; if the pore mouth has a cross-sectional area of 5-6 water molecules (or solute molecules, if both have the same molecular volume) then a solute molecule would be at the pore mouth for only about 1 % of the time. It would stay there for some 10^{-10} s, then jump back into the solution. It would be about 10^{-8} s on average before another solute molecule arrived at the pore mouth. During this period,

the pore mouth "sees" pure water! A solute molecule present at the pore mouth will obviously retard water flow from the solution into the pore, and will exert a force of attraction on the water in the pore" (for a quantitative development of the theory see Ferrier (1984), Dainty and Ferrier (1989) or Janáček (1997).

Finally, we should like to describe an experiment intended for macroscopic modeling of osmosis across a pore (Janáček 1997, see the setup in Fig. 1). A rubber or polyamide stopper immersed in water represents the membrane and the hole represents the pore. A rubber or polyamide piston rounded at the end simulates the spherical solute molecule. It strikes the opening of the pore at a frequency of 100 Hz. Water comes out of the opening in small droplets and is thus transported upwards through the pore. The arrangement has the following features:

1) Attraction between the piston surface and water does not seem to play a role since the piston works equally well whether it is coated with vaseline or covered with water-soaked deerskin.

2) At least one of the two parts of the setup must be reasonably elastically deformable (if one is made of polyamide, the other must be made of rubber).

It should be noted that, although the overall effect, i.e. the "pumping" or "drawing" of water from one side of the membrane to the other, resembles the action of the model postulated by Ferrier and Dainty, the macroscopic device may differ from it in the nature of the forces at work. Firstly, as shown in the above point (1), the attraction exerted on the water in the pore may not be of great importance here; secondly, it is debatable if its presumed mode of action, i.e. periodical increase in water pressure in the pore, after which water emerges along the pathway of lowest resistance, could work equally at the molecular level. Perhaps, osmotic phenomena do not necessarily depend too much on the hydrophilic properties of the solute particles.

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References

- DAINTY J: Osmotic flow. *Symp Soc Exp Biol* **19**: 75-85, 1965.
- DAINTY J, FERRIER J: Osmosis at the molecular level. *Studia Biophys* **133**: 133-140, 1989.
- FERRIER J: Osmosis and intermolecular force. *J Theor Biol* **106**: 449-453, 1984.
- HAMMEL HT: Forum on osmosis. I. Osmosis: diminished solvent activity or enhanced solvent tension? *Am J Physiol* **237**: R95-R107, 1979a.
- HAMMEL HT: Forum on osmosis. V. Epilogue. *Am J Physiol* **237**: R123-R125, 1979b.
- HAMMEL HT, SCHOLANDER PF: *Osmosis and Tensile Solvent*. Springer Verlag, Berlin, 1976.
- HILDEBRAND JH: Forum on osmosis. II. A criticism of "solvent tension" in osmosis. *Am J Physiol* **237**: R108-R109, 1979.
- JANÁČEK K: Osmotic pressure. *Proc of 7th School on Biophysics of Membrane Transport*, Poland, 1984, pp 166-183.
- JANÁČEK K: Osmotic pressure. *Cell Mol Biol Lett* **2** (Suppl 1): 111-117, 1997.
- JANÁČEK K, SIGLER K: Osmotic pressure: thermodynamic basis and units of measurement. *Folia Microbiol* **41**: 2-9, 1996.
- KEDEM O, KATCHALSKY A: Thermodynamic analysis of the permeability of biological membranes to nonelectrolytes. *Biochim Biophys Acta* **27**: 229-246, 1958.
- KATCHALSKY A: Membrane permeability and the thermodynamics of irreversible processes. In *Membrane Transport and Metabolism*, Academia, Prague, 1961, pp 69-86..
- KOTYK A, JANÁČEK K: *Membrane Transport*, Academia, Prague (also Biomembranes 9, Plenum Press, New York) 1977.
- MAURO A: Forum on osmosis. III. Comments on Hammel and Scholander's solvent tension theory and its application to the phenomenon of osmotic flow. *Am J Physiol* **237**: R110-R113, 1979.
- SOODAK H, IBERALL A: Osmosis, diffusion, convection. *Am J Physiol* **235**: R3-R17, 1978.
- SOODAK H, IBERALL A: Forum on osmosis. IV. More on osmosis and diffusion. *Am J Physiol* **237**: R114-R122, 1979.

Reprint requests

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