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KINETICS OF THE OSMOTIC PROCESS AND THE POLARIZATION EFFECT

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Abstract. Osmosis, i.e. the transport of fluids through a semipermeable membrane, has been investigated for more than a century, using open and closed osmotic devices. We have developed now a novel operative experimental approach, based on a controlled volume variation, to modify the rate of the osmotic process. The new method has been applied for the experimental studies of the evolution of osmotic pressure in aqueous solutions of low molecular weight solutes. Quantitative data about the solvent osmotic rate dependence on the relative solution volume variation have been generated. The dynamic aspects of the process frequently exhibit new specific effects. Such non-trivial effects are the maxima in the rates of solvent transfer established in the experiments. The attempt to interpret such maxima brought in the concept of a polarization effect in the near-membrane space: local dilution of solution, due to the influx of solvent, which in its turn raises a diffusion flux from the bulk. We consider the effects established here by using artificial semipermeable membranes to be of relevance for the biological processes, taking place in the real living cells and tissues.

Keywords: osmotic pressure, osmotic kinetics, concentration polarization

Introduction

Osmosis is a physico-chemical process, in which the concentration difference between two solutions creates pressure difference (*osmotic pressure*) across a separating semipermeable membrane. It plays a primary role in biological systems, as well as in vital technological processes like water purification. The exchange of matter with the medium in all living organisms occurs in such a mode. The solvent transport through the membrane takes place from the more diluted solution to that of higher concentration, until reaching the state of equilibrium. Thus, two types of processes take place: solvent transport through the membrane, which is in principle a hydrodynamic process (momentum transport), and concentration dilution, which is a diffusion phenomenon. The two have different weight in the different part of the osmotic cell. Inside the membrane hydrodynamics is exclusively displayed. In cases where diameter of the membrane pores is much smaller than their length ("thick" membranes), the osmotic flow is governed by the well known Poiseuille law. Actually, the real membranes have fibrous structure, without well-formed channels, and the Poiseuille law must be assumed in an effective sense. Inversely, in the bulk of the cell, diffusion stands up as a fundamental reason for the appearance of the so-called concentration polarization (Zhao et al., 2012; Cath et al., 2006).

Considering the characteristics of the cellular structure, the osmotic transfer may acquire considerable complexity. More noteworthy are the following cases: (i) the pore diameter is comparable to the size of the solvent species. Then the solvent transfer does not obey the Poiseuille law and claims special modeling (Jacobs, 1952; Paganelli & Solomon, 1957; Longuet-Higgins & Austin, 1965); (ii) the pore diameter is comparable to the size of the solute species. This is typical for the process of extraction, where intracellular substances are first dissolved into the squeezing in solvent and then leave the cell with the outflow of solution (Staverman, 1952; Mazur, 1954; Katzir-Katchelsky & Curran, 1965); (iii) osmosis in the cells occurs in confined volumes, which may also impose its specificity (Krustev et al., 2007).

The kinetic studies reported in the literature chiefly treat the above problems, concerning the permeability of the membrane, in particular the case of coupled solvent-solute transport (Katchalsky & Curran, 1965), generalization of the Fick and Poiseuille equations for pores of molecular dimensions (Jacobs, 1952; Paganelli & Solomon, 1957; Longuet-Higgins & Austin, 1965).

The aim of the present investigation has been to bring together our accumulated experimental data, generated by means of the specially designed membrane osmometer and, on that basis, to consider their theoretical interpretation. These tasks entailed a

closer look at possible specific effects, by comparing the osmotic pressure values as a function of solute concentration and time, while using an artificial semipermeable membrane and applying two different experimental regimes: of constant and variable volume. In the latter case limited variable gas (air) volume was also incorporated in the system.

Materials and methods

The membrane osmometer employed in our experiments was specially designed and built for the purpose (Kolikov, 2008; Minkov et al., 2012; 2013). It consists of two cylindrical plastic shells, for solvent and solution, respectively. A semipermeable membrane of 5.0 cm diameter was sealed between the two shells and was supported against deformations by additional plastic porous disks on either side. The active operative area of the membrane (the integral whole surface) was ca. 5 cm^2. Further details about the original device are discussed in the quoted above sources.

In the classical membrane osmometry the osmotic pressure, Π, is directly determined by the hydrostatic pressure value established in an "open mode" – through the rise of the liquid level in the solution compartment. Of course, such an approach is only suitable at moderate elevation – of the order of decimeters – which, accordingly, means small concentration differences: up to a few tens of millimoles per liter. An alternative mode, without such limitations, is conducting the process in a closed constant volume (Paganelli & Solomon, 1957; Longuet-Higgins & Austin, 1965; Katzir-Kathalsky & Curran, 1965) and determining Π by means of an appropriate pressure sensor. The specific tasks of the present investigation required novel approach and modification of the classical experimental setup. Here we put forward an operative hybrid method, which combines the advantages of the two above: it comprises controlled variation of the solution volume, which permits measuring much higher pressure levels in the "open mode".

The specific tests, in particular the comparison between osmotic rates at free (variable) and restricted (constant) volume, required further modifications. Here came in action our hybrid modification of the cell with variation of the solution amount by additional partial volume, plus controlled limited variable gas (air) volume. Thin graduated 1.3 m long plastic tubing of 2 mm radius was attached to the solution chamber to measure the solution level rise at variable volume. Thus, with initial capacity of the solution compartment of 60 ml, the attached tube provided additional volume of 16 ml, that is, a possibility of variation by up to *ca*. 25 %. We consider this sufficient for our present purpose. Of course, we could have supplied even larger span of volume variation, but

such a step would have brought further complication, due to the substantial dilution of the studied solution upon time. The principle of operation and the schematic of the measuring osmotic cell are presented schematically in Fig.1.

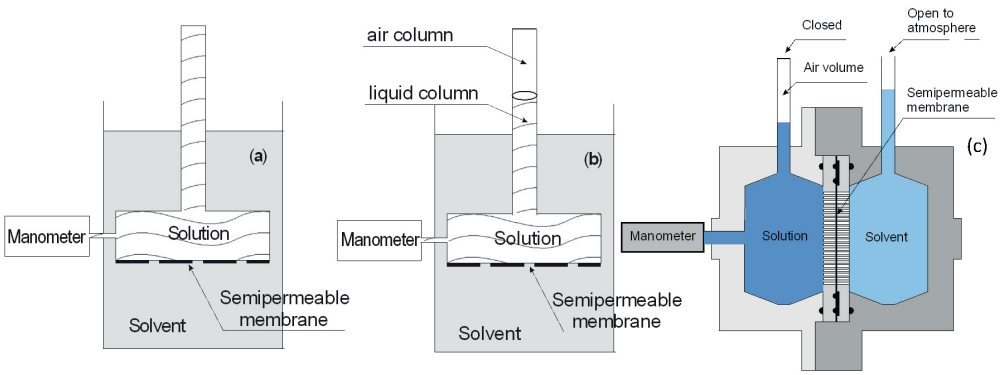

Fig. 1. Representation of the two experimental osmotic regimes: (a) constant volume; (b) variable volume. (c) Schematic of the membrane osmometer (osmotic cell)

All solutions were prepared with Elga Labwater (model PURELAB Option-Q7) deionized water. High purity substances were employed in all experiments – sucrose (Sigma-Aldrich 99+%), pre-ready Glucose solution (Brown®, Germany) for medical applications with concentration C = 0.278 M. Polyamide composite semipermeable Koch RO- (reverse osmosis) membranes were used within the prescribed ranges (pH = 4-11; temperature < 50°C). Our tests confirmed the assertion of Grattoni et al. (2007) that sucrose and glucose are thus totally filtered.

All experimental tests are performed at constant temperature (22^{o}C).

Results and discussion

Further on we shall present the key experimental data, summarized in the current study.

Experimental tests were designed and realized as a function of the solute concentration (at constant additional gas volume), and as a function of the additional gas volume (at constant solute concentration). The experiments have been conducted with two biologically active substances: sucrose and glucose, both used as reference solutes in osmotic studies (Morse et al., 1907; Frazer & Myrick, 1916; Lotz & Frazer, 1921; Stigter, 1960; Granik et al., 2002; Gratoni et al., 2007). The results of the experimental

tests shown in Fig. 2 illustrate the equivalence in the osmotic behaviour of the two species. This is in fact an expected sequence of the van't Hoff law (Eq. 1). Therefore, our further combined handling of the data generated with the two solutes (sucrose and glucose) is fully justified.

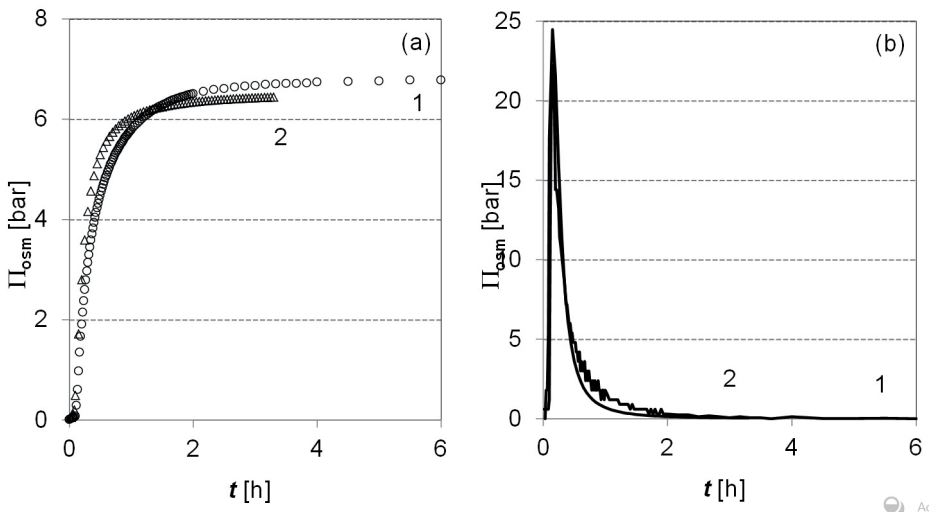

Fig. 2. Panel (a): Osmotic pressure Π vs. time t dependence at constant volume regime for the two different solutes (1 – sucrose; 2 – glucose), of equal concentration (= 0.278 mol/L); Panel (b): Pressure rise rates, dΠ/dt, for the respective two solutes

We must remind here that, as a colligative property of solutions, the osmotic pressure only depends on the solute concentration rather than on the solute nature. To a given bulk concentration of any solute correspond the same equilibrium level, in accord with the van't Hoff (1887) law:

$$\Pi_{eq} = RTc_{eq} \tag{1}$$

Here Π_{eq} is the equilibrium osmotic pressure corresponding to the solute concentration c_{eq}; R is the gas constant and T is the absolute temperature.

Although we are aware of the existence of a number of more complex formulae for the osmotic pressure, produced since (see e.g. (Morse et al., 1907; Frazer & Myrick, 1916; Lotz & Frazer, 1921; Stigter, 1960; Granik et al., 2002; Gratoni et al., 2007), we have found the original van't Hoff equation to be entirely sufficient for the

considered here tasks. Further on, we have used Eq. (1) also to account for the effect of concentration polarization (see Section Osmotic Process Modeling). The results of the extensive study of Grattoni et al. (2007) have shown for a number of nonionic solutes that the deviations between all these equations are insignificant below concentrations of *ca*. 0.5 mol/L, corresponding (at room temperature) to maximal (equilibrium) osmotic pressure values of the order of 12 bar. Therefore, here we operate entirely in the quoted range of moderate levels of osmotic pressure values.

It is important to note that the following Figs. 3 and 4 contain the whole information about the dynamics of osmotic process, which is to be analyzed here.

Three concentrations of sucrose were chosen for the comparison of the osmotic rates for processes at constant and variable solution volume as a function of the solute level: 0.1 M, 0.2 M and 0.5 M. The obtained respective time dependences are presented in Fig. 3:

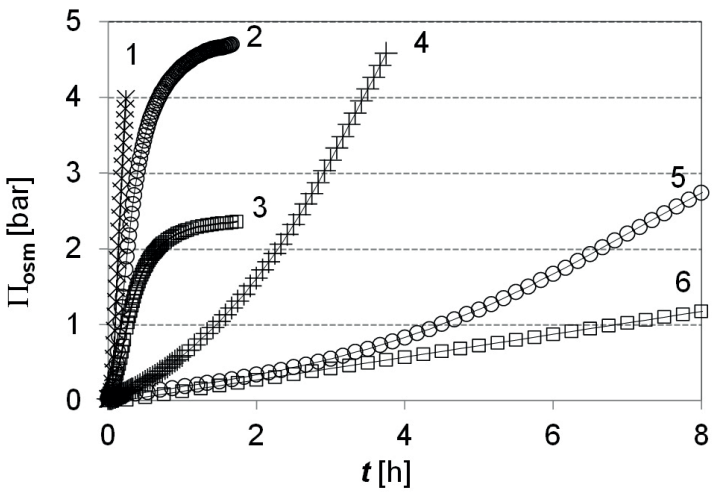

Fig. 3. Osmotic pressure Π vs. time t dependence for three different initial sucrose concentrations at the two regimes: (1) 0.5M (constant volume); (2) 0.2M (constant volume); (3) 0.1M (constant volume); (4) 0.5M (variable volume); (5) 0.2M (variable volume); (6) 0.1M (variable volume)

The juxtaposition of the kinetic dependences presented in Fig. 3 clearly demonstrates the difference in the rates of osmotic pressure rise for the two regimes of constant and varied volume.

Similar pattern – marked differences in the rates of the osmotic pressure rise at the two experimental regimes – we observe in Fig. 4, for the 'osmotic pressure Π vs. time *t*' dependences at constant volume (curve 1) and three different additional (gas) volumes (curves 2-4). The obtained dependences exhibit similar pattern, so that the main difference is in their respective slopes, dΠ/d*t*, diverging already from the onset of the process. It must be noted here that all four Π(*t*) curves in Fig. 4 tend to the same equilibrium plateau levels, as determined by the van't Hoff law (Eq.1).

The difference between initial and final (equilibrium) concentration is determined by the ratio of initial to final solution volume in the chamber. This ratio varies from unity (at constant solution volume), down to *ca*. 0.85 (at the regime of variable volume, in the case of the largest allowed V_{G0} = 16 cm³, relative to the initial 60 cm³). In particular, for the chosen solute concentration and temperature, Π_{eq} = 6.8 bar (curve 1) and Π_{eq} = 5.8, 6.3 and 6.5 bar for the respective curves 2-4.

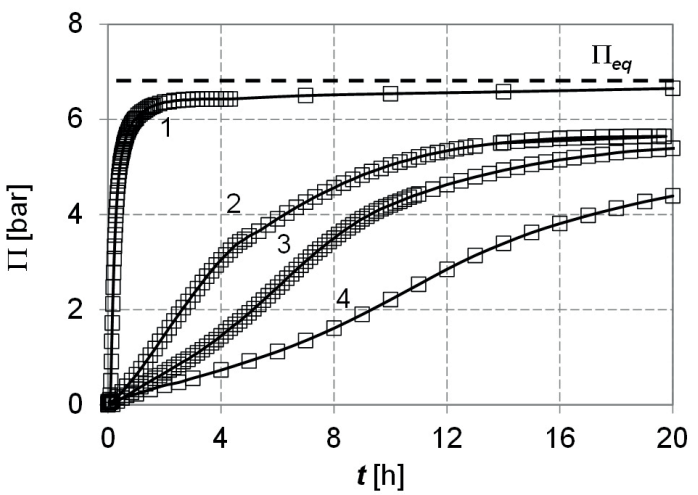

Fig. 4. Osmotic pressure Π vs. time *t* dependences for the two experimental regimes: curve (1) constant volume regime, V_L = 60 cm³; curves (2-4) are for variable additional gas volume (V_G) regime: (2) V_G = 4 cm³; (3) V_G = 8 cm³; (4) V_G = 16 cm³. Solute: 0.278 M aqueous glucose

The effect of the unequal final levels is not really essential for the expressed kinetic differences. Much more pronounced is the scale of disparity in the values of a kinetic parameter like the *relaxation time*, that is, the time of attaining the equilibrium. While

at constant solution volume (curve 1) equilibrium is reached within 2 hours, at variable volume the system may be away of equilibrium even after twenty-four-hour period. As we shall see, the basis of this divergence is the different amount of solvent passing through the membrane into the solution chamber at the different regimes. Respectively, these differences depend on the compressibility of the fluids in the osmotic chamber. At the regime of constant volume, water compressibility is the determining factor, while at variable volume determining is the gas compressibility.

It can be seen from both Figs. 3 and 4 that at variable volume, the osmotic pressure rise occurs at much slower rate. The vast divergence may seem surprising at first sight but, in fact, can be regarded as a quite natural result.

These drastic differences are direct consequence from the mechanical properties of the closed osmotic cell at the two regimes. We shall remind that at constant volume in the solution chamber there is only liquid, while at variable volume gas phase is also present. The latter drastically increases (by five orders of magnitude!) the compressibility and, consequently, the liquid volumes required to raise the pressure. The amount of solvent, which has to pass into the solution compartment of the cell, in order to lift the osmotic pressure, differs dramatically in the two regimes. For example, employing the value for the coefficient of compressibility of pure water of 4.6×10^{-5} bar^{-1}, one estimates that for a closed cell of solution volume of 60 cm^3 the amount of solvent needed to raise the pressure by one atmosphere is 2.76×10^{-3} cm^3 (= 1.53×10^{-4} moles H_2O). Concurrently, in our case of limited volume variation by additional 16 cm^3 of gas to the initial 60 cm^3 of liquid, the amount of solvent necessary to lift the pressure up to a level of $\Pi = 1.0$ bar will be ca. 8.5 cm^3 (= 0.47 moles of water). The latter amount is some 3000 times larger than that at constant volume and, of course, will definitely require longer time of transport.

For the sake of comparison we can also employ the classical case of unlimited solution volume variation. For an osmotic cell connected to an open tube of radius as small as 2 mm, the amount of solvent necessary to lift the solution level by 10.2 m (in order to impose hydrostatic pressure of 1 atmosphere) would be $4\pi\times10^{-2}(cm^2)\times1.02\times10^3$ (cm) = 128 cm^3.

Osmotic process modeling

As it should be expected, the differential analysis of the kinetic dependences can provide further insight into the mechanism of the process. Fig.5 presents the results obtained for $d\Pi/dt$ vs Π, as derived from the integral dependences in Fig. 4. The remarkable novelty here is the appearance of extremes in the rates of pressure rise at

constant solution volume (Fig.5a), as well as at varied volume (Fig.5b).

In effect, the presence of maxima in the rates of solvent transfer is already hinted by the S-shaped integral dependences Π(*t*) and expressed clearer on curves 2-4 (see Fig. 4). According to the non-equilibrium thermodynamics of discontinued systems (de Groot & Mazur, 1962) the osmosis kinetics is governed by the difference in the solvent chemical potential on the two sides of the membrane. Written for diluted solution, it takes the form:

$$j_{osm} = \lambda(RTc - \Pi), \tag{2}$$

with j_{osm} [m/s] as solvent influx (or osmotic flux, see Fig.6), λ as membrane permeability, and *c* as solute concentration.

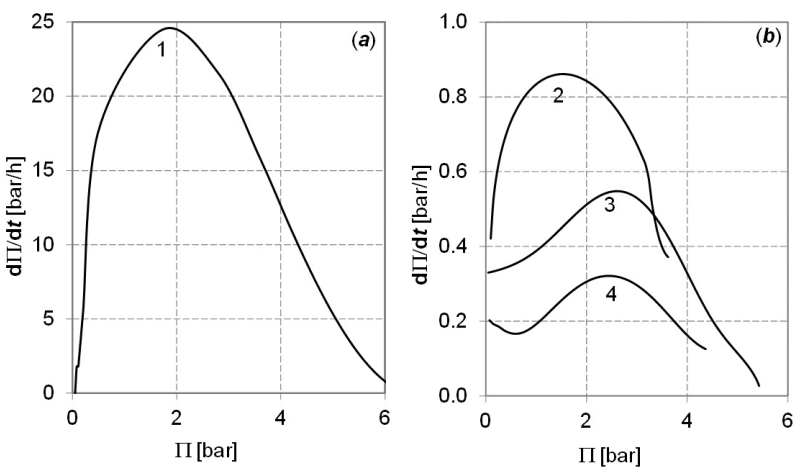

Fig. 5. Osmotic pressure rise differential dependences **d**Π **/d*t*** *vs.* Π for the two regimes: (**a**) curve (1) constant volume regime, (**b** curves (2-4) variable additional volume (V_{G0}) regime: (**2**) V_{G0} = 4 cm³; (**3**) V_{G0} = 8 cm³; (**4**) V_{G0} = 16 cm³

We shall remind that, by definition, the solvent influx is related to the velocity of transfer:

$$d(V_L)/dt = j_{osm}S \tag{3}$$

with S as an effective membrane area and V_L.as liquid volume in the closed chamber. We must point out that the membrane permeability λ is particularly important parameter for the osmosis, especially with respect to living cells, but its investigation goes beyond the structure of the present work. Subject of our treatment are the other parameters in the expression for solvent flux.

According to the non-equilibrium thermodynamics of discontinued systems scheme (Gratoni et al., 2007), the driving force of the process (the fluxes) is determined by the difference in the parameter values on the two membrane surfaces. For osmosis, this refers to the difference in the chemical potentials (of the solvent), that is: in the driving force ($RTc - \Pi$) of flow j_{osm}, all parameters must acquire the instant values at the membrane walls. As the process is isothermal, the temperature T is homogeneous over the whole system. There are global differences in pressure for the system, but the pressure jump is restricted to the (highly dissipative) membrane zone. In the separate chambers pressure is constant (although different on either side of membrane), which gives us the right to consider osmotic pressure as a function of time alone, $\Pi(t)$.

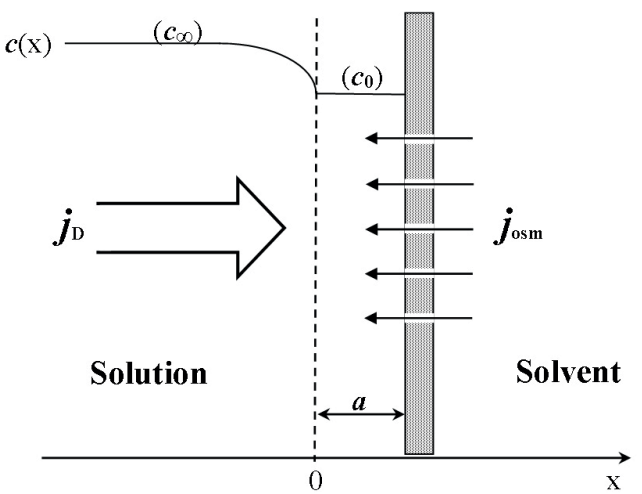

Fig. 6. Schematic of the osmotic concentration polarization

Much different is, however, the behaviour of the solute concentration, c in the expression for the solvent influx, j_{osm}. In contrast to the equilibrium state (j_{osm}=0), where the concentration is uniform in the whole chamber ($c = c_{eq}$) in the course of the process

(j_{osm}≠0), the solute concentration immediately at the membrane surface may differ from the concentration at a distance from membrane (c_∞) (Fig.6). Principal reason for this difference is the solvent influx j_L, which locally dilutes the solution in the membrane vicinity: $c_0 \leq c_\infty$, where c_0 denotes the concentration on the membrane surface. Evidently, the local dilution generates diffusion flow (j_D), which tends to level the concentrations in the chamber.

The osmotic process is thus composed of two conjugated, solvent $j_{osm} = \lambda(RTc_0 - \Pi)$ and diffusion, j_D. fluxes. The solute concentration is a function of the distance from membrane (x) and time (t): $c(x, t)$, while c_0 and Π are uniquely functions of time: $c_0(t)$, Π(t) (see e.g. (Zhao et al., 1012; Cath et al., 2006)).

The near-membrane concentration is controlled by the balance of the two flows j_L и j_D, of the kind:

$$dc_0 / dt \sim j_D - j_{osm} \tag{4}$$

Substantiating the above balance calls for additional clarification of the model of dilution, which is not on hands at the moment. The concentration distribution and its evolution are determined in the frame of the Fick equation. Without entering into details, for the incomplete formulation of the dilution balance, we shall point out that the problem of $c(x, t)$ involves the solution of Fick equation in the simplest form of one-dimensional distribution at boundary conditions $c(x = 0, t) = c_0(t)$ and, for example, $c(x = \infty, t) = c_\infty$. The second boundary condition expresses the assumption that the chamber is sufficiently deep, as to comprise regions which are not affected by dilution. The initial condition, $c(x, t = 0) = c_\infty$, is also obvious. The condition $c_\infty = c_{eq}$ evidently follows from the stipulation about the chamber size, that is, the transferred amount of solvent practically does not alter the initial concentration (equal to its equivalent value).

Concluding remarks

The proposed here osmotic kinetics model emphasizes upon one important concurrent process: the local dilution of the solution in the membrane vicinity, which is known as polarization effect.

The emergence of concentration polarization is a well-known effect, observed at both forward and reverse osmosis; see e.g. (Sutzkover et al., 2000). The models as developed are not of general scope but rather aim at serving various specific cases. Thus, they are not directly applicable to our experimental conditions, which are also specific and significantly different from those in the industrial desalination devices. The

search of an appropriate model corresponding to describe here experiment will be the chief purpose of our future study.

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