

Biophysical Chemistry 91 (2001) 263-271

### Biophysical Chemistry

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# Studies on the structural properties of porous membranes: measurement of linear dimensions of solutes

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Received 6 March 2001; received in revised form 14 May 2001; accepted 14 May 2001

#### **Abstract**

This work is concerned with a novel way of studying the basic structural and transport properties of porous membranes. Formulae have been derived for: the total number (N) of pores in the membrane; and mean square radius  $(r_k)$  of pores and for selective membranes: the mean square radius  $(r_{ka})$  of pores impermeable to solutes and mean square radius  $(r_{kb})$  of permeable pores. The result of the investigation is the proposal of a new research procedure (osmotic) for the determination of the linear dimensions of solutes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Porous membranes; Substance transport; Osmosis; Pore distribution; Solute; Molecular dimensions

### 1. Introduction

By porous membrane we mean a thin solid partition that has a statistical number N of pores of relatively small sizes, which are, however, permeable for the solvent. In a typical porous

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membrane like cellophane, nephrophane or collodion membranes, the pore linear dimensions (the radii of their cross-sections) are randomly distributed. Such a model membrane is assumed to have cylindrical pores oriented normal to its surface. The pore distribution within a membrane is also random. They can, however, be ordered in a series from the smallest pores  $(r_1^{\min})$  to the largest ones  $(r_N^{\max})$ .

Therefore, we assume that in such membranes

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pore size distributions [11,15] can be expressed by the function:

$$\frac{\mathrm{d}n}{N\mathrm{d}r} = f(r)$$

where dn is the number of pores of radii within the interval  $r \div r + dr$ .

The problem of permeability of such membranes towards solvent and solute molecules is, in general, very complicated as shown in the papers [1–7,9,10,12,13,16,18]. Without going into details, one can say that permeability is determined by the physico-chemical properties of membranes and the solutions they separate. In the case of non-electrolytes, it is reasonable to assume that the main determinants of permeability are the dimensions and number of pores within membrane as well as the linear dimensions of solute and solvent molecules. Based on this, membranes can be classified as non-selective (permeable), selective and semi-permeable.

A membrane is termed non-selective if all of its pores are permeable both to solvent and solute molecules. However, for a given membrane, a solute (of molecular radius  $r_s$ ) can be chosen, which does not permeate through a certain number  $(n_a)$  of pores of dimensions from the interval  $(r_1^{\min} \div r_a < r_s)$ . The remaining pores  $n_b = N - n_a$ , of radii within the interval  $(r_s < r_b \div r_N^{\max})$  are permeable to the solute molecules. The membrane is then treated as selective [10,16].

A special case is when all the pores of a membrane are impermeable to the chosen solute. This occurs when  $r_N^{\text{max}} < r_s$ . A membrane satisfying this condition is called semipermeable.

For such membranes we firstly consider the problem, known from literature [15] as the determination of the total number of pores N and their mean square radius  $r_k = \sqrt{\overline{r^2}}$ .

Next, we postulate as previously stated [10,16], that a single pore has a reflection coefficient  $\sigma_p=1$  or 0. From this we derive the formulae for the mean square radii of permeable and impermeable pores of a selective membrane, i.e.  $\overline{r_a^2}$  and  $\overline{r_b^2}$ , and their mean square radii where  $r_{ka}=\sqrt{\overline{r_a^2}}$  and  $r_{kb}=\sqrt{\overline{r_b^2}}$ . This, essentially, is the new contribution of this paper.

Finally, we postulate based on literature data [10,11,15–17], that the distribution of pore linear dimensions in a porous membrane has a Gaussian probability density. Consequently, we attempt to determine the pore size (radii) distribution in a membrane. We also propose a new research procedure for the determination of linear dimensions of solute molecules using membranes. The procedure has been verified experimentally (using a nephrophane membrane) for the molecular radii of glucose and sucrose in solution.

To these introductory remarks we should add that certain membrane methods for finding the solute molecular sizes have been applied by other authors [5–7,19]. These earlier methods have been mostly based on the membrane transport equations derived by Kedem and Katchalsky within the framework of thermodynamics of irreversible processes [12]. Interpretation of these equations is unclear. Therefore, unclear too are the methods based on them.

On the other hand, our method is based on mechanistic considerations. Its interpretation is thus, entirely clear.

This paper creates, in our opinion, new possibilities for further studies, both biophysical and technological, on finding solute molecular sizes as well as structural properties of porous membranes.

### 2. Determination of the total number N of pores in a membrane and their mean square radius

### 2.1. Analytical considerations

The subject of our considerations here is a porous membrane M of active surface S (which is the area of its contact with the bathing solutions on both sides) and thickness d, containing a statistical number of pores N permeable to the solvent. A typical porous membrane like cellophane, nephrophane or collodion membranes, has its pores varying with respect to linear dimensions (radii). They are also randomly distributed within the membrane. In such a model membrane one can assume that the pores are of cylindrical shape and perpendicular to its surface. With re-

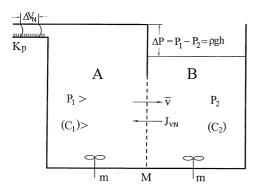


Fig. 1. Membrane system (A,B, compartments; M, membrane;  $K_p$ , capillary; m,m, stirrers;  $C_1$ , $C_2$ , concentrations;  $P_1$ , $P_2$ , mechanical pressure;  $J_{vN}$ , flux; and  $\bar{v}$ , average velocity).

spect to sizes, the pores can be arranged in a sequence that begins with the smallest  $(r_1^{\min})$  and ends with largest  $(r_N^{\max})$ :

$$r_1^{\min} < r_2 < \dots < r_i < \dots < r_N^{\max}$$
.

Let us consider the situation when the membrane separates two compartments A and B containing a solvent ( $C_1 = C_2 = 0$ ) with viscosity coefficient  $\eta$ . Let the solvent be subject to different mechanical pressures  $P_1$  and  $P_2$ . Such a situation is illustrated in Fig. 1. Due to the pressure difference  $\Delta P = P_1 - P_2 > 0$ , the solvent flows through the pores with various velocities:

$$v_1^{\min} < v_2 < \dots < v_i < \dots < v_N^{\max}$$
.

Applying the Poisseuille law to the respective flows (see [7,9,11,14,15]), we obtain:

$$\bar{v} = \frac{\Delta P}{8\eta d} \bar{r}^2 \tag{1}$$

where

$$\bar{v} = \frac{1}{N} \sum_{i=1}^{N} v_i \tag{2}$$

is the mean velocity and

$$\overline{r^2} = \frac{1}{N} \sum_{i=1}^{N} r_i^2 \tag{3}$$

is the mean square radius.

Let us now recall the definition of the mean velocity of solvent flow through a pore of cross-section  $\overline{S} = \pi r^2$ , i.e.

$$\bar{v} = \frac{\Delta \bar{V}}{\bar{S}t} = \frac{\Delta \bar{V}}{\pi r^2 t} \tag{4}$$

where  $\Delta \overline{V}$  is the volume of solvent that has flowed through a pore of mean cross-section  $\overline{S}$  in time t.

Using that definition, Eq. (1) can be rearranged to the form:

$$\Delta \overline{V} = \frac{\pi \left(\overline{r^2}\right)^2}{8\eta d} \Delta Pt. \tag{5}$$

Since there are N pores in the membrane, we have  $\Delta V_N = N\Delta \overline{V}$ . Hence, the total flux across the membrane equals:

$$\Delta V_N = \frac{N\pi \left(\overline{r^2}\right)^2}{8md} \Delta Pt. \tag{6}$$

The unknown quantities in this formula are N and  $\overline{r^2}$ . We need a second equation to find them. Let us then consider the volume  $\Delta V_p$  of the solvent that fills the membrane pores. This quantity can be written as:

$$\Delta V_p = N \pi \overline{r^2} d. \tag{7}$$

Eqs. (6) and (7) constitute a system with two unknowns (N and  $\overline{r^2}$ ). Solving this system of equations we obtain the formulae [15]:

$$N = \frac{\Delta V_p^2 \Delta Pt}{8\eta \pi d^3 \Delta V_N},\tag{8}$$

and

$$\overline{r^2} = \frac{8\eta d^2 \Delta V_N}{\Delta V_p \Delta P t}$$
 and  $r_k = \sqrt{\overline{r^2}} = \sqrt{\frac{8\eta d^2 \Delta V_N}{\Delta V_p \Delta P t}}$ , (9)

where  $r_k$  is the mean square radius. Based on the above formulae, and knowing  $\Delta V_N$ ,  $\Delta V_p$ ,  $\Delta P$ , t,  $\eta$ 

and d, one can, for a given membrane, calculate N,  $\overline{r^2}$ ,  $r_k = \sqrt{\overline{r^2}}$  and also the total cross-section area of all pores:

$$S_N = N\pi \overline{r^2}. (10)$$

Continuing the considerations, we divide Eq. (6) by  $S_N t$  and obtain:

$$\frac{\Delta V_N}{S_N t} = \frac{\overline{r^2}}{8\eta d} \Delta P. \tag{11}$$

This equation can also be rewritten as:

$$J_{vN} = L_{pN} \Delta P \tag{12}$$

where

$$L_{pN} = \frac{\overline{r^2}}{8\pi d} \tag{13}$$

is the real filtration coefficient (hydraulic conductance) of the membrane, and

$$J_{vN} = \bar{v} = \frac{\Delta V_N}{S_N t} \tag{14}$$

is the real volume flux.

At this point we stress that in research practice, conducted mainly with the use of the Kedem-Katchalsky formalism [8,12,13], the following definition of volume flux is used:

$$J_v = \frac{\Delta V}{St}$$

Table 1 Data for nephrophane membrane

for many membranes the strong inequality $S \gg S_N$							
holds, but it becomes weaker the more porous the							
membrane. It is very often assumed that $S_N = S$ ,							
which seems a crude approximation.							
2.2. Sample experimental results							

where S is the so-called active surface of a mem-

brane (i.e. membrane area in contact with the bathing solutions). It should also be noted that

We apply the analytical results presented above to selected experimental data for nephrophane membrane. Using the measuring system presented schematically in Fig. 1, it was shown that the membrane (of effective area  $S=7\times 10^{-4}$  m<sup>2</sup> and thickness  $d=2.5\times 10^{-4}$  m) is permeated by a volume of water  $\Delta V_N=8.25\times 10^{-9}$  m<sup>3</sup>, during time t=300 s and under a mechanical pressure  $\Delta P=P_1-P_2=8338.5$  Nm<sup>-2</sup>. Next, it has been determined by weighing a wet and a dry disk of the membrane of radius  $r_0=1.5\times 10^{-2}$  m, that the water volume contained within membrane pores (and thus, the pore volume) is  $\Delta V_p=11\times 10^{-9}$  m<sup>3</sup>.

Now, taking into account Eqs. (8)–(10), (12) and (14), the quantities  $\overline{r^2}$ ,  $r_k = \sqrt{\overline{r^2}}$  and N have been calculated. Also the real values of the effective area  $S_N$ , volume flux  $J_{vN}$ , and filtration coefficient  $L_{pN}$ , have been determined. Values of these quantities are given in Table 1.

From these calculations it follows that the effective membrane area is  $S = 7 \times 10^{-4} \text{ m}^2$  and is significantly larger than the real effective area  $S_N$  of the membrane  $(S_N = N\pi r^2 = 4.38 \times 10^{-4} \text{ m}^2)$ . This section, together with Table 1, is the starting point for further analysis.

$r^2$ (m <sup>2</sup> )	r <sub>k</sub> (m)	N	$S_N = N\pi r^2$ (m <sup>2</sup> )	$J_{vN} = (ms^{-1})$	$\frac{L_{pN}}{(\text{m}^3\text{N}^{-1}\text{s}^{-1})}$
$1.5 \times 10^{-18}$	$1.2247 \times 10^{-9}$	$9.3 \times 10^{13}$	$4.38 \times 10^{-4}$	$6.278 \times 10^{-8}$	$7.52 \times 10^{-12}$

Other data:  $\Delta V_p = 11 \times 10^{-9}$  (m³); d = 2.5 × 10<sup>-5</sup> (m);  $\Delta P = 8338.5$  (N m<sup>-2</sup>);  $\Delta V_N = 8.25 \times 10^{-9}$  (m³);  $\rho_{\rm H2O} = 0.9982 \times 10^3$  (kg m<sup>-3</sup>);  $\rho_{\rm H2O} = 1.005 \times 10^{-3}$  (N s m<sup>-2</sup>); and t = 300 (s).

## 3. Determination of membrane reflection coefficients and mean square radii: $r_{ka}$ (of impermeable pores) and $r_{kb}$ (of permeable pores)

### 3.1. Analysis

Let us now consider the case when compartment A of the membrane system presented in Fig. 1 is filled with a non-electrolyte solution of concentration  $C_1$ . Compartment B is filled with a solution of the same substance of concentration  $C_2$  lower than  $C_1$ ; possibly  $C_2 = 0$ . On the membrane separating the compartments there now is, besides mechanical pressure  $\Delta P = P_1 - P_2$ , osmotic pressure  $\Delta \pi = RT(C_1 - C_2)$ , where R is the gas constant and T the temperature. Let us assume that the solute molecules are approximately spherical in shape with radii  $r_s$  within the interval  $r_1^{\min} < r_s < r_N^{\max}$ . This means that a certain number  $n_a$  of pores (from the total number N), have radii smaller than  $r_s$ . In other words, these pores are impermeable to the given solute. Applying the notion of the membrane reflection coefficient  $\sigma$  to individual pores, thus introducing a local interpretation of the parameter [10,16], we postulate that the reflection coefficient of each of the  $n_a$  pores is  $\sigma = 1$ . The remaining pores  $n_b =$  $N-n_a$ , are permeable to the solute. The reflection coefficient of each of these pores is  $\sigma_b = 0$ . Thus, we consider here a selective membrane.

Let us denote by  $L_{pNa}$ , the resultant filtration coefficient of impermeable pores  $(n_a)$  and by  $L_{pNb}$  — the resultant filtration coefficient of permeable pores  $(n_b)$ . Since there are pressure differences  $\Delta P$  and  $\Delta \pi$  on the membrane, we can write the following equation for the volume flux  $J_{vNa}$  that permeates the solute-impermeable pores [10]:

$$J_{vNa} = L_{pNa} \Delta P - L_{pNa} \Delta \pi \tag{15}$$

since  $\sigma_a = 1$ .

On the other hand, the volume flux through permeable pores is given by the equation [10,16]:

$$J_{vNh} = L_{pNh} \Delta P \tag{16}$$

since  $\sigma_b = 0$ .

Since the resultant volume flux  $J_{vN}$ , generated in the system is the sum of fluxes  $J_{vNa}$  and  $J_{vNb}$ , which is expressed by the formula:

$$J_{vN} = J_{vNa} + J_{vNb} \tag{17}$$

and taking into account Eqs. (15) and (16), we obtain:

$$J_{vN} = L_{pN} \Delta P - L_{pN} \sigma \Delta \pi \tag{18}$$

where

$$L_{pN} = L_{pNa} + L_{pNb} \tag{19}$$

The quantity  $\sigma$  appearing in Eq. (18), and given by the relation:

$$\sigma = \frac{L_{pNa}}{L_{pN}} \tag{20}$$

is treated as the membrane reflection coefficient. In order to better explain this quantity, let us consider Eq. (18). It shows that there exists such a value of pressure difference  $\Delta P = \Delta P_m$  for which,  $J_{vN}=0$  with  $\Delta \pi={\rm constant}>0$ . For this pressure difference we have:

$$\Delta P_m = \sigma \Delta \pi.$$

Hence, it follows that [10,16]:

$$\sigma = \left(\frac{\Delta P_m}{\Delta \pi}\right)_{J_{vN}=0}.$$
 (21)

This expression for the reflection coefficient is identical to that obtained by Kedem and Katchalsky [12,13].

Now, considering Eqs. (19) and (20), we obtain the following expressions:

$$L_{pNa} = \sigma L_{pN} \tag{22}$$

$$L_{pNh} = (1 - \sigma)L_{pN}. \tag{23}$$

These expressions are very important in what follows, since they allow determination of the coefficients  $L_{pNa}$  and  $L_{pNb}$  when  $L_{pN}$  and  $\sigma$  are

known. However, we first rearrange Eqs. (15) and (16) to the form:

$$J_{vNa} = L_{nN} \sigma(\Delta P - \Delta \pi), \tag{24}$$

$$J_{vNb} = L_{pN}(1 - \sigma)\Delta P. \tag{25}$$

The equations for the fluxes  $J_{vNa}$  and  $J_{vNb}$  can also be written in a form analogous to Eq. (12). Then they have the form:

$$J_{vNa} = \frac{\overline{r_a^2}}{8\pi d} (\Delta P - \Delta \pi), \tag{26}$$

$$J_{vNb} = \frac{\overline{r_b^2}}{8 \, \text{nd}} \, \Delta P. \tag{27}$$

From the above four equations, we get

$$\frac{\overline{r_a^2}}{8\eta d} = L_{pN}\sigma$$
 and  $\frac{\overline{r_b^2}}{8\eta d} = L_{pN}(1-\sigma)$ .

Hence, it follows that:

$$\overline{r_a^2} = 8\eta dL_{pN}\sigma, \qquad (28)$$

$$\overline{r_h^2} = 8\eta dL_{nN}(1 - \sigma), \tag{29}$$

and

$$r_{ka} = \sqrt{8\eta dL_{pN}\sigma} , \qquad (30)$$

$$r_{kb} = \sqrt{8\eta dL_{pN}(1-\sigma)}, \qquad (31)$$

where  $r_{ka}$  and  $r_{kb}$  are the mean square radii of pores  $n_a$  and  $n_b$ , respectively. The last four equa-

tions allow us to determine  $\overline{r_a^2}$ ,  $\overline{r_b^2}$ ,  $r_{ka}$  and  $r_{rb}$ . In the following sections we use the values of  $r_{ka}$  just computed to determine the solute molecular radii  $r_s$ .

### 3.2. Sample experimental results

Using Eqs. (18) and (21) obtained in the preceding section, one can routinely determine [8] the reflection coefficient  $\sigma$  and filtration coefficient  $L_{pN}$  of a membrane. To this end, it is necessary to measure (using the set-up shown in Fig. 1) the volume flux  $J_{vN}$  generated by the pressure difference  $\Delta P$  (with  $\Delta \pi = 0$ ). Then from Eq. (18) we find the coefficient  $L_{pN}$ . Next, after measuring  $\Delta P = \Delta P_m$  (for which  $J_{vN} = 0$ ), we find from Eq. (21) the reflection coefficient  $\sigma$  for the solute. Knowing these parameters (i.e.  $L_{pN}$  and  $\sigma$ ), it is easy to calculate from Eqs. (30) and (31) the mean square radii  $r_{ka}$  (for impermeable pores) and  $r_{kb}$  (for permeable pores).

Sample results for nephrophane membrane and water solutions of glucose and sucrose are given in Table 2.

Especially important are data referring to  $\sigma$ ,  $r_{ka}$ ,  $\sigma^s$  and  $r_{ka}^s$ . They allow determination of the mean square radius  $r_s$  of glucose molecules and the mean radius  $r_s^s$  of sucrose molecules.

### 4. Distribution of pore radii in a membrane. An attempt at determination of the linear dimensions of solute molecules

Let us take a porous membrane with a statistical number N of pores with random cross-section radii. The pore radii can be arranged in a series:

$$r_1^{\min} < r_2 < \dots < r_i < \dots < r_N^{\max}$$
.

Table 2
Experimental data for nephrophane membrane with glucose and sucrose as solutes

Glucose solutions			Sucrose solution		
σ	$r_{ka}$ (nm)	$r_{kb}$ (nm)	$\sigma^s$	$r_{ka}^{\text{s}}$ (nm)	$r_{kb}^{\rm s}$ (nm)
0.067	0.3178	1.187	0.093	0.3749	1.1708

Other data:  $C_1 = 100 \text{ (mol m}^{-3}\text{)}; C_2 = 0; S_N = 4.38 \times 10^{-4} \text{ (m}^2\text{)}; d = 2.5 \times 10^{-5} \text{ (m)}; \eta = 1.005 \times 10^{-3} \text{ (N s m}^{-2}\text{)}; and } L_{pN} = 7.52 \times 10^{-12} \text{ (m}^3 \text{ N}^{-1} \text{ s}^{-1}\text{)}.$ 

This means that in porous membranes the pore radii distribution can be expressed as:

$$\frac{\mathrm{d}n}{N\mathrm{d}r} = f(r) \tag{32}$$

where dn is the number of pores whose dimensions are in the interval  $r \div r + dr$ .

Based on various published reports [11,15,17], we postulate that in a typical porous membrane such as cellophane, nophrophane or collodion membranes, the pore radii distribution of pores permeable to a solvent is the Gauss function, i.e. the normal distribution of probability density of a random variable. This function can, for pores of such a membrane, be written as:

$$\frac{dn}{Ndr} = f(r) = \frac{h}{\sqrt{\pi}} e^{-h^2(r - r_p)^2},$$
(33)

where  $r_p$  is the most probable radius, h a parameter, and f(r) is the probability density of the random variable r. A plot of this function is presented in Fig. 2. It is symmetrical with respect to  $r = r_p$ , where it has a maximum, and a bell-like shape. For such a curve it may be assumed that  $r_k = r_p$ , where  $r_k = \sqrt{\overline{r^2}}$  is the mean square radius of pores permeable to the solvent. An ordinate at the point  $r = r_p = r_k$  halves the area under the curve. It should be explained here that the chosen value of parameter h should ensure a maximum at  $r = r_k$  and the plot running near the point  $r_1^{\min} = 0.15$  nm when water is the solvent. Such are the approximate linear dimensions of water molecules [5,6]. The membrane can't contain even a single very large pore, or a number of such, as this would disqualify the membrane as appropriate for example osmotic processes.

For a membrane with a Gaussian pore distribution, one can select a solute of molecular radius  $r_s$  that satisfies the relation  $r_1^{\min} < r_s < r_N^{\max}$ . A straight line drawn at  $r = r_s$  in the co-ordinate system in Fig. 2, divides the area under the curve into two parts, namely  $S_a$  and  $S_b$ . This means that pores from within the interval  $(r_1^{\min} \div r_a < r_s)$  are impermeable for the solute, and the remaining pores  $n_b = N - n_a$ , i.e. pores within the interval  $(r_s < r_b \div r_N^{\max})$ , are permeable for that solute.

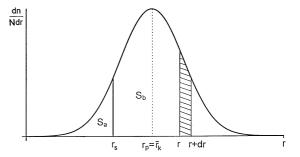


Fig. 2. Pore size distribution in the membrane (description in text)

The considerations described above constitute the starting point for an attempt to elaborate the procedure for determining the linear dimensions  $(r_s)$  of molecules of various solutes.

In order to illustrate such a procedure, let us take, for instance, the nephrophane membrane previously studied. For that membrane we have shown that the mean square pore radius  $r_k = 1.2247$  nm. Thus, we can write the Gauss function [Eq. (33)] as follows:

$$\frac{dn}{Ndr} = f(r) = \frac{h}{\sqrt{\pi}} e^{-h^2(r - r_k)^2}.$$
 (34)

This Gaussian has a maximum for  $r=r_k=1.2247$  nm, and its graph stretches from 0 to  $\infty$ . We are looking for a particular shape that reflects the pore distribution for pores permeable to water, i.e. pores from  $r_1=r_w=0.15$  nm to  $r_N^{\rm max}$ . Therefore, we need a value of parameter h for which the Gaussian approximately stretches from  $r_1=r_w$  to  $r_N^{\rm max}$  (see Fig. 3). We require that the left tail passes near point  $r_1=r_w$  and the right tail — near  $r=r_N^{\rm max}$ . For these points, the values of the Gaussian ought to be sufficiently small. We estimate that the left tail of the Gaussian passes sufficiently close to the point  $r_1=r_w$ , based on the criterion that the area  $S_0$  under the curve (see Figs. 4 and 5) equal

$$S_0 = \int_0^{r_w} f(r) \mathrm{d}r,$$

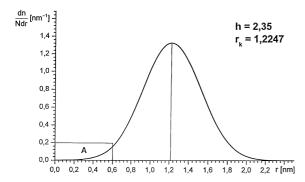


Fig. 3. Gaussian distribution curve of pore sizes in nephrophane membrane obtained for h = 2.35.

is negligible compared to the area

$$S_1 = \int_0^{r_s} f(r) \mathrm{d}r$$

i.e.  $S_0 \ll S_1$ . With this strong inequality, the number of pores represented by the area  $S_0$  is even more negligible compared to the total number of pores N in the membrane studied.

In order to satisfy  $S_0 \ll S_1$ , we start with h = 2.29 in Eq. (34) and gradually increase this value. We determined that h = 2.35 fulfils the inequality  $S_0 \ll S_1$  sufficiently well. Based on this, we claim that the Gaussian [Eq. (34)] with h = 2.35 adequately reflects the pore distribution in the studied membrane. As an additional justification of

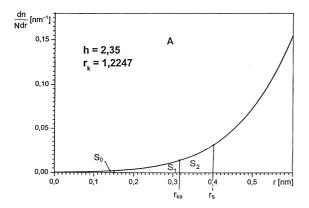


Fig. 4. A fragment of the Gaussian distribution curve of pore sizes in nephrophane membrane (description in text).

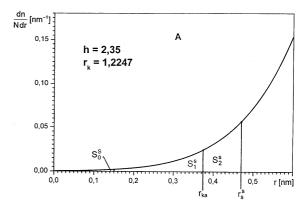


Fig. 5. A fragment of the Gaussian distribution curve of pore sizes in nephrophane membrane (description in text).

this criterion (and also the value of h = 2.35), we note that radius  $r_s$  (for glucose molecules) is very close to the radius  $r_s$  (of this solute molecule) obtained by crystallographic method [18].

Having selected a value of h as described in the preceding paragraphs we applied Gaussian [Eq. (34)] with h = 2.35 in the formula for the average impermeable pore size  $r_{ka}$ :

$$r_{ka} = \frac{\int_0^{r_s} r \exp\left[-h^2(r - r_k)^2\right] dr}{\int_0^{r_s} \exp\left[-h^2(r - r_k)^2\right] dr}.$$
 (35)

The parameter  $r_s$  is the unknown quantity in Eq. (35), while  $r_{ka}$  is determined for a particular membrane and the particular solute as shown in Section 3.1. The integrals were numerically computed and the roots of Eq. (35) found using Mathematical routines.

In particular, Eq. (35) was applied to glucose and sucrose for which mean square radii of impermeable pores were found (see Table 2). For glucose, we have  $r_{ka} = 0.3178$  nm. Substituting this value to Eq. (35) we get  $r_s = 0.406$  nm. Similarly for sucrose,  $r_{ka}^s = 0.3749$  nm, which yields  $r_s^s = 0.470$  nm. These values are somewhat lower than obtained for the same solutes by other membrane methods ( $r_s = 0.44$  and 0.53 nm, respectively) [19]. However, they are close to those

obtained for glucose by crystallographic methods [18], i.e.  $r_s = 0.356$  nm.

### 5. Conclusion

The present work is a novel approach to the basic problems concerning the structural and transport properties of porous membranes. We derive equations which can be used, e.g. for determination of the number of pores N in a membrane and their mean square radius  $r_k$ . For selective membranes, analytical expressions for the mean square radii  $r_{ka}$  (of pores impermeable for solute molecules) and  $r_{kb}$  (of permeable pores) have been derived. Especially important is the expression for the mean square radius of permeable pores:

$$r_{ka} = \sqrt{8\eta dL_{pN}\sigma} .$$

It creates new research possibilities. Based on this we designed a procedure for determining (by using porous membranes) linear dimensions of solute molecules. The analysis presented in this work has been illustrated and verified with experimental results. They refer to nephrophane membrane and water solutions of glucose and sucrose. The determination of molecular radii of glucose and sucrose is the final research result. The values of the radii are  $r_s = 0.406$  and  $r_s^s = 0.470$  nm, respectively. These values are somewhat smaller than the ones mentioned in the literature [19] (i.e.  $r_s = 0.44$  and  $r_s^s = 0.53$  nm, respectively) and obtained from other membrane techniques. We would like to point out though, that our result for glucose ( $r_s = 0.406$  nm) is close to the one obtained from the crystallographic method [18], i.e.  $r_s = 0.356$  nm.

The results obtained in this work verify, to a certain degree, the assumption that the pore size distribution in a membrane is approximately Gaussian.

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