
PERMEATION AND SORPTION METHODS FOR THE DETERMINATION OF TRANSPORT PARAMETERS OF GASES AND VAPOURS THROUGH FLAT MEMBRANES

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Dedicated to late Academician Eduard Hála.

New relations were derived for the determination of diffusion coefficients, coefficients of permeability, and sorption coefficients of gases and vapours through flat membranes by means of the permeation and sorption methods. To verify these relations, a polyurethane filled with silicium oxide (Silica) was chosen as a model system. Transport parameters of water vapours at the temperature of 25°C were determined for this system by the sorption and permeation methods. Both the methods yield practically the same transport parameters especially after evacuating the membrane before the measurement by the permeation technique.

Transport properties of gases and vapours through flat membranes, to which pertain diffusion coefficient, coefficient of permeability, and sorption coefficient, serve for their characterization in studying the effect of structure on the separation properties of a membrane. The given characteristics may be utilized, e.g., in the membrane technology of separating mixtures of gases and mixtures of gaseous isotopes, for separating components by the method of evaporating the mixture through a membrane, in packing, in the technology of manufacturing the composites for the fancy-goods and boot-and-shoe industry, and in other branches of industrial practice.

Hitherto we fail to theoretically predict the values of transport parameters, and therefore as the only reliable method remains their experimental determination. In the following chapters, the permeation and sorption methods for determining the transport properties of gases and vapours through a flat membrane will be described.

The experimental set-up of the permeation method¹ consists of a chamber partitioned with a membrane. One side of the membrane is flowed round by a carrier gas and the second side by a mixture composed of the carrier gas and the gas or vapour whose permeability through the membrane is measured. The gas permeated through the membrane is mixed with the carrier gas, and the composition of the mixture is

determined in terms of the change of thermal conductivity of the system. The voltage signal incoming the recorder is proportional to the measured gas concentration and is connected with the diffusion flow density of a gas or vapour through the membrane which is directly related to the coefficient of permeability of the gas applied.

The experimental apparatus for the sorption method² consists of a spiral quartz balance placed in a glass tempered jacket connected to a manometer and metering device of gas or vapour controlled by a manostat. The membrane specimen is suspended on the spiral balance, the mass changes of the membrane during sorption are evaluated at the given time from the balance stretching read by means of a cathetometer. The measurement is taken at constant pressure which can be maintained in the apparatus as well in terms of a vapour-liquid equilibrium system at a preset cryostat temperature. The adsorbate permeability is found from the sorption rate and from the sorption of adsorbate in equilibrium.

THEORETICAL

Mass transfer through a flat membrane of thickness l is a superposition of the processes of sorption combined with the adsorbate transfer through the gas (g) and solid phase boundary brought about by the difference of chemical potentials $X = \mu_g - \mu$ and by the diffusion accompanied by the substance dissolution brought about by the gradient of chemical potential $Y = \Delta\mu/l$. In the quantitative treatment of this complex process, a question arises whether it is possible to insert simultaneously both the forces X and Y into the transfer equation. Considering that force X pertains to the tensor of the zeroth order (difference of scalar quantity) and force Y is the tensor of the first order — vector (gradient of scalar quantity), both the quantities are not of the same vector order and must not be added in one transfer equation according to the Curie theorem³. The theorem can be satisfied by treating all the problem either in terms of the transfer laws

$$J = bX \quad (1)$$

or the diffusion laws

$$J = LY. \quad (2)$$

Transfer law (1) is to be easily transformed to diffusion law (2)

$$J = LX/l, \quad (3)$$

where J is the diffusion flow, $b = L/l$ is the transfer coefficient, and L is the coefficient of diffusion conductivity of the system. For a polymer membrane of finite dimensions bounded by planes $z = 0$ and $z = l$, the solution of the 2nd Fick law for constant

diffusion coefficient D , $\partial c/\partial t = D\partial^2 c/\partial z^2$, under the initial and boundary conditions

$$\begin{aligned} c &= c_1 & z &= 0 & t &\geq 0 \\ c &= 0 & z &= l & t &\geq 0 \\ c &= 0 & 0 < z < l & t &= 0 \end{aligned} \quad (4)$$

leads⁴ to the relation

$$c = c_1 - c_1 z/l - (2c_1/\pi) \sum_{n=1}^{\infty} (1/n) \sin(n\pi z/l) \exp(-Dn^2 \pi^2 t/l^2), \quad (5)$$

which expresses the dependence of concentration of diffusing substance in membrane on the position and time. The rate with which the diffusing substance leaves the unit area of membrane at $z = l$ is given by the diffusion flow density $J = -D(\partial c/\partial z)_{z=l}$ which is expressed, on the basis of Eq. (5), by the relation

$$J = (Dc_1/l) \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-Dn^2 \pi^2 t/l^2) \right]. \quad (6)$$

It follows from this relation that in steady-state for $t \rightarrow \infty$, the density of diffusion flow J_s is

$$J_s = Dc_1/l. \quad (7)$$

By dividing Eqs (6) and (7), we obtain the ratio of the densities of the diffusion flow and the steady-state diffusion flow of substance:

$$J/J_s = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-Dn^2 \pi^2 t/l^2). \quad (8)$$

On neglecting all the terms with $n \geq 4$, we get

$$\ln [(1 - \alpha)/2 + \beta - \gamma] = -D \pi^2 t_\alpha / l^2, \quad (9)$$

where

$$\alpha = J/J_s, \quad (10)$$

t_α is the time corresponding to the given value of α , l is the membrane thickness, and the correction terms β and γ are defined by

$$\beta = \exp [4 \ln (1 - \alpha)/2], \quad (11)$$

and

$$\gamma = \exp [9 \ln (1 - \alpha)/2]. \quad (12)$$

From Eq. (9) we get for the diffusion coefficient

$$D = -(l^2/\pi^2 t_\alpha) \ln [(1 - \alpha)/2 + \beta - \gamma]. \quad (13)$$

The alternative procedure of solution of the given problem stems from the relation which was obtained by Rogers, Buritz and Alpert⁵ on solving the 2nd Fick law under the initial and boundary conditions given by Eqs (4). They expressed the density of diffusion flow at $z = l$ as a function of time t by the relation

$$J = (4Dc_1/\pi^{0.5}l) (l^2/4Dt)^{0.5} \sum_{m=0}^{\infty} \exp [-(2m + 1)^2 l^2/4Dt]. \quad (14)$$

The series in Eq. (14) converges rapidly, and therefore we can write for $m > 0$

$$J = (4Dc_1/\pi^{0.5}l) (l^2/4Dt)^{0.5} \exp (-l^2/4Dt). \quad (15)$$

The combination of Eqs (15) and (7) leads to the expression

$$J/J_s = (4/(2\pi)^{0.5}) (l^2/2Dt)^{0.5} \exp (-l^2/4Dt). \quad (16)$$

With regard to Eq. (10) we can write after rearranging

$$2 \ln [\alpha(2\pi)^{0.5}/4] = \ln X_\alpha - X_\alpha, \quad (17)$$

where

$$X_\alpha = l^2/2Dt_\alpha. \quad (18)$$

On rearranging Eq. (18) we get the relation for diffusion coefficient

$$D = l^2/2X_\alpha t_\alpha. \quad (19)$$

Under the experimental conditions given by Eqs (4), gas permeates through a flat membrane at a constant density of diffusion flow. The measurement then takes place in a stationary non-equilibrium system. In the sorption method, the density of diffusion flow changes with time and in equilibrium takes its zero value. Gas or vapour penetrates inside the membrane from both sides with a low intensity. The experimental conditions correspond to the measurement in the non-stationary quasi-equilibrium system. If we denote by a the adsorbate amount of substance which diffused into the membrane in time t , and a_∞ corresponds to the equilibrium value of the adsorbate amount of substance at $t = \infty$, the calculation of diffusion coefficient is carried out in terms of the first Fick law for unidirectional diffusion

$$J = -D \, dc/dz \quad (20)$$

under the initial and boundary conditions

$$\begin{aligned} a &= 0 & t &= 0 & z &= 0 \\ a &= a_\infty & t &= \infty & z &= -l/2 \quad \text{and} \quad z = +l/2, \end{aligned} \quad (21)$$

which has in an approximate solution⁶ the form

$$\begin{aligned} a/a_\infty &= 2(Dt/l^2)^{0.5} \{ \pi^{-0.5} + 2 \sum_{n=0}^{\infty} (-1)^n [\exp(-nl^2/4Dt) - \\ &\quad - nl/2(Dt)^{0.5} \operatorname{erfc}(nl/2(Dt)^{0.5})] \}. \end{aligned} \quad (22)$$

For the time interval in which the diffusing adsorbate does not reach the membrane centre, it is possible to be content with the first term of Eq. (22) and to calculate the diffusion coefficient from the line slope of linear segment of the function

$$a/a_\infty = 2(D/\pi l^2)^{0.5} t^{0.5}. \quad (23)$$

Coefficient of permeability P is an important experimental quantity. It gives the amount of gases or vapours passed through the membrane unit area for a time unit at the unit pressure gradient. In the first Fick law (20), the gradient of concentration of a gas or vapour dc/dz in the membrane occurs. On integrating Eq. (20) for the initial and boundary conditions $c = c$ at $z = 0$ and $c = 0$ at $z = l$ in time $t \geq 0$, we find for the density of diffusion flow

$$J = Dc/l. \quad (24)$$

The usually used linear relation between the gas concentration in membrane c and the equilibrium pressure p (Henry sorption isotherm)

$$c = p/k_1 \quad (25)$$

is a limiting relation which is fulfilled only at low equilibrium pressures. By analyzing the experimental data on the sorption of water vapour on different polymers⁷, it was found that the sorption isotherms are of the third type with respect to the Brunauer classification⁸ and have the form

$$c = p/(k_1 - k_2 p) \quad (26)$$

or

$$1/c = k_1/p - k_2, \quad (27)$$

which enables to calculate constants k_1 and k_2 from the sorption or permeation data. Concentration c in Eqs (24)–(26) is the adsorbate concentration in equilibrium related to the membrane volume unit $c = a_\infty/V$ where a_∞ is the adsorbate amount of substance found on the membrane specimen suspended on the sorption balance and volume V is calculated from the geometrical properties of membrane as $V = Al$ where A is the area and l the membrane thickness. By combining Eqs (24) and (26) we get

$$J = Dp/(k_1 - k_2p)l \quad (28)$$

or also

$$J = DS p/l, \quad (29)$$

where

$$S = a_\infty/Vp = (k_1 - k_2p)^{-1} \quad (30)$$

is the sorption coefficient (often called solubility coefficient) and the product

$$P = DS \quad (31)$$

in Eq. (28) is the coefficient of permeability which is the measured quantity. Considering that in the permeation method the density of diffusion flow is proportional to the flow rate of gas mixture, voltage signal, and thickness of membrane, the relation was derived⁹ on the basis of Eq. (28) for calculating the coefficient of permeability P

$$P = K'vm_s l \quad (32)$$

and

$$P_i = K'vm_s l p_b/p_i, \quad (33)$$

where

$$K' = 273 \cdot 15k/(101 \ 325AT) \quad (34)$$

and k is the proportionality constant obtained by calibrating the apparatus, A is the membrane area, v the flow rate of gas mixture, m_s the voltage signal in steady state, l the membrane thickness, T the temperature of measurement, p_b the atmospheric pressure, and p_i the partial pressure of gases or vapours at temperature T . Constants k_1 and k_2 of sorption isotherm (26) can be determined conveniently by the permeation method if we determine diffusion coefficient D according to Eq.

(13) or (19) and the coefficient of permeability P according to Eq. (33) for at least two values of equilibrium pressure p . By rearranging Eq. (31) and on inserting for S from Eq. (30) we find that

$$D/P = k_1 - k_2 p. \quad (35)$$

When measuring the coefficient of permeability by the sorption method, it is necessary to respect the fact that the membrane dimensions change owing to the presence of sorbed molecules. This difficulty may be overcome by the convention to relate all the quantities used for the description of the system to the initial state of the system before sorption. When defining the model, we stem from the experimentally verified fact that the process takes place with low intensity, and therefore it is simple to maintain the chemical potential of the gas phase μ_g constant. Since in the experimental investigation with the sorption method only the adsorbate molecules are available which are bound to a membrane by the dispersion forces or by the electrostatic forces of the proton-donor type, it is suitable to lead the boundary area A between the membrane surface and the gas phase in the distance delimited by the action of these forces. With homogeneous membranes it is possible to assume the boundary curve to be identical with the geometrical area A . Further we presume that gas or vapour permeates through the membrane from one side and boundary area A is the place of the chemical potential jump given by the difference

$$X = \mu_g - \mu, \quad (36)$$

where μ is the chemical potential of adsorbate in the membrane. At a constant temperature, the amount of substance of gas or vapour which passes through the boundary area in time dt is given by

$$da = Ab(\mu_g - \mu) dt, \quad (37)$$

where b is the transfer coefficient. With regard to Eq. (36) we can also write

$$da/dt = AbX. \quad (38)$$

In the same time the chemical potential of adsorbate in the adsorbed layer increases by

$$d\mu = -dX. \quad (39)$$

To derive the time dependence of X we introduce

$$da = K d\mu, \quad (40)$$

where K represents the change of the adsorbate amount of substance related to the unit chemical potential. By combining Eqs (38) and (40) we obtain

$$dX/X = -(Ab/K) dt. \quad (41)$$

By integrating in limits from 0 to t and from X_0 to X we find

$$X = X_0 \exp(-t/C), \quad (42)$$

where X_0 is the difference of chemical potentials at the beginning of the process (at $t = 0$) and $C = K/Ab$ is the time constant. The condition of thermodynamic equilibrium $X = 0$ follows from Eq. (42) for $t = \infty$. The dependence of the adsorbate amount of substance a on time t is found by combining Eqs (38) and (42) and by integrating in the limits from 0 to t and from 0 to a :

$$a = AbX_0C[1 - \exp(-t/C)] \quad (43)$$

or

$$a = a_\infty[1 - \exp(-t/C)], \quad (44)$$

where

$$a_\infty = AbX_0C \quad (45)$$

denotes the adsorbate amount of substance in equilibrium. Eq. (44) can be rearranged into the form

$$\ln [a_\infty/(a_\infty - a)] = t/C \quad (46)$$

from which it is possible to find, by means of experimental data, time constant C which is important for calculating the density of molar flow of adsorbate through a membrane. This flow can be expressed as

$$J_m = A^{-1} da/dt. \quad (47)$$

It follows from Eq. (44)

$$J_m = (CA)^{-1} a_\infty \exp(-t/C) \quad (48)$$

and, on inserting back, also

$$J_m = (CA)^{-1} (a_\infty - a). \quad (49)$$

The comparison of the results of measurements found by the sorption and permeation methods can be carried out by passing from the non-stationary quasi-equilibrium sorption system to the stationary non-equilibrium permeation system by introducing

the mean density of molar flow $\langle J'_m \rangle$, which can be obtained by solving the integral

$$\langle J'_m \rangle = (a_\infty CA)^{-1} \int_0^{a_\infty} (a_\infty - a) da = a_\infty / 2CA. \quad (50)$$

In the sorption method, the specimen of the membrane is suspended on the sorption balance and gas or vapour penetrates into the membrane from both sides. Physically it is the same situation as if adsorbate permeates through the membrane of thickness l from one side with twofold intensity. Then the mean density of molar flow obtained from the sorption measurements can be expressed as

$$\langle J_m \rangle = \langle J'_m \rangle / 2 = a_\infty / 4CA, \quad (51)$$

where a_∞ is the adsorbate amount of substance in equilibrium which has been sorbed by the membrane specimen of area A suspended on the sorption balance. If we express Eq. (3) for the mean density of molar flow

$$\langle J_m \rangle = L_m \Delta\mu / l \quad (52)$$

and the difference of chemical potentials on both sides of the membrane is

$$\Delta\mu = V_m \Delta p, \quad (53)$$

where V_m is the molar volume of gas or vapour and Δp represents the pressure difference on both sides of membrane, on inserting into Eq. (52) we can write

$$\langle J_m \rangle = L_m V_m \Delta p / l \quad (54)$$

or also

$$\langle J_m \rangle = L_m V_m p / l \quad (55)$$

if the pressure on the second side of membrane is zero. On comparing with Eq. (51) we find, for the molar coefficient of permeability of adsorbate through a membrane, the relation

$$P = a_\infty l / 4CAp \quad (56)$$

if

$$P = L_m V_m, \quad (57)$$

where L_m is the coefficient of molar diffusion conductivity of membrane. The diffusion coefficient of adsorbate can be also calculated by means of the coefficient of permeability in Eq. (35) purely from the sorption data if they satisfy Eq. (26).

EXPERIMENTAL

To compare both the methods, the membranes were selected prepared from aliphatic polyester-urethane (PUR) - Impranal ELH (30% solution in the 1 : 1 : 1 mixture of ethylene glycol monoethyl ether, isopropyl alcohol, and toluene), (Bayer) and from the filler, Silica FK 160 (Degussa), of specific surface area $160 \text{ m}^2/\text{g}$, particle size $18 \mu\text{m}$, bulk density $60 \text{ g}/\text{dm}^3$, purity 99.5%, $\text{pH} \sim 5.5$. The membranes of thickness $156 \mu\text{m}$ and $200 \mu\text{m}$ containing 30 mass % Silica filler were prepared. Water vapour was used as an adsorbate.

RESULTS AND DISCUSSION

The kinetics of sorption was measured on both membranes at the temperature of 25°C for various relative pressures of water vapour. The specimens were evacuated before each measurement by using a diffusion pump at the experimental temperature. Two series of measurements were carried out by the permeation method at the temperature of 25°C and relative pressure $p_{\text{rel}} = 1.00$. In the first series of measurement, the specimen was not pretreated, for the second series of measurement the specimen was evacuated by the diffusion pump at experimental temperature. The transfer of water vapour through the system is mostly determined by the nature of filler but the transfer depends also on the amount of filler in the membrane, on the size and spacing of its particles in the membrane. Thus, it is the manifestation of the membrane as a composite system. The sorption processes on the composite materials take place through a complex mechanism, and therefore the transport parameters reported in this work are the effective values. The diffusion coefficients found out by the permeation method were calculated from Eq. (19) and the coefficients of permeability from Eq. (33). The diffusion coefficients found by the sorption method were calculated from the dependence of $a/a_\infty - t^{0.5}$ given by Eq. (23). This dependence for the membrane of thickness $l = 156 \mu\text{m}$ is illustrated in Fig. 1. For thicker membrane, the series of curves is similar. The succession of curves is determined by the dependence of diffusion coefficient on the sorbed amount which goes through a maximum as it is shown in Fig. 2. The occurrence of maximum can be explained on the basis of the superposition of interactions of polymer chains mutually, the adsorbate molecules with polymer chains, and the adsorbate molecules mutually. At low relative pressures when the sorption of water vapour is small, the value of diffusion coefficient grows to its maximum. In this region, the interactions of adsorbate with polymer chains prevail, the interactions between the polymer chains turn weak, the polymer structure turns "open", the molecule mobility grows. At higher relative pressures, the mutual interactions of the adsorbate molecules begin to prevail, hydrogen bonds immobilize the water molecules, and the values of diffusion coefficient decrease. The inflexion point on the sorption isotherm of water vapours on the membrane depicted in Fig. 3 corresponds to the maximum of values of diffusion coefficients. The initial part of the dependence $a/a_\infty - t^{0.5}$ is experimentally

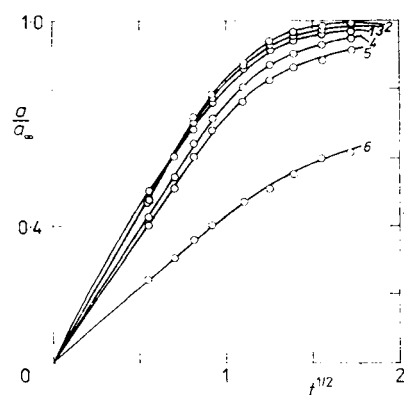


FIG. 1

Dependence $a/a_\infty - t^{0.5}$ in $(10^3 \text{ s})^{1/2}$ in the system PUR + 30 mass % Silica, $l = 156 \mu\text{m}$, temperature 25°C , p_{rel} : 1 0.20, 2 0.40, 3 0.60, 4 0.80, 5 0.90, 6 1.00

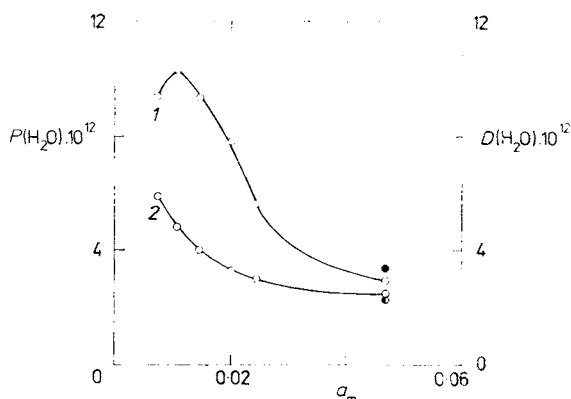


FIG. 2

Dependence of $D(\text{H}_2\text{O})$ ($\text{m}^2 \text{s}^{-1}$) and $P(\text{H}_2\text{O})$ ($\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$) on the sorbed amount a_∞ (gram adsorbate/gram adsorbent) in PUR + 30 mass % Silica, $l = 156 \mu\text{m}$, temperature 25°C ; 1 $D(\text{H}_2\text{O})$, 2 $P(\text{H}_2\text{O})$, ● $D(\text{H}_2\text{O})$ (Eq. (19)), ○ $P(\text{H}_2\text{O})$ (Eq. (33))

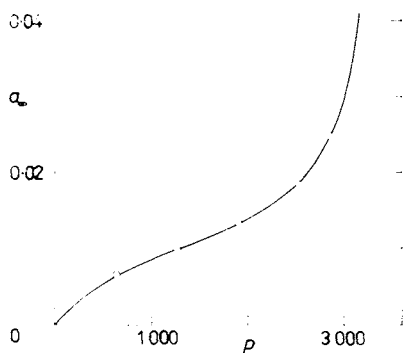


FIG. 3

Dependence of a_∞ (gram adsorbate/gram adsorbent) on pressure p (Pa) (sorption isotherm) for water vapour in PUR + 30 mass % Silica, $l = 156 \mu\text{m}$, temperature 25°C

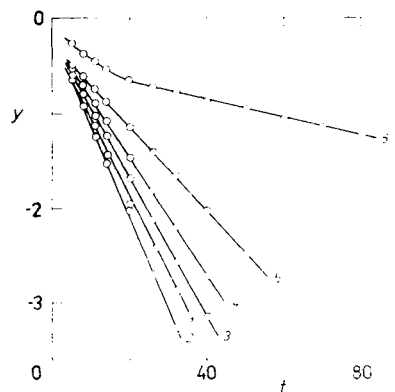


FIG. 4

Dependence $y = \ln [1 - (a/a_\infty)] \cdot t$ (min) in PUR + 30 mass % Silica, $l = 156 \mu\text{m}$, temperature 25°C , p_{rel} : 1 0.20, 2 0.40, 3 0.60, 4 0.80, 5 0.90, 6 1.00

accessible with difficulty because after admitting the adsorbate, the membrane specimen suspended on the balance is made to oscillate. To calculate the diffusion coefficient, the linear part of the curve was employed. For comparison, the diffusion coefficients were calculated from Eq. (31), too. The sorption coefficients were calculated from Eq. (30) and the coefficients of permeability by the sorption method from Eq. (56). The results obtained are given in Tables I and II. The equilibrium values of sorption a_{∞} in Eq. (56) plotted against equilibrium pressure p yield the sorption isotherm whose form can be seen in Fig. 3. Time constant C is found by

TABLE I

Transport parameters of water vapour in the membrane PUR + 30 mass % Silica of thickness $l = 156 \mu\text{m}$; D ($10^{-12} \text{ m}^2 \text{ s}^{-1}$) diffusion coefficient, P ($10^{-12} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) coefficient of permeability, S ($\text{mol m}^{-3} \text{ Pa}^{-1}$) sorption coefficient

P_{rel}	D			P		S
	Eq. (23)	Eq. (31)	Eq. (19)	Eq. (56)	Eq. (33)	Eq. (30)
0.20	9.330	8.900		5.880		0.661
0.40	10.300	9.820		4.780		0.487
0.60	9.330	8.980		4.040		0.450
0.80	7.820	7.130		3.260		0.457
0.90	5.620	6.090		3.010		0.494
1.00	2.910	3.380	2.480	2.480	2.240	0.852

TABLE II

Transport parameters of water vapour in the membrane PUR + 30 mass % Silica of thickness $l = 202 \mu\text{m}$; D ($10^{-12} \text{ m}^2 \text{ s}^{-1}$) diffusion coefficient, P ($10^{-12} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) coefficient of permeability, S ($\text{mol m}^{-3} \text{ Pa}^{-1}$) sorption coefficient

P_{rel}	D			P		S
	Eq. (23)	Eq. (31)	Eq. (19)	Eq. (56)	Eq. (33)	Eq. (30)
0.20	9.300	7.280		4.410		0.606
0.40	10.100	8.580		3.860		0.450
0.60	11.800	8.970		3.650		0.407
0.80	10.140	8.260		3.470		0.420
0.90	8.210	6.270		3.260		0.520
1.00	3.820	3.610	3.780	2.730	2.125	0.756

treating the kinetic measurements according to Eq. (46). The dependence of $\ln [1 - (a/a_\infty)] - t$ for the membrane of thickness $156 \mu\text{m}$ at various relative pressures is demonstrated in Fig. 4. For the membrane of thickness $202 \mu\text{m}$, a similar diagram is obtained. The large distance between the straight lines measured at relative pressures 0.9 and 1.0 is caused by the intense increase of sorption in the final part of isotherm.

The diffusion coefficient of the specimen of the membrane thickness $l = 156 \mu\text{m}$ obtained by the permeation method according to Eq. (19) is $D = 5.12 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$, for the evacuated specimen $D = 3.38 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. These values correspond to the results found by the sorption method according to Eq. (23) for the relative pressure of water vapour $p_{\text{rel}} = 1.0$, where $D = 2.91 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The diffusion coefficient of the specimen of the membrane thickness $l = 202 \mu\text{m}$ obtained by the permeation method according to Eq. (19) is $D = 4.72 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$, for the evacuated specimen $D = 3.78 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The last value is in excellent agreement with the result found out by the sorption method according to Eq. (23) for the relative pressure of water vapour $p_{\text{rel}} = 1.0$, where $D = 3.82 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

The coefficient of permeability of the specimen of the membrane thickness $l = 156 \mu\text{m}$ obtained by the permeation method according to Eq. (33) is $P = 1.91 \cdot 10^{-12} \text{ p.u.}^*$, for the evacuated specimen $P = 2.24 \cdot 10^{-12} \text{ p.u.}$ These values agree well with the results found out by the sorption method according to Eq. (56) for the relative pressure of water vapour $p_{\text{rel}} = 1.0$, where $P = 2.48 \cdot 10^{-12} \text{ p.u.}$ The coefficient of permeability of the specimen of the membrane thickness $l = 202 \mu\text{m}$ obtained by the permeation method according to Eq. (33) is $P = 1.78 \cdot 10^{-12} \text{ p.u.}$, for the evacuated specimen $P = 2.12 \cdot 10^{-12} \text{ p.u.}$ These values correspond to the results found out by the sorption method according to Eq. (56) for the relative pressure of water vapour $p_{\text{rel}} = 1.0$, where $P = 2.73 \cdot 10^{-12} \text{ p.u.}$ The decrease of coefficient of permeability P with increasing sorbed amount in Fig. 2 can be explained by the immobilization of water molecules penetrating through the membrane owing to hydrogen bonds.

On comparing the results of transport properties of water vapour through the flat membrane, obtained by the permeation and sorption methods, it is possible to state good agreement. Although different theoretical and experimental approaches are concerned, both yield practically well utilizable transport parameters.

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* p.u. \equiv permeability unit $\equiv \text{mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$.

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