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Application of Nonlinear Frequency Response to Investigation of Membrane Transport

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Abstract: The concept of higher order frequency response functions, used for investigation of weekly nonlinear systems by frequency response techniques, is applied to investigation of membrane systems. Isothermal permeation of single gases through non-porous and porous membranes is analysed for three transport mechanisms: solution-diffusion, pore-surface diffusion, and viscous-flow. In the course of definition of the transmembrane transport in dynamic conditions, a new concept of generalized membrane permeability, defined as an indefinite sequence of the permeabilities of the first, second, third, . . . order, dependent on the equilibrium and transport parameters of the membrane in steady-state, is introduced. A simple two-reservoir system, with variation of the volume of one reservoir, is defined and its first and second order frequency response functions are derived. It is shown that these functions can be used for identification of the transport mechanism, i.e., of the corresponding model and for estimation of the model parameters: permeabilities of different orders, as well as the separate values of the relevant equilibrium and transport parameters.

Keywords: Membrane transport, nonlinear frequency response, higher order frequency response functions, generalized membrane permeability, solution-diffusion model, pore-surface diffusion model, viscous-flow model, parameter estimation

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INTRODUCTION

Nonlinear frequency response (FR) is a response of a nonlinear system to a sinusoidal or a cosinusoidal input perturbation. It has been proven to be a very useful tool for practical investigation of weekly nonlinear systems (1). A convenient approach used for treatment of frequency response of weakly nonlinear systems is the concept of higher order frequency response functions (FRFs), which is based on Volterra series and generalized Fourier transform (1). For some time, this concept has been used for analysis of weakly nonlinear electrical and mechanical systems, as well as in control engineering (1). In our work, we have been using it for investigation of adsorption kinetics and equilibria (2–7). The most important results of this investigation are that it is possible to reliably discriminate between different kinetic mechanisms using higher order FRFs (5, 7), and that both kinetic and equilibrium parameters, including the ones defining the system nonlinearity, can be estimated from the same set of experimental data (3, 4). The investigation presented in this paper is the first attempt to apply the nonlinear frequency response method to investigation of membrane systems.

More details about nonlinear FR and the concept of higher order FRFs can be found in our previous publications (2, 3). Below we give only some basics:

Contrary to the linear FR, which consists only of the basic (first) harmonic, the nonlinear FR also contains a nonperiodic (DC) component and an indefinite number of higher harmonics (Fig. 1, Equation (1)).

$$\begin{aligned} y &= y_s + y_{DC} + y_I + y_{II} + y_{III} + \cdots \\ &= y_s + y_{DC} + B_I \cos(\omega t + \varphi_I) \\ &\quad + B_{II} \cos(2\omega t + \varphi_{II}) + B_{III} \cos(3\omega t + \varphi_{III}) + \cdots \end{aligned} \tag{1}$$

The concept of higher order FRFs assumes replacement of the nonlinear model **G** with an indefinite sequence of linear functions (FRFs) of the first, second, third, etc. order (G_1, G_2, G_3, etc.) (1). This sequence is often called the generalized transfer function (8). The output of a weakly nonlinear system can be represented in a Volterra series form (1). For a single harmonic input, the Volterra series becomes:

$$\begin{aligned} y &= y_s + \frac{A}{2}\{G_1(\omega)e^{j\omega t} + G_1(-\omega)e^{-j\omega t}\} \\ &\quad + \left(\frac{A}{2}\right)^2 \{G_2(\omega, \omega)e^{2j\omega t} + G_2(-\omega, -\omega)e^{-2j\omega t} + 2G_2(\omega, -\omega)e^0\} \\ &\quad + \left(\frac{A}{2}\right)^3 \{G_3(\omega, \omega, \omega)e^{3j\omega t} + G_3(-\omega, -\omega, -\omega)e^{-3j\omega t} \\ &\quad + 3G_3(\omega, \omega, -\omega)e^{j\omega t} + 3G_3(-\omega, -\omega, \omega)e^{-j\omega t}\} + \cdots \end{aligned} \tag{2}$$

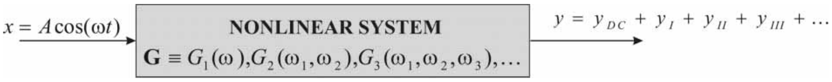

Figure 1. Frequency response of a nonlinear system.

By collecting the constant terms in Equation (2), we obtain the DC component:

$$y_{DC} = 2(A/2)^2 G_2(\omega, -\omega) + 6(A/2)^4 G_4(\omega, \omega, -\omega, -\omega) + \cdots \qquad (3),$$

by collecting the periodic terms of frequency ω, the first harmonic:

$$\begin{aligned} y_I &= B_I \cos(\omega t + \varphi_I) \\ &= \{(A/2)G_1(\omega) + 3(A/2)^3 G_3(\omega, \omega, -\omega) + \cdots\}e^{j\omega t} \\ &\quad + \{(A/2)G_1(-\omega) + 3(A/2)^3 G_3(\omega, -\omega, -\omega) + \cdots\}e^{-j\omega t} \qquad (4), \end{aligned}$$

by collecting the periodic terms of frequency 2ω, the second harmonic:

$$\begin{aligned} y_{II} &= B_{II} \cos(2\omega t + \varphi_{II}) \\ &= \{(A/2)^2 G_2(\omega, \omega) + 4(A/2)^4 G_4(\omega, \omega, \omega, -\omega) + \cdots\}e^{2j\omega t} \\ &\quad + \{(A/2)^2 G_2(-\omega, -\omega) + 4(A/2)^4 G_4(\omega, -\omega, -\omega, -\omega) + \cdots\}e^{-2j\omega t} \\ &\qquad (5), \end{aligned}$$

by collecting the periodic terms of frequency 3ω, the third harmonic:

$$\begin{aligned} y_{III} &= B_{III} \cos(3\omega t + \varphi_{III}) \\ &= \{(A/2)^3 G_3(\omega, \omega, \omega) + 5(A/2)^5 G_5(\omega, \omega, \omega, \omega, -\omega) + \cdots\}e^{3j\omega t} \\ &\quad + \{(A/2)^3 G_3(-\omega, -\omega, -\omega) \\ &\quad + 5(A/2)^5 G_5(\omega, \omega, -\omega, -\omega, -\omega) + \cdots\}e^{-3j\omega t} \qquad (6), \end{aligned}$$

etc.

The first order function $G_1(\omega)$ corresponds to the dominant term of the first harmonic, the second order function $G_2(\omega,\omega)$ to the dominant term of the second harmonic, the second order function $G_2(\omega,-\omega)$ to the dominant term of the DC component, the third order function $G_3(\omega,\omega,\omega)$ to the dominant term of the third harmonic, etc. There are established procedures for estimation of the FRFs from harmonic data (9).

This paper is an attempt to apply the concept of higher order FRFs to investigation of membrane transport. For the time being we restrict our analysis to investigation of isothermal permeation of pure gases through membranes, for three different transport mechanisms: sorption-diffusion through dense membranes, pore-surface diffusion through adsorbing porous membranes, and viscous flow through nonadsorbing porous membranes.

DEFINITION OF TRANSPORT MECHANISMS IN DYNAMIC CONDITIONS

Frequency response is defined as a response to periodic input change around a predefined steady-state. For that reason, we will start our investigation with analysis of the nonlinear dynamics for the simplest case of dynamic trans-membrane transport, presented in Fig. 2: in steady state the whole system is in equilibrium (the pressures at both sides of the membrane are equal to p_s, the concentration in the membrane is uniform and equal to the equilibrium concentration $Q_s = \Phi(p_s)$, and the flux through the membrane J_s is zero). In Fig. 2, Δp_1, Δp_2, ΔQ and ΔJ represent deviations of the pressures p_1 and p_2, concentration in the membrane Q and flux through the membrane J, from their steady-state values.

When a perturbation to this system is introduced ($\Delta p_1 \neq 0$ and/or $\Delta p_2 \neq 0$) the flux and the concentration in the membrane become nonlinear functions of time and the position x in the membrane. The nature of this nonlinearity depends on the transport mechanism. We will consider the mean value of the flux within the membrane, as a representative of the net transport:

$$\langle J \rangle = \frac{1}{L}\int_0^L J(x)dx \tag{7}$$

We will derive expressions that correlate the mean flux to the perturbations Δp_1 and Δp_2, for three different transport mechanisms: solution-diffusion, pore-surface diffusion and viscous flow.

Solution-Diffusion Mechanism (10)

This mechanism of membrane transport is characteristic for defect-free dense membranes. The gas molecules are sorbed (dissolved) in the membrane

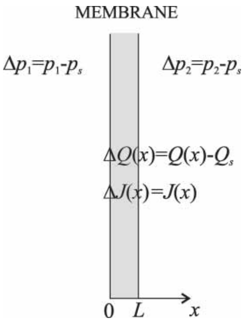

Figure 2. Schematic representation of membrane transport in dynamic conditions.

material and the sorbed molecules are transported through the membrane by Fickian diffusion. For the case of zero steady-state flux under consideration ($J_s = 0$), the flux at position x is:

$$J(x) = \Delta J(x) = -D_m \frac{dQ}{dx} = -D_m \frac{d\Delta Q}{dx} \tag{8}$$

where D_m is the diffusion coefficient through the membrane material. If diffusion through the membrane is the only resistance to mass transfer, the concentrations of the sorbed gas in the membrane at both membrane boundaries are in local equilibrium with the gas phases. This equilibrium relation is generally nonlinear. For our analysis it is convenient to represent it in the Taylor series form:

$$x = 0 : Q(0) = \Phi(p_1) = Q_s + a\Delta p_1 + b\Delta p_1^2 + c\Delta p_1^3 + \cdots \tag{9}$$

$$x = L : Q(L) = \Phi(p_2) = Q_s + a\Delta p_2 + b\Delta p_2^2 + c\Delta p_2^3 + \cdots \tag{10}$$

where a, b, c, … are the coefficients of the Taylor series, which are proportional to the first, second, third, … order derivatives of the equilibrium relation (adsorption isotherm) Φ, corresponding to p_s:

$$a = \left.\frac{d\Phi}{dp}\right|_s, \quad b = \frac{1}{2}\left.\frac{d^2\Phi}{dp^2}\right|_s, \quad c = \frac{1}{6}\left.\frac{d^3\Phi}{dp^3}\right|_s, \ldots \tag{11}$$

The diffusion coefficient D_m is generally concentration dependent, and this dependence is generally nonlinear. It will also be represented in the Taylor series form:

$$D_m = D_{m,s} + D_m^{(1)}\Delta Q + D_m^{(2)}\Delta Q^2 + D_m^{(3)}\Delta Q^3 + \cdots \tag{12}$$

where $D_{m,s}$ is the steady-state value of the diffusion coefficient (corresponding to Q_s) and:

$$D_m^{(1)} = \left.\frac{dD_m}{dQ}\right|_s, \quad D_m^{(2)} = \frac{1}{2}\left.\frac{d^2 D_m}{dQ^2}\right|_s, \quad D_m^{(3)} = \frac{1}{6}\left.\frac{d^3 D_m}{dQ^3}\right|_s, \ldots \tag{13}$$

Taking into account Equation (12), Equation (8) can be rewritten in the following form:

$$\begin{aligned} J(x) &= -(D_{m,s} + D_m^{(1)}\Delta Q + D_m^{(2)}\Delta Q^2 + \cdots)\frac{d\Delta Q}{dx} \\ &= -D_{m,s}\frac{d\Delta Q}{dx} - \frac{D_m^{(1)}}{2}\frac{d\Delta Q^2}{dx} - \frac{D_m^{(2)}}{3}\frac{d\Delta Q^3}{dx} + \cdots \end{aligned} \tag{14}$$

Using Equation (7), the mean flux in the membrane will be:

$$\begin{aligned}\langle J\rangle &= -D_{m,s}\frac{1}{L}\int_0^L d\Delta Q(x) - \frac{D_m^{(1)}}{2}\frac{1}{L}\int_0^L d\Delta Q^2(x)\\ &\quad - \frac{D_m^{(2)}}{3}\frac{1}{L}\int_0^L d\Delta Q^3(x) - \cdots\\ &= -\frac{D_{m,s}}{L}(\Delta Q(L)-\Delta Q(0))\\ &\quad - \frac{D_m^{(1)}}{2L}(\Delta Q^2(L)-\Delta Q^2(0)) - \frac{D_m^{(2)}}{3L}(\Delta Q^3(L)-\Delta Q^3(0)) - \cdots \end{aligned} \tag{15}$$

By applying the boundary conditions (9) and (10), the final expression for the mean flux in the membrane, corresponding to the solution-diffusion mechanisms, is obtained:

$$\begin{aligned}\langle J\rangle &= D_{m,s}a\frac{\Delta p_1-\Delta p_2}{L} + \left(D_{m,s}b + \frac{D_m^{(1)}a^2}{2}\right)\frac{\Delta p_1^2-\Delta p_2^2}{L}\\ &\quad + \left(D_{m,s}c + D_m^{(1)}ab + \frac{D_m^{(3)}a^3}{3}\right)\frac{\Delta p_1^3-\Delta p_2^3}{L} + \cdots\end{aligned} \tag{16}$$

If the diffusion coefficient can be regarded as constant in the investigated range of concentrations, this expression reduces to:

$$\langle J\rangle = D_m a\frac{\Delta p_1-\Delta p_2}{L} + D_m b\frac{\Delta p_1^2-\Delta p_2^2}{L} + D_m c\frac{\Delta p_1^3-\Delta p_2^3}{L} + \cdots \tag{17}$$

and for the case of constant diffusion coefficient and linear adsorption isotherm, to the classical equation used for steady-state permeation through dense membranes (10):

$$\langle J(x)\rangle = D_m a\frac{\Delta p_1-\Delta p_2}{L} = D_m\frac{dQ}{dp}\frac{\Delta p_1-\Delta p_2}{L} \tag{18}$$

Pore-Surface Diffusion Mechanism (11)

This mechanism takes place when a sorbing gas permeates through a defect-free porous membrane. The total concentration in such a membrane can be obtained as a weighted sum of the concentrations in the gas phase present in the pores and in the solid (adsorbed) phase:

$$Q(x) = \varepsilon C_i(x) + (1-\varepsilon)Q_i(x) = \frac{\varepsilon}{R_gT}p_i(x) + (1-\varepsilon)Q_i(x) \tag{19}$$

where ε is the membrane porosity, C_i the concentrations in the membrane pores, p_i the corresponding pressure, Q_i the concentration in the solid phase and R_g and T are the universal gas constant and the absolute temperature. Local equilibrium at any position within the pores is usually assumed, and the equilibrium relation is generally nonlinear. Again, we will represent it in the Taylor series form:

$$Q_i = \Phi(p_i) = Q_{i,s} + \Delta Q_i = Q_{i,s} + a\Delta p_i + bp_i^2 + c\Delta p_i^3 + \cdots \tag{20}$$

ΔQ_i and Δp_i are the deviations of the corresponding variables from their steady-state values, and a, b and c are defined in analogous way as in Equation (11).

Generally, the membrane transport takes place by two parallel mechanisms: by molecular diffusion of the gas molecules in the membrane pores, and by surface diffusion of the adsorbed molecules. For the case under consideration of zero steady-state flux ($J_s = 0$), the flux through the membrane is:

$$\begin{aligned} J(x) &= -\varepsilon D_p \frac{\partial C_i}{\partial x} - (1-\varepsilon) D_s \frac{\partial Q_i}{\partial x} \\ &= -\frac{\varepsilon D_p}{R_g T} \frac{\partial \Delta p_i}{\partial x} - (1-\varepsilon) D_s \frac{\partial \Delta Q_i}{\partial x} \end{aligned} \tag{21}$$

D_p and D_s are the pore and surface diffusion coefficients, respectively. Usually, concentration dependence of the surface diffusion coefficient D_s is significant and has to be taken into account. Being generally nonlinear, this concentration dependence will again be represented in a Taylor series form:

$$D_s = D_{s,s} + D_s^{(1)} \Delta Q_i + D_s^{(2)} \Delta Q_i^2 + D_s^{(3)} \Delta Q_i^3 + \cdots \tag{22}$$

where $D_{s,s}$ is the surface diffusion coefficient corresponding to the steady-state concentration $Q_{i,s}$ and $D_s^{(1)}$, $D_s^{(2)}$, $D_s^{(3)}$,... are defined in an analogous way as $D_m^{(1)}$, $D_m^{(2)}$, $D_m^{(3)}$,... in Equation (13).

The boundary conditions at both sides of the membrane are:

$$x = 0 : p_i(0) = p_1 \Longrightarrow \Delta p_i(0) = \Delta p_1 \tag{23}$$

$$x = L : p_i(L) = p_2 \Longrightarrow \Delta p_i(L) = \Delta p_2 \tag{24}$$

Taking into account Equations (20) and (22), Equation (21) can be written in the following form:

$$\begin{aligned} J(x) = &-\frac{\varepsilon D_p}{R_g T} \frac{\partial \Delta p_i}{\partial x} - (1-\varepsilon)\{D_{s,s} + D_s^{(1)}(a\Delta p_i + b\Delta p_i^2 + \cdots) \\ &+ D_s^{(2)}(a\Delta p_i + b\Delta p_i^2 + \cdots)^2 + \cdots\} \\ &\times \left\{ a\frac{\partial \Delta p_i}{\partial x} + b\frac{\partial \Delta p_i^2}{\partial x} + c\frac{\partial \Delta p_i^3}{\partial x} + \cdots \right\} \end{aligned} \tag{25}$$

After rearranging Equation (25) and applying Equation (7), the mean flux in the membrane is:

$$
\begin{aligned}
\langle J\rangle = & -\left(\frac{\varepsilon D_p}{R_gT}+(1-\varepsilon)D_{s,s}a\right)\frac{1}{L}\int_0^L d\Delta p_i(x)\\
& -(1-\varepsilon)\left(D_{s,s}b+\frac{D_s^{(1)}a^2}{2}\right)\frac{1}{L}\int_0^L d(\Delta p_i(x))^2\\
& -(1-\varepsilon)\left(D_{s,s}c+D_s^{(1)}ab+\frac{D_s^{(2)}a^3}{2}\right)\frac{1}{L}\int_0^L d(\Delta p_i(x))^3-\cdots
\end{aligned}
\tag{26}
$$

and by applying the boundary conditions (23) and (24) the final expression is obtained:

$$
\begin{aligned}
\langle J\rangle = & -D_{eff}a_{eff}\frac{\Delta p_1-\Delta p_2}{L}-(1-\varepsilon)\left(D_{s,s}b+\frac{D_s^{(1)}a^2}{2}\right)\frac{\Delta p_1^2-\Delta p_2^2}{L}\\
& -(1-\varepsilon)\left(D_{s,s}c+D_s^{(1)}ab+\frac{D_s^{(2)}a^3}{2}\right)\frac{\Delta p_1^3-\Delta p_2^3}{L}-\cdots
\end{aligned}
\tag{27}
$$

In this expression we introduce the commonly used definitions of effective or apparent diffusivity (12):

$$
D_{eff}=\frac{\varepsilon D_p+(1-\varepsilon)D_{s,s}aR_gT}{\varepsilon+(1-\varepsilon)aR_gT}
\tag{28}
$$

and slope of the adsorption isotherm

$$
a_{eff}=\frac{\varepsilon}{R_gT}+(1-\varepsilon)a=\left.\frac{dQ}{dp}\right|_s
\tag{29}
$$

If the surface diffusion coefficient can be regarded as constant in the concentration range of interest, Equation (27) reduces to:

$$
\begin{aligned}
\langle J\rangle = & D_{eff}a_{eff}\frac{\Delta p_1-\Delta p_2}{L}+(1-\varepsilon)D_sb\frac{\Delta p_1^2-\Delta p_2^2}{L}\\
& +(1-\varepsilon)D_sc\frac{\Delta p_1^3-\Delta p_2^3}{L}+\cdots
\end{aligned}
\tag{30}
$$

and for the case of constant diffusion coefficients and linear adsorption isotherm, it reduces to the classical form valid for steady-state permeation through sorbing porous membranes:

$$\langle J\rangle = J(x) = D_{eff}a_{eff}\frac{\Delta p_1 - \Delta p_2}{L}$$
$$= \left(\frac{\varepsilon D_p}{R_g T} + (1-\varepsilon)D_s\frac{dQ_i}{dp_i}\bigg|_s\right)\frac{\Delta p_1 - \Delta p_2}{L} \tag{31}$$

Viscous-Flow Transport Mechanism (11)

This pressure driven transport mechanism takes place in porous non-sorbing membranes with relatively large pores. The flux through the membrane for this case can be defined as:

$$J(x) = -\varepsilon\frac{B_0}{\mu R_g T}p_i\frac{dp_i}{dx} = -\varepsilon\frac{B_0}{\mu R_g T}(p_s + \Delta p_i)\frac{d\Delta p_i}{dx} \tag{32}$$

where p_i is the pressure in the membrane pores, ε the membrane porosity, μ viscosity and B_0 the so-called viscous flow parameter. The boundary conditions at both sides of the membrane are:

$$x = 0 : p_i(0) = p_1 \Longrightarrow \Delta p_i(0) = \Delta p_1 \tag{33}$$

$$x = L : p_i(L) = p_2 \Longrightarrow \Delta p_i(L) = \Delta p_2 \tag{34}$$

and the mean flux in the membrane is:

$$< J > = -\frac{\varepsilon B_0 p_s}{\mu R_g T}\frac{1}{L}\int_0^L d\Delta p_i(x) - \frac{\varepsilon B_0}{\mu R_g T}\frac{1}{2L}\int_0^L d(\Delta p_i(x))^2$$
$$= \frac{\varepsilon B_0 p_s}{\mu R_g T}\frac{\Delta p_1 - \Delta p_2}{L} + \frac{\varepsilon B_0}{2\mu R_g T}\frac{\Delta p_1^2 - \Delta p_2^2}{L} \tag{35}$$

Generalized Concept of Membrane Permeability

The derived expressions for the mean flux in the membrane in dynamic conditions, for all three cases under consideration (Equations (16), (27) and (35)) can be represented in the same general form:

$$\langle J(x)\rangle = P_I\frac{\Delta p_1 - \Delta p_2}{L} + P_{II}\frac{\Delta p_1^2 - \Delta p_2^2}{L} + P_{III}\frac{\Delta p_1^3 - \Delta p_2^3}{L} + \cdots \tag{36}$$

i.e. as an infinite series of terms of different orders: the first one proportional to the difference of the pressure deviations (linear driving force term), the second one to the difference of the squares of the pressure deviations (quadratic driving force term), the third one to the difference of the cubes of the pressure deviations (cubic driving force term), etc., with constant coefficients P_I, P_{II}, P_{III}, etc, which depend on the steady-state conditions. The first term in Equation (36) corresponds to the conventional definition of steady-state trans-membrane transport, where P_I corresponds to permeability (10). Accordingly, we will call P_I permeability of the first order, and in analogy with that, P_{II}, P_{III}, etc, will be called the permeabilities of the second, third etc., order. In this way, we define a generalized dynamic permeability, which is generally represented by an infinite sequence of constant values P_I, P_{II}, P_{III}, etc, dependent on the steady state around which the system is perturbed. The definitions of the first three members of these sequences for the three mechanisms analysed in this work are summarized in Table 1. It should be noticed that for the solution-diffusion and for the pore-surface diffusion mechanism the generalized permeabilities are indefinite sequences, while for the viscous-flow mechanism it reduces only to two terms (P_I and P_{II}), while all the permeabilities of the third and higher orders are 0.

A TWO-RESERVOIR SYSTEM FOR INVESTIGATION OF NONLINEAR FREQUENCY RESPONSE OF MEMBRANE SYSTEMS

Different designs could be used for investigation of membrane systems by nonlinear FR. We propose a two-reservoir system, presented in Fig. 3, which is similar to the two-resonator system analyzed by Sun and Do (13).

The system is composed of two batch reservoirs filled with the same pure gas, and divided by the investigated membrane. At steady state, the pressures in both reservoirs are equal (p_s) and the concentration in the membrane is uniform and in equilibrium with p_s (Q_s). The volume of the second reservoir V_2 is constant, while the volume of the first reservoir V_1 can be varied using a bellow, causing variations of the pressures p_1 and p_2, as well as of the concentration in the membrane Q. During the FR experiments, V_1

Table 1. Permeabilities of the first, second and third order, for three transport mechanisms

Mechanism	P_I	P_{II}	P_{III}
Solution-diffusion	$D_{m,s}\,a$	$D_{m,s}b + \frac{D_m^{(1)}a^2}{2}$	$D_{m,s}c + D_m^{(1)}ab + \frac{D_m^{(2)}a^3}{3}$
Pore-surface diffusion	$D_{eff}\,a_{eff}$	$(1-\varepsilon)\left(D_{s,s}b + \frac{D_s^{(1)}a^2}{2}\right)$	$(1-\varepsilon)\left(\frac{D_{s,s}c + D_s^{(1)}ab + D_s^{(2)}a^3}{3}\right)$
Viscous-flow	$\frac{\varepsilon B_0 p_s}{\mu R_g T}$	$\frac{\varepsilon B_0}{2\mu R_g T}$	0

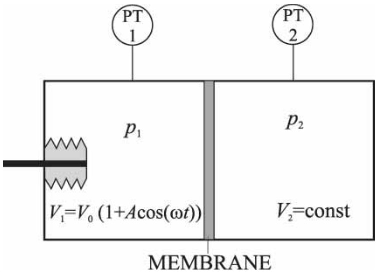

Figure 3. A schematic representation of the proposed two-reservoir experimental system.

is varied in a cosinusoidal way. When a periodic quasi-steady state is reached, the pressures p_1 and p_2, the concentration in the membrane Q and the flux through the membrane J, become complex periodic functions of the input frequency, of the form shown in Fig. 1 and Equations (2–6).

Definition of the Generalized Transfer Functions (Sets of FRFs)

Each of the system outputs can be related to the periodic change of the volume V_1 via its generalized transfer function (set of FRFs). The pressures p_1 and p_2, which can be measured continuously, can be used for estimation of the corresponding sets of FRFs. We will denote the FRFs relating p_1 to V_1 as $F_1(\omega)$, $F_2(\omega_1,\omega_2)$, $F_3(\omega_1,\omega_2,\omega_3),\ldots,$ and the FRFs relating p_2 to V_1 as $G_1(\omega)$, $G_2(\omega_1,\omega_2)$, $G_3(\omega_1,\omega_2,\omega_3),\ldots,$ Both sets of FRFs contain information about the permeation mechanism and the corresponding parameters. Nevertheless, another set of FRFs would be of greater interest, as it defines the membrane transport more directly: the set relating the change of p_2 to the change of p_1. We will denote this set of FRFs as $Z_1(\omega)$, $Z_2(\omega_1,\omega_2)$, $Z_3(\omega_1,\omega_2,\omega_3),\ldots.$

The F- and G-functions could be estimated from experimentally measured quasi-stationary responses of p_1 and p_2 to a cosinusoidal change of V_1. On the other hand, the Z-functions, which correspond to the response of p_2 to a cosinusoidal change of p_1, can be calculated from the G- and F-functions. The G-functions actually correspond to a series connection of two nonlinear elements defined by the F- and the Z-functions (the block diagram illustrating the relations among the F-, G- and Z-functions is given in Fig. 4). For example, for the first and second order FRFs, the series rules can be written in the following way (1):

$$G_1(\omega) = Z_1(\omega)F_1(\omega) \tag{37}$$

$$G_2(\omega_1,\omega_2) = Z_1(\omega_1+\omega_2)F_2(\omega_1,\omega_2) + Z_2(\omega_1,\omega_2)F_1(\omega_1)F_1(\omega_2) \tag{38}$$

The Z-functions can be calculated from these equations. For the case of our interest, when the input (V_1) is a single harmonic function, the frequencies

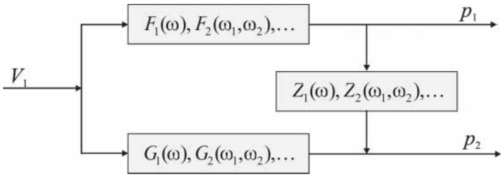

Figure 4. Block diagram defining the FRFs for the system shown in Figure 3.

ω_1 and ω_2 can be either ω or $-\omega$. The *Z*-function for that case can be calculated using the following recurrent formulae:

$$Z_1(\omega) = \frac{G_1(\omega)}{F_1(\omega)} \tag{39}$$

$$Z_2(\omega, \omega) = \frac{G_2(\omega, \omega) - Z_1(2\omega)F_2(\omega, \omega)}{F_1^2(\omega)} \tag{40}$$

$$Z_2(\omega, -\omega) = \frac{G_2(\omega, -\omega) - Z_1(0)F_2(\omega, -\omega)}{F_1(\omega)F_1(-\omega)} \tag{41}$$

Similar formulae can be derived for the third and higher order Z-functions.

In the next section we will derive the *Z*-functions for the three mechanisms of membrane transport analysed in the second section of this manuscript: solution-diffusion, pore-surface diffusion and viscous flow.

THE *Z*-FUNCTIONS

We will limit our efforts to derivation and analysis of only the first and second order FRFs. The reason for that is that the complexity of the algebra involved, as well as of the derived expressions, increases considerably with the increase of the FRF order. On the other hand, the main idea about the applicability of the higher order FRFs can be clearly seen even from the analysis of the first two functions. Nevertheless, the procedure for derivation of higher order functions is straightforward and can be continued using the same methodology, when needed for practical applications.

Mathematical Models

In order to derive the FRFs, it is necessary to postulate the nonlinear mathematical model of the system presented in Fig. 3. The following material balances have to be defined:

- Material balance for the membrane:

$$\frac{\partial Q}{\partial t} = -\frac{\partial J}{\partial x} \tag{42}$$

– Material balance for reservoir 1:

$$\frac{d(V_1C_1)}{dt} = -SJ|_{x=0} \tag{43}$$

– Material balance for reservoir 2:

$$V_2\frac{dC_2}{dt} = SJ|_{x=L} \tag{44}$$

In these equations, S is the membrane surface area, V_1 the variable volume of reservoir 1 and V_2 the constant volume of reservoir 2. C_1 and C_2 are the concentrations in reservoirs 1 and 2, respectively (for isothermal systems, proportional to the pressures p_1 and p_2). All other variables have been defined previously.

The expression for the flux in Equations (42–44), as well as and the boundary conditions for Equation (42), depend on the mechanism of membrane transport. For the three mechanisms under consideration, they can be found in the second section of this manuscript.

One way to derive the Z-functions would be to derive the F- and G-functions first, solving the model equations for a cosinusoidal change of V_1, and than use Equations (39–41). Nevertheless, there is another, shorter way to derive the Z-functions, solving the model equations for cosinusoidal change of the pressure p_1. In that case, the model reduces only to the material balances for the membrane and reservoir 2 (Equations (42) and (44)), with the appropriate boundary conditions. These model equations, for the three mechanisms under consideration, are listed in Table 2. All concentrations in these equations are defined as nondimensional deviations from their steady-state values, as this form is more convenient for analysis in the frequency domain. The definitions of the nondimensional concentrations are listed in Table 3, together with the definitions of some parameters in the model equations.

First and Second Order Z-Functions

The starting point in derivation of the Z-functions is the fact that they correlate the change of the pressure (concentration) in the second reservoir (output) to the change of the pressure (concentration) in the first reservoir (input). If the input change is a single harmonic function:

$$c_1(t) = A\cos(\omega t) = \frac{A}{2}(e^{j\omega t} + e^{-j\omega t}) \tag{58}$$

according to Equations (3–6) the output function will be:

$$c_2(t) = \frac{A}{2}(Z_1(\omega)e^{j\omega t} + Z_1(-\omega)e^{-j\omega t}) + \left(\frac{A}{2}\right)^2(Z_2(\omega,\omega)e^{2j\omega t} + Z_2(-\omega,-\omega)e^{-2j\omega t} + 2Z_2(\omega,-\omega)e^0) + \cdots \tag{59}$$

Table 2. Model equations for derivation of the Z-functions, for three mechanisms of transport through gas membranes

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Solution-diffusion mechanism

Material balance for the membrane

$$\frac{\partial q}{\partial t} = \frac{\partial}{\partial x}\left((D_{m,s} + \tilde{D}_m^{(1)} q + \tilde{D}_m^{(2)} q^2 + \cdots)\frac{\partial q}{\partial x}\right) \tag{45}$$

Boundary conditions

$$x = 0 : \ q = \tilde{a}c_1 + \tilde{b}c_1^2 + \tilde{c}c_1^3 + \ldots \tag{46}$$

$$x = L : q = \tilde{a}c_2 + \tilde{b}c_2^2 + \tilde{c}c_2^3 + \ldots \tag{47}$$

Material balance for reservoir 2

$$\frac{dc_2}{dt} = -K\left((D_{m,s} + \tilde{D}_m^{(1)} q + \tilde{D}_m^{(2)} q^2 + \cdots)\frac{\partial q}{\partial x}\right)\bigg|_{x=L} \tag{48}$$

Pore-surface diffusion mechanism

Material balance for the membrane

$$\begin{aligned} &\varepsilon' \frac{\partial c_i}{\partial t} + (1-\varepsilon)\frac{\partial q_i}{\partial t} \\ &= \frac{\partial}{\partial x}\left(\varepsilon' D_p \frac{\partial c_i}{\partial x} + (1-\varepsilon)(D_{s,s} + \tilde{D}_s^{(1)} q_i + \tilde{D}_s^{(2)} q_i^2 + \cdots)\frac{\partial q_i}{\partial x}\right) \end{aligned} \tag{49}$$

Local equilibrium within the pores

$$\forall x : q_i = \tilde{a}c_i + \tilde{b}c_i^2 + \tilde{c}c_i^3 + \ldots \tag{50}$$

Boundary conditions

$$x = 0 : c_i = c_1 \tag{51}$$

$$x = L : c_i = c_2 \tag{52}$$

Material balance for reservoir 2

$$\frac{dc_2}{dt} = -K\left(\varepsilon' D_p \frac{\partial c_i}{\partial x} + (1-\varepsilon)(D_{s,s} + \tilde{D}_s^{(1)} q_i + \tilde{D}_s^{(2)} q_i^2 + \cdots)\frac{\partial q_i}{\partial x}\right)\bigg|_{x=L} \tag{53}$$

Viscous flow

Material balance for the membrane

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left(\beta_0 (1 + c_i)\frac{\partial c_i}{\partial x}\right) \tag{54}$$

Boundary conditions

$$x = 0 : c_i = c_1 \tag{55}$$

$$x = L : c_i = c_2 \tag{56}$$

Material balance for reservoir 2

$$\frac{dc_2}{dt} = -K\beta_0\left((1 + c_i)\frac{\partial c_i}{\partial x}\right)\bigg|_{x=L} \tag{57}$$

Table 3. Definitions of the nondimensional concentrations and the modified parameters appearing in the model equations listed in Table 2

Solution-diffusion mechanism

Nondimensional concentrations

$$c_1 = \frac{C_1 - C_s}{C_s} = \frac{p_1 - p_s}{p_s}, \; c_2 = \frac{C_2 - C_s}{C_s} = \frac{p_2 - p_s}{p_s}, \; q = \frac{Q - Q_s}{Q_s}$$

Modified parameters

$$\tilde{a} = \left.\frac{dQ}{dp}\right|_s \frac{p_s}{Q_s} = a\frac{p_s}{Q_s}, \; \tilde{b} = \frac{1}{2}\left.\frac{d^2Q}{dp^2}\right|_s \frac{p_s^2}{Q_s} = b\frac{p_s^2}{Q_s}, \; \tilde{c} = \frac{1}{6}\left.\frac{d^3Q}{dp^3}\right|_s \frac{p_s^3}{Q_s} = c\frac{p_s^3}{Q_s}, \cdots$$

$$\tilde{D}_m^{(1)} = \left.\frac{dD_m}{dQ}\right|_s Q_s = D_m^{(1)} Q_s, \; \tilde{D}_m^{(2)} = \frac{1}{2}\left.\frac{d^2D_m}{dQ^2}\right|_s Q_s^2 = D_m^{(2)} Q_s^2, \cdots \; K = \frac{S}{V_2}\frac{Q_s}{C_s}$$

Pore-surface diffusion mechanism

Nondimensional concentrations

$$c_1 = \frac{C_1 - C_s}{C_s} = \frac{p_1 - p_s}{p_s}, \; c_2 = \frac{C_2 - C_s}{C_s} = \frac{p_2 - p_s}{p_s},$$

$$c_i = \frac{C_i - C_s}{C_s}, \frac{p_i - p_s}{p_s}, \; q_i = \frac{Q_i - Q_{is}}{Q_{is}}$$

Modified parameters

$$\tilde{a} = \left.\frac{dQ_i}{dp_i}\right|_s \frac{p_s}{Q_{i,s}} = a\frac{p_s}{Q_{i,s}}, \; \tilde{b} = \frac{1}{2}\left.\frac{d^2Q_i}{dp_i^2}\right|_s \frac{p_s^2}{Q_{i,s}} = b\frac{p_s^2}{Q_{i,s}},$$

$$\tilde{c} = \frac{1}{6}\left.\frac{d^3Q_i}{dp_i^3}\right|_s \frac{p_s^3}{Q_{i,s}} = c\frac{p_s^3}{Q_{i,s}}, \cdots$$

$$\varepsilon' = \varepsilon\frac{C_s}{Q_s}, \; \tilde{a}_{eff} = a_{eff}\frac{p_s}{Q_s} = \varepsilon' + (1 - \varepsilon)\tilde{a}, \; D_{eff} = \frac{\varepsilon' D_p + (1 - \varepsilon)\tilde{a} D_{s,s}}{\varepsilon' + (1 - \varepsilon)\tilde{a}}$$

$$\tilde{D}_s^{(1)} = \left.\frac{dD_s}{dQ_i}\right|_s Q_{i,s} = D_s^{(1)} Q_{i,s}, \; \tilde{D}_s^{(2)} = \frac{1}{2}\left.\frac{d^2D_s}{dQ_i^2}\right|_s Q_{i,s}^2 = D_s^{(2)} Q_{i,s}^2, \cdots \; K = \frac{S}{V_2}\frac{Q_{i,s}}{C_s}$$

Viscous flow mechanism

Nondimensional concentrations

$$c_1 = \frac{C_1 - C_s}{C_s} = \frac{p_1 - p_s}{p_s}, \; c_2 = \frac{C_2 - C_s}{C_s} = \frac{p_2 - p_s}{p_s}, \; c_i = \frac{C_i - C_s}{C_s} = \frac{p_i - p_s}{p_s}$$

Modified parameters

$$\beta_0 = \frac{B_0 p_s}{\mu}, \; K = \frac{S\varepsilon}{V_2}$$

The derivation procedure is similar to the one used for adsorption systems (4–6). Here, we give only the final expressions for the derived first and second order Z-functions, corresponding to the three mechanisms of membrane transport under consideration.

First Order Function $Z_1(\omega)$

For all three mechanisms, the first order Z-function can be represented in the same form:

$$Z_1(\omega) = \frac{\psi\sqrt{\omega}}{j\omega \sinh(\alpha\sqrt{\omega}L) + \psi\sqrt{\omega}\cosh(\alpha\sqrt{\omega}L)} \tag{60}$$

Nevertheless, the definitions of the parameters α and ψ are different for different mechanisms:

- *For solution-diffusion mechanism*:

$$\alpha = \sqrt{\frac{j}{D_{m,s}}},\ \psi = K\tilde{a}\sqrt{jD_{m,s}} \tag{61a}$$

- *For pore-surface diffusion mechanism*:

$$\alpha = \sqrt{j\frac{\varepsilon' + (1-\varepsilon)\tilde{a}}{\varepsilon D_p + (1-\varepsilon)D_{s,s}\tilde{a}}} = \sqrt{\frac{j}{D_{eff}}},$$
$$\psi = K(\varepsilon' + (1-\varepsilon)\tilde{a})\sqrt{jD_{eff}} = K\tilde{a}_{eff}\sqrt{jD_{eff}} \tag{61b}$$

- *For viscous-flow mechanism*:

$$\alpha = \sqrt{\frac{j}{\beta_0}},\ \psi = \varepsilon K\sqrt{j\beta_0} \tag{61c}$$

Second Order Function $Z_2(\omega,\omega)$

The second order functions $Z_2(\omega,\omega)$ for the three mechanisms can again be put into the same form:

$$Z_2(\omega, \omega) = Z_1(2\omega) \times \left\{\Sigma_1(\omega) + \Sigma_2(\omega)\cosh(\alpha\sqrt{2\omega}L) + \Sigma_3(\omega)\sinh(\alpha\sqrt{2\omega}L)\right\} \tag{62}$$

The terms Σ_1, Σ_2 and Σ_3 are complex functions of frequency, which differ for different mechanism:

– *For solution-diffusion mechanism*:

$$\Sigma_1(\omega) = \frac{\tilde{D}_m^{(1)}\tilde{a}}{D_{m,s}} \frac{(Z_1^2(\omega)+1)/2 - Z_1(\omega)\cosh(\alpha\sqrt{\omega}L)}{\sinh^2(\alpha\sqrt{\omega}L)} + \left(\frac{\tilde{b}}{\tilde{a}} + \frac{\tilde{D}_m^{(1)}\tilde{a}}{D_{m,s}}\right) \qquad (63a-1)$$

$$\Sigma_2(\omega) = -\frac{\tilde{D}_m^{(1)}\tilde{a}}{D_{m,s}} \frac{(Z_1^2(\omega)+1)/2 - Z_1(\omega)\cosh(\alpha\sqrt{\omega}L)}{\sinh^2(\alpha\sqrt{\omega}L)} - \left(\frac{\tilde{b}}{\tilde{a}} + \frac{\tilde{D}_m^{(1)}\tilde{a}}{D_{m,s}}\right) Z_1^2(\omega) \qquad (63a-2)$$

$$\Sigma_3(\omega) = \frac{\sqrt{2}\tilde{D}_m^{(1)}\tilde{a}}{2D_{m,s}} \frac{Z_1^2(\omega)\cosh(\alpha\sqrt{\omega}L) - Z_1(\omega)}{\sinh(\alpha\sqrt{\omega}L)} \qquad (63a-3)$$

– *For pore-surface diffusion mechanism*:

$$\begin{aligned}\Sigma_1(\omega) = {} & 2(1-\varepsilon)\left(\frac{D_{s,s}\tilde{b} + \tilde{D}_s^{(1)}\tilde{a}^2/2}{D_{\mathit{eff}}\tilde{a}_{\mathit{eff}}} - \frac{\tilde{b}}{\tilde{a}}\right) \\ & \times \frac{(Z_1^2(\omega)+1)/2 - Z_1(\omega)\cosh(\alpha\sqrt{\omega}L)}{\sinh^2(\alpha\sqrt{\omega}L)} \\ & + (1-\varepsilon)\left(2\frac{D_{s,s}\tilde{b} + \tilde{D}_s^{(1)}\tilde{a}^2/2}{D_{\mathit{eff}}\tilde{a}_{\mathit{eff}}} - \frac{\tilde{b}}{\tilde{a}}\right) \qquad (63b-1)\end{aligned}$$

$$\begin{aligned}\Sigma_2(\omega) = {} & 2(1-\varepsilon)\left(\frac{\tilde{b}}{\tilde{a}} - \frac{D_{s,s}\tilde{b} + \tilde{D}_s^{(1)}\tilde{a}^2/2}{D_{\mathit{eff}}\tilde{a}_{\mathit{eff}}}\right) \\ & \times \frac{(Z_1^2(\omega)+1)/2 - Z_1(\omega)\cosh(\alpha\sqrt{\omega}L)}{\sinh^2(\alpha\sqrt{\omega}L)} \\ & + (1-\varepsilon)\left(\frac{\tilde{b}}{\tilde{a}} - 2\frac{D_{s,s}\tilde{b} + \tilde{D}_s^{(1)}\tilde{a}^2/2}{D_{\mathit{eff}}\tilde{a}_{\mathit{eff}}}\right) Z_1^2(\omega) \qquad (63b-2)\end{aligned}$$

$$\begin{aligned}\Sigma_3(\omega) = {} & \sqrt{2}(1-\varepsilon)\left(2\frac{D_{s,s}\tilde{b} + \tilde{D}_s^{(1)}\tilde{a}^2/2}{D_{\mathit{eff}}\tilde{a}_{\mathit{eff}}} - \frac{\tilde{b}}{\tilde{a}}\right) \\ & \times \frac{Z_1^2(\omega)\cosh(\alpha\sqrt{\omega}L) - Z_1(\omega)}{\sinh(\alpha\sqrt{\omega}L)} \qquad (63b-3)\end{aligned}$$

– *For viscous flow mechanism*

$$\Sigma_1(\omega) = \frac{(Z_1^2(\omega)+1)/2 - Z_1(\omega)\cosh(\alpha\sqrt{\omega}L)}{\sinh^2(\alpha\sqrt{\omega}L)} + 1 \qquad (63\text{c} - 1)$$

$$\Sigma_2(\omega) = -\frac{(Z_1^2(\omega)+1)/2 - Z_1(\omega)\cosh(\alpha\sqrt{\omega}L)}{\sinh^2(\alpha\sqrt{\omega}L)} - Z_1^2(\omega) \qquad (63\text{c} - 2)$$

$$\Sigma_3(\omega) = \frac{\sqrt{2}}{2}\frac{Z_1^2(\omega)\cosh(\alpha\sqrt{\omega}L) - Z_1(\omega)}{\sinh(\alpha\sqrt{\omega}L)} \qquad (63\text{c} - 3)$$

Second Order Function $Z_2(\omega, -\omega)$

The common form of the expressions for the second order function $Z_2(\omega, -\omega)$ is:

$$Z_2(\omega, -\omega) = \Lambda(1 - Z_1(\omega)Z_1(-\omega)) \qquad (64)$$

The parameter Λ also have different definitions for different mechanisms: *For solution-diffusion mechanism*:

$$\Lambda = \frac{D_{m,s}\tilde{b} + \tilde{D}_m^{(1)}\tilde{a}^2/2}{D_{m,s}\tilde{a}} \qquad (65\text{a})$$

For pore-surface diffusion mechanism:

$$\Lambda = \frac{(1-\varepsilon)(D_{s,s}\tilde{b} + \tilde{D}_s^{(1)}\tilde{a}^2/2)}{D_{eff}\tilde{a}_{eff}} \qquad (65\text{b})$$

For viscous-flow mechanism:

$$\Lambda = \frac{1}{2} \qquad (65\text{c})$$

Simulation Results

The derived mathematical expressions for the first and second order Z-functions corresponding to the three models under investigation are rather complex for direct analysis. For that reason, these expressions were used for computer simulation which can be used for analysis of the main features of these functions and for comparison between different models.

The parameter values used for simulation are listed in Table 4. Although they do not correspond to any specific systems, these values have realistic orders of magnitude. Different values of the membrane thickness were used for different models, as they correspond to different membrane types. Also, different values of the parameter K were used for

Table 4. Values of the model parameters used for simulation

Solution-diffusion model	Pore-surface diffusion model	Viscous-flow model
$\tilde{a} = 0.8$	$\tilde{a} = 0.8$	$\beta_0 = 0.001\,\mathrm{s}^{-1}$
$\tilde{b} = -0.2$	$\tilde{b} = -0.2$	$L = 0.01\,\mathrm{cm}$
$D_{m,s} = 1 \times 10^{-8}\,\mathrm{cm}^2/\mathrm{s}$	$D_{s,s} = 1 \times 10^{-7}\,\mathrm{cm}^2/\mathrm{s}$	$K = 10\,\mathrm{cm}^{-1}$
$\tilde{D}_m^{(1)} = 2 \times 10^{-9}\,\mathrm{cm}^2/\mathrm{s}$	$\tilde{D}_s^{(1)} = 2 \times 10^{-8}\,\mathrm{cm}^2/\mathrm{s}$	$\varepsilon = 0.5$
$L = 1 \times 10^{-5}\,\mathrm{cm}$	$D_p = 5 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{s}$	
$K = 100\,\mathrm{cm}^{-1}$	$L = 2 \times 10^{-4}\,\mathrm{cm}$	
	$K = 100\,\mathrm{cm}^{-1}$	
	$\varepsilon = 0.5$	
	$\varepsilon' = 0.0003$	

the solution-diffusion and for the pore-surface diffusion models on one hand, and for the viscous flow model on the other, owing to different definitions of this parameter.

The simulated Z-functions of the first and second order are given in Figure 5 for the solution-diffusion model, Figure 6 for the pore-surface diffusion model and Figure 7 for the viscous-flow model. All FRFs are presented in the form of standard Bodé-plots (amplitude vs. frequency in log-log, and phase vs. frequency in semi-log diagrams).

The following conclusions can be withdrawn by inspection of Figures 5–7:

- *First order functions* $Z_1(\omega)$: The shapes of the first order functions are same for all three mechanisms: the amplitudes of $Z_1(\omega)$ have horizontal low-frequency asymptotes (the asymptotic values are equal to 1) and two distinct changes of slope; the phases tend to 0 for $\omega \to 0$, have plateaus at the level $-\pi/2$, and tend to $-\infty$ for $\omega \to \infty$.
- *Second order functions* $Z_2(\omega,\omega)$: The amplitudes have similar behavior in the low- and high-frequency range (tend to 0 both for $\omega \to 0$ and $\omega \to \infty$). Nevertheless, in the middle range of frequencies, the amplitudes for the solution-diffusion and viscous-flow mechanisms are essentially linear and parallel to the first order curves, while for the pore-surface mechanism the amplitude has more complex shape with several inflection points. The phase functions have similar shapes (and similar to those of the first order functions, but the asymptotic values for the solution-diffusion and pore-surface diffusion mechanism for $\omega \to 0$ are $-\pi/2$, while for the viscous-flow mechanism it is $+\pi/2$.
- *Second order functions* $Z_2(\omega, -\omega)$: The shapes of these functions are same for all three mechanisms: the amplitudes tend to 0 for $\omega \to 0$ and to constant values for $\omega \to \infty$ and the phases are constant. The only difference is that for the solution-diffusion and for the pore–surface diffusion model

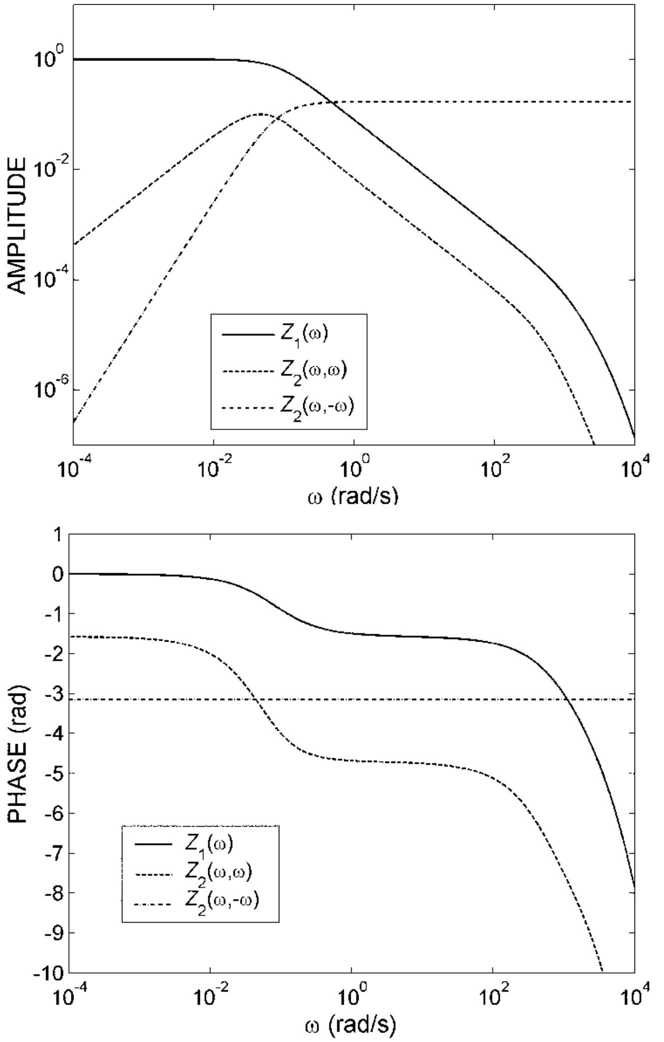

Figure 5. The first and second order Z-functions for the solution-diffusion model.

the phase is $-\pi$ (meaning that the DC component is negative), while for the viscous-flow mechanism the phase is 0 (meaning that the DC component is positive).

Based on the characteristics of the first and second order Z-functions, it would be possible to distinguish between different permeation mechanisms and to identify the real one: the pore-surface diffusion mechanism can be identified based on the shape of the amplitude of $Z_2(\omega,\omega)$, and the viscous-flow based on the phase of $Z_2(\omega,\omega)$ or $Z_2(\omega, -\omega)$.

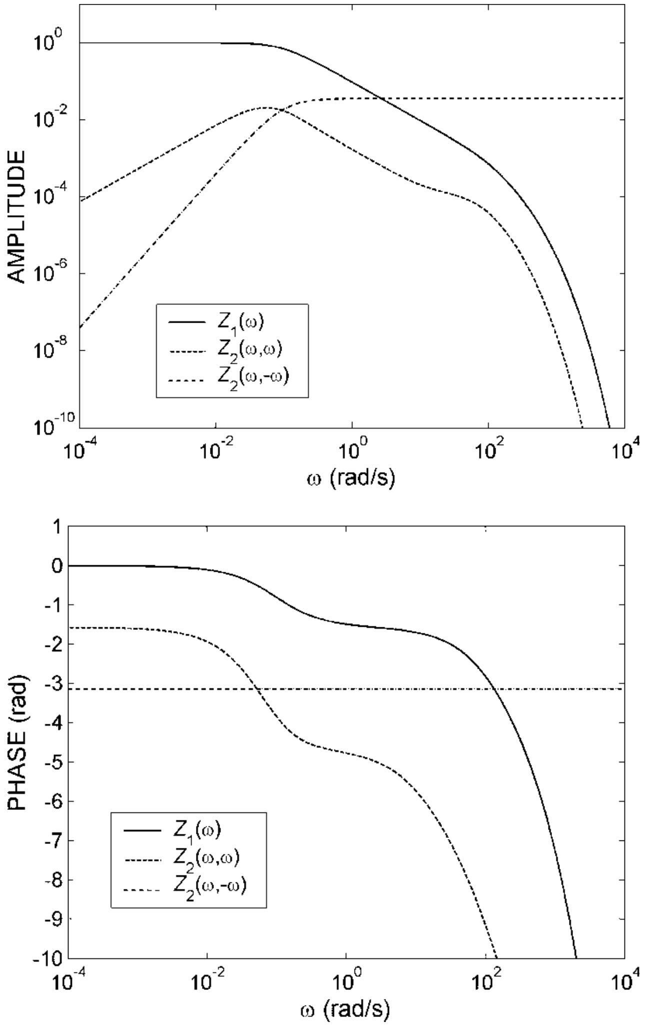

Figure 6. The first and second order *Z*-functions for the pore-surface diffusion model.

ESTIMATION OF THE MODEL PARAMETERS FROM THE FIRST AND SECOND ORDER FRFs

Parameters Estimated From the First Order FRF

One of the important and useful results of the investigation of frequency response of adsorption systems is that the so-called out-of-phase function (14), which is actually the negative imaginary part of the first order frequency response function (15), has a maximum, the position of which is

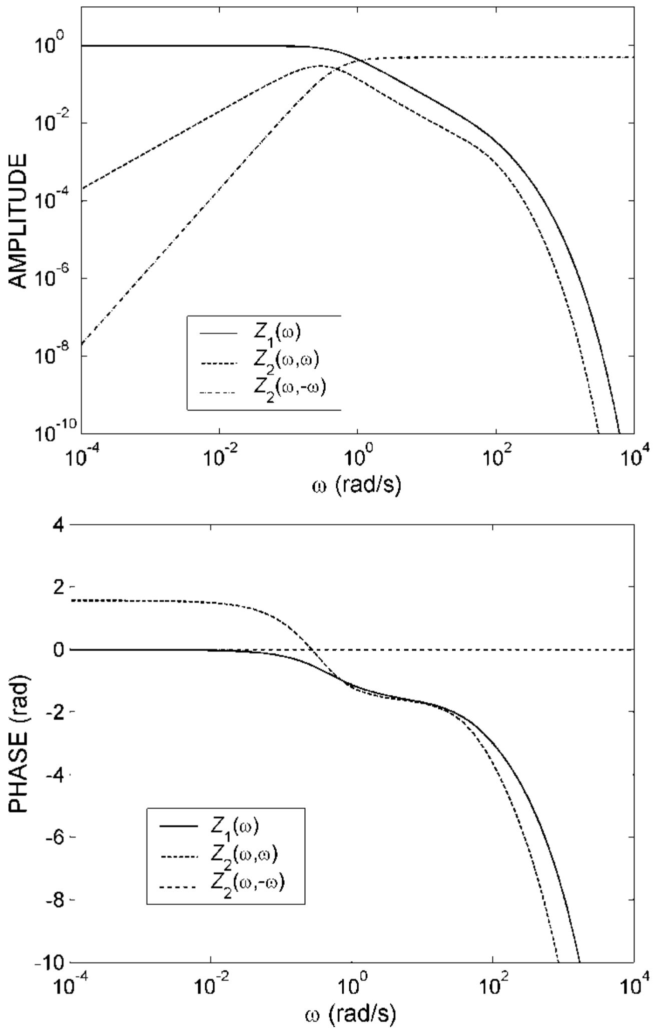

Figure 7. The first and second order Z-functions for the viscous-flow model.

directly related to the main transport parameter of the system (14). This fact is used for estimation of the transport parameters, such as diffusion coefficients, using the frequency response method (14).

A similar result is obtained for the membrane systems investigated in this paper. In Fig. 8, we show the imaginary parts of the first order function $Z_1(\omega)$ for the three mechanisms of membrane transport under investigation. As can be seen from this figure, the curves corresponding to the three different models practically overlap. This was achieved by using nondimensional frequency on the abscisa, defined as a ratio of the dimensional frequency and a characteristic

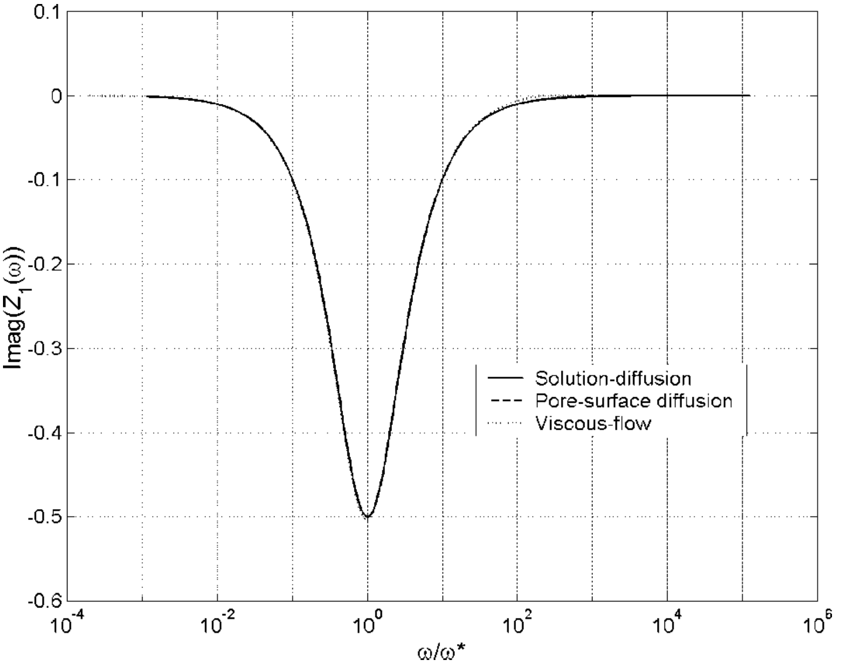

Figure 8. Imaginary part of the first order Z-function

frequency ω^*. The definitions of the characteristic frequencies for the three transport mechanism under consideration are:

- For the solution-diffusion mechanism

$$\omega^* = \frac{D_{m,s}\tilde{a}K}{L} \tag{66}$$

- For the pore-surface mechanism

$$\omega^* = \frac{D_{eff}\tilde{a}_{eff}K}{L} \tag{67}$$

- For the viscous-flow mechanism

$$\omega^* = \frac{\beta_0 K}{L} \tag{68}$$

As it can be seen from Fig. 8, the minimum of the function $\mathrm{Imag}(Z_1(\omega))$ is obtained for $\omega/\omega^* = 1$, i.e. for $\omega = \omega^*$.

On the other hand, by using the definitions of the first order permeabilities given in Table 1, and the definitions of the nondimensional parameters given in Table 3, it can be shown that for all three models under consideration the first order permeability can be determined from the characteristic frequency, i.e. from the locus of the minimum of the imaginary part of $Z_1(\omega)$, using the following common expression:

$$P_I = \frac{V_2 L}{S R_g T}\omega^* \tag{69}$$

It should be noticed that the characteristic frequency ω^* depends, not only on the equilibrium and transport parameters of the investigated membrane, but also on the geometry of the experimental system, i.e. on the ratio of the membrane surface area S and the volume of the reservoir V_2. In designing the experimental system this ratio can be chosen in such a way that the characteristic frequency is in the physically attainable range, even when investigating systems with fast kinetics. By doing this, the main problem of application of the frequency response method in investigation of chemical systems, that input changes with frequencies higher than 10 Hz can not be produced (16), is resolved.

The first order permeability corresponding to the solution-diffusion or to the pore-surface diffusion model is essentially a products of an equilibrium (the first isotherm derivative) and a kinetic parameters (the diffusion coefficient). Using the first order Z-function, these parameters can be estimated individually, as shown below.

Solution-Diffusion Model

It can be shown that the first derivative of the Z_1-function has a finite low-frequency asymptotic value, which is, according to the L′Hopital's rule same as the asymptotic value of the ratio of Imag($Z_1(\omega)$) and ω:

$$\begin{aligned}\lim_{\omega\to 0}\left|\frac{dZ_1(\omega)}{d\omega}\right| = \lim_{\omega\to 0}\left|\frac{\mathrm{Im}(Z_1(\omega))}{\omega}\right| &= \frac{L}{D_{m,s}\tilde{a}K} + \frac{L^2}{2D_{m,s}} \\ &= \frac{1}{\omega^*} + \frac{L^2}{2D_{m,s}}\end{aligned} \tag{70}$$

Regarding the fact that the characteristic frequency is obtained from the locus of the minimum of Imag($Z_1(\omega)$), the low-frequency asymptote defined by Equation (70) enables estimation of the diffusion coefficient $D_{m,s}$ corresponding to the steady state pressure p_s (concentration Q_s). Knowing $D_{m,s}$, it is possible to calculate the first derivative of the adsorption isotherm for the same steady-state, a, as a ratio of the first order permeability P_I and $D_{m,s}$ ($a = P_I/D_{m,s}$).

Pore-Surface Diffusion Mechanism

The low-frequency asymptote of the first derivative of $Z_1(\omega)$ for this mechanism has an analogous form as for the solution-diffusion case:

$$\lim_{\omega\to 0}\left|\frac{dZ_1(\omega)}{d\omega}\right| = \lim_{\omega\to 0}\left|\frac{\mathrm{Im}(Z_1(\omega))}{\omega}\right| = \frac{L}{D_{eff}\tilde{a}_{eff}K}+\frac{L^2}{2D_{eff}}$$

$$=\frac{1}{\omega^*}+\frac{L^2}{2D_{eff}} \tag{71}$$

and can be used for estimation of the effective diffusivity coefficient D_{eff}, and further, of the effective slope of the adsorption isotherm a_{eff} ($a_{eff} = P_I/D_{eff}$).

Parameters Estimated From the Second Order FRFs

In Section 2.4. we defined the so-called second order permeability. Using the expressions given in Table 1 and the parameters defined in Table 3, it can be shown that the following result is valid for all three mechanisms:

$$\lim_{\omega\to\infty} Z_2(\omega, -\omega) = \frac{P_{II}}{P_I}p_s \tag{72}$$

With the first order permeability P_I estimated from the first order FRF $Z_1(\omega)$, Equation (72) enables direct estimation of the second order permeability P_{II} corresponding to the steady-state pressure p_s.

Again, for the solution-diffusion and pore-surface diffusion mechanisms, some additional parameters can be estimated individually, from the second order Z-functions.

Solution-Diffusion Mechanism

The low-frequency asymptotic value of the first derivative of the second order function $Z_2(\omega,\omega)$ (which is, according to the L′Hopital's rule the same as the low-frequency asymptotic value of the ratio $Z_2(\omega,\omega)/\omega$) is:

$$\lim_{\omega\to 0}\left|\frac{dZ_2(\omega,\,\omega)}{d\omega}\right| = \lim_{\omega\to 0}\left|\frac{Z_2(\omega,\,\omega)}{\omega}\right|$$

$$=2\frac{L}{D_{m,s}\tilde{a}K}\frac{\tilde{b}D_{m,s}+\tilde{D}_m^{(1)}\tilde{a}^2/2}{D_{m,s}\tilde{a}}+\frac{L^2}{2D_{m,s}}\frac{\tilde{D}_m^{(1)}\tilde{a}^2}{D_{m,s}\tilde{a}}$$

$$=2\frac{p_s}{\omega^*}\frac{P_{II}}{P_I}+\frac{L^2p_s}{2D_{m,s}^2}D_m^{(1)}a \tag{73}$$

Equation (73) enables estimation of the first derivative of the diffusion coefficient $D_m^{(1)}$, and with previously estimated values of ω^*, P_I, P_{II}, $D_{m,s}$ and a, also the second derivative of the adsorption isotherm b.

Pore-Surface Diffusion Mechanism

The low-frequency asymptote of the first derivative of $Z_2(\omega,\omega)$, is:

$$\begin{aligned}\lim_{\omega\to 0}\left|\frac{dZ_2(\omega,\omega)}{d\omega}\right| &= \lim_{\omega\to 0}\left|\frac{Z_2(\omega,\omega)}{\omega}\right| \\ &= (1-\varepsilon)\left|\frac{\tilde{b}D_{s,s}+\tilde{D}_s^{(1)}\tilde{a}^2/2}{D_{eff}\tilde{a}_{eff}}\left(\frac{L^2}{D_{eff}}-\frac{2L}{D_{eff}\tilde{a}_{eff}K}\right)-\frac{L^2}{D_{eff}}\frac{\tilde{b}}{\tilde{a}_{eff}}\right| \\ &= p_s\left|\frac{P_{II}}{P_I}\left(\frac{L^2}{D_{eff}}-\frac{2}{\omega^*}\right)-\frac{L^2}{D_{eff}}\frac{(1-\varepsilon)b}{a_{eff}}\right| \qquad (74)\end{aligned}$$

The second derivative of the adsorption isotherm b can be estimated using Equation (74), assuming that P_I, P_{II}, ω^*, D_{eff} and a_{eff} have been estimated previously.

The third order permeability P_{III} and the equilibrium and transport parameters related to it could be estimated from he third order function $Z_3(\omega,\omega,\omega)$ and the higher order permeabilities from the functions of higher order.

CONCLUSIONS

The aim of this paper was to analyse the possibilities of application of the nonlinear frequency response method for investigation of membrane transport. The analysis was limited to permeation of pure gases for three transport mechanisms: solution-diffusion, pore-surface diffusion, and viscous-flow.

The first result of our analysis was that, in dynamic conditions, the mean flux through the membrane can be represented as an infinite series. The first member of this series is proportional to the difference of the pressures at both sides of the membrane, the second to the difference of the squares of pressures, the third to the difference of cubes, etc. This led us to the definition of the generalized permeability, as a sequence of values (which we called permeability of the first, second, third, etc., order). These values depend on the steady state around which the system is perturbed, i.e. on the equilibrium and transport parameters corresponding to that steady-state.

A simple two-reservoir system with modulation of the volume of one of them was proposed for investigation of membrane transport by frequency response. The generalized transfer function (a set of FRFs) relating the pressure changes in the two reservoirs (the Z-functions) was chosen as the most convenient and informative. Starting from the nonlinear mathematical models, the expressions for the first and second order Z-functions corresponding to the three mechanisms under consideration were derived. Computer simulation of the first and second order Z-functions, based on these expressions, showed that the second order functions corresponding to different mechanisms have different shapes, and that they contain enough information for discrimination between different mechanisms.

On the other hand, the analysis of the derived Z-functions showed that for each of the three mechanisms the first order permeability could be estimated from the first order function $Z_1(\omega)$, more precisely from the locus of the minimum of its imaginary part. Also, the second order permeability for each mechanism could be estimated from the second order functions, e.g. from the high frequency asymptote of the function $Z_2(\omega, -\omega)$.

It was also shown that the first and second order Z-functions can be used for estimation of the equilibrium and kinetic parameters (such as the isotherm derivatives and the diffusion coefficients), separately.

Although in this paper we derived and analysed only the first and second order frequency response functions, the analysis could be extended to the third and higher order functions, which could be used for estimation of the third and higher order permeabilities.

Being the first attempt at applying the nonlinear FR technique to investigation of membrane systems, this study was limited to the simplest case, membrane transport of pure gases. Investigations of application of the method to multicomponent gas systems and to liquid membrane systems should follow this work. We expect the method to be applicable to investigations of membrane transport of gas mixtures and for liquid separations. Naturally, new, different definitions of the permeabilities and transfer functions, as well as different designs of the experimental setups will be needed for these cases.

NOTATION

A	amplitude
a	first derivative of the adsorption isotherm, mol/cm^3/kPa
a_{eff}	effective first derivative of the adsorption isotherm, mol/cm^3/kPa
b	second derivative of the adsorption isotherm, mol/cm^3/kPa^2
B_0	viscous-flow parameter
C	concentration in the gas phase, mol/cm^3
c	nondimensional pressure or concentration in the gas phase

C_i	concentration in the gas within the membrane pores, $\mathrm{mol/cm^3}$
c_i	nondimensional pressure or concentration in the gas within the membrane pores
D_{eff}	effective diffusion coefficient, $\mathrm{cm^2/s}$
D_m	membrane diffusion coefficient (solution-diffusion model), $\mathrm{cm^2/s}$
$D_m^{(1)}$, $D_m^{(2)}$, $D_m^{(3)}$	Taylor series expansion coefficients for the membrane diffusion coefficient
D_p	pore diffusion coefficient, $\mathrm{cm^2/s}$
D_s	surface diffusion coefficient, $\mathrm{cm^2/s}$
$D_s^{(1)}$, $D_s^{(2)}$, $D_s^{(3)}$	Taylor series expansion coefficients for the surface diffusion coefficient
F	FRFs relating pressure (conc.) in reservoir 1 to the change of volume of reservoir 1
G	FRFs relating pressure (conc.) in reservoir 2 to the change of volume of reservoir 1
J	flux, $\mathrm{mol/cm^2/s}$
L	membrane thickness, cm
K	capacity parameter, defined in Table 3, $\mathrm{m^{-1}}$
P_I	first order permeability, mol/cm/s/kPa
P_{II}	second order permeability, $\mathrm{mol/cm/s/kPa^2}$
P_{III}	third order permeability, $\mathrm{mol/cm/s/kPa^3}$
p	pressure, kPa
p_i	pressure in the membrane pores, kPa
Q	concentration in the membrane, $\mathrm{mol/cm^3}$
Q_i	concentration in the solid phase, $\mathrm{mol/cm^3}$
q_i	nondimensional concentration in the solid phase
R_g	gas constant, J/mol/K
T	temperature, K
t	time, s
S	membrane surface area, $\mathrm{cm^2}$
V	volume, $\mathrm{cm^3}$
x	position within the membrane, cm
Z	FRFs relating pressure (conc.) in reservoir 2 to pressure (conc.) in reservoir 1

Greek Letters

β_0	modified viscous-flow parameter, defined in Table 3
ε	membrane porosity
ε’	modified membrane porosity, defined in Table 3
μ	viscosity, Pas
ω	frequency, rad/s
ω^*	characteristic frequency, rad/s

Subscripts

1	reservoir 1
2	reservoir 2
s	steady-state

Embellishments

$\sim$	modified parameters, defined in Table 3
$\langle\,\rangle$	mean value

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