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Photoacoustic detection of drug diffusion into a membrane: theory and numerical analysis

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Abstract

Possibility of the analysis of drug penetration through membranes using photoacoustic effect is considered. Based on Fick's second law the problem of the spatial and time dependent distribution of drugs in membranes is solved. The solution allows to derive the distribution of heat sources arising in the membrane from intensity modulated light illumination. Subsequently the temperature of the illuminated membrane surface is analysed numerically. This temperature is directly correlated to the signal registered in photoacoustic measurements. The influence of different parameters of the theoretical model on the ac component of the temperature of illuminated membrane surface has been analysed. Conclusions about possibilities and limitations of the considered method are discussed.

1. Introduction

Photoacoustic and photothermal effects are widely used in the investigation of different materials and physical processes. The photothermal effect is referred to the perturbation of temperature fields caused by energy absorption from modulated light. If this disturbance leads to the generation of acoustic signals the phenomenon is called photoacoustic effect. The main advantage of photoacoustic and photothermal measurements is their nondestructive character. Numerous examples of recent applications of both effects may be found in [1]. Christ and co-workers proposed the use of the photoacoustic effect for the investigation of drug diffusion through membranes [2]. The authors registered the time evolution of the photoacoustic signal in organic membranes, were diffused the pharmaceutical drug dithranol. The results have confirmed the possibility to use this technique for the study of diffusion processes. Unfortunately, because of a lack of proper theoretical analysis of signal formation in the experiment mentioned above, a quantitative interpretation of the experimental data was impossible. In a recently published paper [3] Christ and Szurkowski used Crank's theory [4] for the analysis of the experimental data, but they did not solve the problem to determine the diffusion coefficient. The knowledge of the diffusion coefficient however is essential for the analysis of a mass transport. For instance in pharmaceutical applications it would be a possibility to predict the efficiency of drug transports through artificial membranes or from ointments through the skin into human body, respectively.

The aim of this paper is the analysis of the applicability of photoacoustic measurements for the investigation of diffusion and the determination of parameters of diffusion. For the solution of this problem a theoretical model is proposed. The model consists of the description of diffusion in a layered system and the analysis of the formation of the acoustic signal, when the system is illuminated by intensity modulated light. Based on the obtained results a numerical analysis of the dependence of the photoacoustic signal on parameters of the model is carried out, and conclusions about the optimal configuration of the experiment are drawn. Because of the complexity of the model possible simplifications for a preliminary data analysis are considered.

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Nomenclature

A	a constant
D	the diffusion coefficient
I	the light intensity in the membrane
I_0	the maximum intensity of incident light
I_{in}	the intensity of incident light
L	the thickness of the layer
N	the number of space grid points
N_Σ	the number of addends in a sum
n	the concentration
n_0	the concentration of diffusing matter in the source
q	the density of heat sources in the membrane
PAS	the photoacoustic signal
R	the thickness of the membrane
S	the density of surface heat sources at the membrane–source interface
T	the temperature
t	the time
x	the coordinate

Greek symbols

α	the mass transfer coefficient
α_0	the optical absorption coefficient of the membrane
α_a	the total optical absorption coefficient
α_d	the factor of proportionality between the concentration of the diffusing matter and its optical absorption coefficient
β	the thermal diffusivity
Γ	a complex constant
Δt	the time grid increment
Δx	the space grid increment
ε	the coefficient depending on the thermal diffusivity and grid increments
θ	the ac temperature component
κ	the thermal conductivity
μ	the root of the equation $\operatorname{ctg}\mu = \mu(D/\alpha R)$
μ_M	the thermal diffusion length in the membrane
τ	the characteristic time of the diffusion process
ω	the modulation frequency

Subscripts and superscripts

A	an air
j, n	superscripts for j, n node on the grid, describing space and time points, respectively
k	an index for layer (k = A, M, S)
M	the membrane
S	the source

2. Theoretical model

The analysis of the temperature field was carried out for the system schematically shown in Fig. 1. The system consists of three layers: the source of diffusion, the membrane through which diffusion proceeded and the air above it. It was assumed that the concentration of diffusing matter is constant within the source and is a function of time and position in the membrane. The system is uniformly illuminated by intensity-modulated light. According to the classical theory of the photoacoustic effect [5] one has to calculate the temperature field in the sample (the membrane and the source) and in the air, in order to estimate the measured signal. The temperature field in the system is determined by heat sources arising as a result of light absorption. In the considered case it is assumed that light absorption takes place in the membrane and at the boundary towards the source. The second assumption is that light absorption in the source is very strong, and therefore the light is practically fully absorbed near the membrane–source boundary. It should also be noticed, that the density of heat sources in the membrane depends both on the local concentration of diffusing matter and on the optical properties of the membrane. Because the light intensity is low in typical experiments, the disturbance of the temperature field caused by light absorption is weak and a dependence of transport properties on temperature is omitted.

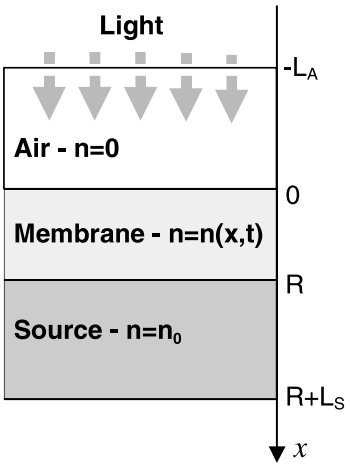

Fig. 1. Geometry of the considered system.

The theoretical analysis can be divided into the following four stages:

- description of the concentration of diffusing matter in the membrane,

- description of heat sources in the system,
- analysis of the temperature field in the system,
- analysis of the photoacoustic signal.

2.1. Diffusion process

The concentration $n(x,t)$ of diffusing matter in the membrane can be calculated based on Fick's second law

$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2}, \tag{1}$$

where D is the diffusion coefficient. In order to obtain a proper solution of the equation above it has to be completed with border conditions. The following conditions are assumed:

1. $n(x,t) = 0$ for $t < 0$ and $x \leqslant R$: there is no diffusing matter in the membrane, before the diffusion is started,
2. $-D(\partial n/\partial x)|_{x=0} = 0$: there is no mass flux into the air,
3. $-D(\partial n/\partial x)|_{x=R} = \alpha[n(R,t) - n_0]$, where α is the mass transfer coefficient: the mass flux from the source to the membrane is proportional to the difference of concentrations at the boundary.

In order to solve this problem one can take advantage of a solution for the problem of heat transport in a homogeneous infinite plate with a thickness of $2R$ placed in a medium with constant temperature. Such a problem is described for instance in textbook [6]. Using the result sketched there and adopting it to the problem considered here, one can obtain the formula describing the concentration of diffusing matter in the membrane

$$n(x,t) = n_0\left[1 - 2\sum_{i=1}^{\infty}\frac{\exp\left(-\mu_i^2\frac{Dt}{R^2}\right)\cos\left(\mu_i\frac{x}{R}\right)\sin\mu_i}{\mu_i + \sin\mu_i\cos\mu_i}\right], \tag{2}$$

where μ_i are roots of equation

$$\operatorname{ctg}\mu = \mu\frac{D}{\alpha R}. \tag{3}$$

The diffusion process in the membrane is characterized by time constants

$$\tau_i = \frac{R^2}{\mu_i^2 D}. \tag{4}$$

These characteristic times are defined by the diffusion coefficient and the membrane thickness, but also depend on the mass transfer coefficient. It follows from Eq. (3) that this dependence may be omitted when α is high enough. Then roots of Eq. (3) are equal to odd multiples of $\pi/2$. For small values of α these roots are smaller and characteristic times are longer. It means that the efficiency of mass transfer at the source–membrane boundary slows down the diffusion.

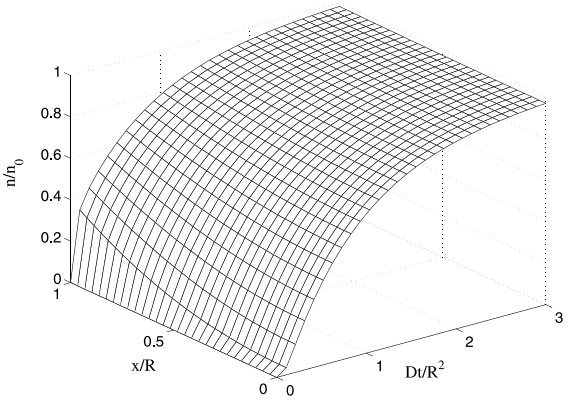

Fig. 2. Normalised concentration of diffusing matter for $D\alpha^{-1}R^{-1} = 1$.

Successive characteristic times rapidly decrease with increasing μ_i. In Fig. 2 the normalized concentration of diffusing matter in the membrane is shown as a function of dimensionless variables DtR^{-2} and xR^{-1} for $D\alpha^{-1}R^{-1} = 1$. The calculation is carried out based on Eq. (2) for the first 100 terms of the infinite sum. Of course it may be expected that in practice, for longer observation times, the infinite sum in Eq. (2) may be replaced by a few, or even only the first term. This conclusion is confirmed by results of numerical analysis. It may be shown that using the first 10 terms only very good approximation is obtained, and for $DtR^{-2} > 0.3$ and $D\alpha^{-1}R^{-1} = 1$, the time evolution of concentration of the diffusing matter at the membrane top surface ($x = 0$) is sufficiently described by the first term of the sum.

2.2. Heat sources

As it is mentioned above the theoretical analysis of a photoacoustic experiment requires the description of heat sources in the investigated system. There are two types of heat sources in the considered system—volume heat sources in the membrane and the surface heat source at the membrane–source interface.

Volume heat sources in the membrane are caused by light absorption by the diffusing matter and the membrane itself. Assuming that all absorbed energy is converted into heat the density of heat sources is

$$q(x,t) = \alpha_a(x,t)I(x,t), \tag{5}$$

where α_a is an absorption coefficient and I, the light intensity. The absorption coefficient is a sum of two terms

$$\alpha_a(x,t) = \alpha_0 + \alpha_d n(x,t), \tag{6}$$

where α_0 is the absorption coefficient of the membrane; $\alpha_d n$, the absorption coefficient of the diffusing matter,

which is assumed to be proportional to its concentration with the material depending factor of proportionality α_d.

The light intensity in the membrane may be derived from the equation

$$dI = -\alpha_a I\,dx. \tag{7}$$

Using (2) and (6) one can obtain the following formula

$$I(x,t) = I_{in}(t)\exp\left\{-R\left\{\alpha_0\frac{x}{R} + \alpha_d n_0\left[\frac{x}{R} - 2\sum_{i=1}^{\infty}\frac{\exp\left(-\mu_i^2\frac{Dt}{R^2}\right)\sin\left(\mu_i\frac{x}{R}\right)\sin\mu_i}{(\mu_i + \sin\mu_i\cos\mu_i)\mu_i}\right]\right\}\right\}, \tag{8}$$

where $I_{in} = 0.5I_0[1-\cos(\omega t)]$ is the light intensity in the membrane at $x = 0$ and ω, the frequency of modulation. It can be shown that the formula describing volume heat sources may also be written in the compact form

$$q(x,t) = -\frac{\partial I(x,t)}{\partial x}. \tag{9}$$

Based on (2), (5) and (8) the distribution of the density of volume heat sources in the membrane may be calculated. An exemplary result of calculations for amplitude of light intensity and heat sources density in the membrane is shown in Figs. 3 and 4, respectively. The calculation was carried out using dimensionless variables DtR^{-2} and xR^{-1}, the same as in Fig. 2, and the following other parameters of the system: $D\alpha^{-1}R^{-1} = 1$, $\alpha_0 = 10^4$ m^{-1}, $\alpha_d n_0 = 10^5$ m^{-1}, and $R = 20$ μm.

According to the earlier assumption, that the diffusion source is optically opaque, the density of surface heat sources at the membrane–source interface is equal to the light intensity at $x = R$

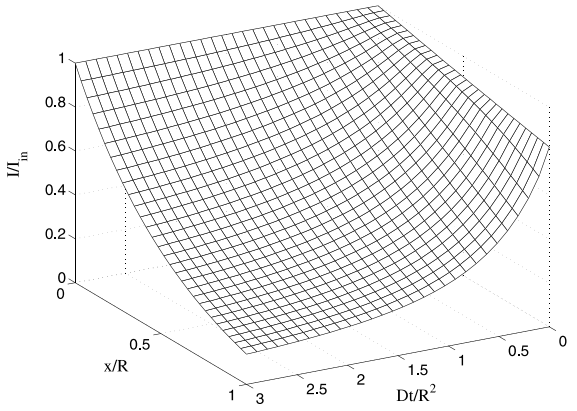

Fig. 3. Distribution of the amplitude of light intensity in the membrane (detailed description in the text).

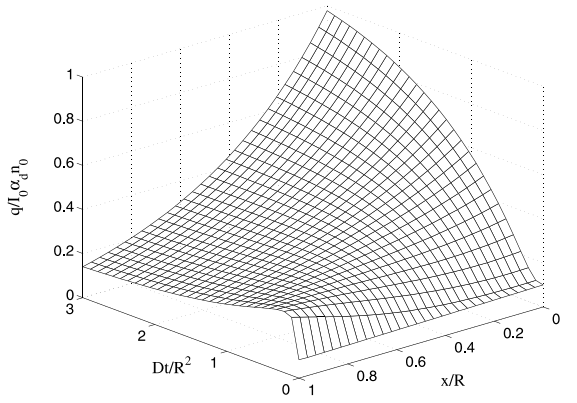

Fig. 4. Distribution of the amplitude of volume heat sources in the membrane (detailed description in the text).

$$S(t) = I(R,t) = I_{in}(t)\exp\left\{-R\left\{\alpha_0 + \alpha_d n_0\left[1 - 2\sum_{i=1}^{\infty}\frac{\exp\left(-\mu_i^2\frac{Dt}{R^2}\right)\sin^2\mu_i}{(\mu_i + \sin\mu_i\cos\mu_i)\mu_i}\right]\right\}\right\}. \tag{10}$$

Therefore the time evolution of the amplitude of the surface heat source calculated for the same parameters as for volume sources can be read from Fig. 3 for $xR^{-1} = 1$.

2.3. Temperature field

The description of the temperature field in the system requires the solution of Fourier–Kirchhoff equations for the air, the membrane and the source, respectively

$$\begin{aligned}\frac{\partial^2 T_A(x,t)}{\partial x^2} &= \frac{1}{\beta_A}\frac{\partial T_A(x,t)}{\partial t},\\ \frac{\partial^2 T_M(x,t)}{\partial x^2} &= \frac{1}{\beta_M}\frac{\partial T_M(x,t)}{\partial t} - \frac{q(x,t)}{\kappa_M},\\ \frac{\partial^2 T_S(x,t)}{\partial x^2} &= \frac{1}{\beta_S}\frac{\partial T_S(x,t)}{\partial t},\end{aligned} \tag{11}$$

where κ_k is the thermal conductivity and β_k, the thermal diffusivity of the kth layer. This set of equations has to be completed with boundary conditions for temperature and heat flux continuity

$$\begin{aligned}&T_A(0,t) = T_M(0,t), \quad T_M(R,t) = T_S(R,t),\\ &-\kappa_A\left.\frac{\partial T_A(x,t)}{\partial x}\right|_{x=0} = -\kappa_M\left.\frac{\partial T_M(x,t)}{\partial x}\right|_{x=0},\\ &-\kappa_M\left.\frac{\partial T_M(x,t)}{\partial x}\right|_{x=R} = -\kappa_S\left.\frac{\partial T_S(x,t)}{\partial x}\right|_{x=R} + S(t).\end{aligned} \tag{12}$$

It is also assumed that at the beginning of the diffusion process the temperature of the system is T_0, and the temperature of outer boundaries of the system remains constant

$$T_A(x,0) = T_M(x,0) = T_S(x,0) = T_0,$$
$$T_A(-L_A,t) = T_S(R+L_S,t) = T_0. \tag{13}$$

Because of the complex form of heat sources an analytical solution of the problem described above has not been found. Therefore further analysis has to be carried out numerically.

2.4. Photoacoustic signal

In typical photoacoustic experiments a lock-in signal detection is used, so only the signal component at the modulation frequency ω should be taken into account. The temperature of the top membrane surface can be written as a sum of two components

$$T_M(0,t) = T(t) + \theta_M(t)\exp(i\omega t), \tag{14}$$

where the second term describes the ac temperature component at the frequency ω. According to the classical Rosencwaig–Gersho theory the photoacoustic signal is proportional to this temperature component [7]

$$\mathrm{PAS}(t) = \Gamma\theta_M(t), \tag{15}$$

where Γ is a complex constant. This theory may be applied, when the gas column over the sample is thermally thick. An extension of the Rosencwaig–Gersho theory to arbitrary gas length L_A was proposed by Korpiun and Büchner [8]. These authors took into account the reflection of thermal waves from a glass window closing the cell. Of course it leads to more complex considerations. But in spite of it one can show that with boundary condition (13) Eq. (15) remains correct, but with a different constant Γ. This is why the numerical analysis in the next chapter is restricted to the calculation of the ac component of the temperature at the sample surface θ_M only.

3. Numerical analysis

The analysis of the temperature field in the system under consideration is based on Frankel–Dufort method of solving parabolic differential equations [9]. The method is direct and always convergent. The temperature in the system is calculated on a grid schematically shown in Fig. 5. The temperature at j, $n+1$ node inside each layer is defined by the formula

$$\begin{aligned}
T_A^{j,n+1} &= \frac{1-\varepsilon_A}{1+\varepsilon_A}T_A^{j,n-1} + \frac{\varepsilon_A}{1+\varepsilon_A}\left(T_A^{j+1,n} + T_A^{j-1,n}\right),\\
T_M^{j,n+1} &= \frac{1-\varepsilon_M}{1+\varepsilon_M}T_M^{j,n-1} + \frac{\varepsilon_M}{1+\varepsilon_M}\left(T_M^{j+1,n} + T_M^{j-1,n}\right)\\
&\quad + \frac{1}{1+\varepsilon_M}\frac{q[(j-1)\Delta x_M,(n-1)\Delta t]}{\kappa_M},\\
T_S^{j,n+1} &= \frac{1-\varepsilon_S}{1+\varepsilon_S}T_S^{j,n-1} + \frac{\varepsilon_S}{1+\varepsilon_S}\left(T_S^{j+1,n} + T_S^{j-1,n}\right),
\end{aligned} \tag{16}$$

where $j = 2,3,\ldots,N_k-1$, N_k is the number of space grid points in the kth layer, $\varepsilon_k = 2\beta_k\Delta t\Delta x_k^{-2}$; Δx_k, the space grid increment in the kth layer; Δt, the grid increment in time. The temperature at the interfaces between adjacent layers is calculated using equations

$$\begin{aligned}
T_A^{N_A,n+1} = T_M^{0,n+1} &= \frac{\frac{\kappa_A}{\Delta x_A}\left(4T_A^{N_A-1,n+1} - T_A^{N_A-2,n+1}\right) + \frac{\kappa_M}{\Delta x_M}\left(4T_M^{2,n+1} - T_M^{3,n+1}\right)}{3\left(\frac{\kappa_A}{\Delta x_A} + \frac{\kappa_M}{\Delta x_M}\right)},\\
T_M^{N_M,n+1} = T_S^{0,n+1} &= \frac{\frac{\kappa_M}{\Delta x_M}\left(4T_M^{N_M-1,n+1} - T_M^{N_M-2,n+1}\right) + \frac{\kappa_S}{\Delta x_S}\left(4T_S^{2,n+1} - T_S^{3,n+1}\right) + 2I(R,n\Delta t)}{3\left(\frac{\kappa_M}{\Delta x_M} + \frac{\kappa_S}{\Delta x_S}\right)},
\end{aligned} \tag{17}$$

which is derived from heat flux continuity conditions. The temperature of the outer boundaries of the system according to the conditions (13) remains constant for any n:

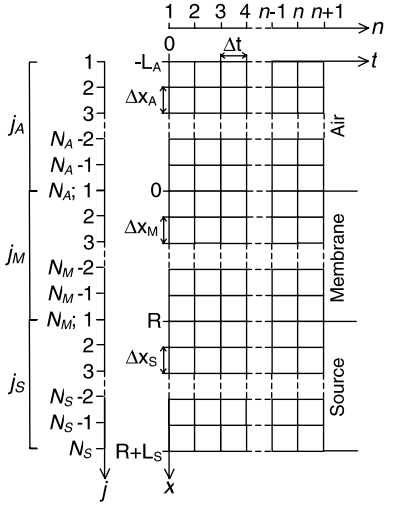

Fig. 5. Space and time grid for the numerical analysis of the temperature field.

$$T_{\mathrm{A}}^{1,n} = T_{\mathrm{S}}^{N_{\mathrm{S}},n} = T_0. \tag{18}$$

As it is mentioned above the Frankel–Dufort method is always convergent. The method is exact, if the time steps are small enough. It means, that time steps should fulfil the condition:

$$\Delta t \ll \min\left(\frac{\Delta x_{\mathrm{A}}^2}{\beta_{\mathrm{A}}}, \frac{\Delta x_{\mathrm{M}}^2}{\beta_{\mathrm{M}}}, \frac{\Delta x_{\mathrm{S}}^2}{\beta_{\mathrm{S}}}, \frac{2\pi}{\omega}\right). \tag{19}$$

The numerical analysis is focused on the influence of different parameters of the model onto the time dependence of the amplitude and the phase of θ_{M}. The phase is calculated relative to the phase of the modulated light. Let us remind that θ_{M} is proportional to the photoacoustic signal. The analysis should also allow to answer the question, if it is possible to obtain quantitative information about the diffusion process from photoacoustic measurements.

The basic dataset for the calculation is as follow:

air layer: $\kappa_{\mathrm{A}} = 2.60 \times 10^{-2}$ W m^{-1} K^{-1}, $\beta_{\mathrm{A}} = 2.18 \times 10^{-4}$ m^2 s^{-1}, $L_{\mathrm{A}} = 350$ μm, $N_{\mathrm{A}} = 20$;
membrane: $\kappa_{\mathrm{M}} = 1.70 \times 10^{-1}$ W m^{-1} K^{-1}, $\beta_{\mathrm{M}} = 1.15 \times 10^{-7}$ m^2 s^{-1}, $R = 20$ μm, $N_{\mathrm{M}} = 20$;
source: $\kappa_{\mathrm{S}} = 2.40 \times 10^{-1}$ W m^{-1} K^{-1}, $\beta_{\mathrm{S}} = 8.53 \times 10^{-8}$ m^2 s^{-1}, $L_{\mathrm{S}} = 60$ μm, $N_{\mathrm{S}} = 20$;
parameters of the diffusion process: $D = 10^{-12}$ m^2 s^{-1}, $\alpha = 10^{-6}$ m s^{-1};
optical constants: $\alpha_0 = 10^4$ m^{-1}, $\alpha_{\mathrm{d}} n_0 = 10^5$ m^{-1};
other parameters: $T_0 = 300$ K, $I_0 = 10^4$ W m^{-2}, $\omega = 1000\pi$ s^{-1}, $N_\Sigma = 20$, where N_Σ is the number of addends of infinite sums taking into account in the calculations.

Thermal parameters of the membrane and the source used in this simulation are similar to thermal parameters of organic materials.

The basic parameter characterising the diffusion process is the diffusion coefficient D. In Fig. 6 the influence of the diffusion coefficient on the time dependence of amplitude and phase of θ_{M} is shown. Based on it one can state that the value of this parameter has a strong impact on the temperature distribution and on the photoacoustic signal. This result might be expected. According to Eq. (4) all characteristic times of the diffusion process are inversely proportional to the diffusion coefficient.

Very interesting is the influence of the mass transfer coefficient D on the analysed dependencies. As it follows from Fig. 7 for a given value of the diffusion coefficient the changes of the mass transfer coefficient have not impact on the diffusion process if this coefficient is large enough. But if this coefficient is very small the diffusion is significantly slowed down. It means that the diffusion process may be controlled by modifications of the properties of the source–membrane interface.

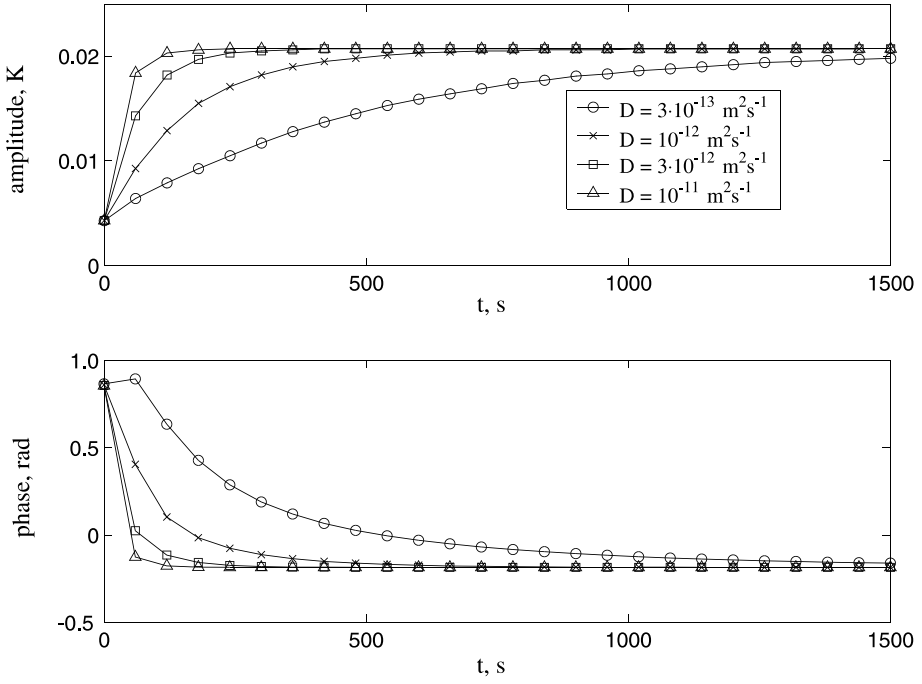

Fig. 6. Time evolution of the ac temperature amplitude and phase at the front membrane surface ($x = 0$) for different diffusion coefficients.

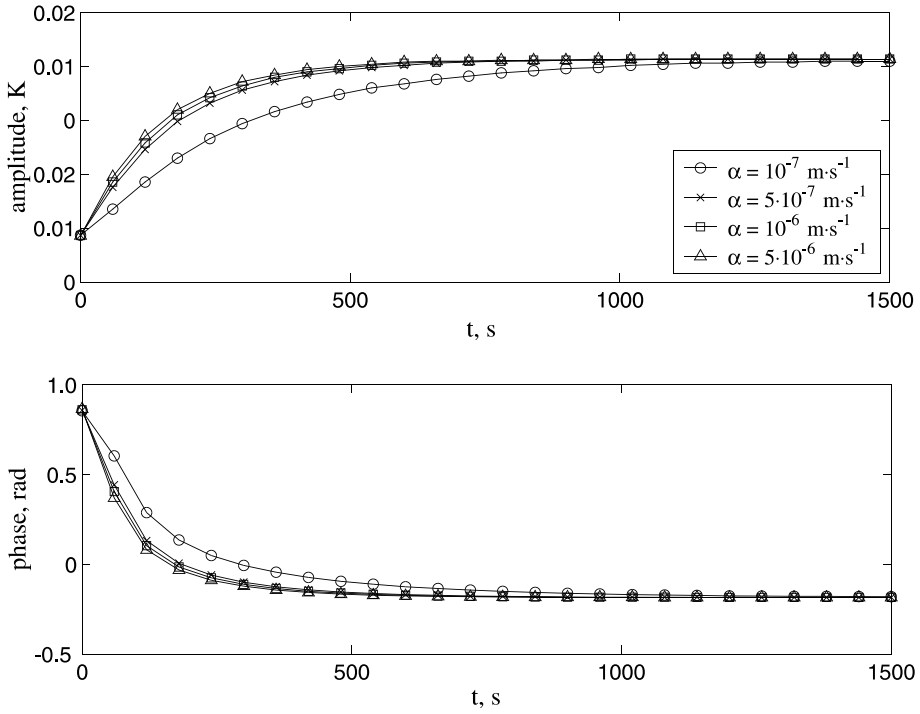

Fig. 7. Influence of the mass transfer coefficient at the membrane–source interface on the time evolution of the ac temperature amplitude and phase at the front membrane surface.

The next group of parameters, which may influence the temperature distribution in the membrane, consists of the thermal properties of the membrane and the source. The numerical analysis shows that in realistic ranges of thermal diffusivities and thermal conductivities for these layers their influence on the time evolution of the temperature at the membrane's top surface is rather weak. From all enumerated parameters the biggest importance for the temperature distribution comes from the thermal diffusivity of the membrane. The thermal diffusivity of the membrane defines the thermal diffusion length

$$\mu_{\mathrm{M}} = \sqrt{2\beta_{\mathrm{M}}/\omega}. \tag{20}$$

This is the thickness of the subsurface layer, from which the information about the temperature disturbance reaches the surface within one modulation period. The properties of this layer may be determined from the photoacoustic signal. As it follows from Eq. (20) the thickness of the layer depends also on the modulation frequency, and the signal changes caused by increasing the thermal diffusivity are similar to the changes caused by decreasing the modulation frequency.

The last group of parameters of the model, which is considered in this analysis, is related to the optical parameters of the membrane and the diffusing matter, or more accurately their absorption coefficients. Dependencies of the temperature of the front membrane surface calculated for different absorption coefficients of the membrane material and the diffusing matter are shown in Fig. 8. More exactly the normalised changes of the temperature amplitude calculated as $[|\theta_{\mathrm{M}}(t)| - |\theta_{\mathrm{M}}(t=0)|]/[|\theta_{\mathrm{M}}(t=1200\ \mathrm{s})| - |\theta_{\mathrm{M}}(t=0)|]$ are shown. It should be emphasised that absolute amplitude changes strongly depend on the absorption coefficient of the diffusing substance and are very small for low values of this coefficient. As it follows from Fig. 8, when the light absorption of the membrane is not too high (in the analysed case not higher than about $10^5\ \mathrm{m}^{-1}$), this parameter practically does not influence the dependence of the relative amplitude on time. On the other hand this dependence apparently changes with variations of the optical properties of diffusing matter. The characteristic time of the analysing dependence becomes apparently shorter for high absorption coefficients of the diffusing matter, as a result of saturation of the photoacoustic signal. When the absorption coefficient of the diffusing matter is very low, the amplitude dependence changes its character. It is interesting to notice, that there are not such distinct changes in the phase dependences. Only for very high membrane absorption the phase remains practically constant.

The aim of the paper is the analysis of the possibility of using the photoacoustic phenomenon for the investigation of a diffusion process. Because of the complexity

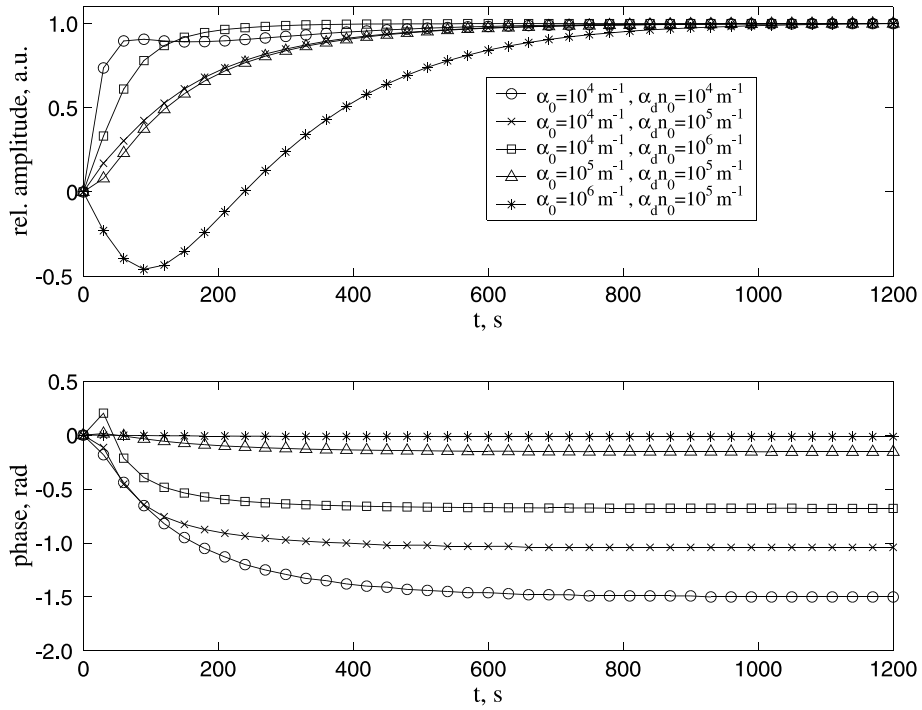

Fig. 8. Time evolution of the normalised changes of the ac temperature amplitude and phase of the front membrane surface for different optical absorption coefficients of the membrane and the diffusing matter.

of the analytical expressions describing heat sources in the considered system, the solution of an inverse problem, i.e. the determination of parameters of the model from experimental data will be difficult. The possible way to overcome this difficulty is using a simplified method for the analysis of the data. As it is shown above, for observation times being long enough the concentration of the diffusing matter may be described by the first term of the infinite sum in Eq. (2) only. But even with such a simplification the formula for the distribution of volume heat sources remains quite complicated. On the other hand preliminary analysis of experimental data carried out in [2] shows that the time dependence of the amplitude of photoacoustic signal can be described by a sum of two exponents. This is why the authors of the present paper have decided to fit the dependencies calculated in numerical analysis with a sum of a few exponents only

$$f(t) = A_0 + \sum_i A_i \exp(-t/\tau_i), \tag{21}$$

where A_i, τ_i are constants, and than to compare the obtained characteristic times with times calculated from Eq. (4). For the majority of the datasets used in the numerical analysis there is a good correlation between the dependences of the signal amplitude calculated from the exact theory and the fitted simplified dependences. For instance for the basic parameter set the correlation between these two dependences is better than 99.99%. It is also very important that the first characteristic time obtained from the fitting procedure is 1.775×10^{-2} s while the theoretically predicted one is 1.787×10^{-2} s. So the difference is less than 1%. But the characteristic time of the second fitted exponent is more than four times longer than the theoretical one. This behaviour was found for almost all analysed cases. The difference between the first characteristic time obtained from the theory and the fitted one is typically smaller than 5%. So one can expect that this time may be easily evaluated from photoacoustic measurements. This difference is higher for a larger diffusion coefficient but the simplified analysis still gives satisfactory evaluation of the first characteristic time. Only when the absorption coefficient of diffusing matter is very high and saturation of photoacoustic signal takes place the simplified analysis leads to characteristic times much shorter than real characteristic times of the diffusion. On the other hand the fitted values of the second characteristic time are quite random.

4. Conclusions

The analysis carried out in the paper shows that the photoacoustic effect may be used for the investigation of

diffusion processes. Changes of concentration of diffusing matter cause changes in the distribution of heat sources, and in combination with absorption of modulated light lead to changes of the photoacoustic signal. As it follows from the theoretical analysis the diffusion process is described by a infinite set of characteristic times, defined by the diffusion coefficient D, the mass transfer coefficient α and the thickness R of the membrane through which the diffusion proceeds. These times are defined by consecutive solutions of Eq. (3). The numerical analysis shows that in the majority of cases, the first characteristic time may be evaluated from photoacoustic measurements using a simple fitting procedure. This information gives a rough estimate on the strength of the diffusion process, which influences the time to the settlement of a homogeneous concentration distribution in the membrane, but is not enough for the determination of $D\alpha^{-1}R^{-1}$. To obtain a value for this combination of parameters one should know at least two consecutive characteristic times with good accuracy. As the higher characteristic times mainly influence the beginning of the diffusion process, where the approximate description cannot be used, the only way to solve the problem is the analysis of the beginning of the process based on exact theory. But such an analysis seems to be rather difficult.

A separate problem is a possible influence on the time dependence of the photoacoustic signal coming from parameters other than those describing diffusion. From the numerical analysis it follows, that the fitted characteristic times are considerably shorter than the theoretically predicted times, when diffusing matter is a very strong light absorber. This conclusion is important, because in photoacoustic experiments the wavelength of light is usually chosen for the absorption peaks of diffusing matter. This assures high changes in the measured signal due to the diffusion component, but may lead to considerable errors. From the analysis follows, that the penetration depth of the light should be comparable with the membrane thickness.

For weak absorption of diffusing matter as well as of the membrane, light can penetrate into the source of diffusion and the assumption, that there is only a surface heat source at the source–membrane interface is not fulfilled. Volume heat sources inside the source of diffusion should be taken into account. But if the membrane is thermally thick this sources do not influence the temperature of the membrane surface. It means that in this case the considered model properly describes the experiments. For the membrane parameters assumed above the membrane is thermally thick for frequencies higher than 180 Hz.

As a summary one can state that photoacoustic measurements give the possibility for the investigation of diffusion, especially its kinetics, in relatively long time periods. It is possible to study the influence of different parameters of the model on the diffusion. For instance the process may be slowed down for low values of the mass transfer coefficient α. When planning an experiment special attention should be paid for proper choose of the modulation frequency and the wavelength of light. It seems to be reasonably to choose such a light wavelength that even for high concentration of diffusing matter light can penetrate all the membrane. Additionally the membrane should be thermally thick to avoid the influence of thermal and optical properties of the diffusion source on the measured signal.

The second part of the paper in which a comparison of theory with the experimental results is done is under preparation.

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