DETERMINATION OF DIFFUSION COEFFICIENTS OF GASES THROUGH A FLAT POLYMERIC MEMBRANE BY THE METHOD OF NON-LINEAR REGRESSION

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Received November 12, 1992
Accepted December 16, 1992

Non-linear regression was applied for calculation of diffusion coefficients of gases through a flat polymeric membrane from the experimental data obtained by the flow permeation method with the thermal conductivity detection of composition of gaseous mixture. To verify this method a polyethylene and carbon dioxide was chosen. Diffusion coefficients of carbon dioxide in the low-density polyethylene of two different thickness at the temperature of 25 °C were determined with precision about ±2.5% in agreement with literature.

The mass transport through an isotropic non-porous membrane caused by the gradient of chemical potential is influenced by properties of both, the membrane and the penetrating substance, being characterized by the diffusion coefficient. Permeation and sorption measurements are two experimental methods commonly used to determine the transport parameters of gases through a membrane[1,2].

The experimental set-up of the differential (flow) permeation method consists of a cell partitioned with a flat membrane. One side of the membrane is flowed round by a carrier gas (at a constant rate) and the second side by a gas (or vapour) whose permeability through the membrane is measured. The sample gas penetrated through the membrane is mixed with the carrier gas, and the composition of the gaseous mixture is determined in terms of the change of thermal conductivity of the system[3 - 6]. The change of thermal conductivity is proportional to the measured gas concentration and is connected with the diffusion flux density of a gas through the membrane which is directly related to the permeability coefficient of the sample gas.

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A source of error in differential permeation method derives from the fact that a measured transient signal always includes contributions of spurious time lags, such as holdup times in feed effluent lines, residence and mixing times in the cell and instrument response times. The aim of present work has been to show that the method of non-linear regression enables to determine the diffusion coefficient of gases in a membrane without the knowledge of experimental spurious time lags values.

THEORETICAL

The mass balance of the sample gas M and the carrier gas N in the upper compartment of the permeation cell at unit area of the membrane yields to the equations (see Fig. 1)

$$V \frac{dc_M}{d\tau} + F_M - J_M = 0, \tag{1}$$

$$V \frac{dc_N}{d\tau} + F_N - G_N + J_N = 0. \tag{2}$$

Since

$$F_M = c_M 0, \tag{3}$$

$$F_N = c_N 0, \tag{4}$$

and assuming that the permeation fluxes J_M and J_N do not affect one another we can obtain from Eqs (*1*) – (*4*) that[5]

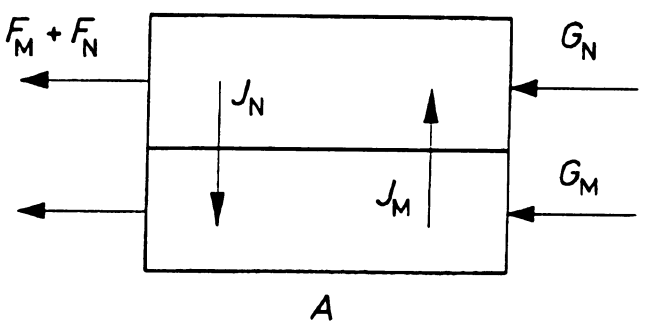

FIG. 1
The mass balance of gases in the permeation cell

$$J_M = V \frac{dc_M}{d\tau} + c_M 0 . \tag{5}$$

The solution of this differential equation for $c_M = 0$ at $\tau = 0$ leads to the relation

$$c_M = \frac{J_M}{0} \left[1 - \exp\left(- \frac{0}{V} \tau \right) \right] , \tag{6}$$

from which it follows that in steady state for $\tau \to \infty$

$$c_{M\infty} = \frac{J_{M\infty}}{0_\infty} . \tag{7}$$

During experiment the flow rates G_M and G_N are kept constant. Therefore a change of the flow rate of gas mixture leaving the cell can be caused by change of the diffusion flux of carrier gas J_M into the carrier gas or by change of the diffusion flux of carrier gas J_N into the sample gas only.

If it is supposed that the ration of $0/0_\infty$ equals to one, than, with respect to Eq. (7), the Eq. (6) can be rearranged to the form

$$\frac{c_M}{c_{M\infty}} = \frac{J_M}{J_{M\infty}} \left[1 - \exp\left(- \frac{0}{V} \tau \right) \right] . \tag{8}$$

The change of the thermal conductivity of the carrier gas is detected by a couple of thermistors as the thermal conductivity detector (TCD) which are installed in the Wheatstone bridge circuit. At the low concentration the dependence of the output voltage of TCD on the volume concentration of sample gas c_M is given by ref.[7]

$$c_M = k U . \tag{9}$$

A combination of Eqs (8) and (9) leads to the relation which expresses the dependence of output voltage of TCD on time

$$U = U_\infty \frac{J_M}{J_{M\infty}} \left[1 - \exp\left(- \frac{0}{V} \tau \right) \right] . \tag{10}$$

Ratio of the density of diffusion flux at time τ to the density of diffusion flux at steady state through the membrane of finite dimensions bounded by planes $z = 0$ and

$z = l$ for constant diffusion coefficient and under the initial and boundary conditions which correspond to experiment, i. e. the constant concentration of sample gas at $z = 0$, constant, zero concentration of sample gas at $z = l$ and zero concentration of sample gas in membrane at $\tau = 0$, is given by refs[4,5,8]

$$\frac{J_M}{J_{M\infty}} = 1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left[-D\,\frac{n^2\pi^2\tau}{l^2}\right]. \qquad (11)$$

The alternative procedure of solution of the given problem stems from the relation which was obtained by Rogers, Buritz and Alpert[9]. Solving the second Fick law under the given initial and boundary conditions they obtained the relation

$$\frac{J_M}{J_{M\infty}} = 2\sqrt{\frac{l^2}{\pi D\tau}}\sum_{m=0}^{\infty} \exp\left[-\frac{(2m+1)^2 l^2}{4D\tau}\right]. \qquad (12)$$

The combination of Eqs (*10*) with (*11*) or (*12*) leads to the expressions

$$U = U_\infty\left[1 - \exp\left(-\frac{0}{V}\tau\right)\right]\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-D\,\frac{n^2\pi^2\tau}{l^2}\right)\right] \qquad (13)$$

and

$$U = 2U_\infty\left[1 - \exp\left(-\frac{0}{V}\tau\right)\right]\sqrt{\frac{l^2}{\pi D\tau}}\sum_{m=0}^{\infty}\exp\left[-\frac{(2m+1)^2 l^2}{4D\tau}\right]. \qquad (14)$$

Equations (*13*) and (*14*) express the dependence of output voltage of TCD on time, diffusion coefficient and thickness of the membrane and enable us to determine the diffusion coefficient of gases through the membrane of given thickness by several different methods including the method of non-linear regression.

Determination of Diffusion Coefficient by Non-Linear Regression

The simplex method[10] solved successfully simulated data. The sum of squared residuals is formulated by

$$S = \sum_{i=1}^{i} (U_{exp} - U_{calc})^2, \qquad (15)$$

where j is the number of experimental points and the model function U_{calc} is defined by Eq. (*13*)

$$U_{calc} = A_1 [1 - \exp(-A_3 (\tau - A_4))] \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{n^2 \pi^2 (A_4 - \tau)}{A_2}\right)\right], \qquad (16)$$

where

$$A_1 = U_\infty \qquad A_2 = l^2/D$$
$$A_3 = 0/V \qquad A_4 = \tau_p \qquad (17)$$

or by Eq. (*14*)

$$U_{calc} = \frac{2 A_1^*}{\sqrt{\pi (\tau - A_4)}} [1 - \exp(-A_3 (\tau - A_4))] \sum_{m=0}^{\infty} \exp\left(\frac{A_2 (2m + 1)^2}{4 (A_4 - \tau)}\right), \qquad (18)$$

where

$$A_1^* = U_\infty (l^2/D)^{1/2} \qquad (19)$$

and A_2, A_3, A_4 being defined by the same relations as in Eq. (*17*).

Parameter A_4 in both model functions represents spurious time lag, i.e. transport delay of gas from the valves to membrane, residence and mixing times in the cell, response time of TCD, etc.

Determination of Permeability Coefficient

The values of U_∞ enable to calculate the permeability coefficient of sample gas by relation[3-6]

$$P = K\, 0\, U_\infty\, l, \qquad (20)$$

where

$$K = (k\, T_0/A\, p_0\, T). \qquad (21)$$

EXPERIMENTAL

Differential permeation method with a thermal conductivity detection of composition of gaseous mixture was used for the experimental determination of membrane transport parameters of gases.

A couple of thermistors installed in the Wheatstone bridge was the thermal conductivity detector (TCD). Output voltage of TCD is proportional to the composition of the gaseous mixture and to the permeation flux as well. Both the composition and the consequently recorded output voltage may change with time up to the constant maximum values which correspond to establishment of steady state.

The permeability and diffusion coefficients can be determined from the maximum value and the time dependence of output voltage if the flow rate of the carrier gas is kept constant and TCD sensitivity is constant, too.

The apparatus for determination of permeability and diffusion coefficients together with operating procedure was described in detail previously[6].

The system polyethylene–carbon dioxide was chosen as a model. Commercial, low-density polyethylene BRALEN (Slovnaft Bratislava, The Slovak Republic) has a density $\rho = 0.92$ g cm^{-3}.

RESULTS AND DISCUSSION

In objective function the sum of an infinite series in Eqs (*16*) and (*18*) is necessary to substitute by the partial sum of series. To accelerate the calculation it is convenient to use the partial sum of series with the lowest number of members. But a great reduction of number of the partial sum of members influences negatively on the accuracy and precision of determination minimum of the objective function.

If in the wide interval of experimental time the expression $\exp(-\tau\ 0/V)$ tends to zero, than the parameter A_3 is in an objective function ill-conditioned and the non-linear regression algorithm does not work. The ill-conditioning this parameter has no influence on an accuracy of other parameters estimated.

Before evaluation of experimental data the objective function and algorithm of non-linear regression were verified on simulated data. System of low-density polyethylene and carbon dioxide at the temperature of 25 °C was chosen as model because for this system a lot of published experimental data[3,4,11] is available.

The determination of global minimum of objective function by evaluation of the experimental data is quite fast. The precision of estimates may be decided on the base of analysis of residuals. Residuals have no trend, their signs change sufficiently. The value of the residuals mean is comparable with the experimental error (see Figs 2 and 3).

The diffusion coefficients on the basis of relations (*16*) – (*19*) were determined, and for determination of permeability coefficients the relations (*20*) and (*21*) with the following experimental parameters were used:

$$k = 8.5897 \cdot 10^{-3}\ \mathrm{V}^{-1},\ 0 = 4 \cdot 10^{-7}\ \mathrm{m}^3\ \mathrm{s}^{-1},\ A = 4.908 \cdot 10^{-4}\ \mathrm{m}^2,\ T = 298.15\ \mathrm{K}.$$

The values of diffusion coefficients and permeability coefficients of carbon dioxide in low-density polyethylene at temperature of 25 °C and membrane thickness $l = 5 \cdot 10^{-5}$ m and $l = 1 \cdot 10^{-4}$ m are given in Table I. The average values of D and P with the standard deviation σ are shown in Table II. The permeability coefficients were calculated with precision of about ±2.0%, the diffusion coefficients with precision about ±2.5%.

The method of moments published by Felder[12] to determine D in the same specimens of polyethylene[13] was also used for comparison, because the Felder's method gives the possibility to determine diffusion coefficients with high precision. The average values of D with the standard deviation are given in Table III.

It is known that permeability and diffusivity of gases depends mainly on the density and degree of crystallinity of polyethylene (PE), on the thickness of polymer samples, on the method of sample preparation and many other factors[2,11]. From this point of view our values of permeability and diffusion coefficients are in relatively good agreement with the literature data, obtained by asymptotic solution of the diffusion equations. Michaels and Bixler[11] published for PE (density $\rho = 0.9137$ g cm^{-3}, volume fraction of amorphous phase $\alpha = 0.57$ and thickness of PE specimens in the range of $2.4 \cdot 10^{-4}$ m to $1.78 \cdot 10^{-3}$ m) the values of $P = 9.474 \cdot 10^{-17}$ m^3(STP) m (m^2 s Pa)$^{-1}$ and $D = 3.72 \cdot 10^{-11}$ m^2 s^{-1}.

Pasternak, Schimscheimer and Heller[4] also used the differential permeation method and published for low-density PE of thickness $l = 8.64 \cdot 10^{-5}$ m, $P = 8.70 \cdot 10^{-17}$ m^3(STP) m (m^2 s Pa)$^{-1}$ and $D = 3 \cdot 10^{-11}$ m^2 s^{-1}, for PE of $l = 12.74 \cdot 10^{-5}$ m, $P = 7.951 \cdot 10^{-17}$ m^3(STP) m (m^2 s Pa)$^{-1}$ and $D = 3.70 \cdot 10^{-11}$ m^2 s^{-1}.

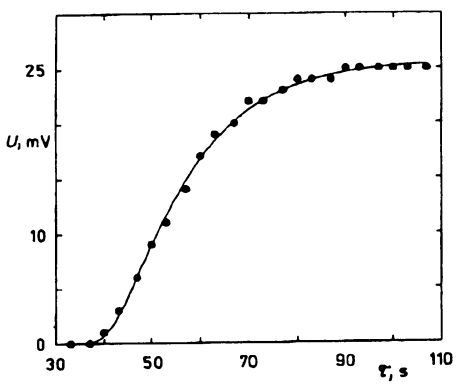

FIG. 2
Time dependence of experimental and calculated output voltage U in experiment No. 15 (see Table I)

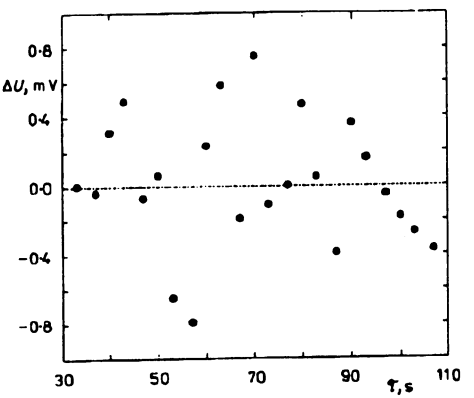

FIG. 3
Time dependence of residuals of experimental and calculated output voltage U in experiment No. 15 (see Table I)

TABLE I
Experimental results in polyethylene–carbon dioxide system at 298.15 K; diffusion, D, and permeability, P, coefficients for membranes of two different thickness, l [a]

No.	$D \cdot 10^{11}$ $m^2\ s^{-1}$	$P \cdot 10^{17}$ $m^3(STP)\ m\ (m^2\ s\ Pa)^{-1}$	No.	$D \cdot 10^{11}$ $m^2\ s^{-1}$	$P \cdot 10^{16}$ $m^3(STP)\ m\ (m^2\ s\ Pa)^{-1}$
1	2.154	8.147	20	4.155	1.187
2	1.615	8.125	21	3.496	1.263
3	1.574	8.356	22	3.470	1.237
4	1.827	8.041	23	3.516	1.111
5	1.993	8.372	24	3.188	1.222
6	1.691	8.363	25	4.092	1.172
7	1.703	8.200	26	4.135	1.126
8	1.818	8.194	27	3.584	1.153
9	1.631	8.181	28	4.101	1.057
10	2.134	7.833	29	3.464	1.121
11	2.014	7.825	30	3.325	1.104
12	1.738	7.672	31	3.298	1.095
13	1.740	7.726	32	3.490	1.159
14	1.779	7.613	33	3.025	1.041
15	1.786	7.776	34	3.407	1.040
16	1.890	7.175	35	3.976	1.005
17	1.762	7.662	36	3.595	1.369
18	2.124	7.381	37	3.756	1.048
19	1.720	7.703	38	3.645	1.067
			39	3.786	1.221

[a] For Nos 1 – 19, $l \approx 5 \cdot 10^{-5}$ m; for Nos 20 – 39, $l \approx 1 \cdot 10^{-4}$ m.

TABLE II
Permeability, P, and diffusion, D, coefficients of CO_2 through PE membrane of thickness l obtained by non-linear regression

l, m	D, $m^2\ s^{-1}$	P, $m^3(STP)\ m\ (m^2\ s\ Pa)^{-1}$
$5 \cdot 10^{-5}$	$(1.826 \pm 0.041) \cdot 10^{-11}$	$(7.913 \pm 0.079) \cdot 10^{-17}$
$10 \cdot 10^{-5}$	$(3.625 \pm 0.073) \cdot 10^{-11}$	$(1.140 \pm 0.020) \cdot 10^{-16}$

TABLE III
Diffusion coefficient, D, of CO_2 through PE membrane obtained by Felder's method of moments[12,13]; l is membrane thickness

l, m	D, $m^2 s^{-1}$
$5 . 10^{-5}$	$(1.871 \pm 0.063) . 10^{-11}$
$10 . 10^{-5}$	$(3.170 \pm 0.061) . 10^{-11}$

It can be concluded that the main advantage of evaluation of experimental data by the non-linear regression consists in fact, that it is not necessary to determine all parameters of given system. Above all, it is not necessary to know exactly the spurious time which is not easy to determine[12]. The method of non-linear regression is generally applicable for any combination of experimental conditions and in comparison to other methods an evaluation of experimental data by this method is possible without simplifying assumptions.

SYMBOLS

A	membrane area, m^2
c	volume concentration of gas
D	diffusion coefficient, $m^2 s^{-1}$
F	flow rate of gas outgoing the cell, $m^3 s^{-1}$
G	flow rate of gas ingoing to the cell, $m^3 s^{-1}$
j	number of experimental points
J	permeation flux of gas, $m^3 s^{-1}$
k	constant of proportionality (determined by calibration of apparatus), V^{-1}
K	constant defined by Eq. (*21*)
l	membrane thickness, m
p_0	standard pressure, 101.325 kPa
P	permeability coefficient, m^3(STP) m $(m^2 s Pa)^{-1}$
S	objective function given by Eq. (*15*)
T	temperature, K
T_0	standard temperature, 273.15 K
U	output voltage, V
V	volume of the upper compartment of the cell, m^3
z	plane position, m
θ	flow rate of gas mixture outgoing the cell, $m^3 s^{-1}$
σ	standard deviation
τ	time, s
τ_p	parasitic time, time lag, time delay, s

Subscripts

M	sample gas
N	carrier gas
∞	steady state
exp	experimental value
calc	model value

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Translated by the author (M. Š.).