DETERMINATION OF DIFFUSION COEFFICIENT OF CARBON DIOXIDE IN POLYETHYLENE BY THE METHOD OF MOMENTS

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By using the method of moments, the values of diffusion coefficients of carbon dioxide in high-pressure polyethylene of two different thicknesses were determined at 25 °C. The values of diffusion coefficients determined with the accuracy of about ±3% are in good agreement both with the values obtained by the optimization method, and with the published values determined on the basis of asymptotic solutions of diffusion equations.

To determine the diffusion coefficients of gases in polymer membranes, the differential or integral permeation method[1,2] is used besides the sorption method. In the differential (flow) permeation method, the membrane is on one side in contact with the measured gas which permeates through the membrane into the carrier gas flowing at a constant velocity on the opposite side of membrane. The time change of concentration of the measured gas in the carrier gas can be monitored on the basis of the thermal conductivity change of gas mixture indicated with a thermal conductivity detector (TCD), e.g., by a pair of thermistors built into the Wheatstone resistance bridge, in the form of voltage signal[3 – 6]. The time dependence of the voltage signal makes it possible to determine the diffusion coefficient of gas in polymer membrane, e.g., by asymptotic solution of diffusion equations[1 – 6].

With the permeation methods it is, however, difficult to determine the time corresponding only to the passage of gas through the membrane for the total time of experiment comprises also the parasitic time connected with the gas transport to the membrane surface. This problem is solved by the Felder method of moments for determining diffusion coefficients[7 – 9] and a new method of determining diffusion coefficients by evaluating experimental data by the method of non-linear regression (so-called optimization)[10].

The aim of this work is to determine diffusion coefficients of gas in membrane by the Felder method and to compare the obtained values above all with the values obtained by the optimization method or by the asymptotic solution of diffusion equations. The

model system polyethylene–carbon dioxide at the temperature of 25 °C was chosen for the experiments.

THEORETICAL

The moment[7] which is defined by the relation

$$\tau_p = \int_0^\infty [1 - (J(t)/J_s)]dt \,, \tag{1}$$

where $J(t)$ is the diffusion flux of the measured gas through the membrane in the dependence on time t and J_s is the steady-state value of this diffusion flux (at time $t \to \infty$), can be utilized for calculating the diffusion coefficient, D, in terms of the relation derived for a so-called time-lag method:

$$D = l^2/(6\tau_p) \,, \tag{2}$$

where l is the membrane thickness. It is possible to prove[9] that the moment τ_p and the time lag are equal.

Experimentally accessible is the quantity τ which is obtained by integrating the time dependence of voltage signal TVD, $m(t)$:

$$\tau = \int_0^\infty [1 - (m(t)/m_s)]dt \,, \tag{3}$$

where m_s is the steady-state value of voltage signal $m(t)$.

On the assumption of linear dependence of voltage signal on diffusion flux[5], Eq. (3) turns into Eq. (1). Quantity t, however, corresponds to the entire measuring system, and therefore it is necessary to determine, on the basis of analysis of moments, the value τ_m which corresponds to the membrane itself.

Considering that the measuring system is a series of its single components (connecting tubes, measuring chamber, membrane, thermistors), it is possible to assign voltage signal $m_i(t)$ to each of them, representing the response to the step concentration change, and a moment, τ_i, defined by the relation

$$\tau_i = \int_0^\infty [1 - (m_i(t)/m_{is})]dt \,. \tag{4}$$

It is possible to prove[8] that all these moments τ_i, which have the physical meaning of mean residence times of gas in single components of measuring system, are additive, i.e.

$$\tau = \sum_{i=1}^{n} \tau_i , \tag{5}$$

On using the flow method with the thermal-conductivity detection of the gas phase composition, it is possible to express the total moment τ as a sum of three contributions:

a) transport delay τ_d corresponding to the transport of gas through the connecting lines;

b) moment τ_k corresponding to the filling of measuring cell with gas;

c) moment τ_m corresponding to the diffusion of gas in membrane:

$$\tau = \tau_d + \tau_k + \tau_m = \tau_r + \tau_m , \tag{6}$$

where τ_r is the spurious moment comprising τ_d and τ_k.

As far as the membrane is excluded from the measuring system, and the response $m_r(t)$ is monitored, it is possible to determine the value of τ_r by numerical integration in terms of Eq. (4). The determination of single values of τ_d and τ_k is no longer substantial for evaluating the experiment (see Eq. (6)).

EXPERIMENTAL

An apparatus based on the differential permeation method with the thermal conductivity detection of the gas mixture composition was used for the experiments whose detailed description along with the procedure of measurement had been published previously[6]. As the material studied, a membrane of high-pressure polyethylene (Bralen; Slovnaft, Bratislava, Slovak Republic) was chosen with density 0.92 g cm^{-3} and of two different thicknesses, about 0.05 mm and 0.1 mm. All the measurements were carried out at the temperature of 25 °C.

For the determination of the spurious moments, the method of impulse characteristics was chosen for the voltage response $m_r(t)$ is too high so that the condition of its linear dependence on concentration[5] is not fulfilled. It was necessary to determine the course of response $m_r(t)$ by the numerical integration of the unit impulse response, $g_r(t')$:

$$m_r(t) = \int_0^t g_r(t') dt' , \tag{7}$$

$$m_{rs} = \int_0^\infty g_r(t') dt' . \tag{8}$$

Since it was not possible to exclude entirely the membrane from the measuring cell (pressure shocks would have taken place), the membrane was replaced by a very permeable layer of unsized paper. Values of τ_r were found on the basis of Eqs (4), (7) and (8) from the impulse characteristics for various numbers of paper layers to be able to determine, by extrapolating, the value of τ_r^0 corresponding to the state when the membrane would be completely excluded. In this way, the value

$$\tau_r^0 = 38 \text{ s}$$

was found out.

The value of τ_r^0 is, however, subject to a certain error resulting from the assumption that the ratio of diffusion fluxes is equal to the ratio of voltage signals[5]. In fact, the relation

$$J/J_s = (m/m_s) \{1 - \exp[-\alpha(t - \tau_d)]\}^{-1} \quad (9)$$

holds where $\alpha = v/V$, v is the flow rate of carrier gas (24 cm^3 min^{-1}), V is the volume of the cell measuring compartment (2.454 cm^3). The corrected value determined on the basis of Eqs (1) and (9) is then

$$\tau_{r, corr}^0 = 37 \text{ s} .$$

During the measurements of diffusion coefficients of carbon dioxide in polyethylene, the moment τ is calculated in terms of Eq. (3), the correction with respect to Eq. (9) not being necessary to carry out as it was when calculating τ_r. In case of the polyethylene–carbon dioxide system, the time of experiment is so long that the assumption of equality of the ratio of diffusion fluxes and the ratio of voltage signals is then justified (see Eq. (9)), and the caused error in value τ does not exceed ±0.1 s. The diffusion coefficient is calculated from Eq. (2) where

$$\tau_p = \tau_{m, corr} \approx \tau - \tau_{r, corr}^0 . \quad (10)$$

RESULTS AND DISCUSSION

The values of diffusion coefficients of carbon dioxide in high-pressure polyethylene (PE) are given in Table I for the thickness of about 0.05 mm and in Table II for the thickness of about 0.1 mm. For the comparison, the values of diffusion coefficients determined by the method of non-linear regression (so-called optimization)[10] are given in Tables I and II as well, the non-differentiating method of flexible polyhedron (Simplex) having been chosen as an algorithm. The model function consists in the solution of the 2nd Fick law according to Rogers et al.[11] rearranged to the form suitable for optimization:

$$m_{\text{model}} = 2 A_1 \frac{1}{\sqrt{(\pi (t - A_4))}} \{1 - \exp[-A_3 (t - A_4)]\} \sum_{m=0}^{\infty} \exp[-\frac{(2 m + 1)^2 A_2}{4 (t - A_4)}] \quad (11)$$

with the parameters $A_1 = m_s \sqrt{(l^2/D)}$, $A_2 = l^2/D$, $A_3 = v/V$, $A_4 = \tau_z$,

where τ_z is a so-called effective transport lag. The mean value of τ_z found by optimizing is 37 s, which is quite in agreement with the value of spurious moment, $\tau_{r, corr}^0$.

The diffusion coefficient of CO_2 in PE of the thickness 0.05 mm has an average value $(1.871 \pm 0.063) . 10^{-11}$ m^2 s^{-1}, the average error of arithmetic mean being given

in parenthesis. The average value found by the optimization method is (1.826 ± 0.041) . 10^{-11} m^2 s^{-1}. It is apparent that both the values are in very good agreement.

In case of PE of thickness 0.1 mm, the mean value of diffusion coefficient of CO_2 (3.170 ± 0.061) . 10^{-11} m^2 s^{-1} was measured whereas the optimization method gives the result (3.625 ± 0.073) . 10^{-11} m^2 s^{-1}. The agreement of these results is no more so good which can be accounted for by the fact that thicknesses of single used specimens of thicker PE were rather different (see Table II), and these differences were reflected on the greater scatter of values obtained by the optimization method. Nevertheless if we calculate the standard deviation, s, which is for the method of moments ± 0.274 . 10^{-11} m^2 s^{-1} and for the optimization method ± 0.328 . 10^{-11} m^2 s^{-1}, we can state that even in this case, the results of both the methods are commensurable.

It is well-known that the diffusion coefficients of gases depend mainly on the PE density, on the membrane thickness and on the way of its preparation and furthermore on a number of other factors[2,12]. From this point of view, the values of diffusion coeffi-

TABLE I
Values of diffusion coefficient, D, of carbon dioxide in polyethylene of thickness $l \approx 0.05$ mm at the temperature of 25 °C (D_{optim} is diffusion coefficient obtained by optimization)

l . 10^5, m	D . 10^{11}, m^2 s^{-1}	D_{optim} . 10^{11}, m^2 s^{-1}
4.9	2.042	2.154
	1.366	1.615
	1.450	1.574
	1.576	1.827
4.8	1.864	1.993
	1.607	1.691
	1.662	1.703
	1.613	1.818
4.8	1.530	1.631
	2.032	2.134
	2.182	2.014
4.9	2.011	1.738
	2.140	1.740
	1.991	1.779
	2.151	1.786
4.9	2.011	1.890
	2.128	1.762
	2.011	2.124
	2.175	1.720

cients measured by us are in relatively good agreement with the published values obtained by asymptotic solution of diffusion equations. For instance, Michaels and Bixler[12] report for PE of density 0.9137 g cm^{-3} and of membrane thickness within 2.4 . 10^{-4} to 1.78 . 10^{-3} m, the value of diffusion coefficient of CO_2 equal to 3.72 . 10^{-11} m^2 s^{-1}. Pasternak et al.[4] used also the differential permeation method and obtained the value of diffusion coefficient of CO_2 equal to 3 . 10^{-11} m^2 s^{-1} for high-pressure PE of the membrane thickness 8.64 . 10^{-5} m and the value 3.7 . 10^{-11} m^2 s^{-1} for the membrane thickness 12.74 . 10^{-5} m.

The main advantage of the moment method and the optimization method is the possibility of eliminating the parasitic time when calculating the diffusion coefficients. In the moment method, this parasitic time can be directly experimentally determined as an apparatus constant. On the other hand, in the optimization method, the parasitic time is

TABLE II
Values of diffusion coefficient, D, of carbon dioxide in polyethylene of thickness $l \approx 0.1$ mm at the temperature of 25 °C (D_{optim} is diffusion coefficient obtained by optimization)

l . 10^5, m	D . 10^{11}, m^2 s^{-1}	D_{optim} . 10^{11}, m^2 s^{-1}
10.9	3.311	4.155
	3.793	3.496
	3.345	3.470
	3.173	3.516
9.9	3.347	3.188
	3.432	4.092
	3.123	4.135
	3.148	3.584
9.9	3.053	4.101
	3.111	3.464
	3.117	3.325
	2.896	3.298
10.1	3.014	3.490
	2.729	3.025
	2.774	3.407
	2.896	3.976
12.9	3.698	3.595
	3.529	3.756
	2.941	3.645
	3.232	3.786

one of parameters of model function, and therefore it can be obtained as a result of non-linear regression.

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