

Application of Thermal Conductivity Detection for Investigating the Diffusion of Component X in the System: A Mixture of Vapors of X and Y Substances–Polymer Membrane–Y Substance Vapor

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Synopsis

Thermal conductivity detection has been applied for determining the mass transport coefficients of vapor through polymer membranes in the presence of another vapor being in equilibrium with polymer. Apparatus and measuring technique have been described. Diffusion, permeability, and solubility coefficients have been determined for systems comprising polyethylene membrane and two-component vapor mixtures of selected substances. It has been found that the presence of nonpolar substances affected diffusion, permeability, and solubility coefficients of polar penetrants in the systems investigated. Analysis of the results obtained in evaluating the possibility and correctness of the determination of diffusion and permeability coefficients derived from mathematical descriptions of the process of permeating a single substance has been carried out.

INTRODUCTION

In the classical partition-cell techniques for determining the diffusion coefficient D and permeability coefficient P of gases and vapors through polymer membranes, a quantity of permeating agent is usually determined volumetrically or manometrically. The partition-cell technique may be also applied for investigating the mass transport of mixtures of gases and vapors after its proper adaptation relying upon a selective detection of mixture components. Recently, there have been published more and more works dealing with mass transport problems in which chromatography or its elements have been applied.¹⁻⁹ Two research trends may be distinguished among them. In some of the papers,^{1-5,8} the application of thermal conductivity detector was described. It is placed in a carrier gas flux (usually H_2) flowing through one part of diffusion cell at a penetrant's downstream side. The second part of diffusion cell is supplied with a mixture of carrier gas and vapor under examination. A detector's signal quantity is proportional to the downstream mass flux of the penetrant. The recorded signal changes with time make it possible to determine diffusion and permeability coefficients of vapor, assuming that a carrier gas is "inert."

Other works deal with permeation process of the mixtures of gases or vapors through polymer membranes.⁶⁻⁹ In this case, the measurement of changes in the thermal conductivity of a mixture flowing out of the diffusion cell is not sufficient to determine the mass transport coefficients, due to

the fact that the detector signal is affected by all the fractions of particular mixture components. For this reason, the carrier gas eluting the components of the penetrating mixture is periodically supplied to a chromatographic column for their resolution and quantitative determination. The measuring techniques used for investigating the permeation process of gas or vapor mixtures, described in the literature cited, should be, in our opinion, critically compared with permeation models assumed in the methods for determining the D and P coefficients with the conditions of the used techniques. Both D and P coefficients are determined from analytical formula describing the models of permeating the single penetrant. These formula do not consider the effect of mixture components on the distribution of their concentrations within a polymer membrane in a function of time and space. It results in a discrepancy between the data obtained by different authors.

The aim of this work is to present the method based on thermal conductivity detection for determining the diffusion and permeability coefficients of vapor in the presence of another vapor being in equilibrium with polymer membrane. The D and P coefficients determined by the technique described can be used in basic research dealing with the mass transport mechanisms of mixtures through polymer membranes, as well as for practical purposes concerning the separation of gaseous mixtures by means of polymer membranes.

EXPERIMENTAL

For experiments, the following elements of the Chrom 41 chromatograph were used: flow controller, thermostatic chamber, and detector TC with supply. The diffusion cell having inserted therein a polyethylene foil under test was mounted in place of chromatographic columns. The diffusion cell was made of stainless steel. It was divided into two parts by means of the polymer membrane. A detector signal was relayed to compensator equipped with the TZ 21S type recorder. The measurements were carried out applying 90-mA bridge current. A carrier gas (hydrogen) was supplied to the flow controller through absorbers containing a drying agent therein. The mixtures of carrier gas and vapors were prepared by saturating the gas flux in a thermostatic vaporizer which was filled with a liquid to be tested, followed by diluting it with the carrier gas to the concentration required. Two procedures of preparing the vapor mixtures were used depending on a solubility of mixture components in a liquid phase. In the case of the X and Y components, practically insoluble in a liquid phase, the flow system shown schematically in Figure 1 was used. In this system two streams of carrier gas I and II have been saturated with vapor of substance Y in saturators 10 and 12. Saturators were double, connected in a row washers, equipped with bubblers of sintered glass and filled with liquid substance Y. The washers were thermostated with measuring accuracy ± 0.1 K. The stream of carrier gas after passing through the saturator achieved the state of vapor saturation, determined by the pressure of saturated vapor p^0 , corresponding to temperature of a liquid in washers.

Valves 4 and 7 enabled dilution of saturated with vapor gas streams I

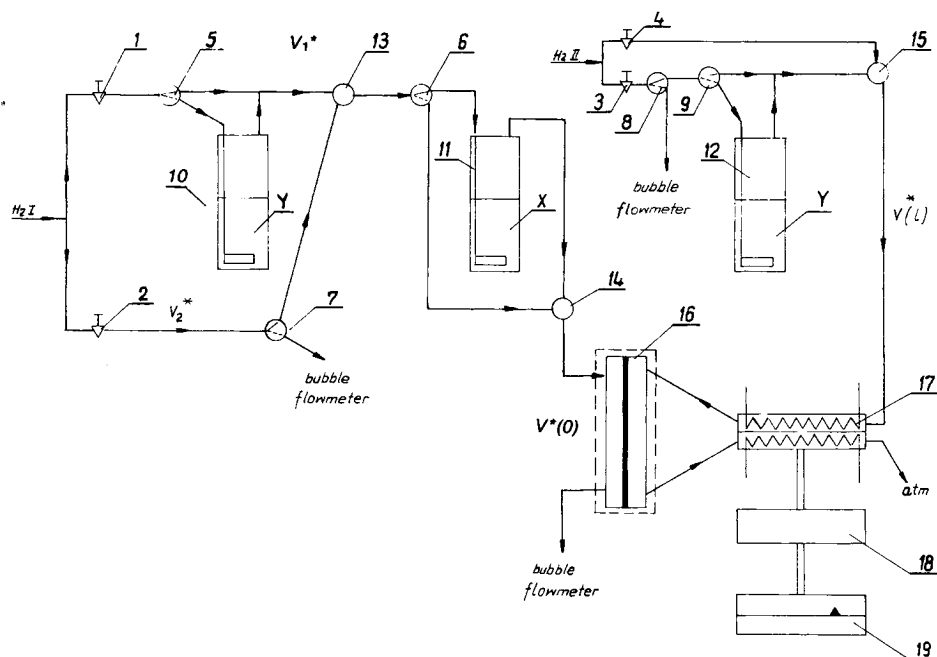


Fig. 1. Diagram of the measuring system for determining the permeability of substance X vapor in the presence of substance Y vapor (immiscible liquids in a liquid phase): (1-4) flow control valves; (5-9) three-way valves; (10-12) thermostatic vaporizers; (13-15) agitators; (16) diffusion cell; (17) detector TC; (18) detector supply; (19) recorder.

and II up to the required partial pressure of the component Y. Within the system of getting mixtures in the places of gases in flow with different composition there were placed mixers 13, 14, and 15, where a strong streams swirl took place, which ensured mixtures homogenization.

One of the streams (determined with symbol I on Figure 1) was sent by means of an adequate setting of a multiway valve 6 either directly or through the vaporizer 11 with liquid X to one chamber of diffusion cell and then into the atmosphere. By taking into consideration the insolubility of substances X and Y in the liquid phase, the partial pressure of the component Y in the mixture brought upstream to the diffusion cell depends on the temperature of vaporizer 10 and on the relation of volumetric rate of flow of the gas carrier V_1^* and V_2^* .

Pressure of penetrant's vapor X equals to saturated vapor pressure (p_X^0) in the vaporizer 11 temperature. Such a system of making mixtures made possible carrying out measurements of vapor X permeability when $p_X = p_X^0$ and when component Y had variable partial pressure within the range from 0 to p_Y^0 .

Component intensity of flow V_1^* and V_2^* was measured separately by means of bubble flow meters and, by the same method, the total intensity flow of mixture outflowing from the diffusion cell. These measurements formed a control of partial mixture components pressure additivity and enabled calculation of p_Y partial pressure. Flux of carrier gas II flows through one branch of TC detector, further through the second chamber of

diffusion cell (downstream) to the second detector's branch and from it into the atmosphere. Partition of this flux by means of 3 and 4 cocks and steering by its one part to the saturator 11 enables the getting of a mixture, which has the same partial pressure value Y as in the flux of gas I.

In the case of vapor mixture of the X and Y substances characterized by an unlimited solubility in a liquid phase, the measuring system presented schematically in Figure 2 was used. Such a character of mutual solubility required a separate preparation of carrier gas mixture and vapor of substance Y , as well as a mixture of a carrier gas and vapor of substance X , and then their mixing in a proper relation. A proper selection of particular rates of flow V_1 , V_2 , and V_3 measured at the valves 2, allowed one to prepare vapor mixtures of the required composition. This system made it possible to perform measurements for mixtures of the following composition:

$$0 < p_X < \frac{V_3 \cdot p_X^0}{V_1 + V_3} \quad \text{and} \quad 0 < p_Y < \frac{V_1 \cdot p_Y^0}{V_1 + V_3}$$

where

$$p_X = \frac{V_3 \cdot p_X^0}{V_1 + V_2 + V_3} \quad \text{and} \quad p_Y = \frac{V_1 \cdot p_Y^0}{V_1 + V_2 + V_3}$$

Prior to the measurement, the flow velocities of the carrier gas were adjusted and determined for both systems, i.e., immiscible liquids. The same

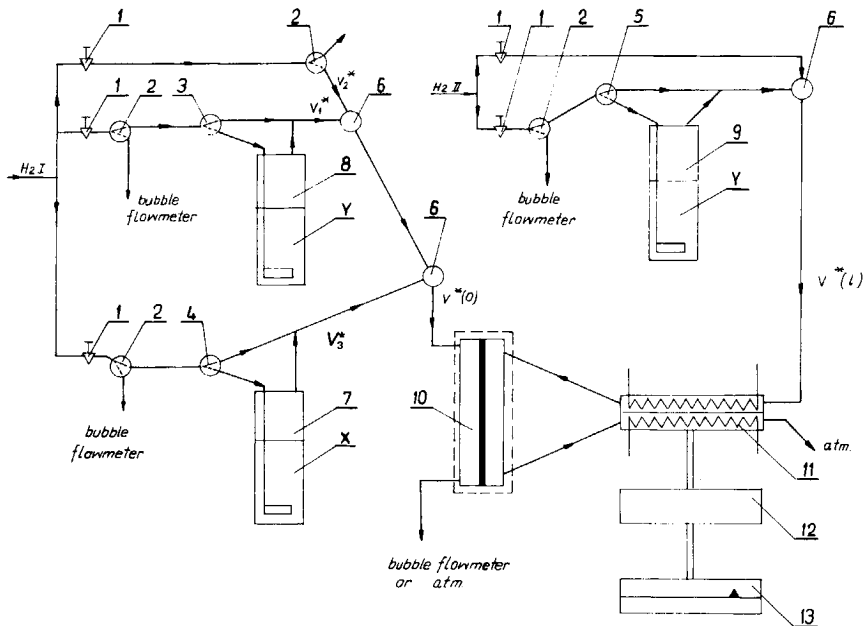


Fig. 2. Diagram of the measuring system for determining the permeability of substance X vapor in the presence of substance Y vapor (miscible liquids in a liquid phase): (1) flow control valves; (2-5) three-way valves; (6) agitators; (7-9) thermostatic vaporizers; (10) diffusion cell; (11) detector TC; (12) detector supply; (13) recorder.

intensity quantities of a carrier on both sides of membrane as well as open to atmosphere outlets of both diffusion cell chambers are causes of the same total pressure on both its sides. When reaching a proper stability of the measuring system (basic zero line), the multiway valves were adjusted in such a way that both sides of polymer membrane were in contact with the carrier gas and Y substance vapor fluxes. When a proper zero line was attained, then the measurement was started by supplying the appropriate carrier gas flux through the liquid X containing vaporizer. A signal recorded was proportional to the mass of the X component permeating the membrane in the diffusion cell. Typical record of change of the U signal quantity against time is shown in Figure 3.

The record was then used to calculate the diffusion coefficient of the X substance vapor in the presence of the Y substance vapor based on the Ziegel's method,² in which the analytical formula has a form as follows:

$$D = \frac{l^2}{7.199 \cdot t_{1/2}} \quad (1)$$

For a steady state permeation, the function given below is also correct:

$$\lim_{t \rightarrow \infty} \frac{dQ_t}{dt} = Q_{X,\infty}^* = P \cdot \frac{A}{l} \cdot p_X(0) \quad (2)$$

Furthermore, the permeation rate of the penetrant through a membrane is proportional to the product of detector signal U_∞ and carrier gas volume flow $V^*(l)$ at the downstream side of the membrane, i.e.,

$$Q_{X,\infty}^* = \alpha U_\infty V^*(l) \quad (3)$$

$$\alpha = \frac{P_{\text{cal}}}{U_{\text{cal}}} \quad (4)$$

Finally, eq. (2)–(4) can be transformed to the formula

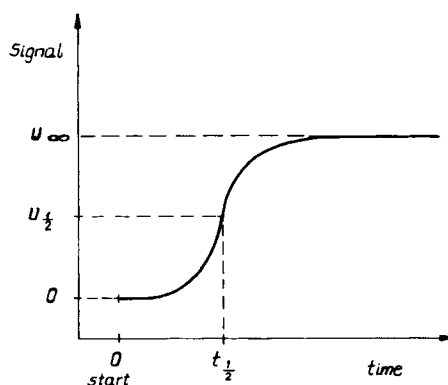


Fig. 3. Typical signal record in the measurement of vapor permeability through polymer membrane.

$$P = \frac{l}{A} V^*(D) \frac{U_{\infty} P_{\text{cal}}}{U_{\text{cal}} p_X(0)} \quad (5)$$

which in turn is used for calculating the permeability coefficient.

The α factor was determined when calibrating the detector. The calibration procedure comprised the flow of a mixture of carrier gas and Y vapor through one detector TC branch and the simultaneous flow of a mixture of carrier gas and X and Y vapors of different X component partial pressure. The calibration plots of U against p_X were then used to calculate the α factor. In Figure 4 there are shown several calibration plots.

RESULTS AND DISCUSSION

The suitability of the method for determining the D and P coefficients described therein has been evaluated based on the measurements performed for different combinations of two-component mixtures comprising carbon tetrachloride, benzene, *n*-heptane, methanol, and water. All the measurements were carried out at a temperature of 303 K using a commercial polyethylene membrane of 0.919 g/cm³ in density and $36 \pm 3 \mu\text{m}$ thickness.

Table I shows the effect of water vapor on both D and P coefficients of carbon tetrachloride, benzene, and *n*-heptane. It can be seen that the presence of water vapor affects these quantities. Generally, they are several percent lower in comparison with corresponding quantities determined when water vapor was absent. Assuming that the mass transport process in the systems under examination may be described by Fick's and Henry's laws, then it is possible to determine the S solubility coefficient from the equation $P = S \times D$. The results obtained prove that solubilities of carbon tetrachloride and *n*-heptane do not change in the presence of water vapor

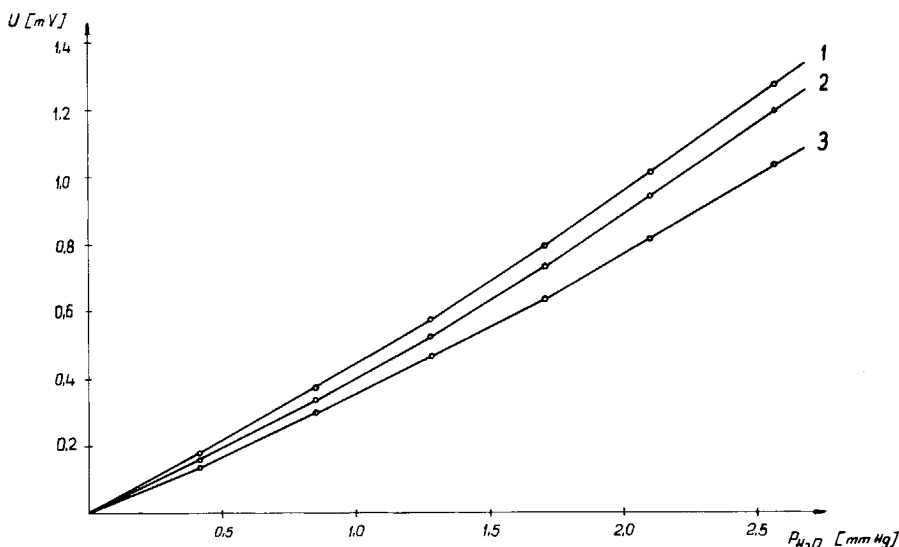


Fig. 4. Calibration curves for TC detector: (1) plot of $U = f'(p_{\text{H}_2\text{O}})$ in the absence of another vapor; (2) plot of $U = f'(p_{\text{H}_2\text{O}})$ in the presence of *n*-C₇H₁₆ (3.5 mm Hg); (3) plot of $U = f(p_{\text{H}_2\text{O}})$ in the presence of *n*-C₇H₁₆ (10.5 mm Hg).

TABLE I
 Diffusion, Permeability, and Solubility Coefficients of Vapors of Nonpolar Substances (X) in Presence of Water Vapor (Y)^a

No.	X	Substance		$D_X \times 10^8$ (cm ² /s)	$P_X \times 10^6$ [cm ³ (STP)/cm s mm Hg]	$S_X = P_X/D_X$ [cm ³ (STP)/cm ³ mm Hg]
		$P_X(O)$ (mm Hg)	Y			
1	CCl ₄	89.6	H ₂ O	0.69	0.65	0.94
				0.57	0.50	0.88
2	n-C ₇ H ₁₆	35.4	H ₂ O	1.10	1.26	1.15
				0.80	1.07	1.34
3	C ₆ H ₆	74.7	H ₂ O	0.83	1.18	1.42
				0.72	1.35	1.87

^a $T = 303 \pm 0.5$ K.

TABLE II
 Diffusion, Permeability, and Solubility Coefficients of Water Vapor (X) in Presence of Nonpolar Substance Vapor (Y)^a

Substance		$p_x(O)$ (mm Hg)	Y	p_y (mm Hg)	$D_x \times 10^8$ (cm ² /s)	$P_x \times 10^8$ [cm ³ (STP)/cm s mm Hg]	$S_x = P_x/D_x$ [cm ³ (STP)/cm ³ mm Hg]
1	X		—	—	2.9	0.44	0.15
2	H ₂ O	17.5	CCl ₄	89.6	1.9	1.31	0.69
3			n-C ₇ H ₁₆	35.4	2.0	0.82	0.41
4			C ₈ H ₆	74.7	2.1	0.49	0.23

^a $T = 303 \pm 0.5$ K.

within experimental error limits. A measurable increase of solubility coefficient of benzene indicates that benzene becomes more soluble in polyethylene under the influence of water vapor.

The effect of CCl_4 , $n\text{-C}_7\text{H}_{16}$, and C_6H_6 vapors on both diffusion and permeability coefficients of water vapor is completely different. Table II shows that in all the cases the values of D decrease while those of P increase. Diffusion coefficient of water vapor decreases by about 25%, whereas its permeability coefficients increase variedly, i.e., four times in the presence of carbon tetrachloride vapor and only 1.5 times when benzene is present. It can be explained by a greater solubility of water vapor in polyethylene in the presence of nonpolar substances. The increase of water solubility in polyethylene can be attributed to a change of intermolecular interaction between polymer and penetrant in the presence or absence of the Y component. Hence, the examined substances can be ordered in terms of their interaction power in the following succession:



Due to the fact that carbon tetrachloride affects most significantly the diffusion and permeability coefficients of water vapor through polyethylene membrane, it was decided to perform a series of measurements aiming at determination of the effect of its concentration of these quantities. The results obtained were compiled in Table III and in Figure 5. It was found that the value of water vapor permeability coefficient increased three times while the value of diffusion coefficient decreased by about 30% at a partial pressure of CCl_4 vapor equal to about 90 mm Hg in comparison with corresponding values found in absence of carbon tetrachloride. It corresponds with 5.5 times increase of water vapor solubility in polyethylene.

Table IV presents diffusion and permeability coefficients of methanol vapor in the presence of water vapor. It can be stated that the presence of water vapor does not affect the D and P values of methanol vapor. The differences are insignificant and fall within experimental error limits, however, when increasing the water vapor partial pressure the D value increases, while the P value decreases.

In Table V there are collected the methanol vapor permeability data determined in the presence of carbon tetrachloride vapor of different partial pressure. It may be seen that the increase of carbon tetrachloride vapor

TABLE III
Effect of Partial Pressure of CCl_4 Vapor (Y) on Diffusion, Permeability, and Solubility of Water Vapor (X)

No.	$P_{\text{H}_2\text{O}}$ (mm Hg)	P_{CCl_4} (mm Hg)	$D_{\text{H}_2\text{O}} \times 10^8$ (cm^2/s)	$P_{\text{H}_2\text{O}} \times 10^8$ [cm^3 (STP)/ cm s mm Hg]	$S = P/D$ [cm^3 (STP)/ $\text{cm}^3 \text{ mm Hg}$]
1		—	2.95 ± 0.14	0.43 ± 0.04	0.15
2		8.4	2.74 ± 0.17	0.50 ± 0.02	0.18
3	14 ± 1	16.7	2.43 ± 0.20	0.67 ± 0.02	0.28
4		25.0	2.20 ± 0.15	0.89 ± 0.02	0.40
5		89.6	1.90 ± 0.16	1.31 ± 0.03	0.69

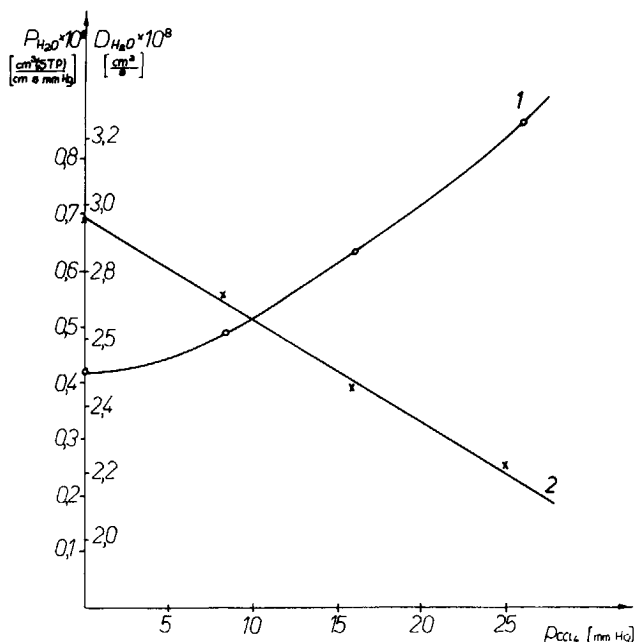


Fig. 5. Plots of permeability (curve 1) and diffusion coefficients (curve 2) of water vapor vs. CCl_4 vapor partial pressure.

partial pressure affects the double increase of methanol vapor permeability coefficient. For these systems it was not possible to determine the D coefficient, due to anomalous course of the permeation curves shown in Figure 6. The distinct inflexions are observed on the curves 2 and 3, i.e., plots of $U = f(t)$. Anomalous course of the permeation curves does not make it possible to apply eq. (1) for determining D . The occurrence of inflexions can be explained by great changes in solubility of CCl_4 in polyethylene membrane under the influence of methanol vapor. Due to the decrease of CCl_4 solubility it becomes partly desorbed from the foil. A stream of desorbed CCl_4 causes an increase of the detector's signal value. Value of this signal is namely a sum of two components, corresponding to two processes: methanol's permeation and CCl_4 desorption from the membrane. These processes have different time courses. Permeation aims at establishing a stationary state and corresponding to it stationary value of signal component. On the

TABLE IV
Effect of Water Vapor (Y) Partial Pressure on Diffusion and Permeability Coefficients of Methanol Vapor (X)^a

No.	$P_{\text{CH}_3\text{OH}}$ (mm Hg)	$P_{\text{H}_2\text{O}}$ (mm Hg)	$D_{\text{CH}_3\text{OH}} \times 10^8$ (cm^2/s)	$P_{\text{CH}_3\text{OH}} \times 10^8$ [cm^3 (STP)/ cm s mm Hg]
1		—	3.30 ± 0.05	0.15 ± 0.01
2	56.4	1.4	3.48 ± 0.07	0.15 ± 0.01
3		2.8	3.57 ± 0.07	0.16 ± 0.01
4		4.3	3.67 ± 0.07	0.16 ± 0.01

^a $T = 303 \pm 0.5$ K.

TABLE V
Effect of Partial Pressure of CCl_4 Vapor (Y) on Diffusion and Permeability Coefficients of Methanol Vapor (X)^a

No.	$P_{\text{CH}_3\text{OH}}$ (mm Hg)	P_{CCl_4} (mm Hg)	$D_{\text{CH}_3\text{OH}} \times 10^8$ (cm^2/s)	$P_{\text{CH}_3\text{OH}} \times 10^8$ [cm^3 (STP)/ cm s mm Hg]
1	56.4	—	3.30 ± 0.05	0.15 ± 0.01
2	55.1	7.0	^b	0.21 ± 0.02
3	55.3	14.1	^b	0.27 ± 0.02
4	57.5	22.2	^b	0.33 ± 0.02

^a $T = 303 \pm 0.5$ K.

^b Anomalous course of permeation curves.

other hand, CCl_4 desorption ends when it achieves a new state of dissolution equilibrium. Corresponding to this process signal component achieves zero value within a determined time. Hence the experimental curves $U = f(t)$ allow one merely to determine the permeability coefficient on the ground of final signal value U_∞ .

The effects of this type were not observed in case of a discussed system $\text{PE}(\text{CCl}_4)\text{-H}_2\text{O}$, although the penetrating agent (water vapor) is also a polar substance. These various sorption-diffusion properties of systems $\text{PE}(\text{CCl}_4)\text{-H}_2\text{O}$ and $\text{PE}(\text{CCl}_4)\text{-CH}_3\text{OH}$ are—in our opinion—strictly connected with the different solubility character of liquid systems $\text{CCl}_4\text{-H}_2\text{O}$ and $\text{CCl}_4\text{-CH}_3\text{OH}$. In the first case the components are in practice insoluble; in the second case we have to do with the unlimited solubility.

Summing up, we can assume that in the investigated systems there is a great influence of nonpolar component vapor upon the values of diffusion coefficients and permeability of polar substance vapor (see Tables II, III, and V). It concerns both the components of unlimited solubility and those which are in practice insoluble in the liquid state.

Polyethelene as a solid crystalline homopolymer can be described as a two-component system, with spatially partitioned phases: amorphous and crystalline. The presence of micromolecular substance in the amorphous

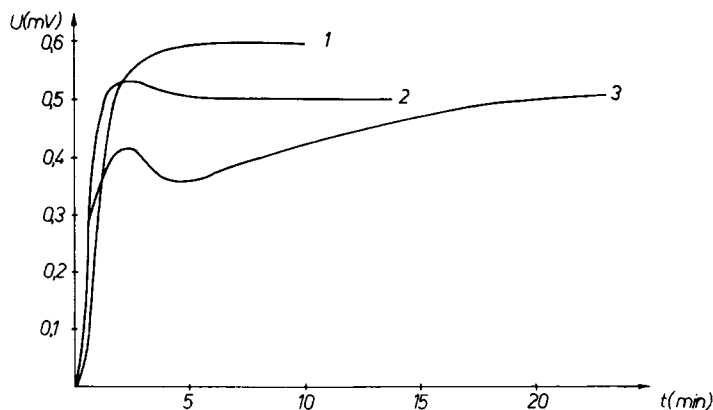


Fig. 6. Permeation curves of methanol vapor: (1) in the absence of CCl_4 vapor; (2) in the presence of CCl_4 vapor (7.0 mm Hg); (3) in the presence of CCl_4 vapor (22.5 mm Hg).

areas may bring a plastifying effect on the tangled polymer's chains. As a consequence, they are locally partitioned by mobile small particles.

In the case of a great substance sorption, the amorphous component becomes swollen. The presence of a crystalline phase protects from a change of specimens shape. As a result the change of polymer foil thickness cannot be observed in case of investigated non-polar substance vapors.

The presence of polar water stream (see Tables I and IV) does not influence in practice the change of diffusion coefficients value and penetrants permeability. It concerns both the polar (CH_3OH) and nonpolar penetrants (CCl_4 , $n\text{-C}_7\text{H}_{16}$, C_6H_6). It is of no importance whether mixture components in liquid phase are soluble or insoluble with each other.

The technique described can be used for determining the mass transport coefficients of one component through membranes in the presence of the second one being in equilibrium with polymer. It concerns mainly the permeability coefficients which are determined when permeation approaches a steady state. Under conditions of performing the measurements, a steady state of permeation is of the first order for the penetrant and of the zero order for the X component, the partial pressure of the latter being kept constant and uniform at both sides of the membrane.

The determination of diffusion coefficients is more complicated, because it is based on a transient state of permeation. The diffusion coefficient can be calculated basing on equations describing diffusion of a single component through membrane, if the X penetrant introduced to the polymer-Y substance system does not interfere with its equilibrium. If not, i.e., when the penetrant interferes with the equilibrium of the system mentioned above, the nontypical curves are obtained at the initial times. The application of these parts of curves needs some mathematical descriptions which should consider a convergence of permeation in the three-component system comprising polymer-Y substance-X penetrant.

NOMENCLATURE

A	active membrane surface (cm^2)
D	diffusion coefficient (cm^2/s)
l	membrane thickness (cm)
P	permeability coefficient [$\text{cm}^3(\text{STP})/\text{cm s mm Hg}$]
p_X^s	saturated vapor pressure of penetrant X (mm Hg)
p_Y^s	saturated vapor pressure of component Y of vapors mixture (mm Hg)
p_X	partial vapor pressure of penetrant X (mm Hg)
p_Y	partial vapor pressure of component Y of vapors mixture (mm Hg)
$p_{X(0)}$	penetrant partial pressure at the upstream side of the polymer membrane (mm Hg)
Q_t	mass quantity penetrant flow through polymer membrane [$\text{cm}^3(\text{STP})$]
\dot{Q}_x, ∞	mass rate of penetrant flow through polymer membrane at a steady state [$\text{cm}^3(\text{STP})/\text{s}$]
S	solubility coefficient [$\text{cm}^3(\text{STP})/\text{cm}^3 \text{ mm Hg}$]
t	time (s)
$t_{1/2}$	time after which half quantity of the signal ($0.5U_\infty$) is achieved at a steady state of penetration (s)
U	signal quantity (mV)

U_{cal}	signal quantity at the p_{cal} vapor pressure during detector calibration (mV)
U_{∞}	signal quantity at a steady state of penetration (mV)
V_1, V_2, V_3	rates of volume flow of the carrier gas (cm ³ /s)
$V^*(l)$	rate of volume flow of the carrier gas at the downstream side of the membrane (cm ³ /s)
α	factor of proportionality in eq. (3) (mm Hg/mV)

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