

Flow Method for Study of Gas Transport in Polymers. Application to the Study of Oxygen, Nitrogen, and Carbon Dioxide Permeation through Cellulose Acetate Membranes

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SYNOPSIS

Transient permeation of oxygen, nitrogen, and carbon dioxide through certain cellulose acetate (CA) dense membranes made from solutions in dioxane and dioxane-added ethanol were studied by the flow method. In order to explain the overshoots for transient permeation rates in the latter case, a new model is proposed. It postulates a time-dependence solubility coefficient, in the form of a series of exponential terms, which is combined in Fick's second law and solved. The model fits well the obtained permeation kinetics, leading to values of the diffusion, and permeation coefficients, and the structure change-related time. The overshoots are explained by the formation of unstable structure from dioxane-ethanol solvent mixtures, a memory effect of aggregated chains, which undergoes consolidation upon gas penetration. The stable state which results from the consolidation process is the same as that of membranes obtained from pure dioxane solutions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Diffusion of low molecular weight species in polymers occurs in many areas of modern technology. It plays an important role in coatings, paintings, fiber-spinning, drying of polymers, controlled-release technologies, and membrane processes. The latter application is specifically based on the control of the diffusion of species in a mixture through polymer films. Gas permeation is becoming a popular membrane separation process in chemical and oil industries. Cellulose acetate used in the present work is an important membrane material for such a process since it allies good selectivity to good intrinsic permeability for many gas mixtures.

The diffusion process in polymer films is generally studied by transient sorption or permeation. In these methods, the polymer is suddenly put into contact with a fluid medium so as to promote the diffusion of the considered species from the fluid into the polymer material. The diffusion rate of the species

is followed by monitoring its uptake by the polymer or its permeation rate through the polymer film. Although the sorption method is often used for such studies, the more recently developed transient permeation method seems to have several advantages.¹ However, since the first use of this method for the determination of transport parameters, i.e. permeability coefficient and diffusion coefficient of gases in polymers, by Yasuda and Rosengren,² relatively few attempts have been made to obtain the values of these fundamental parameters and to develop the method further in order to extend its investigation field. The limitation of the method resides generally in the lack of adequate physical models and convenient mathematical or numerical methods to make possible the extraction of values of different parameters from transient permeation rates. One useful extension would be to different cases of concentration-dependent diffusion coefficients. Extension to the cases of time-dependent mass transport parameters would also be useful. Nevertheless, if the permeant transport depends on both the concentration and time parameters, the distinction of the origins of the two phenomena would be difficult from the global value of permeation rates. However, the cases

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of time-dependence diffusivity can be more easily studied in gas permeation, since the gas solubility in polymers is very low and the diffusion coefficient can be considered to be constant. In the absence of the time dependence of the diffusion coefficient, known analytical solutions of Fick's second law³⁻⁵ fit well the kinetic curves of permeation flux.¹ But these solutions fail to account for overshoots in permeation kinetics, such as those obtained in the present work on cellulose acetate membranes prepared in dioxane-added ethanol medium. Non-Fickian sorption behaviors were analyzed by Crank,⁶ Park,⁷ News,⁸ and others⁹⁻¹¹ on the basis of polymer relaxation due to swelling; their analytical methods were applied to systems with high penetrant solubility (e.g., organic vapors-polymer systems) but not to permeant gas-polymer system in which the permeant solubility is too low to promote swelling-based relaxations. Recently, several authors reexamined theoretical models for transient penetrant diffusion with relaxation or deformation of the **polymer**.¹²⁻¹⁸ Some authors imposed a thermodynamic frame to transport equations.^{15,17,18} These models are useful for an effective description of various unusual behaviors such as discontinuities in the penetrant concentration profiles, overshoots, or oscillations of sorbed mass in a solid polymer. However, their use as methods for the determination of parameters of non-Fickian transient permeation data seems difficult due to their complexity. The dependence of membrane transport properties on crystallinity of polymers was studied by Michaels and Bixler,¹⁹ but this study was limited to the case of steady-state permeation in semi-crystalline films.

In the present work, a new model was proposed to account for changes in the transient permeation rate, and specifically changes due to polymer crystallization or consolidation, in glassy polymers. The model was then applied to data obtained with the flow method in the case of the transient permeation of gases (oxygen, nitrogen, carbon dioxide) through

the cellulose acetate membranes prepared from ethanol-added dioxane solvent medium. The choice of the solvent medium was motivated by the fact that a swelling solvent or a nonsolvent is often added to the solvent in the polymer casting dope to modify the properties of the obtained membrane.

EXPERIMENTAL

Membrane Preparation

Cellulose acetate of average molecular weight 61,000 and of 39.4 wt % acetyl content was purchased from Eastman Kodak Chemicals. Dense membranes were prepared by first dissolving the mentioned cellulose ester (10 wt %) in dioxane. Two series of membranes were made: one with the polymer dissolved in dioxane alone, the other with the polymer dissolved in dioxane to which 1 wt % of ethanol was added. The polymer dope was cast on a glass plate, and the solvent in the film was evaporated in an oven at 60°C. As complete evaporation of solvents from a solvent-cast membrane is generally difficult, the obtained membranes were washed several times with water, then were immersed in a large volume of hot water (at 85°C) for 30 min to leach out residual solvents before drying. In differential scanning calorimetry (Mettler DSC30), the obtained membranes did not show first- or second-order transitions up to 200°C; beyond this temperature, the membranes underwent chemical modifications (oxidation, dehydration). No crystalline structure was detected in wide-angle x-ray scattering (Rigaku, Japan).

Experimental Set-ups

The flow cell for transient permeation is shown schematically in Figure 1. The two reference and test thermistors of the thermal conductivity detector are connected over a Wheatstone bridge circuit. Be-

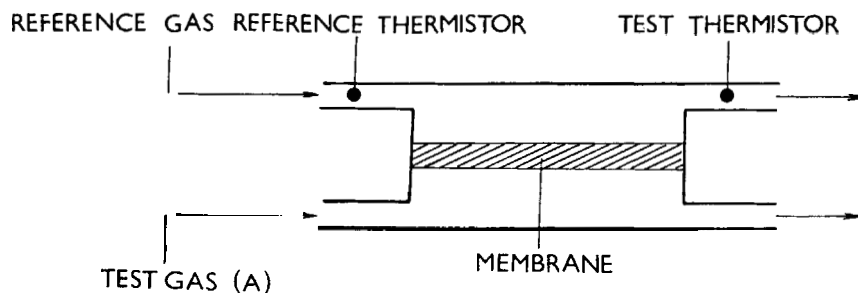


Figure 1 Schematic representation of the experimental set-up.

fore the measurement, the reference gas was simultaneously flushed through both the upstream and downstream compartments. To start the measurement, the reference gas flow through the upstream compartment was suddenly replaced by a flow of the test gas with the same flow rate as the reference gas in the downstream compartment. The basic consideration for the design of the instrument can be found in ref. 2. Depending on the permeation flux through the studied membrane by the test gas, the flow rate through the compartments must be high enough to ensure a practically constant partial pressure of the test gas (p_A) in the upstream compartment and a very low partial pressure of the test gas in the downstream compartment. Since the concentration of the test gas in the downstream compartment was very small, the electrical output of the thermal conductivity detector is proportional to the instantaneous diffusion flux of the test gas through the membrane.^{1,2} The proportionality coefficient can be obtained by calibration. The time-recorded output from the detector was subsequently used in the calculation of gas transport parameters, including the one related to the crystallization or consolidation of the membrane structure, according to the model described below.

BACKGROUND

From the measurement procedure given above, the initial and boundary conditions are as follows (for one-dimensional transport):

$$p_A(l, t) = \text{const.} \quad p_A(0, t) = 0 \quad c(\infty, 0) = 0 \quad (1)$$

where p_A is the partial pressure of the test gas (A) on the membrane surface, l is the membrane thickness, t is the time, and ∞ is the spatial coordinate. $c(\infty, 0) = 0$ means that the membrane initially contains no test gas molecule throughout its structure (Fig. 2).

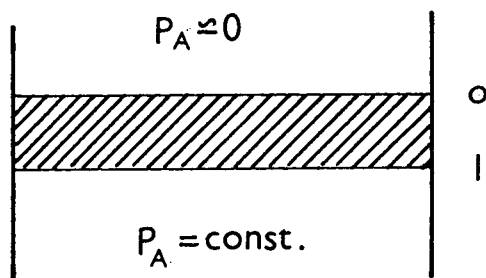


Figure 2 Schematic diagram of the studied boundary conditions.

Using a similar procedure as that given in ref. 2, we obtain the following expression for the membrane gas permeability P :

$$P = \frac{T_N F l}{T p_N A} \cdot \frac{r_s}{\alpha} \quad (2)$$

where T_N and p_N are the standard temperature and pressure resp., F is the flow rate of the reference gas, r_s is the signal output corresponding to the permeation flux at steady state, α is a calibration constant, and A is the membrane surface area.

We assume that the relaxation process of solid polymer structure change, resulting in a time-dependence of concentration at upstream membrane face for $t > 0$, has a "fading" behavior (i.e., the solubility coefficient S is assumed to vary with time according to an exponential function). A generally analytical expression of such behavior can be written in the form of a series of exponential terms:

$$c(l, t) = c_0 \sum_i a_i \exp(-\beta_i t) \quad (3)$$

where c_0 is the initial test gas concentration at the upstream membrane surface, a_i are constants satisfying the relationship $\sum a_i = 1$. The parameters β_i are positive, negative, or equal to zero when $c(l, t)$ decreases, increases, or remains constant with time, resp. Magnitude of absolute value of the parameters β_i determines the rate of relaxation. The model can then accommodate a broader spectrum of features such as the relaxation of chains leading to an increase in solubility, or organization of chains leading to a decrease in solubility. By using the Laplace transformation method²⁰ to solve Fick's second law, we obtain:

$$J = D c_0 \sum_i \frac{a_i \sqrt{\frac{\beta_i}{D}}}{\sin \sqrt{\frac{\beta_i}{D}} l} \exp(-\beta_i t) - 2 \frac{D^2 c_0}{l} \sum_i \sum_k \frac{(-1)^k a_i \lambda_k^2}{\beta_i - \lambda_k^2 D} \exp(-\lambda_k^2 D t) \quad (4)$$

where D is the diffusion coefficient, and $\lambda_k = k\pi/l$ for $k = 1, 2, \dots, \infty$. Note that eq. (4) recovers its well-known form when the solubility coefficient remains constant, indicating that the Fickian behavior^{1,2} corresponds to a special case of the model. Then the parameters D and β_i can be ob-

tained by numerically fitting²¹ the experimental curves with eq. (4).

RESULTS AND DISCUSSION

Behaviors of Differently Prepared Dense Membranes

The membranes prepared from dioxane (or acetone or chloroform) solutions of cellulose acetate exhibited a Fickian behavior whose typical permeation pattern is shown in Figure 3. The diffusion and permeation coefficients of a gas through all these membranes have practically the same values (ca. 2×10^{-8} cm²/s for oxygen). On the contrary, the transient permeation rates of all the three gases (oxygen, nitrogen, and carbon dioxide) through cellulose acetate membranes prepared from ethanol-dioxane solutions exhibit overshoots (i.e., the permeation increases with time to reach a maximum value), then slowly decays to a steady-state value (Figs. 4–6). Assuming that the first part of the transient permeation curve results from a Fickian penetration of gases due to the step change in surface concentration, we fitted this curve with the usual solution of Fick's second law.^{1,2} The agreement is good for this part of the curve (Fig. 5). Consequently, the assumption of an early Fickian diffusion stage in these membranes appears to be valid. Subsequent measurements made on the sample already used in previous measurements yielded typical Fickian permeation curves without overshoots (Fig. 6).

The analysis of the work as a whole suggests that

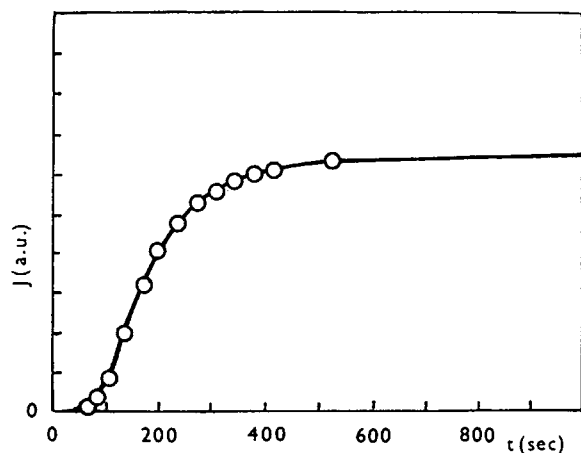


Figure 3 Kinetics of carbon dioxide permeation through cellulose acetate membranes made from pure dioxane solutions. Theoretical curve calculated from the Fickian permeation equation¹ fits well the experimental points.

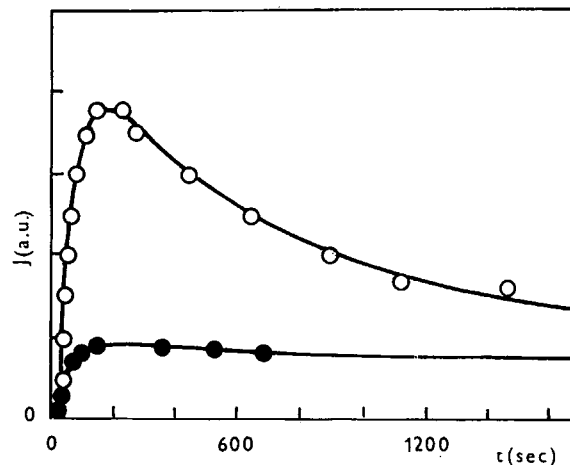


Figure 4 Kinetics of oxygen permeation $J(t)$ through the unstable cellulose acetate membrane made from dioxane-added ethanol solutions (— theoretical curves; O and ● experimental points of the first and second consecutive measurements on the same sample, resp.).

the observed overshoots can be attributed to a decrease in the solubility coefficient with time due to polymer consolidation. We will argue for this suggestion first on the basis of published models, then on the basis of the model proposed in the present work. The physicochemical origin of the observed behaviors will be discussed in the last part.

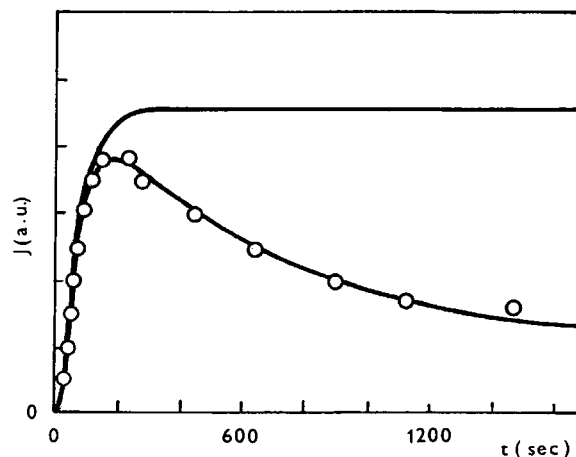


Figure 5 Kinetics of oxygen permeation $J(t)$ through the unstable cellulose acetate membrane made from dioxane-added ethanol solutions in comparison with theoretical curve calculated by assuming Fickian permeation as it were in the early stage (— theoretical curves; O experimental points).

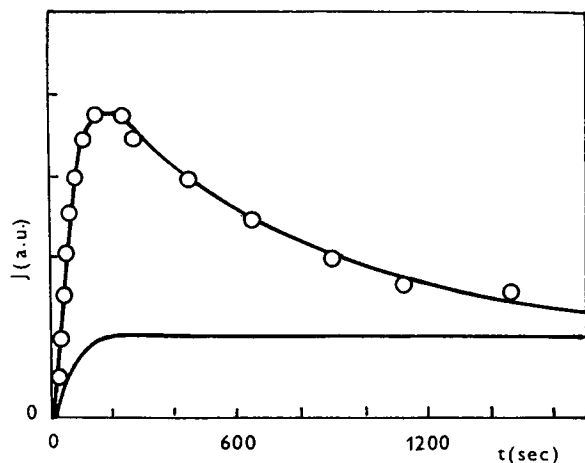


Figure 6 Kinetics of oxygen permeation $J(t)$ through the unstable cellulose acetate membrane made from dioxane-added ethanol solutions in comparison with theoretical curve calculated from parameters obtained by the model when the membrane gets in the stable state (— theoretical curves; \circ experimental points).

Analysis of the Results on the Basis of Published Works

The observed overshoots were obviously not due to a concentration-dependent diffusivity, which is generally considered to increase exponentially with the permeant concentration.⁶ Such an increase, which is compatible with the free-volume concept, cannot lead to a permeation overshoot, as the latter behavior implies a late decrease in the diffusion coefficient. The permeation overshoot does not correspond to the case-II diffusion (according to a classification based on the relative rates of diffusion and polymer relaxation proposed by Alfrey, Gurnee, and Lloyd²²). If case-II was true, we would have observed no flux during a certain time, then a sudden and strong increase in the flux, when the permeant concentration front reaches the downstream face.

Gas sorption and diffusion in membranes are often analyzed on the basis of a dual sorption model.²³ However, the model which postulates the existence of two populations of sorbed species in glassy polymers (one composed of Langmuir-type adsorbed molecules, the other composed of dissolved molecules) cannot account for the observed unusual behavior. In this model, the sorption kinetics are assumed to be very fast compared with the diffusion kinetics, themselves regarded as processes with constant rates; without time-dependences of membrane properties, it is not possible to obtain such a viscoelastic behavior. In fact, in the dual sorption mode, the diffusion transport is Fickian.²³

Permeation processes affected by polymer relax-

ations were usually observed in the transport of organic compounds or water vapors (i.e., condensable species) in glassy polymers.^{6-11,24-29} Some authors consider that the anomalous processes (e.g., those related to internal state changes) influence the permeant diffusivity but have no effects on solubility.^{6,7} On the contrary, other authors consider that anomalous processes affect only the solubility.^{8,28,29} In order to describe the anomalous diffusion, several mathematical models have been proposed. They generally combine the penetrant diffusion, sorption, and polymer relaxation processes, which occur at different relative rates according to the conditions of experiments. Experimental studies mostly concerned the kinetics of organic compound sorption in glassy polymers.^{6-11,24-29} In these cases, the non-Fickian behaviors are caused by polymer chain relaxations due to swelling.⁶⁻¹¹ The overall effect of the chain relaxation is characterized by an increased sorption,^{28,29} and consequently an increased permeation rate. As the gas sorption extent in polymers is generally low, we do not expect any significant film swelling under the low applied pressures used in the present work. Anyway, models of this type can only lead to overshoots for the sorbed mass (and consequently for the permeation rate) if a "negative sorption" is permitted at a certain moment; such a negative coefficient in the relaxation-related term was used by Berens and Hopfenberg^{9,10} for the modeling of the incremental sorption of methanol in PVC, in which an overshoot for the sorbed mass was observed.

Models based on irreversible thermodynamics¹²⁻¹⁸ give only general features. As any nonlinear behavior does come from the change in the transport coefficients with time (or concentration), their use requires explicit expressions for these coefficients.

It should be noted that, although a model which can account for all the known aspects of anomalous diffusion is not yet available, several efforts made in the past decade led to a much better understanding of the variation of different parameters and their influence.^{6-12,28,29}

Analysis of the Results on the Basis of the Proposed Model

As did Bagley and Long,²⁸ Long and Richman,²⁹ or Newns,⁸ we assumed that the internal state changes caused by gas molecule penetration mainly affects the gas solubility. Nevertheless, the underlying mechanism of internal state changes proposed in the present case is quite different from that proposed by the authors mentioned: instead of an increased

solubility due to chain relaxations, we consider a decreased solubility due to a permeant-induced consolidation of the material. A typical consolidation of the polymer structure is that caused by crystallization. According to Michaels and Bixler,¹⁹ the solubility and the diffusion coefficients of a semi-crystalline film are given by:

$$S = \nu_a S_a \quad (5)$$

where ν_a is the volume fraction of the amorphous phase and S_a is the solubility coefficient of the completely amorphous polymer, and

$$D = \frac{D_a}{\tau\gamma} \quad (6)$$

where D_a is the diffusion coefficient of the permeant in the completely amorphous polymer, τ is the tortuosity factor due to the presence of crystals in the diffusion path, and γ is the chain immobilization factor. The dependence of $\tau\gamma$ on the volume fraction of amorphous phase ν_a is very complex.^{19,30} However, as the cellulose acetate membranes are not crystalline, we assume that the diffusion coefficient D is constant, but the solubility coefficient S changes with time due to a change (with time) of the volume fraction in the amorphous phase. The latter phase is probably here a disordered phase which dissolves significantly the gas in the beginning, but much less after its consolidation or ordering (induced by the permeant penetration). We assume further that the kinetics of volume fraction change of this phase is of the first-order type:

$$\frac{\partial \nu_a}{\partial t} = k_c \nu_c - k_a \nu_a \quad (7)$$

where k_a and k_c are the kinetic coefficients (determining the consolidation rate) ν_c is volume fraction of the ordered phase. Solutions of this differential eq. (7) have the following form:

$$\nu_a(t) = a'_1 + a'_2 \exp(-\beta'_2 t) \quad (8)$$

where $a'_1 = k_c / (k_a + k_c)$, $a'_2 = [(k_a + k_c) \nu_a^0 - k_c] / (k_a + k_c)$, $\beta'_2 = k_a + k_c$, and ν_a^0 is volume fraction of disordered phase at the beginning. Combination of eqs. (1), (5), and (8), with the assumption of a linear relationship between the penetrant concentration at the membrane surface and the external pressure ($c = Sp_A$), leads to an eq. which is the simplified form of eq. (3), in which $\beta_1 = 0$, $\beta_2 = \beta'_2$, and $\beta_i = 0$ for $i > 2$, i.e.,

$$c(l, t) = c_0 [a_1 + a_2 \exp(-\beta_2 t)] \quad (9)$$

where $c_0 = p_A(l, 0) \nu_a(0)$.

Berens and Hopfenberg¹⁰ adopted first-order kinetics for the polymer relaxation. However, they use an explicit separation of diffusion and relaxation parameters. The physical situation implied by this model is fundamentally different from the model embodied in eq. (4), since the model with explicit separation of diffusion and relaxation parameters uses a linear superposition of phenomenologically independent contributions (Fickian diffusion and polymer relaxations). The equations for the diffusion and relaxation processes are solved independently by different phenomenological equations. This means that the relaxation process does not influence the transport one. In our model, the permeant concentration, which varies with time according to eq. (9), is included in Fick's second law and the differential equation is solved with the time-dependence concentration. Both the diffusion and the consolidation processes are simultaneously taken into account in Fick's equation.

Equation (4) fits very well the experimental permeation kinetics (Figs. 3, 6, 7). For the case in which the relaxation rate is very high [i.e., $\beta'_2 \rightarrow \infty$ in eq. (8)], we have $\nu_a \simeq a'_1$, and the solubility is constant. This is the case I (i) of Alfrey, Gurnee, and Lloyd's classification.²² For the case in which the relaxation rate is very low (i.e., $\beta'_2 \rightarrow 0$), we have $\nu_a \simeq a'_1 + a'_2$ in eq. (8), and the solubility can also be considered to be constant. This is the case II (ii) of Alfrey, Gurnee, and Lloyd's classification. When $\beta'_2 \rightarrow 0$ (i.e., $\beta_2 \rightarrow 0$ or $\nu_a \simeq a'_1$), we have $a_2 \rightarrow 0$. The fact that

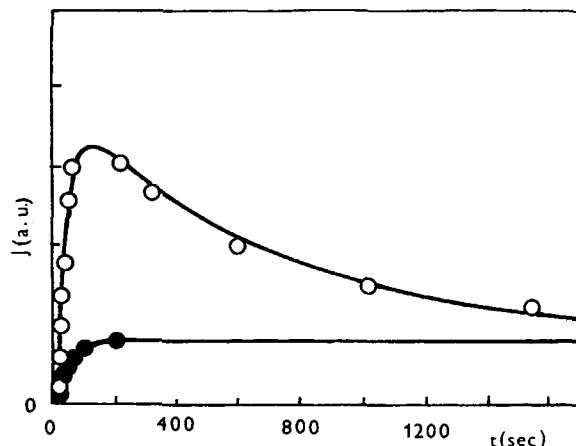


Figure 7 Kinetics of nitrogen permeation $J(t)$ through unstable cellulose acetate membranes (— theoretical curves; \circ and \bullet experimental points of the first and third consecutive measurement, resp.).

eq. (4) can fit different kinetics including the Fickian permeation kinetics (Fig. 7) means that the proposed model is general enough to make possible the study of different permeation features.

Physicochemical Origin of the Observed Behaviors

The transient permeation results showed that the presence of ethanol in the polymer dioxane solution made the prepared film unstable. Under the influence of the penetrant gas, the film underwent structural change toward a denser structure. The good agreement between the experimental permeation data and the model suggests that only part of the unstable material was transformed into a material with lower gas absorption capacity.

In order to explain the influence of ethanol on the film structure, we remind the reader that ethanol is a swelling agent for cellulose acetate but not its solvent. The presence of a small amount of swelling agent (precipitant) in the solvent would lead to formation of polymer aggregates. Such a possibility was experimentally shown in the case of polyetherimide dissolved in *N*-methyl pyrrolidone to which a small amount of water (precipitant) was added.²⁴ In the formation of the solid film by solvent evaporation, such aggregates which were probably not truly thermodynamically stable would be sintered. The polymer chains frozen in this state would be unstable compared with the chains obtained from solutions of polymer in a good solvent. Figure 5 shows that if there was no change in the structure in a later stage ($\beta_2 = 0$ and $S = \text{constant}$), the permeability of the membrane in an unstable state would have been much higher than that of the membrane obtained in the stable state from a good solvent (values given in Tables I and II). The absence of overshoots for

the permeation rates in the second and third measurements on the sample and the low level of the steady-state permeation rate indicate further that the structure change corresponds to a collapse of the initial structure into a stable structure.

We cannot explain why a test gas such as oxygen or nitrogen initiated the change in the polymer structure to a more stable one. As no overshoot was observed with membranes prepared from solutions of the polymer in pure dioxane, one possible explanation is the collapse of the loose structure upon the removal of the residual ethanol additive by the test gas. Nevertheless, such an explanation seems contrary to the known physicochemical properties of cellulose acetate-solvents-gases: as ethanol has a lower boiling point, and weaker affinity to the polymer, than dioxane, it must be more easily removed in the evaporation and washing step. Furthermore, the studied gases do not show any specific affinity to ethanol and therefore would not be more efficient in the removal of ethanol. The other possible explanation is that the penetration of the studied gas induces the structure change in a way similar to that of a catalyst in reaction. In this case, the gas simply lowers the activation energy barrier for local movements of chain segments (mainly rotations about the C—C bonds). A strong global interaction between the permeant and the polymer would not be required; a similar observation was made by Ping et al.²⁶ who observed much stronger crystallization of poly(vinyl alcohol) films when the permeant is a poorer solvent. The values of the beta parameter give an idea about the chain-ordering efficiency of nitrogen, oxygen, and carbon dioxide gases: ($\beta_2(\text{O}_2) > \beta_2(\text{N}_2) > \beta_2(\text{CO}_2)$) (Table II). These results contrast with those obtained by Titow et al.,²⁵ who found that the crystallization of a polycarbonate membrane was strongly induced by its good solvents.

Table I Literature Data on Gas Diffusion Coefficients and Permeabilities in Cellulose Acetate Membranes

Sample	Gas	Temperature (°C)	$D \times 10^9$ (cm ² /s)	P (barrer) ^a
CA ³⁰	O ₂	30		0.78
—	CO ₂	30		22.7
CA (unplasticized) ³¹	CO ₂	20	26	5.2
CA (40% plasticized) ³¹	CO ₂	20	16	3.65
CA ^{32b}	O ₂	25	19	0.46
—	N ₂	25	5.5	0.07
CA ³³	O ₂	25		0.79

^a 1 Barrer = 1×10^{10} cm³ (STP) · cm · cm⁻² · s⁻¹ · cmHg⁻¹.

^b Results obtained by vacuum time-lag method.

Table II Data Obtained by the Experiments of This Work at 25°C

Gas	Measurement	$\beta_2 \times 10^3$	$D \times 10^9$ (cm ² /s)	P_0^a (barrer)	P (barrer)
O ₂	1.	1.53	18	1.12	0.22
O ₂	2.	1.51	19	0.25	0.20
N ₂	1.	1.37	4.3	0.12	0.04
N ₂	3.	0	4.3	0.04	0.04
CO ₂	1.	0.29	11	7.41	0.98
CO ₂	3.	0	9.9	0.91	0.91

^a Gas permeabilities through membranes at the beginning.

It appears from these results that the composition of the solvent medium of the polymer has an important effect on the membrane properties. There would be a kind of memory of the polymer structure in the solution even when the membrane was prepared by evaporation and not by coagulation. However, the gain in permeability, obtained by modifying the composition of the polymer dope, may be unstable in permeation of low affinity components at temperatures well below the glass transition temperature of the polymer.

Whatever the physicochemical mechanism, the proposed model is capable of predicting transport properties of membrane in the stable state from the data obtained in the unstable state. Figure 6 shows how the permeation kinetics of oxygen would look when a membrane gets in the stable state. The predicted results of solubility, diffusivity, and permeability agree with those obtained by measurement from the third measurement (Figs. 4–6) when the

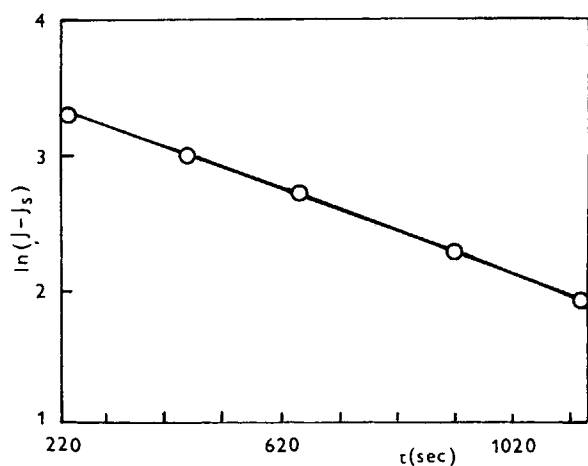


Figure 8 A plot of $\ln(J - J_s)$ versus time t of oxygen for the first measurement in the case of an unstable membrane.

membrane reached its stable state. When $\ln(J - J_s)$ is plotted versus time, combination of eqs. (4) and (9) implies that after achieving the maximum value there would be a linear dependence. Figure 8 obtained from the experimental results shows that the mentioned conclusion is correct. The transport parameters obtained in this work for the stable membranes are compatible with the results reported in the literature^{30–33} (Tables I and II), confirming the validity of the model. The Deborah number suggested by Vrentas and Duda²⁷ as a useful parameter to predict the type of transport in a glassy polymer on the basis of the relative “relaxation” time and to characteristic time of pure diffusion was also calculated from the values obtained from the proposed model. The value of the Deborah number obtained by assuming the “relaxation” time to be the reciprocal of beta is ca. 1000s. According to Doghieri et al.,¹⁸ such a high Deborah value corresponds to viscoelastic behavior of the overshoot or oscillation type.

In summary, the proposed model, illustrated by the results obtained in a case of unusual diffusion (overshoot for permeation rates) proves to be useful to analyze transient permeation data for glassy polymers. The case of polymer relaxation leading to increased solubility can also be analyzed in this model (the beta values are negative in this case). It provides a certain insight into transient behavior which is difficult to study by other methods. Concerning the exact physical mechanism, more investigations on the polymer structure before and after permeation will be needed providing experimental results that we think may be nearer to the real nature of the observed behaviors of the permeation process of the systems studied in this work. Hypotheses in the model need to be proved by other independent experimental methods to show, for instance, removal of residual solvent in membrane; this may be the origin of these seemingly complex effects.

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