

The thermodiffusion analysis of thin polymer films

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Abstract

Although the solubility and diffusivity of gases and vapours through polymers are temperature-dependent properties shown by all such systems, the diffusion of several gases through a polymer and the diffusion of the same gas through different polymers have not been investigated systematically.

We have found that the diffusivity (D), solubility (S), permeability (P) parameters and their temperature dependence for gases in polymers can be used to describe the permeability parameters of other gases and vapours in the polymer materials in question. Noble gases were used as probes to determine the temperature-dependent diffusion and the diagnostics of the permeability features of various gases, i.e. bi- and multi-atomic simple gases, lower hydrocarbons and some acid gases, through polymer thin films

INTRODUCTION

In recent years thin polymer films of specified diffusion properties have gained importance in several fields of science and technology, e.g. in electronics (for coatings), in chemical and nuclear technology (for the separation of gas mixtures) and in agriculture (for the storage of alimentary products under preserving conditions).

As it is very complicated and time consuming to obtain quantitative information on the permeability of various gases through thin polymer films, we attempted to gain the maximum amount of information about these properties of thin films at different temperatures by making the minimum amount of gas diffusion measurements. This was possible by using inert gases to characterize the thin-film diffusion properties. The thermodiffusion analysis based on these measurements was used to predict the permeability through solid polymer films of other gases and vapours of inorganic and organic origin.

Inert gases have been used to study the permeability properties of solids for many years [1–9]. The results of numerous studies on the inert-gas

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release from solids, and the methods of inert gas introduction into solids, etc., have been reviewed by Balek [10].

It has been shown that the thermodiffusion method can be used as a quality-control tool in the manufacture of thin polymer films of specified properties, e.g. gas-permeable membranes, coatings of specific permeability as required by the electronics industry, isolating and preserving coatings, and capsules that give controlled release of the active components of drugs.

Despite considerable theoretical and experimental research into gas transport through various classes of polymers, existing theoretical approaches cannot satisfactorily explain all the observed facts. This is especially true for copolymers and composite polymeric materials, the components of which may be present in different physical and phase conditions. In addition, the current state of knowledge does not allow the formulation of detailed criteria of chemical structure, physical and phase states and other physico-chemical properties that are required to guide the screening or synthesis of homo- and co-polymers for preparing potential coatings and other thin films having controlled selective gas transport.

In the present paper an attempt is made to analyse and describe the known correlations of the permeability parameters of polymers in order to show the possibility of selecting the chemical properties that are most important in controlling the selective permeability of gas transport and of predicting the gas permeability and its temperature dependence of thin polymeric films.

THE MAIN PERMEABILITY PARAMETERS OF THIN POLYMERIC FILMS

Experimental techniques and mathematical methods are available for the analysis of simple and moderately complex diffusion phenomena in polymers. The methods of analysing experimental data on diffusion have been reported in the literature (see, for example, refs. 11–21).

Modern techniques permit the main gas-transfer parameters (i.e. the coefficients of diffusivity D , solubility S and permeability P) to be determined reliably for single gases and vapours in polymers. In the simplest case

$$P = DS = Qh/A\Delta p \quad (1)$$

where Q is the steady-state flux of gas under the pressure difference Δp through an area A of membrane thickness h .

The experimental difficulties connected with the determination of diffusion parameters are not covered here because they have been widely discussed in the literature (see, for example, refs. 11–13, 16–18, 22–24). It is necessary, however, to bear in mind the possibility that gas-permeability parameters depend on concentration, space and time. In particular, they may depend on the extent of cross-linking in the polymer [11,12], the extent

of crystallinity in partly crystalline polymers [25], the annealing temperature and plasticization of glassy polymers [11,12], and the morphology and organization in copolymers and blends of polymers [26–29]. With mixtures of permeants, one penetrant may influence the permeability of another [30] and, especially in glassy polymers under high gas pressures, a fraction of the permeant may be immobilized [16,22,30]. Account must also be taken of the consequences of experimental errors connected with, for example, the variation in the thickness of film samples and the use of approximate methods for treating experimental data [19–21,31]. As permeation through thin polymeric films includes both sorption and desorption, particular caution must be taken when deriving diffusion data solely from kinetic sorption experiments [11–13,22,23].

Bearing in mind that the migration of molecules through solids by diffusion is by molecular thermojumping, if the structure of the polymer does not change over some temperature interval the temperature dependences of the permeability parameters are approximated by exponential functions

$$P = P_0 \exp(-E_P/RT) \quad (2)$$

$$D = D_0 \exp(-E_D/RT) \quad (3)$$

$$S = S_0 \exp(-\Delta H_S/RT) \quad (4)$$

where E_D is the activation energy of gas diffusion and ΔH_S is the heat of gas solution. The balance of the above temperature dependences for a given polymer characterizes its temperature coefficient of permeability.

In this paper the permeability parameters (derived mainly from permeability experiments) for rare gases, a number of permanent gases and hydrocarbons (C_1 to C_4) and a number of polymeric materials are considered. The temperature dependences of these characteristics are also used in the analysis.

The polymers for which data were taken into consideration include polydienes, polysiloxanes, polyolefins, halogen and silicon containing carbon chain polymers, polymeric esters and ketones, polyamides and polyaromatic compounds. In addition, random and block copolymers of polydienes, polydimethyl siloxane (PDMS), polyvinyltrimethylsilane (PVTMS) and polyolefins were included. The data were taken from refs. [25,26,28,31–43].

Equation (1) shows that the permeability coefficient P reflects the kinetic (D) and thermodynamic (S) aspects of gas transfer. The permeability coefficients of, for example, argon vary over eight orders of magnitude in different polymers, while D varies over nine orders and S over 1.5 orders. The ratios of the permeabilities of the different gases vary widely over a range of polymers. For example, for the pair He/Kr the permeability ratio varies from less than 1 in PDMS, NR and PE [32] to more than 10^5 in PAN [34]. (Abbreviations of polymer names are listed in Table 1.)

TABLE 1

The correlation coefficients (eqns. (5) and (8)) for estimating the gas permeability parameters of polymeric films [36,37,41,43]

No	Polymer	Coefficient ($\times 10^2$)				
		K_1	K_2	K_3	K_4	
<i>Homopolymers</i>						
1	Polydimethylsiloxane (PDMS)	-7.85	0.100	-4.70	0.77	
2	Polytrimethylsilylpropyne (PMSP)	-6.94	0.185	-4.07	0.85	
3	Polybutadiene (PB)	-8.15	0.211	-5.47	0.85	
4	Polyethylene (PE) ($\rho = 0.914 \text{ g cm}^{-3}$)	-8.42	0.225	-5.74	0.92	
5	Polyethylene (PE) ($\rho = 0.968 \text{ g cm}^{-3}$)	-8.71	0.250	-5.95	0.79	
6	Polymethylvinylether (PMVE)	-7.83	0.324	-5.56	0.80	
7	Polyvinyltrimethylsilane (PVTMS)	-7.22	0.347	-4.84	0.93	
8	Polyphenylenoxide (PPO)	-7.96	0.373	-4.42	0.94	
9	Polyamide-11 (PA-11)	-8.16	0.427	-5.87	1.02	
10	Polyvinylacetate (PVA) 298 K	-7.40	0.451	-5.41	0.77	
		350 K	-7.43	0.269	-5.16	0.51
		400 K	-7.56	0.108	-5.00	0.37
11	Polyethylmethacrylate (PEMA)	-7.29	0.471	-5.38	0.98	
12	Polyethylterephthalate (PETPH)	-7.73	0.556	-5.52	0.98	
13	Polyvinylacetate (T_g) (PVA)	-7.15	0.578	-5.59	1.01	
14	Polymethylvinylketone (PMVK)	-7.49	0.603	-5.60	0.74	
15	Polyacrylonitrile (PAN)	-7.09	0.947	-5.65	1.47	
<i>Random copolymers</i>						
16	Butadiene styrene	92.8 ^a -8.24	0.184	-5.40	0.72	
17		80:20 -8.00	0.253	-5.63	0.85	
18	Ethylene propylene	50:50 -8.16	0.199	-5.33	0.74	
19	Butadiene acrylonitrile	80:20 -8.04	0.248	-5.60	1.06	
20		73:27 -8.05	0.282	-5.66	1.09	
21		68:32 -7.96	0.316	-5.74	1.14	
22		61:39 -7.97	0.357	-5.78	1.17	
<i>Block copolymers</i>						
23	Polybutadiene polystyrene (ABA)	73.27 -8.47	0.142	-5.50	1.10	
24		59.41 -8.43	0.171	-5.64	1.16	
25	Polyarylate: poly-dimethylsiloxane (AB) _x	46:54 -8.19	0.121	-4.82	0.75	
26	Polyvinyltrimethylsilane polydimethylsiloxane (AB)	80:20 -7.62	0.282	-4.53	0.76	
		64:36 -7.84	0.219	-4.51	0.88	
27		60:40 -7.83	0.188	-4.86	0.80	

^a Parts weight for weight.

Such wide variability in the permeability and selectivity towards gases of organic polymers which, as a class, have rather similar densities and elemental compositions, has led to considerable research into the mechanism of gas diffusion and into the influence of the physical and chemical properties of the polymer on its gas-permeation parameters.

THE CORRELATION OF PERMEABILITY PARAMETERS

Several correlations of the coefficients of diffusivity (D), solubility (S) and permeability (P) of gases and vapours to their properties and those of polymers have already been reported [11–16,22–24]. Correlations between permeabilities and polymer properties (such as density and extent of crystallinity in polyolefins [25], glass transition temperatures and melting points of glassy polymers [12,44], and the cohesive energy density of polyaromatic compounds [45]) have been proposed. Correlations of P with gas properties such as molecular size and critical temperature have been suggested [44, 46,47]. Whilst such correlations are valid only for particular groups of homopolymers and often suffer from errors even in the order of magnitude of the predicted values, they do point the way to a more general approach to the understanding of the gas permeabilities of polymeric materials and membranes.

If the permeabilities of, for example, the rare gases in a series of polymers are considered to depend on any one property of the polymers (such as their densities) or of the gases (for example their atomic weights) it can be seen from Fig. 1 that the permeabilities of the “heavy” gases in polymers such as PDMS, NR, PE and PMSP are high by comparison with those of the “light” ones i.e. $P_{\text{Xe}}/P_{\text{He}} > 1$ [32,48]. However, the opposite is true for polymers such as PAN, PMVK, PVA and PVTMS [33–36]. These correlations of the permeabilities are characterized by different functional graphs which cross one another. For this reason it must be recognized that to base the correlations of P values on any property of the polymer or gas will not be adequate.

There are two possible approaches to relating permeability data to polymer chemical structure: the Permachor and the solubility space factor concepts. The Permachor correlation makes use of a scheme of additive (positive or negative) contributions from the chemical structural elements of the polymer to its permeability [12,13]. However, unlike classical additive properties, these structural contributions are not the same for all gases or for all polymers. The Permachor concept can only be applied to known experimental data of homopolymers. It is not a reliable predictive tool for copolymers, for new polymers or for polymeric blends, composites, and so on.

The solubility space factor method was suggested in an attempt to establish a more general basis for permeability prediction. It allows for the effect of the thermal expansion of the polymeric film. The thermal-expansion coefficient can be estimated by means of a method of additive contributions [13,49]. While this method shows some promise, it has the same disadvantages as the Permachor concept.

The diffusion coefficient (D) of penetrants in a polymer usually decreases with increasing dimensions of the penetrant molecule. The critical volume,

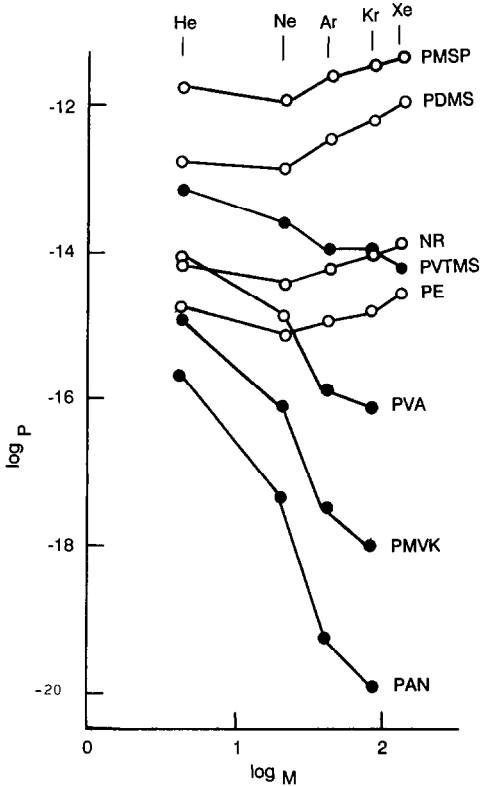


Fig. 1. Dependence of the gas permeability (as $\log P$) on the atomic weights of the inert gases (as $\log M$) at 298 K. PMSP, poly(1-(trimethylsilyl)-1-propyne), PDMS, polydimethylsiloxane, NR, polyisoprene, PVTMS, polyvinyltrimethylsilane; PE, polyethylene, PVA, polyvinylacetate, PMVK, polymethylvinylketone; PAN, polyacrylonitrile. The units of P are $\text{mol m s}^{-1} \text{m}^{-2} \text{Pa}^{-1}$ (see eqn (1))

Van der Waals volume, collision diameter, cross-section or any combination of these may be selected as a measure of the molecular dimension [25,32,36,38,42,50–52]. A number of authors have noted the difficulties of analysing diffusion data using such properties, and several scales of molecular diameters obtained by different calculation methods have been explored [48,53–60].

An analysis of the correlation between D and the molecular diameter has been carried out for more than 50 polymeric materials [36,37]. It was found that the dependence of D on molecular diameter for the rare gases and a number of multi-atomic gases was optimally expressed by

$$\log D_i = K_1 - K_2 \cdot d_i^2 \quad (5)$$

where D_i is in $\text{m}^2 \text{s}^{-1}$ and d_i (in nm) is the effective molecular diameter. These diameters were obtained by comparing the diffusion coefficients of the various gases in different polymers with those of the rare gases [36,43]. The values K_1 and K_2 are dependent on temperature (Table 1).

Equation (5) is valid for homopolymers and copolymers under different phases and physical conditions, and both coefficients in eqn. (5) are isothermally constant for any polymer.

Equation (5) is used on the hypothesis that during diffusion jumps bi- and multi-atomic molecules are oriented in the direction of the maximum molecular dimension of the molecule [25,36,42]. In support of this hypothesis it may be noted that the effective cross-sections of multi-atomic gases obtained by comparison with the rate gases are lower than the gas-phase equilibrium values [43]. In all cases increasing the effective cross-section of the permeant leads to a lowering of D .

The diffusion coefficients of different gases in polymers increase with temperature in accordance with the Arrhenius equation (eqn. (3)). The activation energy increases virtually in proportion to the effective cross-section of the permeant [26,55]; this holds for both the rare gases and multi-atomic gases.

When K_1 and K_2 are known for a polymer, the coefficients of diffusivity and the Arrhenius activation energies in that polymer can be estimated for about 12 gases and a number of hydrocarbons up to C_4 . A large number of K_1 and K_2 values have been published already [36,37]. It should be noted that values of K_1 and K_2 obtained by using data for only two or three rare gases under different temperatures can be used to estimate the permeability of polymeric films to a number of gases at the desired temperature (for some data on different polymeric materials see Table 1). The values of K_1 and K_2 for a new polymer can be obtained by collecting diffusion data on two or three rare gases.

Although the correlation equation (eqn. (5)) can be used satisfactorily to predict the values of D for many gases and vapours in different polymers (including polymers of unknown composition) on the basis of only minimum experimental data, a simple empirical approach is insufficient for estimating the values of K_1 and K_2 . These coefficients are determined not only by the chemical structure of the polymer but also by physical properties such as density, extent of crystallinity, glass temperature, interchain interactions, macrochain packing and supra-molecular organization. For complex polymeric materials, i.e. structured copolymers blends and composites, K_1 and K_2 also depend on the phase structure organization.

Although it must be expected that under isothermic conditions K_1 and K_2 depend on many polymer properties, it should also be noted that there are predominating trends. Thus K_1 varies relatively little from one polymer to another, while K_2 increases continuously with the increasing cohesive energy density (CED) of the polymers. For example: in PDMS (CED = 238 MJ m⁻³), $K_2 = +0.1$; and in PAN (CED = 1033 MJ m⁻³ [49]) $K_2 = +0.947$. This is shown particularly clearly by the values for the homopolymers listed in Table 1. For copolymers, an increase in the mole fraction of the monomer residue possessing the higher CED leads to an increase in K_2

(see, for example, the butadiene:acrylonitrile copolymers in Table 1). It should be noted that the maximum values of K_2 are for glassy polymers with polar side groups attached to the main chain. Medium values of K_2 are found for glassy polymers with non-polar side groups and the smallest values of K_2 are found for rubber-like polymers.

While the kinetic factor (D) in the permeability coefficient decreases with increasing cross-section of the migrating molecule, the thermodynamic factor (S) normally increases. More correctly, the solubilities (S) of gases and vapours in different polymers [11–13,22,25,36–38], by analogy with solubilities in liquids, increase in accordance with T_c , T_b or the force constant of the {6–12} intermolecular potential. Such correlations can be derived theoretically by equating the chemical potentials of the permeant in the gas and in the solid polymeric phase [23]

$$\log S = 0.011(\varepsilon/k) + \text{constant} \quad (6)$$

The temperature coefficient of the solubility can be expressed using the Clausius–Clapeyron equation

$$\log S = \log S_0 - \Delta H_s/2.303 RT \quad (7)$$

where ΔH_s is the molar heat of solution.

Equations (6) and (7) suggest that the index of the exponent (0.011) is independent of the nature of the polymer and that the solubility depends only on the Lennard-Jones potential ε/k .

There is no established view on which property to choose as the characteristic one of a polymer. It is known from experimental data that the greater the free volume fraction of the polymer the greater are the solubilities of gases in it [15,46].

On generalizing this approach, the correlation equation

$$\log S_i = K_3 + K_4(\varepsilon/k) \quad (8)$$

is proposed [36,37,43].

The coefficients K_3 and K_4 obtained from such correlation plots are dependent on temperature and are listed in Table 1. The values of K_3 and K_4 for any polymer can be estimated by determining the solubilities of two or three simple gases, e.g. rare gases. The effective values of ε_i/k which determine the solubilities of other gases in polymers can be obtained from the correlation plots if the solubility of the gases in a single polymer is known [43].

Regarding the values of K_3 and K_4 under isothermic conditions (Table 1), K_4 varies relatively little between different polymers and is quite close to the theoretical value of 0.011. It can be seen, however, that K_4 increases slowly with increasing polarity of the polymer. Although the values of K_3 are not constant the variations are not large and show no clear trend with the chemical composition of the polymer.

Finally, the sorption heats (ΔH_s) are found [55] to depend linearly on the values of ϵ/k , as is consistent with eqn. (7), i.e. the estimation of these values for a number of gases can be based on minimum experimental data obtained for inert gases.

By combining the correlation equations (eqns. (5) and (8)) a general relationship can be obtained for the permeability coefficients of polymeric films

$$\log P_i = \log D_i + \log S_i = K_1 + K_3 - K_2 d_i^2 + K_4 \epsilon_i/k \quad (9)$$

It should be noted that, in rubber-like polymers, including partly crystalline ones and one glassy polymer (PMSP), the solubility of the gases and vapours is the predominant factor and in these cases the permeability of the more soluble gas is greater than that of the less soluble one. However, the reverse is true for glassy polymers. An example of this can be seen in Fig. 1 where, in the rubbery polymer PDMS, P_{He} is less than P_{Xe} , whereas in the

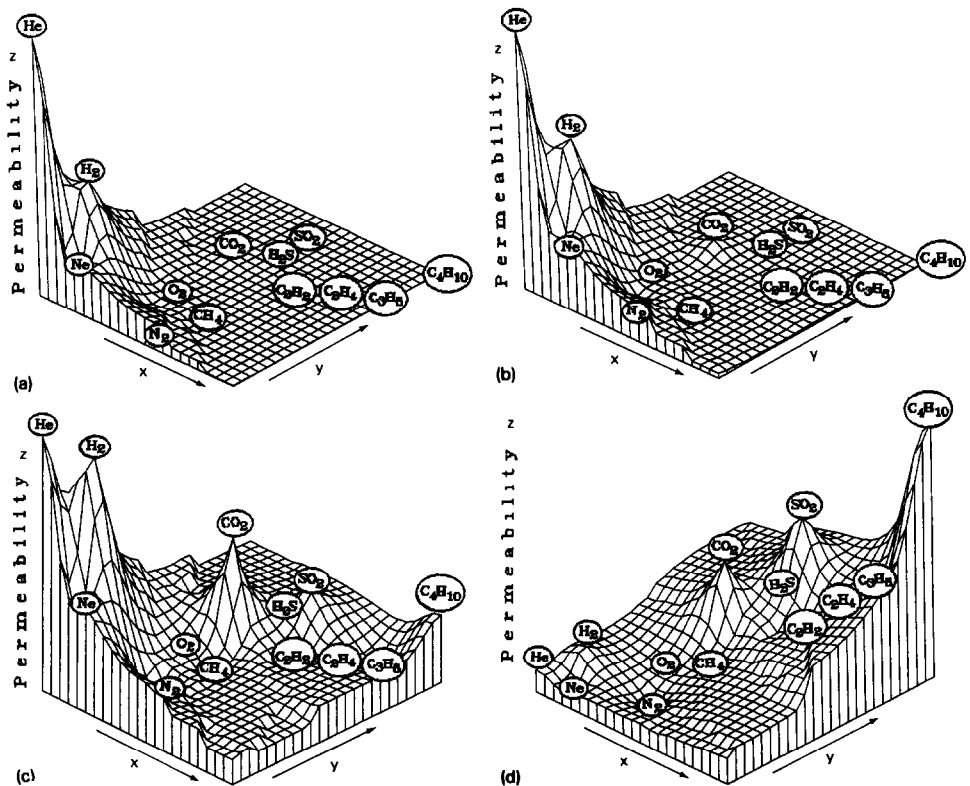


Fig. 2. The gas permeability changes for polyvinylacetate (PVA) at the operating temperatures of (a) 250 K, (b) 300 K, (c) 350 K, (d) 400 K. Axes effective cross section of the diffusant molecule (x), the $\{6-12\}$ -potential force constant of the diffusant molecule (y), and the permeability coefficients for PVA film (z)

glassy polymer PVTMS, P_{He} is greater than P_{Xe} . Other situations are possible and, for example, the selective gas permeability of copolymers can take intermediate values between those of the homopolymers [28]. An example of thermodiffusion analysis for thin films obtained by using data for inert gases is shown in Fig. 2. In this case the reliefs of gas permeability of PVA vary from the unpermeable condition (the exceptions are for He and H_2) at 250 K up to the very permeable condition (in relation to acid gases and hydrocarbons) at 350–400 K.

It should be noted that once the coefficients K_1 to K_4 of a polymer have been established, an estimate can be made of the permeability of any gas for which the effective diameter and force constant are known. Thus the potential of any polymer film to allow the permeation of particular gases can be assessed without carrying out additional experimental work. Since the values of K_1 to K_4 can be determined from a small number of permeability measurements made with inert gases without any knowledge of the chemical composition of the polymer, it is possible to assess the value of commercially available polymeric films and coatings, in terms of their isolating or permeable properties, under operating temperatures other than those for which they were originally produced.

CONCLUSION

The thermodiffusion method can be used to assess the gas-permeability parameters of polymer thin films. The values of the inert gas diffusivity (D), solubility (S), permeability (P) and the thermocharacteristics E_D , ΔH_S and E_P measured in the required temperature region allow the D , S , P , E_D , ΔH_S and E_P values of various other gases and vapours in the polymer film in question to be predicted, even when the chemical composition of the polymer is not available.

The results obtained using the thermodiffusion method can be used in the manufacture and control of thin polymer films having specified properties, such as gas-permeable membranes, coatings of controlled permeability (as required in electronics), isolating and preserving coatings, and controlled-release drug capsules.

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