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# Permeability, Diffusion and Solubility of Gases in Polyethylene, Polyamide 11 and Poly(vinylidene fluoride)

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**Résumé — Perméabilité, diffusion et solubilité des gaz dans le polyéthylène, le polyamide 11 et le polyfluorure de vinylidène** — Les coefficients de transport de gaz, c'est-à-dire la perméabilité, la diffusion et la solubilité, sont déterminés par la méthode du temps retard sur une cellule de perméabilité spécifique. Trois polymères semi-cristallins, le polyéthylène (PE), le polyamide 11 (PA11) et le polyfluorure de vinylidène (PVDF) sont étudiés en présence d'hélium (He), d'argon (Ar), d'azote (N<sub>2</sub>), de méthane (CH<sub>4</sub>) et de dioxyde de carbone (CO<sub>2</sub>) pour des températures de 40 à 80 °C dans le cas du PE et de 70 à 130 °C pour les deux autres matériaux. Les pressions appliquées sont dans la majorité des tests de 10 MPa pour He, Ar, N<sub>2</sub> et CH<sub>4</sub> et de 4 MPa pour le CO<sub>2</sub>, sauf dans quelques cas particuliers où nous avons regardé l'influence de la pression. Dans le cas du PE, l'influence de la fraction volumique de phase amorphe, comprise entre 0,21 et 0,70, de la température et de la nature du gaz sur les processus de transport de gaz est étudiée. L'indépendance de ces phénomènes vis-à-vis de la pression et de l'épaisseur de l'échantillon, comprise entre 0,5 et 6 mm, est également démontrée. En ce qui concerne le PA11, après avoir déterminé l'influence de la température et de la nature du gaz, nous regardons l'effet de l'incorporation de molécules plastifiantes dans cette matrice polymère. Au niveau du PVDF, mis à part les paramètres classiques que sont la température et le type de gaz utilisé, une comparaison des coefficients de transport du CH<sub>4</sub> et du CO<sub>2</sub> dans du PVDF mis en œuvre par extrusion et par moulage en compression est effectuée. Pour chaque polymère étudié, la dépendance de la perméabilité, de la diffusion et de la solubilité peut s'exprimer à partir de lois d'Arrhenius. Il semble également que la diffusion soit liée de façon très étroite à la taille des molécules et que la solubilité puisse être reliée au paramètre  $\varepsilon/K$  des gaz. La comparaison des résultats obtenus avec les données disponibles dans la littérature apparaît satisfaisante.

Mots-clés : perméabilité, diffusion, solubilité, gaz, PE, PA11, PVDF.

**Abstract — Permeability, Diffusion and Solubility of Gases in Polyethylene, Polyamide 11 and Poly(vinylidene fluoride)** — The gases transport coefficients, permeability, diffusion and solubility, are determined by the time lag method on a specific permeation cell. Three semicrystalline polymers, polyethylene (PE), polyamide 11 (PA11) and poly(vinylidene fluoride) (PVDF), are studied in the presence of helium (He), argon (Ar), nitrogen (N<sub>2</sub>), methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) for temperatures ranging from 40° to 80°C in the case of PE, and from 70° to 130°C for both other materials. The applied pressures are, in the majority of tests, of 10 MPa for He, Ar, N<sub>2</sub> and CH<sub>4</sub>, and of 4 MPa for CO<sub>2</sub>, except in some particular cases where the influence of pressure was studied. In the case

of PE, the influence of the volume fraction of the amorphous phase, ranging from 0.21 to 0.70, the influence of temperature and the influence of the nature of the gas on the transport processes are investigated. Also, the independence of these phenomena related to pressure and sample thickness, between 0.5 and 6 mm, is shown. For PA11, after determining the influence of temperature and of the nature of the gas used, the effect of the plasticizer incorporation in this polymer was studied. Regarding PVF<sub>2</sub>, apart the classic parameters that are temperature and the kind of gas used, we compare the coefficients of transport of CH<sub>4</sub> and CO<sub>2</sub> in PVF<sub>2</sub> made up by extrusion or by compression moulding. For each polymer, it is shown that permeability, diffusion and solubility depend on temperature following Arrhenius' laws. It also seems that diffusion is directly related to the gases molecule size and that the solubility coefficient can be linked to the  $\epsilon/K$  gases parameter. The comparison of the results obtained with the available data in the literature seems satisfactory.

Keywords: permeability, diffusion, solubility, gases, PE, PA11, PVF<sub>2</sub>.

## LIST OF THE USED NOTATIONS

### Polymer Characteristics

LDPE	Low density polyethylene
MDPE	Medium density polyethylene
HDPE	High density polyethylene
PA11	Polyamide 11
PVF <sub>2</sub>	Poly(vinylidene fluoride)
$\rho$	Semicrystalline polymer density (g/cm <sup>3</sup> )
$T_f$	Melting point temperature (°C)
$\Delta H_f$	Enthalpy of fusion (J/g)
$X_c$	Degree of crystallinity (weight fraction) (%)
$\Phi_a$	Volume fraction of the amorphous phase
$L_p$	Long period (Å)
$L_a$	Thickness of the amorphous zone (Å)
$L_c$	Thickness of the crystalline zone (Å)

### Gas Transport Coefficients

STP	Standard conditions of temperature (273 K) and pressure (0.1013 MPa)
$P_e$	Permeability coefficient (cm <sup>3</sup> (STP)/cm·s·MPa)
$D$	Diffusion coefficient (cm <sup>2</sup> /s)
$S$	Solubility coefficient (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
$\Theta$	Time lag (s)

### Characteristics of Gases

He	Helium
N <sub>2</sub>	Nitrogen
Ar	Argon
CH <sub>4</sub>	Methane
CO <sub>2</sub>	Carbon dioxide
$T_b$	Boiling point of the gas (K)
$T_c$	Critical temperature of the gas (K)
$P_c$	Critical pressure of the gas (bar)
$\epsilon/K$	Lennard-Jones' parameter of the gas (K)
$\varnothing$	Molecule diameter (Å)

## INTRODUCTION

The gas transport coefficients in semicrystalline polymers are generally complex to determine and to analyse, especially in the field of high pressures and high temperatures. Few literature data on this subject are available. Indeed, the permeability ( $P_e$ ), the diffusion ( $D$ ) or the solubility coefficients ( $S$ ) vary generally with many parameters which can be intrinsic to the polymer, such as the weight fraction of crystallinity, the nature of the polymer or even the thermal history of the sample [1, 2]. The kind of gas used, characterised by its molecule size or thermodynamical parameters, is also a factor influencing these coefficients in the same way as temperature [1, 2].

In this work, the equipment of permeation and the time lag method, described in [3], are used to obtain the transport coefficients of gases in three semicrystalline polymers: polyethylene (PE), polyamide 11 (PA11) and poly(vinylidene fluoride) (PVF<sub>2</sub>). Some of the characteristics of these polymers were determined before and after permeation measurements. Five gases, helium, argon, nitrogen, methane and carbon dioxide, were studied in a temperature range of 40° to 130°C and for pressures ranging from 4 to 12 MPa.

In the case of PE, the measurement repeatability was verified. Then, it was established that the transport coefficients are independent of the membrane thickness. For each polymer, the effects of temperature and of the nature of the gas are discussed and compared with the literature data. In a more specific way, the influence of the plasticizer incorporation in polyamide 11 and the effect of PVF<sub>2</sub> processing conditions are shown.

## 1 EXPERIMENTAL PROCEDURE

### 1.1 Permeability Measurement

The determination of the transport coefficients of various gases is made by a manometric method (pressure accumulation in a closed volume). The precise description of

the “medium pressure” equipment used and its working procedure are detailed in [3]. Permeability, diffusion and solubility are obtained from the experimental curves, by using the “time lag” method. In the studied ranges of pressure and temperature, the diffusion coefficient is assumed to be independent of the gas concentration in the polymer, and it is admitted that the solubility respects Henry’s law. These restrictive assumptions allow to obtain apparent values of  $D$  and  $S$  that are quite realistic when there are few interactions between the gas and the polymer.

Then, the permeability coefficient,  $Pe$ , expressed in  $\text{cm}^3$  (STP)/ $\text{cm}\cdot\text{s}\cdot\text{MPa}$ , is directly proportional to the slope of the straight line representing the gas flow rate *versus* the applied pressure, in steady state, and is written as:

$$Pe = \frac{Ql}{At p} \quad (1)$$

where  $Q$  is the amount of gas in  $\text{cm}^3$  (STP),  $l$  is the membrane thickness in cm,  $A$  is the diffusion area in  $\text{cm}^2$ ,  $t$  is the time in s, and  $p$  is the applied pressure in MPa. The diffusion area was equal to  $12.57 \text{ cm}^2$  [2, 3]. The diffusion coefficient,  $D$ , given in  $\text{cm}^2/\text{s}$ , is obtained from the relation:

$$D = \frac{l^2}{6 \Theta} \quad (2)$$

$\Theta$ , the “time lag” in s, corresponds to the intercept of the  $x$  axis with the straight line in steady state.

The solubility coefficient  $S$ , expressed in  $\text{cm}^3$  (STP)/ $\text{cm}^3 \cdot \text{MPa}$ , is easily calculated as the ratio  $Pe/D$ .

## 1.2 Measurement Repeatability

A rigorous calibration of the permeation cell is very difficult as far as the expected flow ranged from some tenths of  $\text{cm}^3/\text{h}$  to some  $\text{cm}^3/\text{h}$ . Then, the potential drift of the equipment is verified by testing regularly a standard polymer in average conditions.

The chosen polymer is an extruded, 30 m in length and about 2 mm in thickness, band of medium density polyethylene (MDPE) tested under  $\text{CO}_2$  at 4 MPa and  $60^\circ\text{C}$ . The values of the transport coefficients obtained from several tests are given in Table 1.

From these results, it can be concluded that the measurement repeatability is correct in spite of some small variations of temperature and pressure. The experimental uncertainties on  $Pe$ ,  $D$  and  $S$ , calculated in [2], are of the order of some percents for permeability, from 10% to 15% for the diffusion coefficient and about 20% for solubility. Indeed, regarding permeability, the uncertainties depend directly on the sensors used. On the other hand, a very small

TABLE 1  
Permeability, diffusion and solubility of  $\text{CO}_2$  in extruded medium density polyethylene at  $60^\circ\text{C}$  and 4 MPa

$T$ ( $^\circ\text{C}$ )	$p$ (MPa)	$l$ (mm)	$Pe$ ( $10^{-6} \text{ cm}^3(\text{STP})/\text{cm}\cdot\text{s}\cdot\text{MPa}$ )	$D$ ( $10^{-6} \text{ cm}^2/\text{s}$ )	$S$ ( $\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{MPa}$ )
61	3.95	1.71	1.58	1.09	1.45
61	4.0	1.64	1.60	1.10	1.46
60	4.0	1.71	1.54	1.01	1.52
60	4.1	1.65	1.51	1.14	1.32
60	4.1	1.71	1.61	1.03	1.56
60	4.4	1.71	1.67	1.14	1.47
60	4.4	1.64	1.57	1.24	1.27
60	4.5	1.71	1.69	0.99	1.70
60	4.5	1.64	1.60	1.15	1.40
60	4.0	1.73	1.60	0.97	1.65
60	4.0	1.66	1.63	1.03	1.59
60	4.0	1.73	1.62	0.99	1.63
61	4.0	1.65	1.66	0.98	1.70
61	4.0	1.72	1.66	0.93	1.78
62	3.9	1.64	1.67	1.00	1.68
62	3.9	1.73	1.68	0.99	1.70
61	4.1	1.64	1.68	0.94	1.78
61	4.0	1.73	1.61	0.99	1.62
61	4.0	1.64	1.60	1.06	1.55
<b>Mean value</b>			<b>1.62</b>	<b>1.04</b>	<b>1.57</b>
<b>Standard deviation</b>			<b><math>5.0 \cdot 10^{-2}</math></b>	<b><math>8.2 \cdot 10^{-2}</math></b>	<b>0.15</b>
<b>Standard deviation %</b>			<b>3%</b>	<b>8%</b>	<b>9%</b>

variation of the slope in the steady state can entail important variations of the time lag value, and, then, a strong uncertainty on the diffusion coefficient. This will be the case when the time lag is small as, for example, in the diffusion of helium. The relative uncertainty on solubility, calculated by the ratio  $Pe/D$ , is equal to the sum of the relative errors on both coefficients.

### 1.3 Processing Conditions and Polymer Characterisations

Six semicrystalline polymers were used during this study: a low density polyethylene, noted LDPE, a medium density, noted MDPE, two high density, referenced respectively HDPE and HDPE-RI, a polyamide 11, noted PA11 and a poly(vinylidene fluoride), noted PVF<sub>2</sub>. All the polymer samples necessary for the permeation tests were extracted from plane sheets made up by compression moulding of pellets. The processing conditions for each polymer are given below:

- polyethylenes:
  - temperature: 170°C
  - pressure: 10 MPa
  - cooling: air quenched (10°C/min)
- polyamide 11:
  - temperature: 210°C
  - pressure: 10 MPa
  - cooling: air quenched (10°C/min)
- poly(vinylidene fluoride):
  - temperature: 230°C
  - pressure: 10 MPa
  - cooling: air quenched (10°C/min).

The first three polyethylenes, LDPE, MDPE and HDPE, were cooled in a standard way. To increase the degree of crystallinity as more as possible, the last one, HDPE-RI, was cooled slowly at 1°C/min on a programmable press. Before the permeation tests, the polyethylene and PVF<sub>2</sub> samples were maintained at ambient temperature (21°-23°C) in an air-conditioned room. For PA11, the membranes were annealed under vacuum at 80°C during eight hours and, then, kept under vacuum to avoid humidity absorption.

Some polymer characteristics were determined after compression moulding. The density values of the polymer samples were measured on a *Mettler* AE240 balance. This measure is based on Archimedes' principle. The fact that polyethylenes and polyamide 11 have densities close to that of water required the use of ethanol as solvent. For PVF<sub>2</sub>, the measures were performed in water.

A differential scanning calorimeter (*Perkin-Elmer* DSC7) was used to measure the melting temperature and the fusion enthalpy of the studied polymers. DSC (Differential Scanning Calorimetry) spectra, an example of which is given in Figure 1, were obtained at a rate of 10°C/min, under a continuous flow of argon and for a mass of sample of around

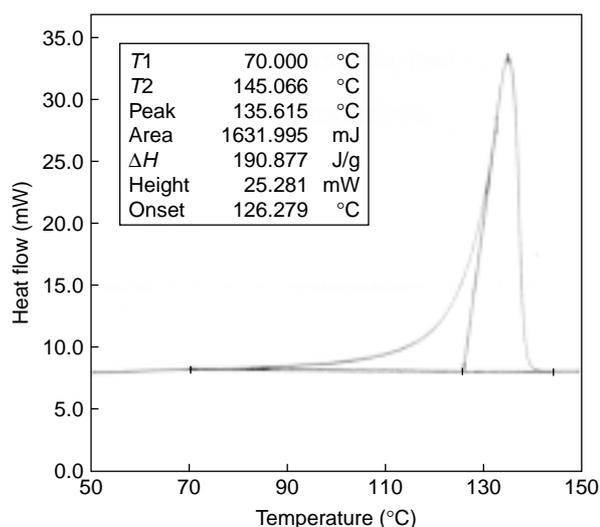


Figure 1  
DSC of HDPE.

5 mg. The ratio of the fusion enthalpy of the semicrystalline samples over the fusion enthalpy of the pure (100%) crystalline polymer gives the degree of crystallinity,  $X_c$ , of each polymer. The enthalpies of fusion of the pure crystalline polymers were taken equal to 290 J/g for polyethylenes [4], to 226 J/g for polyamide 11 [5] and to 100 J/g for PVF<sub>2</sub> [6]. The values of  $X_c$  allowed the calculation of the volume fraction of the amorphous phase, noted  $\Phi_a$ , for every polymer by the relation:

$$\Phi_a = (1 - X_c) \frac{\rho}{\rho_a} \quad (3)$$

$\rho$  is the density of the semicrystalline polymer and  $\rho_a$  is the density of the amorphous phase of the considered polymer. The densities of the amorphous phase were taken equal to 0.855 g/cm<sup>3</sup> for polyethylenes [4], to 1 g/cm<sup>3</sup> for polyamide 11 [7] and to 1.67 g/cm<sup>3</sup> for poly(vinylidene fluoride) [8].

The "long period" of the polymers was determined by tests of small angle X-ray diffraction (SAXS). The equipment and the working procedure are described in [9]. In this system, the incidental bundle presents a surface of 2 mm<sup>2</sup> and the range of the observation angle can vary from 0.1° to 2°. This represents the diffraction of regular structures, the period of repetition of which varies from 40 to 700 Å. It is the case of thin lamellae and interlamellae zones of semicrystalline polymers. The spectrum obtained for this type of polymer (*Fig. 2*) presents an interference peak corresponding to the stack of the crystalline small lamellae separated by the amorphous phase. The long period,  $Lp$ , is calculated from the maximum  $q_{\max}$  of the curve by:

$$Lp = \frac{\lambda}{2 \sin \theta} = \frac{2 \pi}{q_{\max}} \quad (4)$$

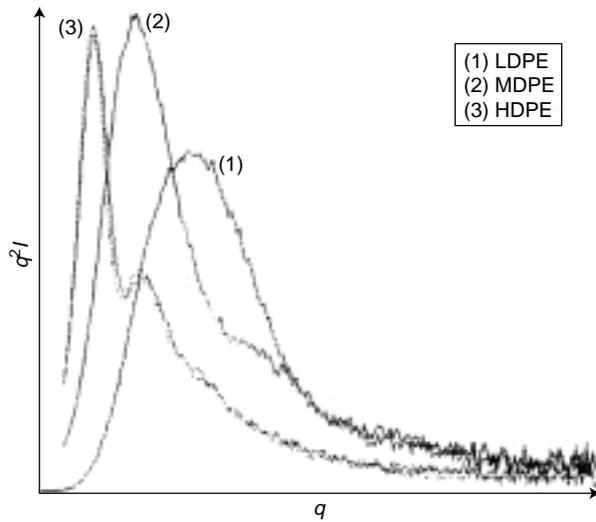


Figure 2  
SAXS spectra.

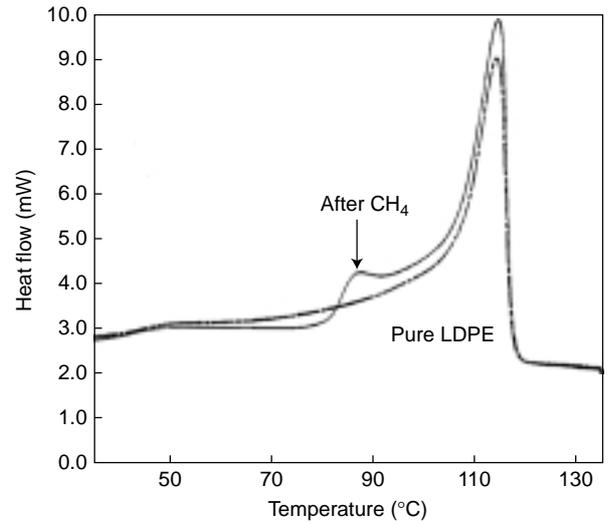


Figure 3  
DSC analysis of pure LDPE and LDPE after a CH<sub>4</sub> permeation test at 80°C.

The degree of crystallinity measured by using DSC allows to obtain the volume fraction of the crystalline phase ( $\Phi_c$ ) contained in the polymers. Then, the thickness of the crystalline zone,  $L_c$ , is calculated using the relation:

$$L_c = L_p \Phi_c \quad (5)$$

The thickness of the amorphous zone,  $L_a$ , is calculated by simple subtraction of  $L_c$  from  $L_p$ .

The polymers characteristics in their initial state, determined by the techniques described above, are recapitulated in Table 2.

Some characterisations were made after the permeation tests in methane at 80° and 40°C, for two of the polyethylenes, LDPE and HDPE-R1. The comparison between the DSC analysis performed at the initial state and after the permeation tests at 80°C, allowed to note a slight increase of the degree of crystallinity of LDPE (Fig. 3). At the same time, the crystallinity of HDPE-R1 remained constant. In the case of the measurements at 40°C, no significant evolution of the permeability was identified.

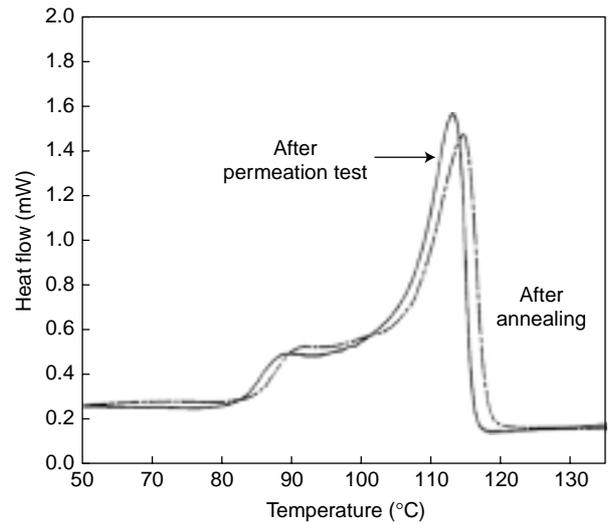


Figure 4  
DSC analysis of LDPE after a CH<sub>4</sub> permeation test at 80°C and after annealing at the same temperature.

TABLE 2

Polymers characteristics before permeation tests

Polymer	$\rho$ (g/cm <sup>3</sup> )	$T_f$ (°C)	$\Delta H_f$ (J/g)	$X_c$ (%)	$\Phi_a$	$L_p$ (Å)	$L_a$ (Å)	$L_c$ (Å)
LDPE	0.920	114	101	35	0.70	124	87	37
MDPE	0.934	129	149	51	0.53	201	107	94
HDPE	0.943	136	193	66	0.37	288	107	181
HDPE-R1	0.978	139	237	82	0.21	308	65	243
PA11	1.037	191	55	24	0.79	96	73	23
PVF <sub>2</sub>	1.757	170	50	50	0.53	107	57	50

Besides, DSC performed on samples annealed at 80°C, during a time equivalent to the duration of the permeation tests, gave identical thermograms (Fig. 4). In the case of LDPE, the temperature of the permeation tests seemed to increase slightly the degree of crystallinity. For all the polymers, no effect of the gas was observed. Finally, the “long period”, measured after the permeation tests, increased slightly, for LDPE, from 124 Å initially to 131 Å, whatever the kind of gas used (but it was not modified for HDPE-RI). This modification was due to the increase of the degree of crystallinity of this polymer.

#### 1.4 Gases Used

Table 3 recapitulates the main characteristics of the tested gases that have a purity greater than 99%. For literature data, like the Lennard-Jones' parameter ( $\epsilon/K$ ) or the molecule diameter, the amplitude of variation is rather wide.

TABLE 3  
Physical properties of gases

	$T_b$ (K)	$T_c$ (K)	$P_c$ (bar)	$\epsilon/K$ (K)	$\varnothing$ (Å)
	[10, 11]	[10, 11]	[11]	[10, 11]	[10, 11]
He	4.2	5.2	2.3	5.5-13	1.78-2.55
Ar	87.3	151	49	93-130	3-3.8
N <sub>2</sub>	77	126	34	71-94	3-4.1
CH <sub>4</sub>	111.6	191	46	140-170	3.2-4
CO <sub>2</sub>	195	304	74	195-230	3.5-5.1

## 2 PERMEATION OF GASES THROUGH POLYETHYLENE

This section is dedicated to the transport phenomena of helium, argon, nitrogen, methane and carbon dioxide in polyethylene [2]. The influence of various parameters such as the temperature, in a range of 40° to 80°C, the thickness of membranes, the type of gas used and the crystallinity, was studied. In some cases, the pressure varied from 4 to 10 MPa to evaluate its effect on the transport coefficients.

Tables 4 to 8 respectively present the transport coefficients of helium, argon, nitrogen, methane and carbon dioxide in the four PE studied at various temperatures and pressures. All the tests were performed on membranes of 2 mm in thickness. These different values will be analysed and discussed in Sections 2.2 and 2.3 dedicated to the effects of the temperature, PE crystallinity and kind of gas used.

### 2.1 Influence of the Sample Thickness

To verify that the thickness of the polymer membranes used does not influence the transport coefficients in a significant way, permeation tests were performed on MDPE in the presence of CO<sub>2</sub> at 80°C and a pressure of 4 MPa. The sample thickness varied from 0.5 to 6 mm. Each test was systematically repeated and the obtained results are given in Table 9.

Considering the experimental uncertainties, the permeability, diffusion and solubility values are not

TABLE 4  
Transport coefficients of He in polyethylene

Polymer	$T$ (°C)	$p$ (MPa)	$l$ (mm)	$Pe$ (10 <sup>-7</sup> cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ (10 <sup>-7</sup> cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
LDPE ( $\Phi_a = 0.70$ )	41	4	1.81	6.4	120	0.05
	40	10	1.86	5.8	140	0.04
	49	5	1.83	8.4	210	0.04
	69	5	1.90	19	210	0.08
	78	4	1.82	25	240	0.11
	80	10	1.81	25	260	0.09
MDPE ( $\Phi_a = 0.53$ )	41	10	1.93	2.8	51	0.06
	60	8	1.96	6.7	65	0.10
	78	10	1.95	11	120	0.09
HDPE ( $\Phi_a = 0.37$ )	40	10	2.11	1.9	76	0.03
	59	7.5	1.95	4.8	45	0.11
	79	10	2.11	8.3	130	0.06
HDPE-RI ( $\Phi_a = 0.21$ )	41	4	1.89	1.2	61	0.03
	41	10	1.77	0.95	78	0.02
	59	7.5	1.75	2.1	57	0.04
	79	10	1.75	4.0	83	0.05
	80	4	1.77	4.4	180	0.03

TABLE 5  
Transport coefficients of Ar in polyethylene

Polymer	$T$ (°C)	$p$ (MPa)	$l$ (mm)	$Pe$ ( $10^{-7}$ cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ ( $10^{-7}$ cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
LDPE ( $\Phi a = 0.70$ )	42	10	1.90	2.19	5.65	0.39
	61	10	1.89	5.82	14.2	0.41
	79	10	1.85	14.2	20.9	0.68
MDPE ( $\Phi a = 0.53$ )	42	10	1.97	1.10	3.03	0.36
	60	10	1.97	2.17	7.95	0.27
	79	10	1.92	4.63	14	0.33
HDPE-R1 ( $\Phi a = 0.21$ )	61	10	1.72	0.76	4.47	0.17
	80	10	1.74	2.06	7.77	0.27

TABLE 6  
Transport coefficients of N<sub>2</sub> in polyethylene

Polymer	$T$ (°C)	$p$ (MPa)	$l$ (mm)	$Pe$ ( $10^{-7}$ cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ ( $10^{-7}$ cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
LDPE ( $\Phi a = 0.70$ )	70	10	1.88	5.1	20	0.26
	80	10	1.82	7.4	24	0.31
MDPE ( $\Phi a = 0.53$ )	69	10	1.97	2.0	11	0.18
	79	10	1.93	2.7	16	0.18
HDPE ( $\Phi a = 0.37$ )	69	10	2.08	1.0	12	0.09
	79	10	2.08	1.6	10	0.16
HDPE-R1 ( $\Phi a = 0.21$ )	69	10	1.93	0.50	6.9	0.07
	80	10	1.93	0.82	5.6	0.15

TABLE 7  
Transport coefficients of CH<sub>4</sub> in polyethylene

Polymer	$T$ (°C)	$p$ (MPa)	$l$ (mm)	$Pe$ ( $10^{-7}$ cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ ( $10^{-7}$ cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
LDPE ( $\Phi a = 0.70$ )	41	4	1.85	4.3	3.4	1.30
	40	10	1.83	3.7	4.2	0.90
	40	7.5	1.82	4.8	3.7	1.30
	59	7.5	1.80	13	10	1.20
	80	4	1.83	29	23	1.30
	80	10	1.91	28	22	1.30
	77	7	2.75	32	26	1.20
MDPE ( $\Phi a = 0.53$ )	39	10	2.01	1.2	1.6	0.78
	39	7	1.92	1.5	2.1	0.74
	60	7	1.99	5	4.7	1.10
	59	4	1.95	3.3	6.5	0.51
	80	4	1.91	12	11	1.10
HDPE ( $\Phi a = 0.37$ )	39	7	2.08	0.92	1.6	0.57
	61	7	1.99	2.6	4.6	0.56
	77	10	2.05	5.1	9.2	0.56
HDPE-R1 ( $\Phi a = 0.21$ )	41	4	1.84	0.5	1.3	0.39
	41	10	1.69	0.37	1.4	0.27
	60	7.5	1.71	1.2	1.9	0.62
	80	4	1.73	2.3	6.9	0.33
	80	10	1.75	2.4	6.5	0.36

TABLE 8  
Transport coefficients of CO<sub>2</sub> in polyethylene

Polymer	<i>T</i> (°C)	<i>p</i> (MPa)	<i>l</i> (mm)	<i>Pe</i> (10 <sup>-7</sup> cm <sup>3</sup> (STP)/cm·s·MPa)	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> /s)	<i>S</i> (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
LDPE (Φ <sub>a</sub> = 0.70)	40	4	1.83	22	6.7	3.30
	60	4	1.80	41	19	2.20
	76	4	2.16	64	22	2.90
MDPE (Φ <sub>a</sub> = 0.53)	39	4	1.95	8.1	3.7	2.25
	61	4	2.03	17	10	1.65
	80	4	1.95	29	17	1.80
HDPE (Φ <sub>a</sub> = 0.37)	40	4	2.01	5.5	4.0	1.40
	60	4	2.09	9.6	8.2	1.20
	81	4	2.07	19	16	1.20
HDPE-RI (Φ <sub>a</sub> = 0.21)	40	4	1.79	2.6	2.8	0.95
	60	4.5	1.73	4.1	4.4	0.93

TABLE 9  
Thickness sample influence on transport coefficients of CO<sub>2</sub> in MDPE at 80°C and 4 MPa

Polymer	<i>l</i> (mm)	<i>Pe</i> (10 <sup>-6</sup> cm <sup>3</sup> (STP)/cm·s·MPa)	<i>D</i> (10 <sup>-6</sup> cm <sup>2</sup> /s)	<i>S</i> (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)	Θ (s)
MDPE	0.57	2.5 ± 0.11	1.3 ± 0.03	1.93 ± 0.10	424 ± 1
MDPE	1.25	2.8 ± 0.16	1.8 ± 0.02	1.62 ± 0.11	1435 ± 3
MDPE	2.11	2.6 ± 0.20	1.9 ± 0.30	1.93 ± 0.11	3970 ± 480
MDPE	3.98	2.4 ± 0.11	1.9 ± 0.10	1.28 ± 0.06	13 200 ± 900
MDPE	5.75	2.4 ± 0.11	1.8 ± 0.12	1.93 ± 0.09	31 100 ± 1500

influenced by the membrane thickness. Nevertheless, for the tests on a sample of 0.5 mm thickness, *D* is a little smaller than in the other cases. This can be explained considering that the value of the time lag is less than 10 min. This implies large uncertainties for the determination of *D*. As shown in Figure 5, the duration of the tests was strongly dependent on

the membrane thickness. In this study, the time lag varied from 10 min, for a thickness of 0.5 mm, to more than 8 h for the highest thickness. A relation of proportionality between Θ and *l*<sup>2</sup> is obtained (Fig. 6). This implies a weak dependence of the diffusion coefficient on the gas concentration in the MDPE samples. Indeed, it is common to compare the speed

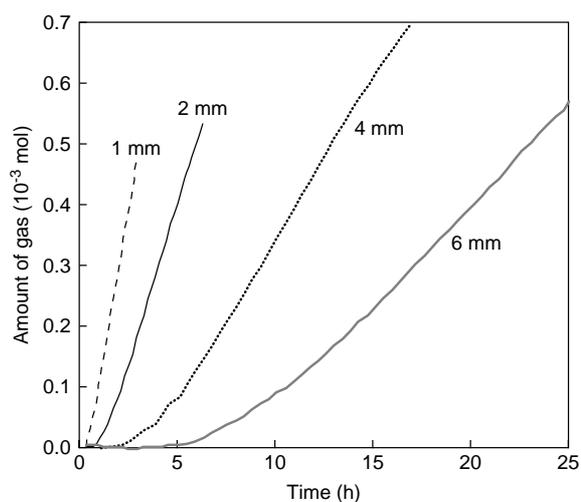


Figure 5  
Permeation curves for MDPE at 80°C and 4 MPa of CO<sub>2</sub>.

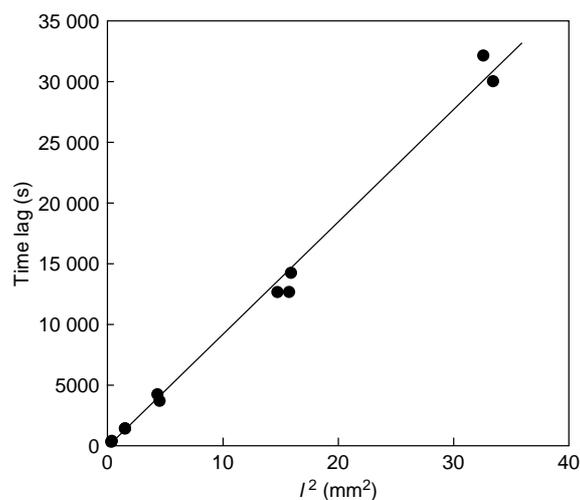


Figure 6  
Relationship between time lag and *l*<sup>2</sup>.

of the gas molecules to the relaxation speed of the polymer chains. Then, the ratio of these speeds allows to separate the various cases of diffusion. The main cases are:

- the relaxation rate of the polymer chains is very high compared to the speed of gas molecules diffusion. Then, the diffusion front propagates at the gas rate in the polymer and the time lag is proportional to the square of the membrane thickness;
- in a second case, the diffusion front moves much more slowly than the gas. The time lag is equal to the time necessary for this front to cross the membrane. This time is directly proportional to the thickness.

By taking into account experimental uncertainties, it was concluded that the transport coefficients seemed independent of the sample thickness and that the diffusion coefficient was apparently slightly dependent on the CO<sub>2</sub> concentration in MDPE. Considering these results, all the permeation tests were made on membranes of 1 or 2 mm in thickness depending on the polymers used.

## 2.2 Influence of the Temperature and Pressure

In the range of used pressures (4 to 10 MPa), no significant effect was noticed on the gas transport coefficients in polyethylene. The values of permeability, diffusion and solubility, for helium and methane tests, rarely exhibited variations greater than the experimental uncertainties. Then, it was difficult to give a reliable conclusion for the pressure effect on the transport coefficients. A similar study showed that the CH<sub>4</sub> and CO<sub>2</sub> solubility in PE seemed independent of pressure in a range from 0.1 to 4 MPa [12]. On the other hand, the diffusion coefficient appeared to depend systematically on concentration. Some other authors have noticed that, in methane or nitrogen sorption tests in PE, *S* became dependent on pressure from 15 MPa [13]. Regarding permeability, a study dealt with ten gases from 0.1 to 13 MPa on polyethylene and polypropylene [14]. The authors noted a slight increase of permeability with the pressure of the most soluble gases in PE, that are CO<sub>2</sub> and CH<sub>4</sub>.

The amorphous phase of the studied polymers consists in entanglements of macromolecular chains. Increasing the permeation tests temperature leads to a simultaneous increase of

the degree of chain mobility and of the gas molecule mobility. It is current to express that the transport coefficients depend on temperature according to Arrhenius' laws of the type:

$$Pe = Pe_0 \exp\left(\frac{-E_{Pe}}{RT}\right) \quad (6)$$

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (7)$$

$$S = S_0 \exp\left(\frac{-\Delta Hs}{RT}\right) \quad (8)$$

where  $E_{Pe}$  and  $E_D$  are the activation energies of permeability and diffusion and  $\Delta Hs$  the apparent heat of the solution [1]. As Figure 7 shows it, the temperature effect on the gas transport in polymers is very important for permeability (Fig. 7a) and diffusion (Fig. 7b) while solubility (Fig. 7c) seems less sensitive to this parameter. The logarithmic representation of *Pe*, *D* and *S* versus 1/*T* allows to obtain straight lines, the slopes of which are proportional to the activation energies of these phenomena. The obtained values of  $E_{Pe}$ ,  $E_D$  and  $\Delta Hs$  for polyethylene and for each gas studied are given in Table 10 and compared with the literature data.

The activation energies obtained during this study agree well with the literature values, especially for permeability or diffusion. On the other hand, the comparison is not suitable for the solubility of some gases as helium, argon or methane. In every case, the calculation of *S* remains based on assumptions that can be restrictive: *D* depends on the gas concentration and *S* respects Henry's law. Furthermore, for helium, as indicated above, a rather important error on the diffusion coefficient may be done, entailing rather important errors on the solubility and finally on  $\Delta Hs$ .

## 2.3 Crystallinity Effect and Influence of the Nature of Gas

The degree of crystallinity of semicrystalline polymers is a parameter that modifies most of the properties of these materials, in particular their transport coefficients [1, 2, 15-17]. To illustrate the crystallinity and the nature of the gas effects, Figure 8 represents the permeability coefficients

TABLE 10  
Apparent activation energies for permeability, diffusion and heat of solutions of gases in polyethylenes

Gas	$E_{Pe}$ (exp) (kJ/mol)	$E_{Pe}$ [15] (kJ/mol)	$E_D$ (exp) (kJ/mol)	$E_D$ [15] (kJ/mol)	$\Delta Hs$ (exp) (kJ/mol)	$\Delta Hs$ [16] (kJ/mol)
He	33-36	30-35	17-20	23-25	18-20	6-11
Ar	40-51	33-45	29-36	33-42	4-13	(-2)-4
N <sub>2</sub>	35-41	40-49	36-46	37-41	5-12	2-8
CH <sub>4</sub>	41-46	40-47	38-41	43-46	3-4	(-3)-2
CO <sub>2</sub>	29-31	30-39	30-34	36-38	(-2)-(-1)	(-5)-0.5

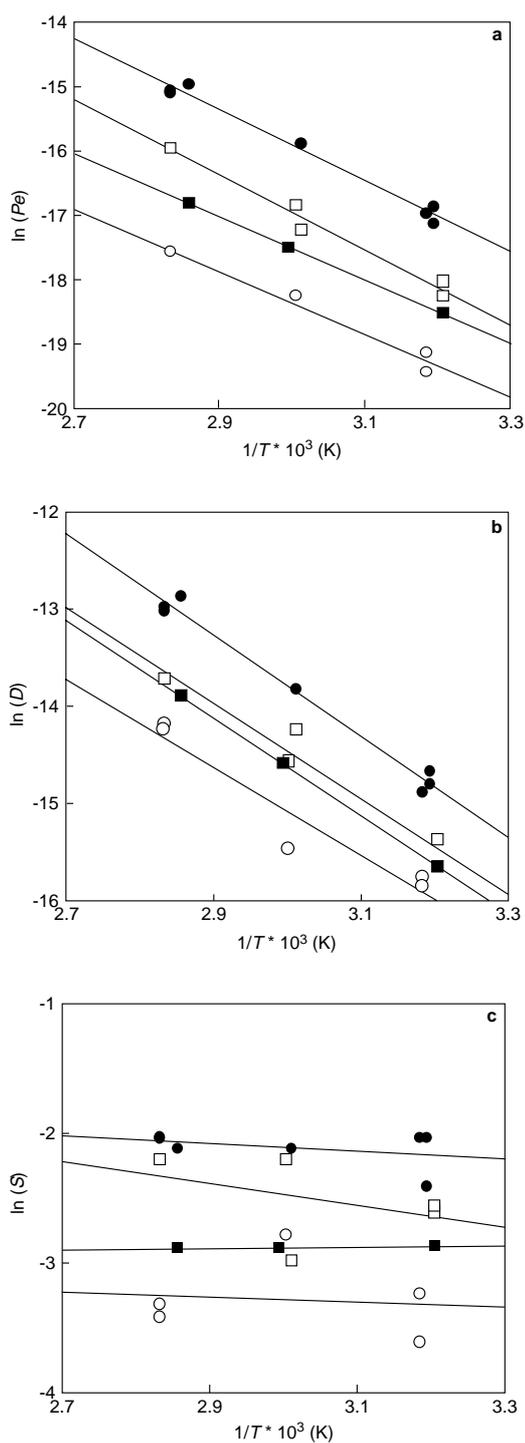


Figure 7

Temperature influence on transport coefficients of CH<sub>4</sub> (80°C, 10 MPa) in various polyethylenes (● LDPE, □ MDPE, ■ HDPE, ○ HDPE-R1).

- (a) Permeability *versus* reciprocal temperature ( $Pe$  in cm<sup>3</sup>(STP)/cm·s·bar).  
 (b) Diffusion *versus* reciprocal temperature.  
 (c) Solubility *versus* reciprocal temperature ( $S$  in cm<sup>3</sup>(STP)/cm<sup>3</sup>·bar).

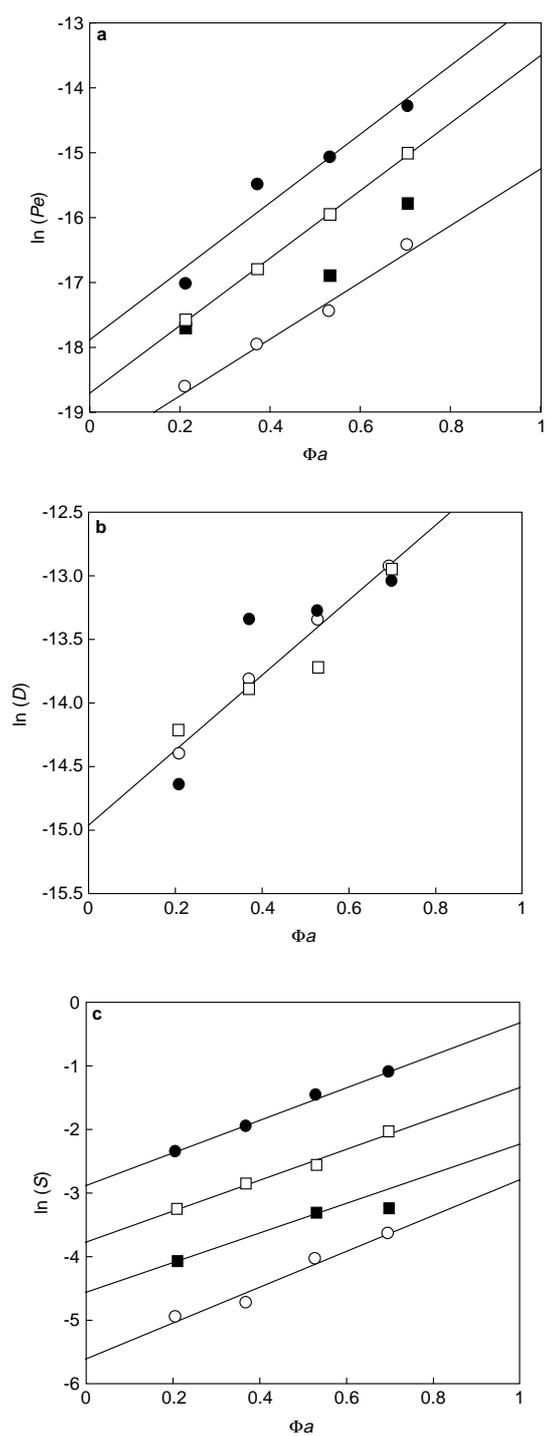


Figure 8

Transport coefficient dependence on volume fraction of amorphous polyethylene for various gases (● CO<sub>2</sub>, □ CH<sub>4</sub>, ■ Ar, ○ N<sub>2</sub>).

- (a) Permeability (cm<sup>3</sup>(STP)/cm·s·bar) *versus*  $\Phi_a$ .  
 (b) Diffusion *versus*  $\Phi_a$ .  
 (c) Solubility (cm<sup>3</sup>(STP)/cm<sup>3</sup>·bar) *versus*  $\Phi_a$ .

(Fig. 8a), the diffusion coefficients (Fig. 8b) and the solubility (Fig. 8c) versus the volume fraction of the amorphous phase contained in the four polyethylenes.

The obtained results (Tables 5-8) let appear a clear influence of the PE crystallinity on the different coefficients. The decrease of the amorphous phase content involves systematically a decrease of  $Pe$ ,  $D$  and  $S$ . These conclusions are in good agreement with those of the literature where the authors correlate the transport coefficients with the crystallinity of polyethylene [15-17]. If the relations do not seem explicit concerning permeability and, more particularly diffusion, solubility seems to linearly depend on the volume fraction of the amorphous phase in PE. In that case, the crystalline phase acts as a barrier for gases, and the gases are only soluble in the amorphous phase. It is then possible to write:

$$S = Sa \Phi a \quad (9)$$

where  $S$  is the solubility coefficient of the gas in semicrystalline PE and  $Sa$  is the gas solubility in a totally amorphous PE.

The values of  $Sa$  at 40°C in Table 11 have been obtained from the slopes of the straight lines represented in Figure 8c for only four of the gases used, namely, argon, nitrogen, methane and carbon dioxide. Indeed, it seemed difficult to take into account the values of the helium solubility as far as the experimental errors in that case are very important. The obtained results are very close to those of the literature (Table 11).

By representing  $\ln(Sa)$  versus Lennard-Jones' parameter ( $\epsilon/K$ ) of gases, a straight line can be plotted (Fig. 9) whose equation is:

$$\ln(Sa) = -4.80 + 0.021 \epsilon / K \quad (10)$$

where the pressure unit for the expression of  $Sa$  is the bar (1 bar = 0.1 MPa). This relation is close to those determined by other authors [16, 18] who found respectively for much larger ranges of gases:

$$\ln(Sa) = -5.07 + 0.022 \epsilon / K \quad (11)$$

$$\ln(Sa) = -4.80 + 0.022 \epsilon / K \quad (12)$$

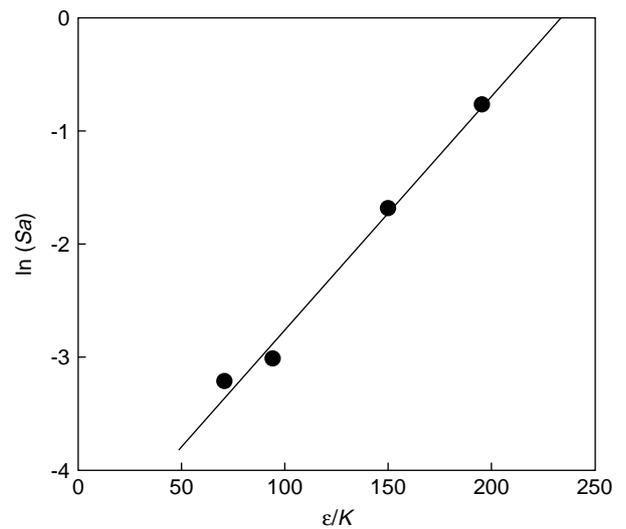


Figure 9

Relationship between solubility in completely amorphous polyethylene ( $Sa$  in  $\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{bar}$ ) and Lennard-Jones' force constant ( $\epsilon/K$ ) of various gases.

Hence, in a first approximation, the solubility coefficient of semicrystalline PE can be estimated in a simple way from  $\epsilon/K$  and from the volume fraction of the amorphous phase.

The relations between the crystallinity of PE and the coefficients of permeability and diffusion are less evident. Indeed, the polymers may be plasticized (in the case of high solubility) or a difference of tortuosity due to the amount of crystalline phase contained in PE [1, 15] may occur. Furthermore, PE is assumed to be a two-phase mixture of crystallites and amorphous polymer. Now, the reality is quite different and the intermediate phases between the amorphous and the crystallites do not present the same behaviour than a perfectly homogeneous amorphous environment. In order to take correctly into account the quantity of amorphous phase in the diffusion process, it would be necessary to know the parameters of the crystalline morphology (distribution, orientation, tortuosity, etc.) and of the amorphous phase (entanglement density, etc.). In the case of permeability, which results from both other phenomena, the difficulty is

TABLE 11  
Gases solubilities in amorphous polyethylene at 40°C

Gas	$Sa$ (exp) (40°C) ( $10^{-2} \text{ cm}^3/\text{cm}^3\cdot\text{MPa}$ )	$Sa$ [16] (25°C) ( $10^{-2} \text{ cm}^3/\text{cm}^3\cdot\text{MPa}$ )	$Sa$ [14] (25°C) ( $10^{-2} \text{ cm}^3/\text{cm}^3\cdot\text{MPa}$ )	$Sa$ [18] (25°C) ( $10^{-2} \text{ cm}^3/\text{cm}^3\cdot\text{MPa}$ )
Ar	49	98	92	105
N <sub>2</sub>	41	41	38	45
CH <sub>4</sub>	188	200	183	ND*
CO <sub>2</sub>	468	445	450	557

\* Not determined.

identical. It is clear that  $Pe$  depends strongly on the crystallinity but in a complex way [1, 2].

Considering the gas effect, it turns out that for a small gas molecule (like helium), the diffusion coefficient governs permeability, while, for larger molecules with similar size, permeability is rather dependent on solubility. All the available data allowed to classify the transport coefficients in polyethylenes according to the nature of the gas and to confirm the previous observation:

– permeability:

$$Pe(\text{CO}_2) > Pe(\text{He}) > Pe(\text{CH}_4) > Pe(\text{Ar}) > Pe(\text{N}_2)$$

– diffusion:

$$D(\text{He}) \gg D(\text{CO}_2) \approx D(\text{Ar}) \approx D(\text{CH}_4) \approx D(\text{N}_2)$$

– solubility:

$$S(\text{CO}_2) \gg S(\text{CH}_4) \gg S(\text{Ar}) > S(\text{N}_2) \gg S(\text{He})$$

### 3 PERMEATION OF GASES THROUGH POLYAMIDE 11

Polyamide 11 was the second polymer studied during this work. The measurements of the transport coefficients were also performed for the five gases. The temperature ranged from 40° to 100°C for He, and from 70° to 130°C for the others. The applied pressure of CO<sub>2</sub> was about 4 MPa while, for the other gases, the pressure was fixed to 10 MPa. All the obtained results are given in Table 12.

#### 3.1 Temperature Influence

Figure 10 illustrates the temperature effect on the transport coefficients in polyamide 11. As in the case of polyethylene, the temperature influence on permeability, diffusion and solubility can be described correctly by Arrhenius' laws for

TABLE 12  
Transport coefficients of gases in PA11

Gas	$T$ (°C)	$p$ (MPa)	$l$ (mm)	$Pe$ ( $10^{-7}$ cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ ( $10^{-7}$ cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
He	41	4	1.87	2.1	54	0.04
	70	10	1.84	5.4	91	0.06
	101	10	1.91	16	130	0.13
Ar	70	10	1.28	0.42	1.1	0.39
	99	10	1.29	1.3	3.9	0.35
	130	10	1.24	3.9	8.9	0.44
N <sub>2</sub>	69	10	1.86	0.16	0.8	0.24
	103	10	1.90	0.80	3.5	0.23
	129	10	1.86	2.1	5.3	0.40
CH <sub>4</sub>	70	10	1.27	0.28	0.62	0.44
	101	10	1.24	1.27	2.0	0.63
	120	10	1.27	1.64	4.8	0.34
	130	10	1.20	2.6	5.7	0.45
CO <sub>2</sub>	71	4.2	1.24	2.31	1.0	2.30
	101	4.3	1.16	5.45	3.54	1.54
	121	3.8	2.15	10	6.4	1.70
	131	4	2.11	12	10	1.20

TABLE 13  
Apparent activation energies for permeability, diffusion and heats of solution of gases in PA11

Gas	$E_{Pe}$ (exp) (kJ/mol)	$E_{Pe}$ [18] (kJ/mol)	$E_D$ (exp) (kJ/mol)	$E_D$ [18] (kJ/mol)	$\Delta H_s$ (exp) (kJ/mol)	$\Delta H_s$ [18] (kJ/mol)
He	28	28	13	22	16	5
Ar	43	42	41	41	-2	(-3)-(-1)
N <sub>2</sub>	42	ND*	45	ND*	-3	ND*
CH <sub>4</sub>	42	ND*	46	ND*	-4	ND*
CO <sub>2</sub>	35	34	40	52	(-10)-(-4)	(-18)-(-13)

\* Not determined.

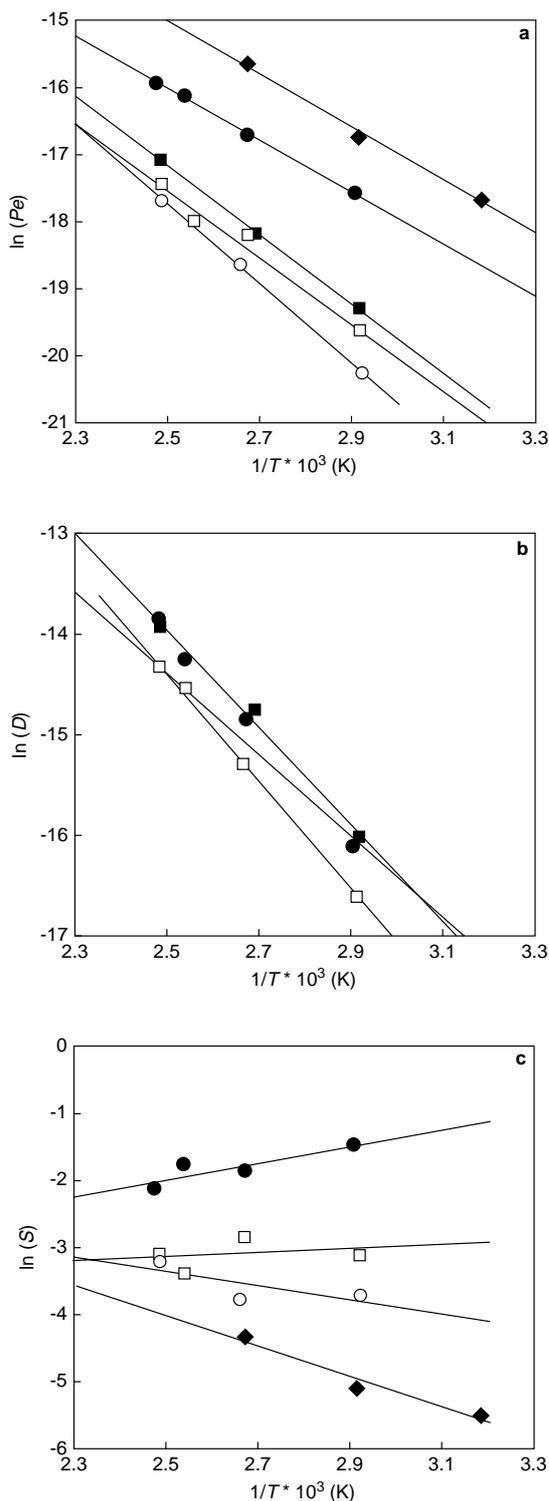


Figure 10

Temperature effect on transport coefficients for various gases in polyamide 11 (●  $\text{CO}_2$ , □  $\text{CH}_4$ , ■ Ar, ○  $\text{N}_2$ , ◆ He).

(a) Permeability ( $\text{cm}^3$  (STP)/ $\text{cm} \cdot \text{s} \cdot \text{bar}$ ) coefficients versus reciprocal temperature.

(b) Diffusion coefficients versus reciprocal temperature.

(c) Solubility ( $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{bar}$ ) versus reciprocal temperature.

each gas. Then, the activation energies  $E_{Pe}$ ,  $E_D$  and  $\Delta H_s$  of each transport phenomenon can be determined (Table 13).

The values of the permeability activation energy determined during this study are in good agreement with those found in the literature. On the other hand, the values of  $E_D$  and  $\Delta H_s$  agree well for argon, but are slightly different from those obtained for the other gases [18].

### 3.2 Influence of the Gas Nature

Figure 10 shows the influence of the gas type on the transport coefficients in polyamide 11. From Table 12, a summary of the results is obtained by a classification of the gases with regard to their transport coefficients in PA11:

– permeability:

$$Pe(\text{He}) > Pe(\text{CO}_2) > Pe(\text{Ar}) > Pe(\text{CH}_4) > Pe(\text{N}_2)$$

– diffusion:

$$D(\text{He}) \gg \gg D(\text{CO}_2) \approx D(\text{Ar}) > D(\text{N}_2) \approx D(\text{CH}_4)$$

– solubility:

$$S(\text{CO}_2) \gg \gg S(\text{CH}_4) \approx S(\text{Ar}) > S(\text{N}_2) > S(\text{He})$$

Due to its high diffusion rate and in spite of its very weak solubility, helium is the gas that presents the highest permeability in PA11 (Fig. 10a). For the four other gases which have very close diffusion coefficients (Fig. 10b), solubility governs permeability and, hence, the rather soluble  $\text{CO}_2$  in PA11 (Fig. 10c) displays a stronger permeability than Ar,  $\text{CH}_4$  and  $\text{N}_2$ .

### 3.3 Influence of the Weight Fraction of Plasticizer

Polyamide 11 has a glass transition temperature of about  $40^\circ\text{C}$  and is rather brittle at ambient temperature. In order to decrease its  $T_g$  value, a plasticizer (*n*-butyl-benzene-sulfonamide (BBSA)) is incorporated into the polymer. For example, in the case of flexible pipes for oil transport, this avoids the risks of brittle fracture during the rolling-up of the structures during storage. In [1], one can notice the plasticizer influence on gas transport phenomena in polymers. Hence, the coefficients of permeability, diffusion and solubility in polyamide 11, containing five different fractions of plasticizer, were measured with methane and carbon dioxide.

The plasticizer was incorporated into the polymer matrix by using a Haake melting compounder [19]. Membranes necessary for the permeation tests were taken from plane sheets processed by compression moulding. In the same way as for polyethylene, some characteristics of these samples were determined (Table 14). The determination of the plasticizer content was performed by a gravimetric method on a microbalance equipped with an infrared spectrometer. Samples of about 10 mg were heated from  $40^\circ$  to  $230^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , then maintained at  $230^\circ\text{C}$  during 80 min.

TABLE 14  
Plasticized PA11 characteristics before the permeation tests

Plasticizer	$\rho$ (g/cm <sup>3</sup> )	$T_f$ (°C)	$\Delta H_f$ (J/g)	$X_c$ (%)	$\Phi_a$	$L_p$ (Å)	$L_a$ (Å)	$L_c$ (Å)
0%	1.037	191	55	24	0.79	96	23	73
7.5%	1.038	188	52	25	0.78	96	24	72
12.5%	1.041	182	49	24	0.79	98	24	74
19%	1.042	179	47	25	0.78	98	24	74
29.5%	1.045	175	39	23	0.80	98	23	75

This technique allowed to know the exact plasticizer contents of membranes before and after the permeation tests. At the initial state, the weight fractions of plasticizer were respectively 0%, 7.5%, 12.5%, 19% and 29.5%.

The permeability measurements were carried out at 120°C and 4 MPa pressure, for membranes of 2 mm in thickness (Table 15). At this temperature and whatever the kind of gas used, no significant loss of plasticizer was noted. It can be concluded that there was no extraction of plasticizer due to temperature. It is necessary to underline that the tests duration was systematically lower than 24 h and that, for longer stays, the plasticizer could be extracted. The long periods measured by SAXS remained also constant after the permeation tests. However, these measurements indicated an increase of the thickness of the crystalline zones. This result was confirmed by the thermal analysis where it could be noted a systematic increase of the PA11 crystallinity of about 4% to 5%.

Figure 11 represents the permeability (Fig. 11a), the diffusion (Fig. 11b), and the solubility (Fig. 11c) of methane and carbon dioxide in PA11 versus the plasticizer content. These three curves confirm the influence of the plasticizer on the gas transport coefficients in PA11. Indeed, the diffusion rate of methane and carbon dioxide is five times slower

through the natural PA11 than through the same polymer containing 30% of plasticizer. The solubility coefficient (Fig. 11c) seems slightly modified by the plasticizer content but relatively sensitive to the nature of the gas used: carbon dioxide is about twice more soluble in PA11 than methane, for all the contents of plasticizer. Hence, the increase of the permeability can be attributed to the large variation of the diffusion coefficient. The plasticizer incorporation in the amorphous phase of PA11 gives more freedom to the macromolecular chains and facilitates the diffusion of the gas molecules. Furthermore, as the diffusion rates of the two gases in PA11 are closed to each other, the difference of permeability can be attributed, at constant plasticizer weight fraction, to the high solubility of CO<sub>2</sub> in this polymer.

#### 4 PERMEATION OF GASES THROUGH POLY(VINYLDENE FLUORIDE)

The last polymer studied during this work was poly(vinylidene fluoride). The coefficients of permeability, diffusion and solubility were determined for He, Ar, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> for temperatures varying from 40° to 130°C, and pressures of 4 MPa for CO<sub>2</sub>, 10 MPa for Ar, N<sub>2</sub> and CH<sub>4</sub> and varying from 4 to 12 MPa for N<sub>2</sub> (Table 16).

TABLE 15  
Transport coefficients of CH<sub>4</sub> and CO<sub>2</sub> in plasticized PA11 at 120°C and 4 MPa

Gas	Plasticizer (%)	$Pe$ (cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ (cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·s·MPa)
CH <sub>4</sub>	0	2.9 10 <sup>-7</sup>	3.0 10 <sup>-7</sup>	1.07
	7.5	7.3 10 <sup>-7</sup>	10 10 <sup>-7</sup>	0.71
	12.5	7.8 10 <sup>-7</sup>	10 10 <sup>-7</sup>	0.80
	19	10.0 10 <sup>-7</sup>	10 10 <sup>-7</sup>	0.99
	29.5	15.9 10 <sup>-7</sup>	15 10 <sup>-7</sup>	1.04
CO <sub>2</sub>	0	10.6 10 <sup>-7</sup>	5.0 10 <sup>-7</sup>	1.96
	7.5	23.5 10 <sup>-7</sup>	12 10 <sup>-7</sup>	2.03
	12.5	36.5 10 <sup>-7</sup>	15 10 <sup>-7</sup>	2.40
	19	35.4 10 <sup>-7</sup>	14 10 <sup>-7</sup>	2.63
	29.5	52.7 10 <sup>-7</sup>	20 10 <sup>-7</sup>	2.60

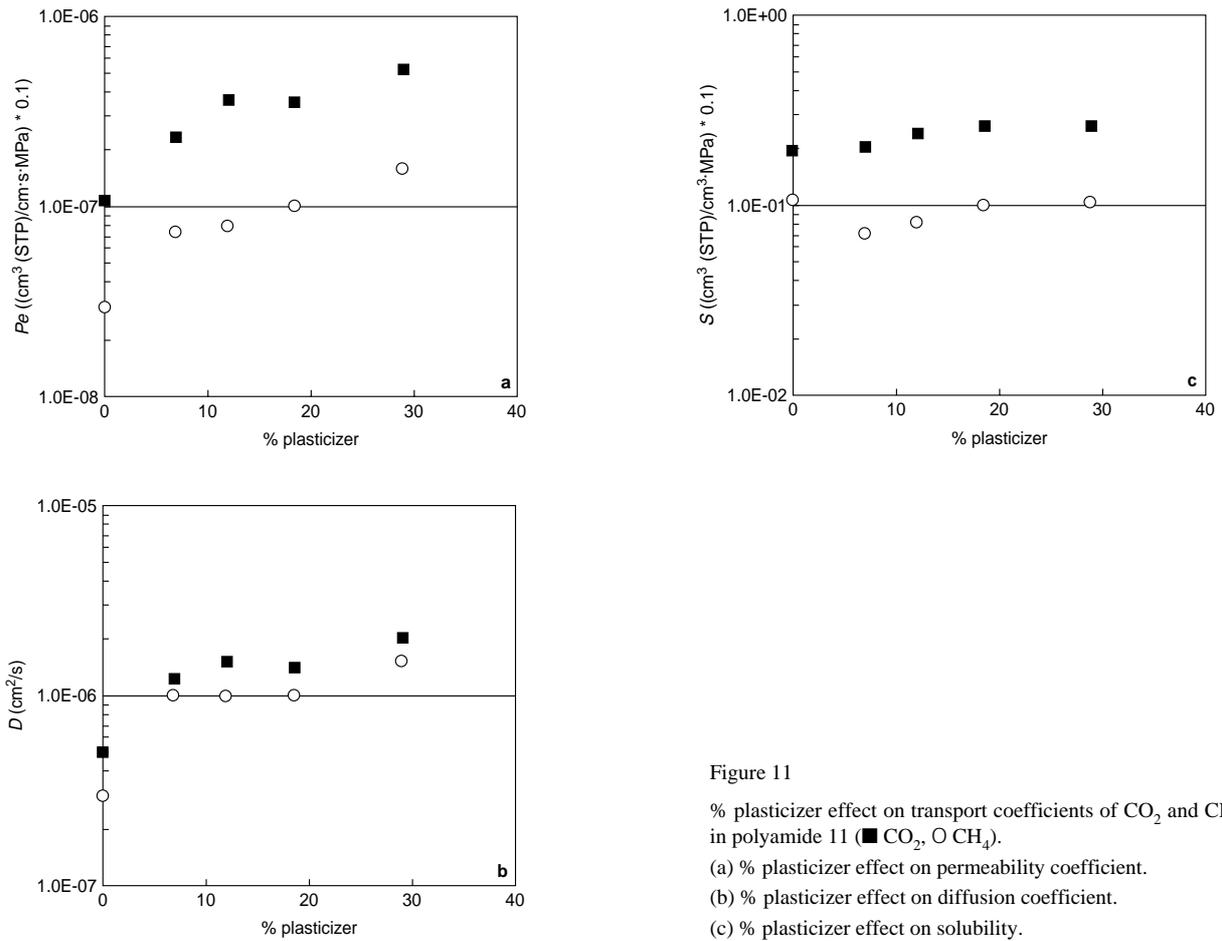


Figure 11  
 % plasticizer effect on transport coefficients of CO<sub>2</sub> and CH<sub>4</sub> in polyamide 11 (■ CO<sub>2</sub>, ○ CH<sub>4</sub>).  
 (a) % plasticizer effect on permeability coefficient.  
 (b) % plasticizer effect on diffusion coefficient.  
 (c) % plasticizer effect on solubility.

TABLE 16  
 Transport coefficients of gases in PVF<sub>2</sub>

Gas	$T$ (°C)	$p$ (MPa)	$l$ (mm)	$P_e$ (10 <sup>-7</sup> cm <sup>3</sup> (STP)/cm·s·MPa)	$D$ (10 <sup>-7</sup> cm <sup>2</sup> /s)	$S$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
He	41	10	2.10	1.4	22	0.06
	69	10	2.13	4.3	46	0.09
	101	10	2.10	14	95	0.15
Ar	70	10	1.20	0.29	0.81	0.36
	98	10	1.21	1.04	3.77	0.28
	130	10	1.17	5.71	9.91	0.58
N <sub>2</sub>	69	10	2.14	0.18	0.77	0.24
	102	10	2.06	0.78	3.3	0.24
	129	10	2.11	2.8	9.2	0.30
	129	4	2.07	3.2	10	0.31
	128	12	2.10	2.8	9.1	0.31
CH <sub>4</sub>	70	10	1.23	0.14	0.41	0.35
	100	10	1.20	0.81	1.93	0.43
	130	10	2.17	3.92	9.25	0.42
CO <sub>2</sub>	70	4	1.18	4.85	0.98	4.93
	101	4	1.16	13.7	3.23	4.24
	110	4.1	1.33	16.7	4.52	3.70
	132	4	2.10	30	12	2.80

#### 4.1 Influence of the Temperature and Pressure

No significant effect of the nitrogen pressure (in the range of 4 to 12 MPa) on the transport coefficients was noticed at 130°C.

For PVF<sub>2</sub>, temperature is an important parameter (Fig. 12). In a same way as for polyethylene and PA11, the activation energies of the transport coefficients of gas in PVF<sub>2</sub> are supplied in Table 17.

TABLE 17

Apparent activation energies for permeability, diffusion and heats of solution of gases in PVF<sub>2</sub>

Gas	$E_{Pe}$ (exp) (kJ/mol)	$E_D$ (exp) (kJ/mol)	$\Delta H_s$ (exp) (kJ/mol)
He	37	24	14
Ar	57	44	-14
N <sub>2</sub>	59	50	8
CH <sub>4</sub>	60-62	59-64	(-3)-0
CO <sub>2</sub>	30-36	44-49	(-20)-(-10)

Few studies concerning this polymer are available in the literature. The values of the activation energies obtained during this work can only be compared to those determined in [20] on the same polymer at a pressure varying from 0.1 to 2.5 MPa: in the case of helium, their  $E_{Pe}$  value is about 36 kJ/mol, that is identical to the results of this study. In the case of methane, the values are also close:  $E_{Pe} = 65$  kJ/mol,  $E_D = 67$  kJ/mol and  $\Delta H_s = -3.5$  kJ/mol.

For gases of similar molecule size, like Ar, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, the  $E_D$  values are about identical. However, the activation energy of permeability to CO<sub>2</sub> is about half that of the three other gases. This can be explained by the high solubility of CO<sub>2</sub> in PVF<sub>2</sub>.

#### 4.2 Influence of the Samples Processing

The permeability measurements performed on PVF<sub>2</sub> membranes taken from plane sheets moulded by compression are compared to those made on samples taken from single-screw extruded bands (Table 18). The characteristics determined on these two types of polymers are similar, in

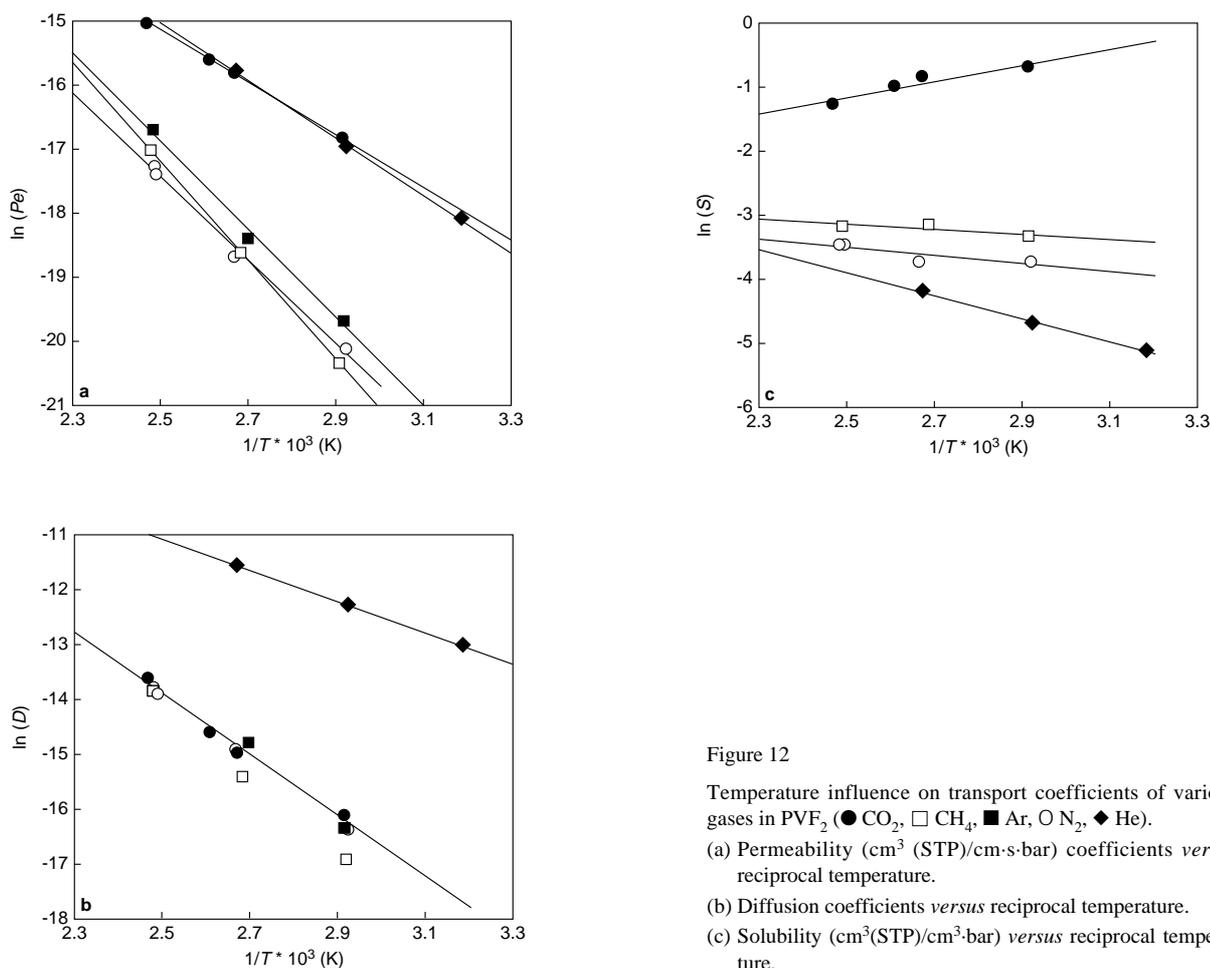


Figure 12

Temperature influence on transport coefficients of various gases in PVF<sub>2</sub> (● CO<sub>2</sub>, □ CH<sub>4</sub>, ■ Ar, ○ N<sub>2</sub>, ◆ He).

(a) Permeability (cm<sup>3</sup> (STP)/cm·s·bar) coefficients versus reciprocal temperature.

(b) Diffusion coefficients versus reciprocal temperature.

(c) Solubility (cm<sup>3</sup>(STP)/cm<sup>3</sup>·bar) versus reciprocal temperature.

TABLE 18  
Gases transport coefficients in extruded PVF<sub>2</sub>

Gas	<i>T</i> (°C)	<i>p</i> (MPa)	<i>l</i> (mm)	<i>Pe</i> (10 <sup>-7</sup> cm <sup>3</sup> (STP)/cm·s·MPa)	<i>D</i> (10 <sup>-7</sup> cm <sup>2</sup> /s)	<i>S</i> (cm <sup>3</sup> (STP)/cm <sup>3</sup> ·MPa)
CH <sub>4</sub>	100	10	1.02	0.9	2.3	0.40
	131	10	1.02	3.5	7.6	0.47
	130	10	1.02	3.7	6.1	0.60
CO <sub>2</sub>	97	4	1.01	7.0	3.0	2.38
	98	4	1.02	6.4	2.8	2.30
	131	4	1.02	29	11	2.60
	131	4	1.01	30	10	2.86

particular the densities and the volume fractions of the amorphous phase.

The comparison of the results obtained on the extruded PVF<sub>2</sub> with those of Table 12, performed in identical operating conditions, lets appear only small differences. In most of the cases, this slight difference is lower than the experimental uncertainty, except for the permeation tests of CO<sub>2</sub> at 100°C. The lower temperature (97°C) at which the permeation tests were made on the extruded sample can be a good explanation of this variation. These observations are confirmed in one study whose authors noticed that the orientation of the polymer chains induced by the extrusion is not sufficient to modify in a significant way the values of gas transport coefficients in this PVF<sub>2</sub> [20].

### 4.3 Effect of the Gas Nature

Figure 12 shows the importance of the type of gas used. From all the available values, it was possible to establish a gas classification for the different transport coefficients:

– permeability:

$$Pe(\text{He}) \approx Pe(\text{CO}_2) \gg Pe(\text{Ar}) > Pe(\text{CH}_4) > Pe(\text{N}_2)$$

– diffusion:

$$D(\text{He}) \gg \gg D(\text{CO}_2) \approx D(\text{Ar}) \approx D(\text{CH}_4) \approx D(\text{N}_2)$$

– solubility:

$$S(\text{CO}_2) \gg S(\text{CH}_4) \approx S(\text{Ar}) > S(\text{N}_2) > S(\text{He})$$

As in the case of PE and PA11, *D* seems to depend strongly on the gas molecule size. Indeed, gases with close diameters have rather similar diffusion coefficients (Fig. 12b). The very high solubility of CO<sub>2</sub> in PVF<sub>2</sub> (Fig. 12c) provides to this gas a permeability (Fig. 12a) almost identical to the permeability to helium which has nevertheless a 50-time higher diffusion coefficient.

## CONCLUSIONS

The transport coefficients of five gases, He, Ar, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, were determined from permeation tests analysed by using the time lag method, for three semicrystalline polymers, PE, PA11 and PVF<sub>2</sub>, in a range of temperature from 40° to 80°C for PE and from 70° to 130°C for the others. The applied pressures varied between 4 and 12 MPa.

For the diffusion and the solubility coefficients, the polymer nature is obviously one of the most important parameters. Whatever the tested gas, polyethylene is more permeable than PA11 and PVF<sub>2</sub>, which present a very similar behaviour. This result is attributed to the high diffusion coefficients of gases in PE. One explanation could be that the permeation tests temperature is closer to the melting point of PE (130°C) than to that of PA11 (190°C) or PVF<sub>2</sub> (170°C). Then, the macromolecular chains of the amorphous phase of PE have a greater mobility than those of the other materials. PVF<sub>2</sub> is twice as permeable to CO<sub>2</sub> than PA11 and represents a particular case. This phenomenon can be explained by the strong interaction between CO<sub>2</sub> and this polymer, resulting in a very high solubility.

In the operating conditions used, the repeatability of the tests is good and the membrane thickness (0.5 mm ≤ *l* ≤ 6 mm) does not modify in a significant way the permeability, diffusion and solubility values.

Arrhenius' laws can describe the temperature influence on the gas transport coefficients in these polymers. The values obtained for the activation energies of these phenomena are in good agreement with those found in the literature.

For polyethylene, the degree of crystallinity is also an important parameter and an increase of the volume fraction of the amorphous phase ( $\Phi_a$ ) results in an increase of *Pe*, *D* and *S*. By assuming the crystalline phase of PE totally impenetrable to gases, an empirical correlation between *S<sub>a</sub>*, the gases solubility in the totally amorphous PE, and the gases parameter,  $\epsilon/K$ , was established. This relation is quite similar to the others found in the literature.

For PA11, the addition of plasticizer in the polymer matrix involves an important increase of the gas transport coefficients.

Regarding PVF<sub>2</sub>, the macromolecular chains orientation induced by extrusion is not sufficient to modify the coefficients  $Pe$ ,  $D$  and  $S$ .

Whatever the studied polymer, some complex relations exist between  $D$  and the gas size. In the case of small molecules such as helium, it seems that the diffusion coefficient governs the permeation phenomenon. On the other hand, for gases of quite similar sizes, having close diffusion coefficients, it seems that permeability is then strongly dependent on the gas-polymer interactions, which are reflected by the solubility coefficient.

To have a better understanding of gas transport phenomena in polymers, various domains should be investigated. In order to quantify more precisely the competition between the effects of the polymer hydrostatic compression and of material plasticizing, it would be interesting to study the very high-pressure field. In the case of mixed gases, it would be important to know if effects of synergy between the gas molecules and a polymer matrix might exist. All this would lead to perform realistic predictions of polymer structures behaviour during the contact of gas under pressure.

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