

Simultaneous measurement of the concentration of a supercritical gas absorbed in a polymer and of the concomitant change in volume of the polymer. The coupled VW-*pVT* technique revisited

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Abstract

The purpose of this article is to re-examine the simultaneous measurements of the concentration of a supercritical gas in a polymer and of the concomitant change in volume of the polymer with the coupled VW-*pVT* technique [Hilic S, P dua AAH, Grolier J-PE. *Rev Sci Instrum* 71 (11) (2000) 4236–41; Hilic S, Boyer SAE, P dua AAH, Grolier J-PE. *J Polym Sci B: Polym Phys* 39 (2001) 2063–2070]. The experimental set-up consists of an original coupling of two techniques, a vibrating-wire sensor VW to weigh the polymer sample during the sorption and a pressure decay *pVT*-method to measure the quantity of gas, transferred from a high-pressure calibrated volume, which is absorbed by the polymer sample. The present study is related to the sorption and desorption of light gases (like CH₄, CO₂, H₂S, N₂) usually found in petroleum products circulating in pipelines made of semicrystalline polymers (like polyolefins and fluorinated polymers).

Results for CO₂ in medium-density polyethylene, MDPE, and in poly(vinylidene fluoride), PVDF (or PVF₂), in the range of temperatures up to 391 K and pressures up to 43 MPa, are reported and discussed. Experiments allow the apparent concentration of gas dissolved in the polymer to be established; the associated swelling of the polymer is estimated using the Sanchez–Lacombe equation of state. Then, the data of the corrected concentration of the gas in the polymer are correlated with the semi-empirical ‘dual-mode’ model. Whenever possible to compare our results are in good agreement with existing literature data.

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1. Introduction

The understanding of {gas–polymer} interactions is essential in many industrial applications of thermoplastic polymers. This is the case where such polymers are processed (foaming, extrusion, molding) to produce end-products. This is also particularly the case in the petroleum industry where these polymers are used as materials for making pipelines or seals. In all cases, polymers are usually submitted to gas sorption under elevated temperatures and high pressures. In this respect, a quantitative evaluation of

the amount of gases (often in supercritical state) in the polymers is of paramount importance.

Basically, the polymers used in the making of pipelines are semicrystalline thermoplastics. The choice result in their main characteristics, i.e. the ease of processing, the lightness and the flexibility of use which make them suitable complements to other materials (essentially metals) utilized in the equipment construction. But polymers, such as polyethylenes, polyamides or fluorinated polymers, have a tendency to absorb gases contained in petroleum products with which they are in contact over extended periods of time in severe environments in terms of *T* and *p*. The consequences of the sorption of easily soluble gases, like CH₄, CO₂ or H₂S, inducing significant dilatation, are particularly damaging for the polymer matrix. Effectively, rupture of the thermodynamic equilibrium due to a sharp pressure drop may eventually end with a local over saturation by the gas in such a way that gas concentration

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and temperature gradients cause irreversible ‘explosive’ deterioration of the polymeric structures. This process manifests itself by cracks, blisters or microstructures-like foams. This blistering phenomenon, usually termed as ‘explosive decompression failure’ (XDF) process is actually dramatic for the material which eventually loses its initial properties. This problem is a real concern in connection with the present exploitation of deeper oil wells with petroleum fluids typically at higher T and p .

The comprehensive investigation of the blistering of semicrystalline polymers implies the understanding from the thermodynamic point of view of the interactions between gases and polymers. Typically, this requires knowledge of the changes in the thermophysical properties of the materials submitted to gas sorption, of the gas solubility in these materials, and the characterization of the structure changes induced by XDF. Results obtained so far [3] concern the behavior of thermoplastics (PA, PE, PP, PVDF), under 100 MPa of gases (CH_4 , CO_2 or H_2S) and temperatures up to 373 K. The saturation is obtained after 72 h and fast decompressions are generated over a time period of 2–30 s. Polyethylene saturated with methane under pressures from 10 to 50 MPa at temperatures up to 343 K have been investigated for decompressions generated during 10–600 s [4]. Most reported studies have been conducted on elastomers. Little is known about the behavior of thermoplastic semicrystalline polymers when blistering occurs. The few available studies concern the thermomechanical properties as well as the gas solubility and the polymer swelling following the gas sorption [5–7].

Sorption, diffusion and permeation of small molecules in polymers must be well documented in order to fully understand the complex phenomena of blistering. Similarly the subsequent changes in the thermophysical properties of polymers and their impact on the mechanical behavior of these materials must be established. Studies on diffusion, permeation and mechanical impacts are beyond the scope of this contribution. However, several reports give a state of the art on such aspects [8–10]. In particular, the solution-diffusion concept is characterized by the permeability coefficient, Pe , which depends on the product of both solubility coefficient, S , and diffusion coefficient, D , as

$$Pe = SD \quad (1)$$

S is a thermodynamic quantity expressed in ($\text{cm}^3(\text{STP}) \text{cm}^{-3}(\text{polymer}) p^{-1}$) and D is a kinetic parameter expressed in ($\text{cm}^2 \text{s}^{-1}$) (STP stands for standard conditions of temperature and pressure, i.e. 273 K and 1 atm = 101 325 Pa).

In transport properties discussion, polymers are often treated as a ‘black box’ [11–15]. The structure of thermoplastic semicrystalline polymers is constituted with a highly ordered polymeric matrix (crystalline phase) and a non-ordered polymeric matrix (amorphous phase) both being characterized by the existence of microvoids (frozen

free volume or a free volume space). Crystallinity reduces the gas permeation by diminishing the polymer free volume which is restricted to the amorphous phase [8–13].

Other parameters can affect the transport properties, i.e. effect of the nature of the gas, of the nature of the polymer, of the type of gas–polymer interactions. For example, small gas molecules can more easily penetrate in the matrix. An increase of the concentration of penetrant in the polymer usually enhances plasticization of the polymer, what facilitates the transport properties. As regards the nature of the polymer, a comprehensive correlation is difficult to elaborate since the change of one feature affects the others. One can note that the incorporation of a plasticizer in a polymer may ‘mechanically’ facilitate the sorption. However, its action may as well be influenced by its proper affinity with the penetrant molecule.

2. Sorption: Sanchez–Lacombe equation of state and ‘dual-mode’ model

Estimation of sorption of supercritical CO_2 (scCO_2) in polymeric materials is extremely important in order to predict the phase changes in solvent–polymer mixtures by using a small number of adjustable parameters. Sorption of a gas in a polymer depends on temperature, pressure, concentration, swelling of the polymeric matrix and time of saturation. In this contribution, two models have been chosen: the Sanchez–Lacombe equation of state [2,16–19] and the ‘dual-mode’ model [20–23].

2.1. Lattice-fluid model

The lattice-fluid model vacancies are introduced to account for compressibility and density changes. The Sanchez–Lacombe equation of state (SL-EOS) was chosen as a model frame for its capability to describe the phase behavior of heavy compounds such as polymers, but it can also be used for light molecules such as CO_2 . Estimation of mixture properties should be based on the state parameters for pure compounds obtained from appropriate equation of state. In this respect, the Sanchez–Lacombe equation of state requires values for the three scaling characteristic parameters, respectively, the temperature, T^* , pressure, p^* , and density, ρ^* , for light and heavy pure compounds. The characteristic parameters for the two polymers, linear PE and PVDF, were obtained by fitting, using SL-EOS, the available (p , T , ρ) data. Respectively, for PE and PVDF, the temperatures are in the range of 303–394 K and of 313–413 K for six isobars (0.1, 20, 40, 60, 80 and 100 MPa) with steps of 10 K. The average deviation for the fit is about 0.5%. In Table 1, are listed the values obtained which are in good agreement with those published by Boudouris et al. [17].

The characteristic parameters of carbon dioxide were

Table 1
Characteristic parameters of the SL-EOS for linear PE, PVDF and CO₂

Reference	p^* (MPa)	T^* (K)	ρ^* (kg m ⁻³)	Range of study
PE _{solid} linear (this work)	537.0	687.2	997.1	(0–100 MPa)–(303–394 K)
PE _{melted} [17]	425.0	649.0	904.0	(0–100 MPa)–(426–473 K)
PVDF _{solid} (this work)	618.2	694.2	1855.8	(0–100 MPa)–(313–413 K)
PVDF _{melted} [17]	424.0	650.0	1771.0	(0–200 MPa)–(453–504 K)
CO ₂ [18]	412.6	316.0	1369.0	

taken from Hariharan et al. [18]; they were determined using the CO₂ vapor pressure of 0.5716 MPa at 219.26 K.

For the description of the SL-EOS, we give only the significant relations [16–18]. In the mixing rule appears the volume fraction of the gas (index 1), ϕ_1 , in the polymer (index 2)

$$p^* = \sum_1 \sum_2 \phi_1 \phi_2 p_{12}^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 \Delta p^* \quad (2)$$

$$T^* = \frac{p^*}{\frac{\phi_1 p_1^*}{T_1^*} + \frac{\phi_2 p_2^*}{T_2^*}} \quad (3)$$

The parameter, Δp^* , represents the interactions in the mixture. It is correlated with the binary adjustable parameter k_{12}

$$\Delta p^* = k_{12} \sqrt{p_1^* p_2^*} \quad (4)$$

The mass fraction of permeant gas, ω_1 , at equilibrium is calculated with

$$\omega_1 = \frac{\phi_1}{\phi_1 + (1 - \phi) \frac{\rho_2^*}{\rho_1^*}} \quad (5)$$

Knowing the characteristic parameters (ρ_1^* , p_1^* , T_1^*) and (ρ_2^* , p_2^* , T_2^*) of pure compounds, only one adjustable variable, k_{12} , have to be fitted for each binary pair by correlating our experimental points, using the SL-EOS.

The associated change in volume, ΔV_{pol} , of the polymer is calculated with the equation proposed by DeAngelis et al. [19]

$$\frac{\Delta V_{\text{pol}}}{V_0} = \frac{1}{\tilde{\rho} \rho^* (1 - \omega_1)} \frac{1}{\tilde{v}_2^0} \quad (6)$$

Parameters, ρ^* and $\tilde{\rho}$, are, respectively, the mixture characteristic and reduced densities, and \tilde{v}_2^0 is the specific volume of the pure polymer at fixed T , p and composition.

2.2. 'Dual-mode' model

The ideal 'dual-mode' model is often used to discuss the solubility of gases. It takes into consideration two types of sorption.

The first one, the Henry's law isotherm coincides to sorption sites in dense polymeric regions

$$C = C_D = k_D p = S p \quad (7)$$

The Henry's law constant, k_D , expressed in (cm³(STP) cm⁻³(polymer) atm⁻¹), is the solubility coefficient, S , of the gas in the polymer and p is the partial pressure of the gas. The concentration, C , is expressed in (cm³(STP) cm⁻³(polymer)) or (cm³(STP) g⁻¹(polymer)). The solvent is supposed to be randomly distributed in the polymeric matrix where the interactions solvent–polymer and solvent–solvent are weak compared to polymer–polymer interactions.

The second one, the Langmuir mode sorption characterizes the free volume regions with the 'hole filling' process and where solvent–polymer interactions are favored. The adsorbed molecules are on specific polymeric sites (microvoids or free volume). The concentration, C , is expressed by

$$C = C_H = \frac{C'_H b p}{1 + b p} \quad (8)$$

where the Langmuir sorption capacity, C'_H , expressed in (cm³(STP) cm⁻³(polymer)), corresponds to a measure of the holes concentration. The Langmuir affinity constant, b , is expressed in (atm⁻¹) and the pressure, p , in (atm). Molecules absorbed in the Langmuir mode are immobilized in a non swelling matrix.

In this 'dual-mode' concept, gas sorption is then represented by the coexistence of two contributions: dissolution of Henry, C_D , into the matrix and the adsorption of Langmuir, C_H , in microvoids domains

$$C = C_D + C_H = k_D p + C'_H \frac{b p}{1 + b p} \quad (9)$$

Consequently the term 'sorption' is used to regroup the phenomena of absorption and of adsorption [20–23]. The concept is based on the distinction of an amorphous phase and of a crystalline phase. The amorphous phase is continuous, quasi-liquid, and permeable to gas, whereas the crystalline phase is dispersed and not permeable to gases. Physical interpretation of the 'dual-mode' model parameters suggests that gas solubility depends on the free volume part [24], gas–polymer interactions [11] and gas critical temperature [25].

3. Materials and experimental section

Sorption of supercritical CO₂ in extruded semicrystalline thermoplastics was investigated on medium-density polyethylene, MDPE (Finathene 3802) crystallinity 0.55 and

poly(vinylidene fluoride), PVDF (Kynar 50HD) crystallinity 0.54. Because of their final use (as materials for making pipelines), commercial polymer samples were supplied by IFP. The Table 2 gives the processing conditions.

The crystallinity characteristics were verified with a temperature modulated-differential scanning calorimeter (Mettler–Toledo) TMDSC type 821e. Thermograms were obtained under a continuous flow of nitrogen (15 ml min^{-1}), for a mass of sample varying between 2 and 5 mg. Modulation conditions of temperature were: temperature rate $q_{\text{TMDSC}} = 2.00 \text{ K min}^{-1}$, amplitude of modulation of temperature $A_T = 0.8 \text{ K min}^{-1}$ and period of modulation $p_{\text{TMDSC}} = 60 \text{ s}$. The degree of crystallinity, X_c , is the ratio of the fusion enthalpy of semicrystalline polymers, $\Delta H_{f,c}$, obtained by integration of the fusion peak, over the fusion enthalpy of the 100% crystalline polymer, $\Delta H_{f,100\%c}$, with the respective values 293.014 J g^{-1} for PE and 104.631 J g^{-1} for PVDF. The volume fraction of the amorphous phase, ϕ_a , is given by Eq. (10)

$$\phi_a = (1 - X_c) \frac{\rho}{\rho_a} \quad (10)$$

ρ is the density of the semicrystalline polymer and ρ_a the density of the amorphous phase. The densities of the amorphous phases are 0.855 g cm^{-3} for PE and 1.67 g cm^{-3} for PVDF, respectively [10]. Our data, given Table 3, are slightly above but in good agreement with the literature values.

Since the thickness of the polymer samples used does not influence the transport coefficients in a significant way, three types of samples have been studied: rods, circular cross section rods and rectangular cross section rods.

Carbon dioxide was purchased from SAGA France and used without further purification. The critical pressure and temperature for CO_2 are, respectively, 7.38 MPa and 304.13 K (Table 4). The density values, ρ , of CO_2 , used in the working equation of the vibrating-wire sensor VW and in the pressure decay measurement pVT -method, were calculated using the equation of state of Ely et al. [26]. The viscosity values, η , of CO_2 were obtained from the correlation of Vesovic et al. [27].

In order to investigate possible hysteresis phenomenon between sorption and desorption, both sorption (measurements made as the experimental pressure was increased) and desorption (measurements made as the experimental pressure was decreased) were performed. Isotherms were obtained using a concept that has the particularity to

Table 2
Processing conditions of polymers

Polymers	$T(\text{K})$	$p(\text{MPa})$	Cooling air quenching (K min^{-1})
Medium density polyethylene	443	10	10
Poly(vinylidene fluoride)	503	10	10

combine two techniques, a vibrating-wire VW sensor and a pressure decay pVT -technique. The vibrating-wire sensor VW is employed as a force sensor to weigh the polymer sample during the sorption: the buoyancy force exerted by the pressurized fluid on the polymer depends on the swollen volume, ΔV_{pol} , of the polymer due to the gas sorption. The pressure decay pVT -method allows to calculate the number of moles, n_{sol} , of gas (which is initially kept in the high-pressure calibrated cell) absorbed in the polymer, from the measurement of pressure at its initial value p_i when the gas enters the measuring cell and its final value p_f after the gas–polymer system has returned to thermodynamic equilibrium. The combined apparatus is designed to measure sorption of gases and the concomitant volume change of polymers at pressures up to 100 MPa from room temperature to 473 K. In this study, the thermodynamic equilibrium, for each pressure steps, is reached between 10 and 24 h for the $\{\text{CO}_2\text{-MDPE}\}$ and between 10 and 72 h for the $\{\text{CO}_2\text{-PVDF}\}$.

4. Results and discussion

4.1. Experimental measurements and data analysis

The experimental method consists in a series of successive transfers of the gas by connecting the reservoir cell, V_1 , and the calibrated transfer cell, V_3 , to the equilibrium cell, V_2 , which contains the polymer. The initial, p_i , and final, p_f , pressures are recorded between each transfer.

The initial methodology developed to simultaneously determine the solubility and the swelling of the polymer was based on the iterative calculation described by Hilic et al. [1, 2]. The iterative operation was designed to simultaneously calculate the solubility and the volume change of the polymer due to sorption, using two rigorous working equations. However, a careful check of the whole procedure showed that the two working equations do not converge.

The working Eq. (11) for the pVT -technique gives the amount of gas entering the polymer sample during the first transfer once equilibration is attained

$$m_{\text{sol}} = \frac{M_g}{RT_f} \frac{p_f}{Z_f} \Delta V_{\text{pol}} + \frac{M_g}{R} \left[\frac{p_i}{Z_i T_i} V_3 - \frac{p_f}{Z_f T_f} (V_2 + V_3 - V_{\text{pol}}) \right] \quad (11)$$

The term m_{sol} is the mass of gas dissolved in the polymer, M_g is the molar mass of the dissolved gas, Z_i with Z_f are the compression factors of the gas entering the polymer, respectively, at the initial (index i) and final (equilibrium sorption, index f) conditions. Volume of the degassed polymer and the volume change due to sorption are represented by V_{pol} and ΔV_{pol} , respectively.

And the total amount of gas absorbed by the polymer

Table 3
Properties of native polymers by TMDSC (before supercritical gas sorption)

Polymers	ρ (g cm ⁻³)	T_f (K)	$\Delta H_{f,c}$ (J g ⁻¹)	X_c (%)	ϕ_a (this work)	ϕ_a [10]
MDPE	0.934 ($T=298$ K)	400.0	142	49	0.55	0.53
PVDF	1.757 ($T=298$ K)	440.9	50	48	0.54	0.53

after completion of the successive transfers is given by Eq. (12)

$$\Delta m_{\text{sol}}^{(k)} = \frac{M_g}{R} \frac{p_f^{(k)}}{Z_f^{(k)}} \frac{\Delta V_{\text{pol}}^{(k)}}{T_f^{(k)}} + \frac{M_g}{R} \left[\frac{p_i^{(k)} V_3}{Z_i^{(k)} T_i^{(k)}} + \frac{p_f^{(k-1)} (V_2 - V_p - \Delta V_{\text{pol}}^{(k-1)})}{Z_i^{(k-1)} T_i^{(k-1)}} - \frac{p_f^{(k)} (V_2 + V_3 - V_{\text{pol}})}{Z_i^{(k)} T_i^{(k)}} \right] \quad (12)$$

$\Delta m_{\text{sol}}^{(k)}$ is the increment in dissolved gas mass resulting from the transfer k and $\Delta V_{\text{pol}}^{(k)}$ is the change in volume after transfer k .

The working Eq. (13) for the vibrating-wire sensor VW relates the mass, m_{sol} , of gas absorbed in the polymer to the change in volume, ΔV_{pol} , of the polymer. The natural angular frequency of the wire, through which the container housing the polymer sample is suspended, depends on the amount of gas absorbed. The physical characteristics of the wire are accounted for in the working Eq. (13) as

$$m_{\text{sol}} = \rho \Delta V_{\text{pol}} + \left[(\omega_B^2 - \omega_0^2) \frac{4L^2 R^2 \rho_s}{\pi g} + \rho (V_c + V_{\text{pol}}) \right] \quad (13)$$

The terms ω_0 with ω_B represent the natural (angular) frequencies of the wire in vacuum and under pressure, respectively, V_c the volume of the container. The symbols L , R and ρ_s are, respectively, the length, the radius and the density of the wire.

A common term appears in both Eqs. (12) and (13), the density, ρ , of the gas

$$\rho_{\text{gas}} = \frac{M_g}{RT} \frac{p_f}{Z_f} \quad (14)$$

Then Eq. (13) can be written

Table 4
Properties of carbon dioxide

Carbon dioxide CO ₂			
Purity	(%)		99.50
Rate of humidity	(%)		< 10
Critical temperature	T_c	(K)	304.13
Critical pressure	p_c	(MPa)	7.37521
Molar weight	M_g	(g mol ⁻¹)	44.0098
Molecule diameter	\emptyset	(Å)	3.5–5.1

$$\Delta m_{\text{sol}}^{(k)} = \rho_{\text{gas}} \Delta V_{\text{pol}} + d \quad (15)$$

The term d represents the apparent concentration of gas in the polymer, i.e. when the change in volume, ΔV_{pol} , is zero.

However, despite the different terms appearing in the two working Eqs. (12) and (13), these two equations can be both expressed by the same reduced Eq. (15) having the slope given by Eq. (14). The vibrating-wire sensor is described with rigorous models yielding a working equation in which all parameters have a physical meaning: ω_0 and ω_B the natural frequencies (Hz), V_c (m³), L (m), R (m) and ρ_s (kg m⁻³) of the wire. The pressure decay technique requires Z , M_g (g mol⁻¹) and the volumes of the cells (m³). The volume of the polymer sample, V_{pol} , with its associated change, ΔV_{pol} , and the total mass of dissolved gas, m_{sol} , are the only unknown terms.

It appears that the vibrating-wire sensor technique is more precise than the pVT -technique since there are no cumulative errors like in the case of the pVT -method, when the successive transfers are performed during an isothermal sorption. Fig. 1 compares the mass of CO₂ dissolved in 4 g of MDPE at 333.15 K obtained with the two methods VW and pVT . With the pressure decay method, after the critical zone (7.65 MPa), uncertainties in the mass dissolved become too large. Evidently, in the pressure critical region, a small variation of pressure leads to a significant variation of the compressibility factor.

The vibrating-wire technique does not require extensive calibrations. Essentially, uncertainties come from the experimentally measured resonance frequencies. Errors are reduced with the new data acquisition permitting the simultaneous recording of the phase with the frequency:

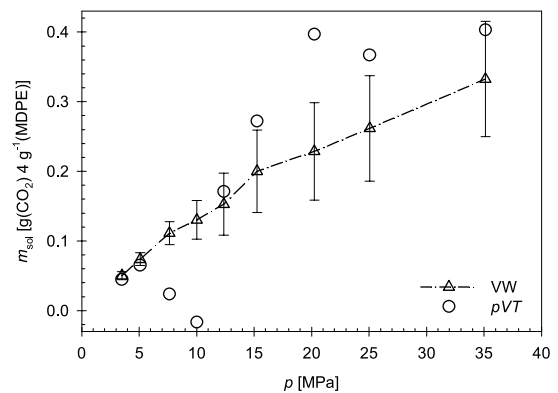


Fig. 1. Comparison of the total mass of dissolved CO₂ in 4 g of MDPE at 333.15 K as obtained with the two methods pVT (open circles) and VW (open triangles) with their respective error bars.

effectively, the phase angle is better suited than the amplitude to detect the natural resonant frequency (and also the half-width). Fig. 2 shows as an example the data obtained with a MDPE polymer sample in presence of scCO₂ at 338.15 K. Experimental amplitude and phase are correctly fitted by the fluid-mechanical theory [1] of the vibrating wire. Standard deviations for both amplitude and phase are also shown.

The main source of uncertainty affecting the evaluation of the gas concentration data comes from the term of Eq. (15) which contains the density of the gas and the change in volume of the polymer.

At this stage, it was then necessary to elaborate a new procedure to unambiguously obtain the apparent solubility of the gas in the polymer and the associated change in volume. For this, the Sanchez–Lacombe equation of state was selected to estimate the change in volume of the polymer at different pressures and temperatures.

4.2. Sorption of carbon dioxide

The extend of the polymer swelling has been estimated

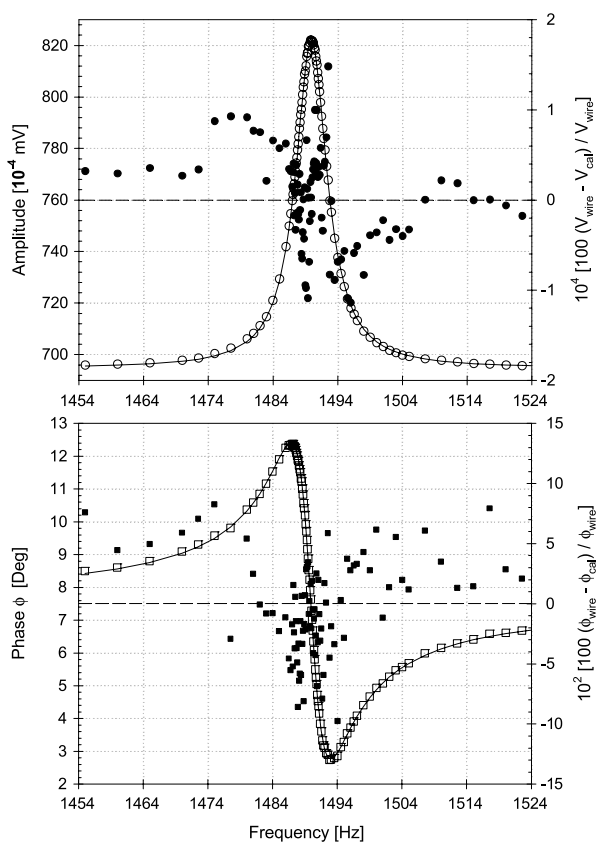


Fig. 2. Comparison of experimentally measured amplitude (open circles) and phase (open squares) of the vibrating-wire sensor. Full lines correspond to the curves calculated with the theoretical model describing the characteristics of the vibrating-wire sensor [1]. Closed symbols represent the deviation between experimental and calculated values.

using the SL-EOS and the ‘dual-mode’ model for comparison.

4.2.1. Medium-density polyethylene (MDPE)

The sorption of carbon dioxide in MD polyethylene was measured along three isotherms up to a pressure of 43 MPa for both sorption and desorption. Measurements were performed on solid polymers of two different types of samples (circular cross section rods): a number of thin rods (length 65.0 mm, diameter 2.1 mm, and total mass 3.750 g) at 333.15 and 338.15 K, one single rod (length 74.7 mm, diameter 4.4 mm, and mass 1.048 g) at 353.15 K (Table 5, Figs. 3–5). The data at 353.15 K are particularly interesting because only 1 g of sample was used: with this small weight we consider that we are close to the detection limit of the instrument.

Estimation of the change in volume of the polymer was made with the SL-EOS, in which the interaction parameter k_{12} minimizes the AAD (average of absolute deviations). The correction of the polymer swelling amounts from 4 to 2.5% depending on the temperature. The results are in good agreement with the experimental measurements realized at IFP using a quite different technique [28]. As expected, swelling increases with solubility and tends to a limit. This tendency would be explained by an increase of the free volume accessible to a penetrant molecule: that is to say a CO₂-induced increase in total free volume or a redistribution of existing free volume.

The correlation of the corrected concentration during sorption and desorption of CO₂ in MDPE was made using the ‘dual-mode’ model. Values for the fitting parameters are listed in Table 6. The results obtained either during sorption or desorption are of the same order of magnitude.

The gas concentration increases with increasing pressure and seems to decrease with increasing temperature. The only literature data for sorption in PE block samples are from Kamiya et al. [5]. They investigated sorption and desorption of CO₂ in low-density polyethylene, LDPE, using a gravimetric method up to 5 MPa at 308.15 K. Our measurements taken in the same conditions are in good agreement.

High pressure data have been obtained for PE in the molten state ($T > T_{\text{fusion}}$), for LDPE by Chaudary and Johns [6] using a gravimetric technique, Magnetic Suspension Device (MSD), and for HDPE by Sato et al. [7] using a pressure decay method with three sorption cells. As expected, the concentration in the solid state is smaller than in the molten state.

4.2.2. Poly(vinylidene fluoride) (PVDF)

Two isotherms for the sorption of carbon dioxide in poly(vinylidene fluoride) at 391.15 K are shown in Fig. 6; the results are summarized Table 7. Measurements were performed on solid polymers of two different types of samples (rods): a number of circular cross section rods (length 58.1 mm, diameter 2.4 mm, and total mass 5.716 g)

Table 5

Comparison of the apparent concentrations determined by the two methods, vibrating-wire sensor and pressure decay measurement, respectively, in MDPE at 333.15, 338.15 and 353.15 K during sorption and desorption

T (K)	p (MPa)	C^{apparent} VW (mg(CO ₂) g ⁻¹ (MDPE))	C^{apparent} pVT (mg(CO ₂) g ⁻¹ (MDPE))
333.15 Sorption	3.51	11.02	11.03
	5.09	16.83	16.11
	7.65	25.98	5.85
	10.02	30.53	0.58
	12.37	35.88	42.38
	15.26	47.37	67.38
	20.25	54.29	98.28
	25.06	62.38	90.91
	35.14	78.88	111.59
333.15 Desorption	25.20	60.58	
	20.58	57.44	
338.15 Sorption	5.84	18.40	
	9.12	23.38	
	10.99	18.86	
	12.46	26.19	
	13.73	26.47	
	15.14	27.10	
	16.91	28.83	
	18.97	30.73	
	21.23	30.14	
338.15 Desorption	16.59	26.11	
	15.12	27.87	
	12.35	14.68	
353.15 Sorption	5.95	15.61	
	2.86	10.19	
	4.04	14.33	
	10.13	40.82	
	22.93	29.11	
353.15 Desorption	25.45	36.97	
	7.98	15.06	
	6.01	9.19	

and a single rectangular cross section rod (length 69.9 mm, width 8.8 mm, thickness 5.1 mm and mass 5.588 g). An apparent convex curve is obtained different of what was observed with MDPE. The apparent concentration goes through a maximum, 18 (cm³(STP) cm⁻³(PVDF)), at 10 MPa, and then decreases with pressure. A similar trend was observed with two different studies. These series of data attest to the reliability of the apparatus. As regards experimental uncertainties, this indicates that the geometry of sample does not influence in a significant way the concentration of the gas as long as the system is at the thermodynamic equilibrium.

The apparent concentration of CO₂ in PVDF, higher than in MDPE, could be attributed to the uncertainty on estimating the polymer swelling, as observed in fitting the apparent concentration with the SL-EOS. The fitted value k_{12} chosen is 0.945. This leads to a variation in volume of 14% at 42 MPa. The corrected concentration in the sorption mode is fitted with the 'dual-mode' model using Eq. (9) with the parameters $k_D = -0.375$, $C'_H = 1403$ and $b = 0.429 \times 10^{-3}$.

Quantitative comparison with the work of Rodgers [29], who studied the same type of polymer under scCO₂ at 373.15 and 398.15 K, confirms that the apparent

Table 6

Correlation with SL-EOS and 'dual-mode' model of the scCO₂-MDPE system during sorption and desorption. k_{12} binary adjustable parameter of SL-EOS, k_D Henry's law constant, C'_H Langmuir sorption capacity, b Langmuir affinity constant

T (K)		SL-EOS k_{12}	'Dual-mode'		
			k_D	C'_H	b
333.15	Sorption	0.8600	-0.375	1403	0.443×10^{-3}
	Desorption	0.8603	-0.375	1403	0.451×10^{-3}
338.15	Sorption	0.8070	-0.0826	162.3	0.160×10^{-2}
	Desorption	0.8060	-0.0826	162.3	0.150×10^{-2}
353.15	Sorption	0.8000	0.1075	3.161	5.004×10^{-1}
	Desorption	0.8060	0.0710	3.161	5.002×10^{-1}

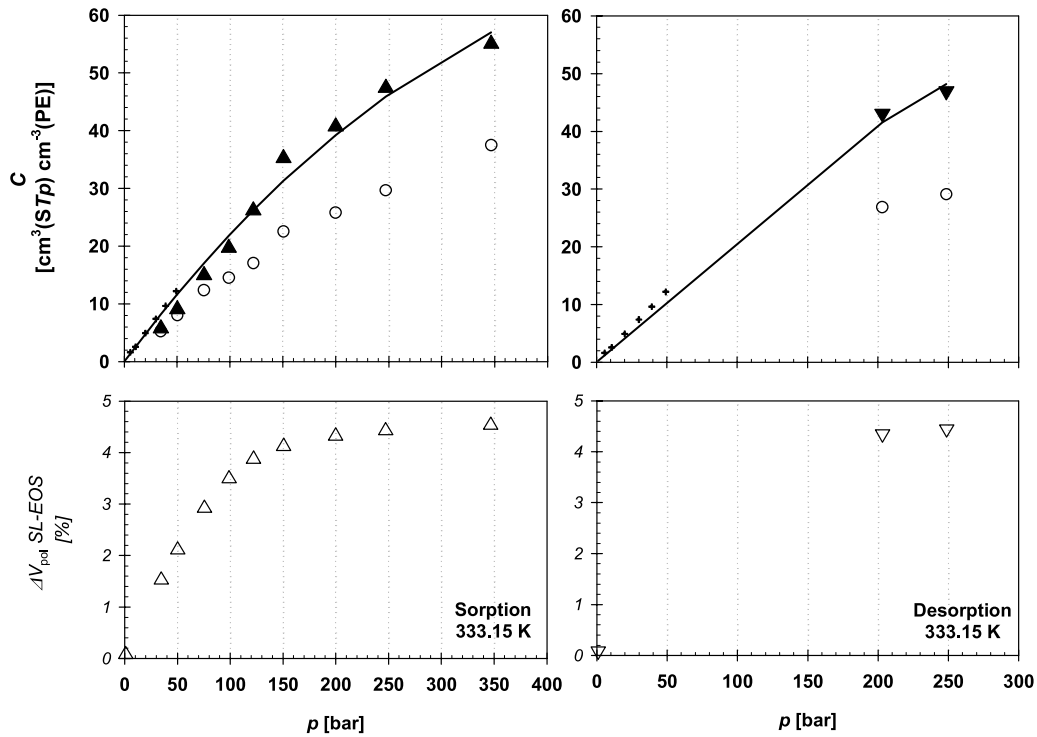


Fig. 3. Sorption (left hand side) and desorption (right hand side) of CO₂ up to 35 MPa in MDPE at 333.15 K. As a function of pressure, apparent concentration (open circles) and corrected values (closed triangles) using the swelling ΔV_{pol} of the polymer estimated using the SL-EOS (open triangles in lower graphs). Fit of the corrected values (full lines) is made with the 'dual-mode' model. +, Kamiya et al. [5] at 308.15 K for LDPE.

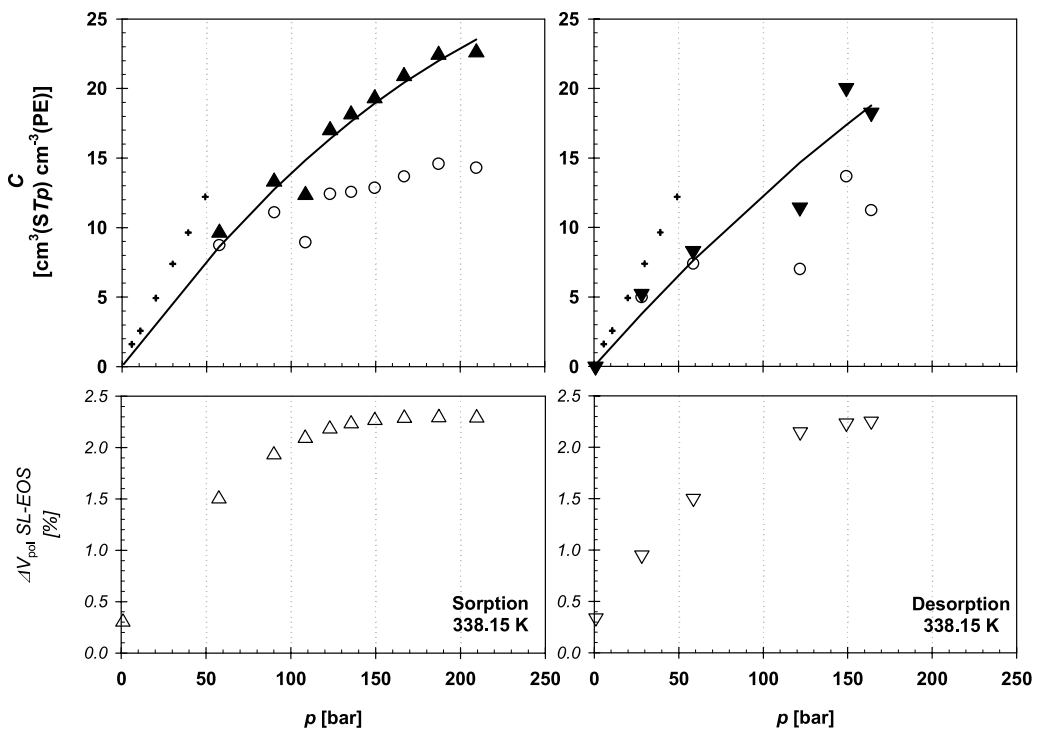


Fig. 4. Sorption (left hand side) and desorption (right hand side) of CO₂ up to 25 MPa in MDPE at 338.15 K. As a function of pressure, apparent concentration (open circles) and corrected values (closed triangles) using the swelling ΔV_{pol} of the polymer estimated using the SL-EOS (open triangles in lower graphs). Fit of the corrected values (full lines) is made with the 'dual-mode' model. +, Kamiya et al. [5] at 308.15 K for LDPE.

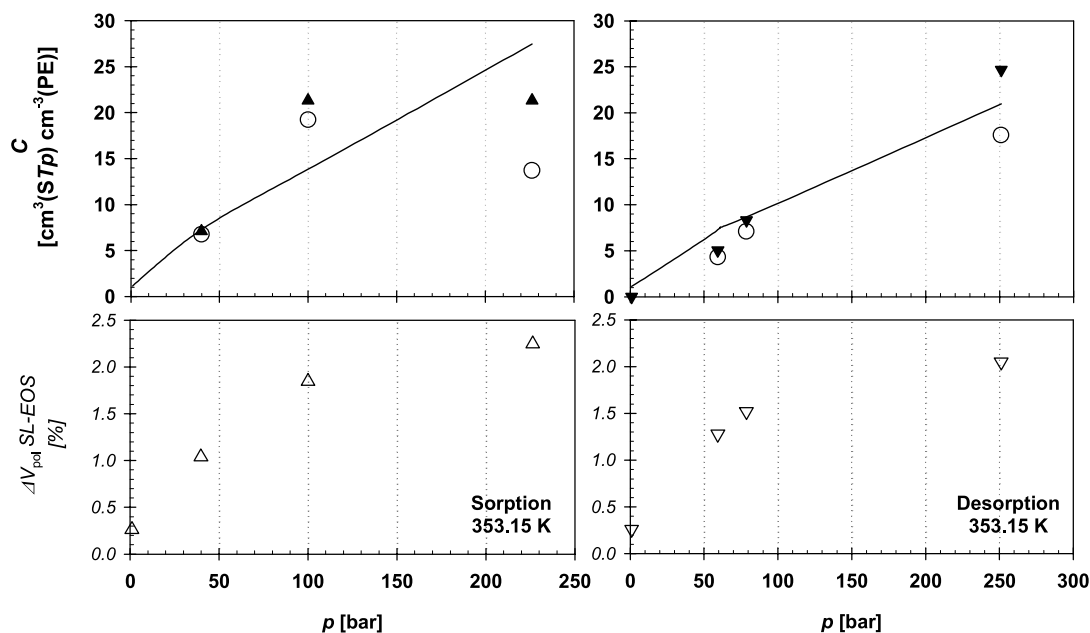


Fig. 5. Sorption (left hand side) and desorption (right hand side) of CO₂ up to 25 MPa in MDPE at 353.15 K. As a function of pressure, apparent concentration (open circles) and corrected values (closed triangles) using the swelling ΔV_{pol} of the polymer estimated using the SL-EOS (open triangles in lower graphs). Fit of the corrected values (full lines) is made with the ‘dual-mode’ model.

concentration is under-estimated as a consequence of the significant contribution of the swelling. At low pressures, up to 10 MPa, neglecting swelling does not affect the solubility, but above 15 MPa the change in volume seems important and can not be ignored.

The conclusion is in good agreement with that of Lorge et al. [30] as regards the variation of mass and the corresponding volume change for the CO₂-PVDF system at 353.15 K, during sorption and desorption at a speed of 0.5 MPa min⁻¹. They determined the gaseous mass uptake using a vibrating beam technique, the dilatation studies being performed using an ultrasonic transducer. Recent calorimetric investigations by Grolier et al. [31] confirm such trend connecting gas solubility, swelling of the polymer during sorption and the associated energy of interaction.

As a final remark, it should be noted that the present results are for the samples investigated as provided by IFP. It is commonly accepted that polymers samples may possibly contain, depending on their origin and on their end usage, specific additives (like inhibitors, antioxidants, customizing agents or residues from polymerization). Influence of such additives as well as of processing conditions have not be considered in this study. This should be the object of further investigations.

5. Conclusion

Development and use of polymer materials require the knowledge of phase equilibria of gas–polymer systems and related properties over large ranges of temperature and

Table 7

Apparent concentration of carbon dioxide in PVDF obtained with the vibrating-wire sensor method at 391.15 K during sorption, under different pressures and with different types of samples (rods)

T (K)	p (MPa)	$C^{\text{apparent}} \text{ VW (mg(CO}_2\text{) g}^{-1}\text{(PVDF))}$
391.05 Sorption circular cross section rods	5.47	11.09
	10.43	18.72
	15.20	16.80
	20.38	14.73
	31.34	8.74
	42.97	5.95
391.50 Sorption rectangular cross section rod	5.36	12.61
	10.63	19.48
	19.64	17.61
	29.75	12.66
	42.70	5.17

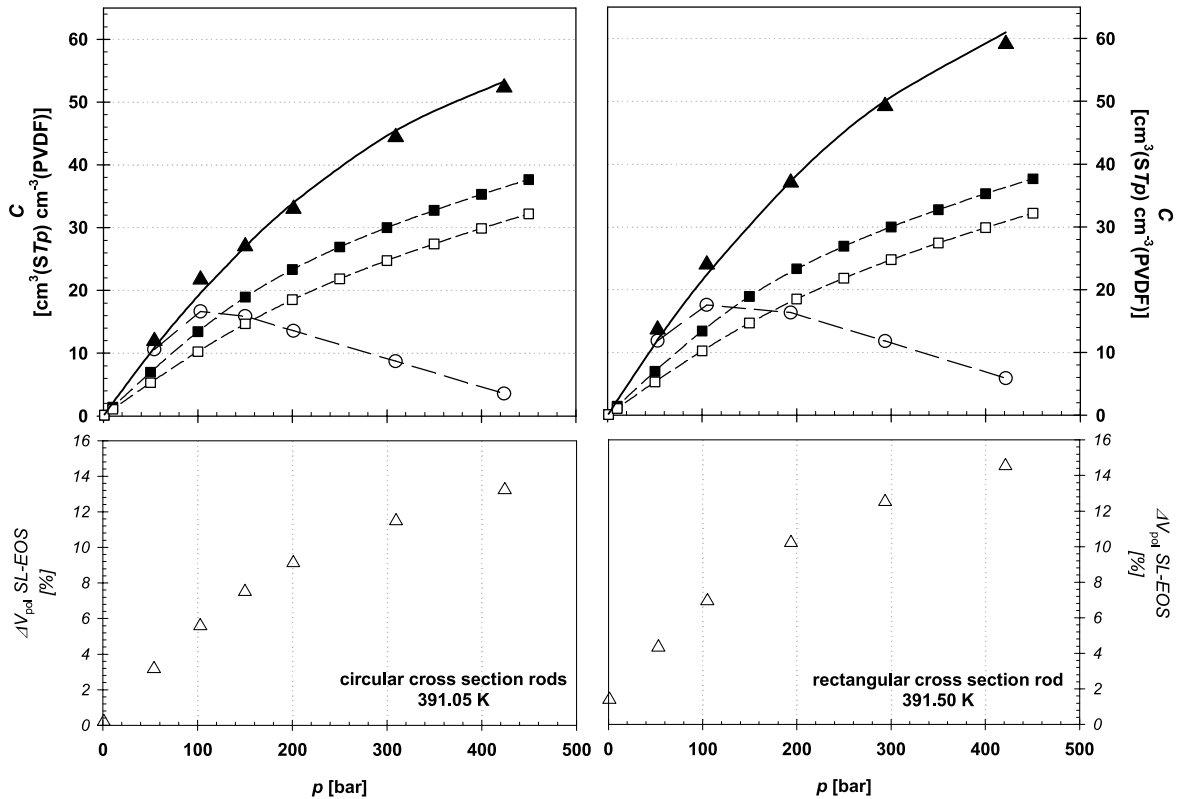


Fig. 6. Apparent concentrations (open circles) of CO₂ in PVDF at 391.15 K as a function of pressure (up to 43 MPa) in two different types of polymer samples (circular cross section rods and rectangular cross section rod). Corrected concentration (open symbols in lower graphs) is obtained using the change in volume of the polymer estimated using the SL-EOS. The fitted value $k_{12}=0.945$ is the value used to correlate the corrected concentration (closed triangles). The correlation (full lines) of the corrected concentration is done using the 'dual-mode' model. Data of Rodgers [29]: at 373.15 K (closed squares) and at 398.15 K (open squares).

pressure. Therefore it is essential that the data used should be critically evaluated. The present thermodynamic approach dealt with the determination of the concentration of supercritical carbon dioxide in two different semicrystalline polymers under elevated T and p . To this end the solubility of gases in polymers was investigated using coupled methods, i.e. a 'weighing technique' making use of a vibrating-wire (VW) sensor and a pVT -technique to perform pressure decay measurements. Particular attention was paid as to improve the accuracy of the entire experimental procedure. At this stage, only the apparent concentration of gas can be directly measured. The working equation, allowing to correlate the concentration of the gas with the density of the fluid, shows the importance of the gaseous density on the gas solubility and confirms that the volume change must not be ignored. An estimation of polymer swelling is necessary and it has been made using the SL-EOS.

Up to now, the evaluation of polymer swelling was usually carried out separately from solubility experiments. Quite recent investigations concern the simultaneous measurement of sorption and of the concomitant swelling in polymeric films making use of a quartz spring balance coupled with a CCD camera method [32].

Principal notations used

AAD	$AAD = \frac{1}{N} \times \sum_{i=1}^N Valeur_i^{exp} - Valeur_i^{cal} $	Average of absolute deviations
C'_H	$(cm^3(STP) cm^{-3} (polymer))$	Langmuir sorption capacity
MDPE		Medium-density polyethylene
PVDF (or PVF ₂)		Poly(vinylidene fluoride)
SL-EOS		Sanchez-Lacombe equation of state
VW		Vibrating-wire sensor
XDF		Explosive decomposition failure
b	(atm^{-1})	Langmuir or holes affinity constant
d	$(g(gas) g^{-1}(polymer))$	Apparent concentration ($\Delta V_{pol}=0 m^3$)
k_D	$(cm^3(STP) cm^{-3} (polymer)^{-1} p^{-1})$	Henry's law constant
k_{12}		Binary adjustable parameter of SL-EOS
scCO ₂		Supercritical carbon dioxide
ΔV_{pol}	(m^3)	Swelling of the polymer
ρ	$(kg m^{-3})$	Density of the fluid

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References

- [1] Hilic S, Pádua AAH, Grolier J-PE. *Rev Sci Instrum* 2000;71(11): 4236–41.
- [2] Hilic S, Boyer SAE, Pádua AAH, Grolier J-PE. *J Polym Sci B: Polym Phys* 2001;39:2063–70.
- [3] Dewimille B, Martin J, Jarrin J. *J de Physique IV* 1993;3(7):1559–64.
- [4] Jarrin J, Dewimille B, Devaux E, Martin J. *Int SPE* 1994;28482: 203–14.
- [5] Kamiya Y, Hirose T, Mizoguchi K, Naito Y. *J Polym Sci B: Polym Phys* 1986;24:1525–39.
- [6] Chaudary BI, Johns AI. *J Cell Plast* 1998;34:312–28.
- [7] Sato Y, Fujiwara K, Takikawa T, Sumarno, Takishima S, Masuoka H. *Fluid Phase Equilibria* 1999;162:261–76.
- [8] Klopffer M-H, Flaconnèche B. *Oil Gas Sci Technol-Rev IFP* 2001; 56(3):223–44.
- [9] Flaconnèche B, Martin J, Klopffer M-H. *Oil Gas Sci Technol-Rev IFP* 2001;56(3):245–59.
- [10] Flaconnèche B, Martin J, Klopffer M-H. *Oil Gas Sci Technol-Rev IFP* 2001;56(3):261–78.
- [11] Michaels AS, Bixler HJ. *J Polym Sci* 1961;50:393–412.
- [12] Michaels AS, Bixler HJ. *J Polym Sci* 1961;50:413–39.
- [13] Michaels AS, Parker RB. *J Polym Sci* 1959;41:53–71.
- [14] Tsujita Y. *Prog Polym Sci* 2003;28:1377–401.
- [15] Hu C-C, Chang C-S, Ruaan R-C, Lai J-Y. *J Membr Sci* 2003;226: 51–61.
- [16] Sanchez IC, Lacombe RH. *Macromolecules* 1978;11(6):1145–56.
- [17] Boudouris D, Constantinou L, Panayiotou C. *Fluid Phase Equilibria* 2000;167:1–19.
- [18] Hariharan R, Freeman BD, Carbonell RG, Sarti GC. *J Appl Polym Sci* 1993;50:1781–95.
- [19] DeAngelis MG, Merkel TC, Bondar VI, Freeman BD, Doghieri F, Sarti GC. *J Polym Sci B: Polym Phys* 1999;37:3011–26.
- [20] Meares P. *J Am Chem Soc* 1954;76:3415–22.
- [21] Barrer RM, Barrie JA, Slater J. *J Polym Sci* 1958;27:177–97.
- [22] Vieth WR, Howell JM, Hsieh JH. *J Memb Sci* 1976;1:177–220.
- [23] Vieth WR, Sladek KJ. *J Colloid Sci* 1965;20:1014–33.
- [24] Koros WJ, Paul DR. *J Polym Sci: B Polym Phys* 1978;16:1947–63.
- [25] Vieth WR, Tam PM, Michaels AS. *J Colloid Interface Sci* 1966;22: 360–70.
- [26] Ely JF, Magee JW, Haynes WM. Thermophysical properties for special high CO₂ content mixtures. Gas Processors Association, 1987 Research Report-110.
- [27] Vesovic V, Wakeham WA, Olchoway GA, Sengers JV, Watson JTR, Millat J. *J Phys Chem Ref Data* 1990;19(3):763–808.
- [28] Bazourdy E, Martin J. Etude de l’influence du confinement sur le comportement de matériaux polymères soumis à de fortes pressions de gaz. IFP report 45 568, June 1999.
- [29] Rodgers P. Equation-of-state predictions of solubility in semi-crystalline poly(vinylidene fluoride). IFP report 39887, July 1992.
- [30] Lorge O, Briscoe BJ, Dang P. *Polymer* 1999;40:2981–91.
- [31] Grolier J-PE, Dan F, Boyer SAE, Orłowska M, Randzio SL. *Int J Thermophys* 2004;25(2):297–319.
- [32] Piccinini E, Giacinti Baschetti M, Sarti GC. *J Membr Sci* 2004;234: 95–100.