Gas Sorption and Dilation in Poly(2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethylene): Comparison of Experimental Data with Predictions of the Nonequilibrium Lattice Fluid Model

M. G. De Angelis,[‡] T. C. Merkel,[†] V. I. Bondar,[†] B. D. Freeman,[†,§] F. Doghieri,[‡] and G. C. Sarti*,[‡]

Department of Chemical Engineering, North Carolina State University,
Raleigh, North Carolina 27695-7905; and Dipartimento di Ingegneria Chimica,
Mineraria e delle Tecnologie Ambientali, Università di Bologna, Viale Risorgimento 2,
40136 Bologna, Italy

Received April 9, 2001

ABSTRACT: The sorption and dilation properties of a series of *n*-alkanes and the corresponding perfluorinated compounds have been examined in two amorphous copolymers of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD), commercially available under the names Teflon AF1600 and AF2400. The analysis was made at three different temperatures: 25, 35, and 45 °C, to test the effect of temperature on solubility and to evaluate the sorption enthalpies. The partial molar volumes of most penetrants have also been determined in both copolymers. The experimental data have been satisfactorily compared with the sorption isotherms predicted or correlated using the nonequilibrium lattice fluid model.

Introduction

The sorption of gases and vapors in polymers and the related swelling of the polymeric matrix are phenomena of significant importance in the field of membrane separations. Traditionally, penetrant sorption isotherms in glassy polymers have been described by a well-established empirical correlation known as the dual-mode sorption model (DMS).[1,2] The physical assumptions of this model, however, give an oversimplified picture of the sorption process, and its three adjustable parameters depend on temperature, pressure, and the specific penetrant−polymer pair.[3] As a consequence, no predictive use can be made of this model. In recent years a thermodynamic formulation proposed by Doghieri and Sarti[4] and known as the nonequilibrium lattice fluid (NELF) model has been developed.[4−8] This model considers the penetrant molecules to be dissolved in a uniform nonequilibrium glassy phase; it can be used in a predictive way, based only on pure component parameters, and has proved to be quite satisfactory for all gas−polymer pairs examined to date. Comparisons between the DMS and NELF models have already been discussed elsewhere[4−8] and are not the focus of this paper. Instead, we will compare the predictions of the NELF model to experimental sorption data for a series of gases and vapors, including hydrocarbon and fluorocarbon analogues, in two glassy perfluoropolymers. The application of the NELF model to this case is rather interesting and meaningful, since the perfluoropolymers considered are endowed with extremely high free volume, so that the basic assumptions of the model are tested more severely than in other cases. Additionally, previously observed differences in hydrocarbon and fluorocarbon solubilities in polymers not anticipated by regular solution theory should provide an interesting test of the NELF model's predictive ability.

Previous sorption studies[9−11] have shown that fluorocarbons are less soluble than the analogous hydrocarbon penetrants in a hydrocarbon-based polymer such as poly(dimethylsiloxane) [PDMS]; the same trend is observed, to a lesser extent, in poly(1-trimethylsilyl-1-propyne) [PTMSP].[12,13] In the case of PDMS, in particular, even when the sorption results are correlated to differences in condensability and molecular size between penetrants, the fluorocarbons follow a separate correlation line, corresponding to lower solubility than for the hydrocarbon analogues.[10] The above results suggest that the solubility of these components in the polymeric matrix is strongly dependent on polymer−penetrant interactions, which favor the mixing of penetrant in a chemically similar polymer. In contrast to the behavior observed in PDMS and PTMSP, fluorinated compounds are more soluble than their hydrocarbon analogues in the fluorocopolymer AF2400, thus confirming the crucial role played by polymer−penetrant interactions.[14] Previous results for modeling equilibrium hydrocarbon and perfluorocarbon solubility in PDMS via the Sanchez−Lacombe model[9] indicate that these polymer−penetrant interactions must be taken into account. In that case, it was found that the zero-order approximation for the binary interaction mixing rule is not always sufficient, particularly so for cases in which the interactions between polymer and penetrant are very different from the interactions between molecules of the pure species.

The polymers investigated in this study are two random, glassy copolymers of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD), containing 65 and 87 mol % BDD and commercially available under the trade names Teflon AF1600 and AF2400, respectively. These perfluoropolymers possess extremely high fractional free volumes and are among the most permeable polymers known.[15−19] In this work,

---

[†] North Carolina State University.

[‡] Università di Bologna.

[§] Present address: Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78758.

10.1021/ma0106090 CCC: $22.00

we refer to the experimental sorption data collected for a large series of penetrants by Merkel et al.[14] For several penetrants, we have also measured the volumetric dilation induced during isothermal sorption, which is crucial information for the use of the NELF model.[4−6] For the sake of review the basic relationships of the NELF model are briefly recalled hereafter.

Background

Sanchez and Lacombe[20−23] and Panayiotou and Vera[24,25] have developed lattice fluid models which have been rather successfully used to describe the behavior of polymers and of polymeric mixtures. The NELF model uses, for the Gibbs free energy of a glassy mixture, the expression proposed by Sanchez and Lacombe in their lattice fluid theory, which for a binary mixture of a low molecular weight species, 1, in a polymer, 2, gives[21]

$$G = RT^*(r_1 n_1 + r_2 n_2)\left\{-\tilde{\rho} + \frac{\tilde{p}}{\tilde{\rho}} + \frac{\tilde{T}}{\tilde{\rho}}[(1-\tilde{\rho}) \ln(1-\tilde{\rho}) + \frac{\phi_1}{r_1}\tilde{\rho}\ln(\phi_1\tilde{\rho}) + \frac{\phi_2}{r_2}\tilde{\rho}\ln(\phi_2\tilde{\rho})]\right\} \quad (1)$$

where R is the ideal gas constant, r_i is the number of lattice sites occupied by a mole of species i, and ϕ_i is the volume fraction of species i, defined in terms of the mass fraction ω_i and of the characteristic densities of the pure components $\rho_i{}^*$ as[21]

$$\phi_i = \frac{\omega_i/\rho_i^*}{\omega_1/\rho_1^* + \omega_2/\rho_2^*} \quad (2)$$

The quantities $\tilde{\rho}$, $\tilde{p}$, and $\tilde{T}$ represent the reduced density, pressure, and temperature of the mixture, respectively, and are defined as follows:

$$\tilde{\rho} = \rho/\rho^* \quad \tilde{p} = p/p^* \quad \tilde{T} = T/T^* \quad (3)$$

The characteristic lattice parameters ρ^* and p^* represent the mass density and cohesive energy density (CED) at close packed conditions, respectively, while T^* is associated with the average interaction energy between the chain segments contained in nearby lattice cells. For a binary mixture, the characteristic parameters can be calculated from the corresponding pure component values using the following three mixing rules:[23]

$$\frac{1}{\rho^*} = \frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*} \quad (4)$$

$$p^* = \phi_1^2 p_1^* + \phi_2^2 p_2^* + 2\phi_1\phi_2 p_{12}^* \quad (5)$$

$$p^* v^* = RT^* \quad (6)$$

The characteristic volumes and densities are related to each other through the usual relationship:

$$\rho_i^* v_i^* = \frac{M_i}{r_i^0} \quad (7)$$

The symbol r_i^0 indicates the number of lattice sites occupied by a mole of species i in the pure component lattice, which is related to the number of lattice sites r_i occupied by a mole of species i in the mixture as follows:

$$\frac{r_i}{r_i^0} = \frac{v_i^*}{v^*} \quad (8)$$

The binary parameter p_{12}^* in eq 5 is constant with respect to composition and temperature and is determined through experimental miscibility data of the binary mixture. As a first approximation, one can estimate its value based only on pure component characteristic pressures: [23]

$$p_{12}^* = \sqrt{p_1^* p_2^*} \quad (9)$$

For the more general case it is also customary to represent the binary parameter p_{12}^* as

$$p_{12}^* = \Psi\sqrt{p_1^* p_2^*} \quad (10)$$

where the quantity Ψ plays the role of an adjustable interaction parameter for the binary mixture.

From eq 1 for the Gibbs free energy, one can obtain the density of the mixture under equilibrium conditions by imposing the minimization of the Gibbs free energy at T, p, and ω_ι with respect to the density. This condition yields an equilibrium PVT equation of state for the mixture, generally known as the Sanchez−Lacombe equation of state:

$$\tilde{\rho} = 1 - \exp\left[-\frac{\tilde{\rho}^2}{\tilde{T}} - \frac{\tilde{p}}{\tilde{T}} - \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] \quad (11)$$

The density of a glassy mixture, however, cannot be calculated through this equation of state, since the system is not at equilibrium. However, it has been demonstrated[5] that when the temperature, pressure and density are treated as independent variables, expression 1 provides the proper and unique nonequilibrium Gibbs free energy for a lattice fluid in which the bulk rheology is governed by a Voigt model. Therefore, it can be assumed that the Gibbs free energy of the glassy mixture can be represented by eq 1 together with the above-mentioned mixing rules.

In the following, we will express the mixture density, ρ, in terms of the polymer partial density, ρ_2, which can be obtained directly from polymer dilation data. By definition,[43] we have

$$\tilde{\rho} = \frac{\rho_2}{\omega_2\rho^*} \quad (12)$$

The density of a glassy mixture gives a measure of the departure from the equilibrium state of the system, when compared with its equilibrium value at the temperature, pressure and composition considered. The polymer density ρ_2 was shown to be the only order parameter required; it is indeed an internal state variable for the glassy phase,[4] i.e., its time rate of change is itself a function of the state of the system. Such a result is obtained based on the bulk rheology of the glassy mixture during sorption or desorption, and allows the use of the thermodynamics of systems endowed with internal state variables to describe the behavior of the glassy mixture. The variables required to define the state of the system are T, p, and ω_1 (as in the equilibrium case) and the polymer density, ρ_2, which characterizes the departure of the system from equilibrium. Nonequilibrium thermodynamic arguments[27] provide an expression for penetrant chemical potential in the glassy phase:

$$\mu_1^{(S)} = \left(\frac{\partial G}{\partial n_1}\right)_{T,p,\rho_2,n_2} \tag{13}$$

Even for glassy mixtures, the phase equilibrium established at the interface with an external fluid containing the penetrant component requires a common value for the penetrant chemical potential both in the solid and in the external phase[5]

$$\mu_1^{(S)}(T, p, \omega_1, \rho_{2,\infty}) = \mu_1^{(E)}(T, p, y_1) \tag{14}$$

where y_1 is the mole fraction of component 1 in the surrounding phase, for the general case in which the external phase is a gaseous mixture. The polymer density reaches an asymptotic value $\rho_{2\infty}$, instead of its equilibrium value because the relaxation of the glassy matrix is kinetically hindered.

The chemical potential of component 1 in the glassy polymeric phase can now be obtained by using eq 13 as a function of ρ, p, T and composition ϕ_1; one finally has

$$\frac{\mu_1^{(S)}}{RT} = \ln(\tilde{\rho}\phi_1) - \left[r_1^0 + \frac{(r_1 - r_1^0)}{\tilde{\rho}}\right]\ln(1 - \tilde{\rho}) - r_1 + 1 - \tilde{\rho}\left[\frac{2r_1^0\, v_1^*(\phi_1 p_1^* + \phi_2 \Psi\sqrt{p_1^*\, p_2^*})}{RT}\right] \tag{15}$$

The above expression for the chemical potential of a pure penetrant in a glassy mixture is the main result of the NELF theory, associated to the use of the Sanchez–Lacombe expression of the Gibbs free energy, and is exactly equivalent to the expression used in previous works.[4–8] By considering the phase equilibrium condition represented by eq 14, one can calculate, at fixed T, p, and ρ_2, the composition ω_1 of the penetrant in the glassy mixture in a pseudoequilibrium state.

The above expression also demonstrates the influence of the binary interaction parameter Ψ on the chemical potential of the penetrant in the solid phase and, therefore, on solubility. The value of Ψ can, in principle, be determined from a single mixture data point, for example at infinite dilution, and either under true thermodynamic equilibrium (rubbery phase) or in pseudoequilibrium conditions (glassy phase). The predicted solubility increases with increasing Ψ because the attraction energy between unlike species increases. Equations 14 and 15 offer an implicit expression for the mass fraction of the penetrant in the polymer as a function of the external activity; an iterative but straightforward procedure is used to calculate ω_1 and thus to obtain the solubility isotherms.

Polymer Density: NELF Predictions and Correlations. The proper use of Equations 14 and 15 for the solubility isotherm requires knowledge of polymer density in the glassy phase, $\rho_{2\infty}$, asymptotically reached under pseudoequilibrium conditions at each penetrant pressure. Equations 14 and 15 are rather sensitive to the polymer density, so its value must be known to good accuracy. To that aim one would require, in principle, measurements of the dilation isotherm during sorption or desorption, in which case one can use the NELF model in an entirely predictive mode. In the absence of specific information on the volumetric isotherm, one can take advantage of the following observations by considering separately swelling and nonswelling penetrants.

i. When the penetrant species has a rather low solubility and is a nonswelling agent, as is the case for permanent gases such as oxygen and nitrogen, the polymer density does not change appreciably with the penetrant pressure, and for all practical purposes, the value $\rho_{2\infty}$ can be replaced by the density of the pure, penetrant-free glassy polymer, ρ_2^0;

ii. For the case of swelling penetrants, it is convenient to consider separately the low-pressure portion of the isotherm from the general case.

In the low-pressure range[6] even for highly swelling penetrants, such as CO_2, the corresponding volume dilations are not significant, so that in such a range one can still use the value of the pure glassy polymer density ρ_2^0 in place of the actual $\rho_{2\infty}$ value.

This approximation is no longer valid at higher pressures for which $\rho_{2\infty}$ becomes significantly smaller than ρ_2^0, and correspondingly the solubility calculated using the true polymer density is larger than the value calculated by neglecting volume dilation.[6] However, the entire solubility isotherm can be reliably calculated in the absence of direct dilation data provided at least one data point of the sorption isotherm is known from experiments. The procedure is illustrated in detail in ref 5 and is briefly summarized here. From the available experimental data on volume dilation in the polymeric matrix during sorption, one realizes that the volume of the glassy phase is typically linearly proportional to the gas pressure. Thus, only one point of the curve is needed to draw the dilation isotherm, once the density of the pure polymer is known. Therefore, for systems whose swelling is expected to be significant, this consideration allows us to treat the value of dilation at one single penetrant pressure as an adjustable parameter. One can choose a single experimental data point in the solubility isotherm and then use it as the input in eq 14 to calculate the value of the polymeric density ρ_2, at the temperature and pressure considered. The volume dilation isotherm is then obtained in a straightforward way at all pressures by simply assuming a proportional relation between pressure and the volume change of the system per unit polymer mass. In this way, one obtains good estimates of polymer density in the glassy phase for any external penetrant pressure, and can thus calculate the solubility isotherm over the entire pressure range of interest. Therefore, in the absence of experimental dilation data, we will use hereafter this method to predict solubility and test the reliability of the NELF model over the entire range of pressures explored experimentally.

Experimental Section

Dilation measurements were conducted using an apparatus described previously.[9] The sample is a polymeric film about 100 mm long suspended in a pressure chamber in which penetrant gas is introduced at the desired pressure. This device monitors the elongation of the sample from which, assuming the dilation to be isotropic, the volume change can be easily calculated. All experiments were conducted at 35 °C after degassing the sample chamber for 24 h. Further details regarding this equipment can be found in ref 9.

Results and Discussion

Evaluation of Sanchez–Lacombe Equation of State Characteristic Parameters. The characteristic parameters p^*, ρ^*, and T^* of the pure polymers are determined by fitting to the Sanchez–Lacombe equation of state experimental *PVT* data above T_g where the equilibrium condition expressed by eq 11 holds true. For AF1600 and AF2400, we used a compilation of volumetric data ranging from 100 to 2000 bar and from 300 to 620 K.[28] As already shown by various authors, use of the Sanchez–Lacombe equation of state with a single set of parameters often cannot accurately describe experimental pressure–volume–temperature data over very wide ranges of temperature and pressure.[29,30] To obtain an accurate representation of the volumetric behavior, it is thus necessary to confine the regression to a more restricted range of experimental data closer to the pressures and temperatures of interest. In this work, we optimized the fitting of volumetric data by considering pressures below 300 bar and temperatures up to 550 K for AF1600 and up to 620 K for AF2400.

The volumetric properties of the copolymers investigated in this study are rather unusual and extremely interesting for industrial applications. In particular, the polymer compressibility is very high as compared to other common polymers and to many simple fluids.[31] The isothermal compressibility, β, is closely related to the characteristic pressure p^* in the Sanchez–Lacombe theory and ultimately to the cohesive energy density of the polymer; in particular, p^* decreases with increasing β. In agreement with this observation the value of p^* obtained from the regression is much lower than the value calculated for all other known polymers. The characteristic pressure is equal to 2800 bar for AF1600 and to 2500 bar for AF2400, while the typical range for polymers is from 3000 to 6000 bar.[32] As a consequence, this polymer is characterized by weak intermolecular forces, that is, by a low value of the cohesive energy density. In the classical theory of regular solutions by Hildebrand and Scatchard,[33] the cohesive energy density of a substance determines its sorption behavior: in particular, two compounds with similar CED must be mutually soluble and vice versa. It is interesting to note that the perfluorocarbon compounds have the lowest values of CED among all organic substances, and that the amorphous Teflons (i.e., AF1600 and AF2400) have the lowest values of compressibility among polymers.

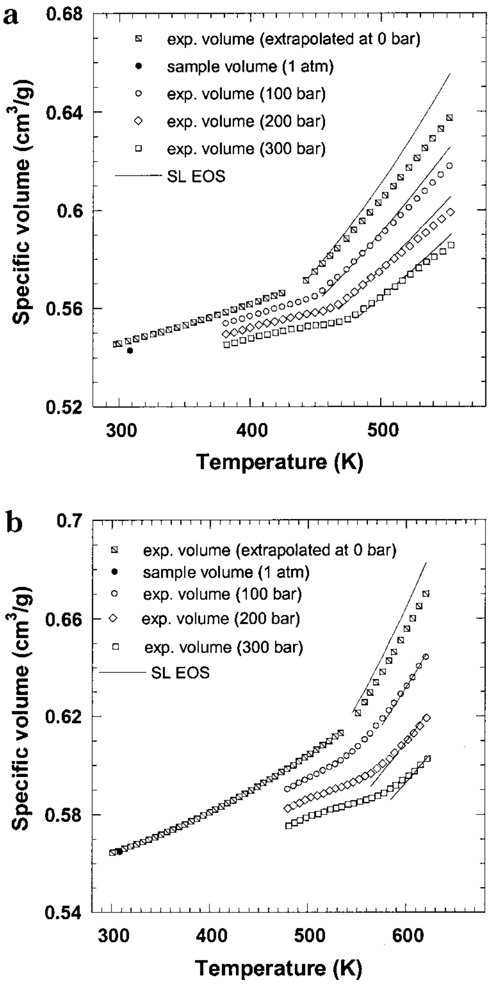

Figure 1. Volumetric properties for AF1600 (Figure 1a) and AF2400 (Figure 1b) and comparison with the Sanchez–Lacombe equation of state, represented by the solid lines. Experimental data were taken from ref 31.

Table 1. SL Equation of State Characteristic Parameters for Polymers

polymer	p^* (bar)	T^* (K)	ρ^* (kg/L)	ref
AF1600	2800	575	2.16	this work
AF2400	2500	624	2.13	this work
PTFE	3710	618	2.25	Sanchez et al.[37]

The compressibility of Teflon AF increases with BDD monomer content, as observed by Walsh et al.,[31] which leads to a clear correlation between volumetric properties and BDD content. The oxygenated BDD ring breaks up chain packing of poly(tetrafluoroethylene) [PTFE] and inhibits crystallization. The resulting copolymers are totally amorphous and exhibit free volumes that are much larger than most other glassy polymers.[19] In addition, the effect of pressure on the glass transition temperature is unusually high, so that, at relatively low pressures (300–400 bar), T_g for AF2400 exceeds 620 K, i.e., the maximum temperature at which the volumetric measurements are available. As a result, there are only a few volumetric data actually available in the rubbery region (cf. Figure 1b), so that it is difficult to determine the exact value of T_g at each pressure. The lack of volumetric information makes the fitting procedure used to retrieve the Sanchez–Lacombe characteristic parameters somewhat less reliable. The set of parameters used in this study are shown in Table 1, and the comparison between experimental volumetric data in the rubbery phase and the corresponding values calculated by the Sanchez–Lacombe equation of state using the former set of parameters is presented in Figure 1, parts a and b. No other set of Sanchez–Lacombe parameters for the amorphous Teflon copolymers was found in the literature. In Table 1, we have listed for comparison the characteristic parameters for PTFE as determined by Sanchez.[34] In parts a and b of Figure 1, the data at low pressure (0 bar) have been extrapolated analytically by assuming the isothermal compressibility coefficient to be constant in the range 0–200 bar since experimental densities at atmospheric pressure were not available in the mentioned compilation of data. The SL parameters reported in Table 1 were determined by fitting v–T curves in the range 100–300 bar, while the extrapolated isobaric curve was only displayed in order to compare it as a first approximation with the value of density of our sample at 308 K and 1 atm as measured before experimental dilation runs. In parts a and b of Figure 1, the filled circle represents the measured specific volume of the samples used in this work: the sample density is equal

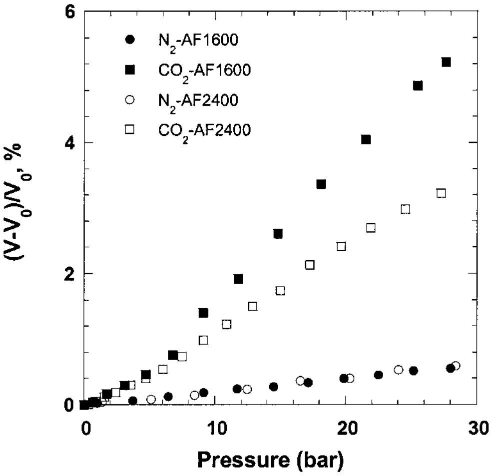

Figure 2. Volume dilation due to sorption of nitrogen and carbon dioxide in AF1600 and AF2400 as measured in this work at 35 °C.

Table 2. SL Equation of State Characteristic Parameters for Penetrants

penetrant	p^* (bar)	T^* (K)	ρ^* (kg/L)	ref	source of *PVT* data
N_2	1600	145	0.943	9	Vargaftik[40]
O_2	2140	180	1.250	9	Vargaftik[40]
CO_2	6300	300	1.515	9	Vargaftik[40]
CH_4	2500	215	0.500	9	Vargaftik[40]
C_2H_6	3300	320	0.640	9	Daubert and Danner[41]
C_3H_8	3200	375	0.690	9	Vargaftik[40]
n-C_4H_{10}	2900	430	0.720		Vargaftik[40]
CF_4	2650	230	1.920	9	Daubert and Danner[41]
C_2F_6	2270	296	1.950	9	Daubert and Danner[41]

to 1.84 g/cm^3 for AF1600 and to 1.77 g/cm^3 for AF2400, in good agreement with the extrapolated data at 0 bar. The SL parameters of gaseous penetrants were taken from previous works, except for n-butane, for which they have been computed, and are listed in Table 2 along with the source of the experimental data used.

Sorption and Dilation Isotherms for Light Gases (N_2, O_2, CO_2). Dilation isotherms were measured in this study for N_2 and CO_2 in AF1600 and AF2400 at 35 °C and up to 30 bar. For these penetrants, the dilation data were used to obtain at each penetrant pressure the mixture density, which is needed as an input variable in calculating the gas solubility through eq 14. Sorption isotherms calculated in this manner were then compared to the experimental data. In the case of O_2, for which volume dilation is typically very small (although it was not experimentally recorded) we followed the low-pressure approximation[6] and considered the polymeric density constant during the sorption process and equal to the pure glassy polymer density. The dilation isotherms at 35 °C of the systems N_2−AF1600, N_2−AF2400, CO_2−AF1600, and CO_2−AF2400 are presented in Figure 2. The relative volume change of the more dense AF1600, at a fixed penetrant pressure and temperature, is slightly greater than the corresponding value for AF2400, due to the higher free volume of the latter polymer. The amount of volume change is about 0.6% at 30 bar for nitrogen in both copolymers, while for CO_2 it is 3.2% and 5.1% at 27 bar in AF2400 and AF1600, respectively.

A comparison between the experimental sorption isotherms of N_2, O_2 and CO_2 and the predictions calculated by the NELF model are shown in Figure 3, parts a−c. For nitrogen dissolution in AF2400 and AF1600, the sorption isotherms are well predicted by the NELF model using no adjustable parameters (i.e., by adopting for the binary interaction parameter Ψ the default value of 1). Similarly for the systems O_2−AF1600 and O_2−AF2400, the sorption isotherms are exactly predicted with no adjustable parameters over the entire pressure range explored, thus confirming the hypothesis made on the amount of dilation to be expected in this case. For CO_2−AF2400 mixtures, the solubility is correctly predicted at low pressures, while the model somewhat underestimates the sorption level at higher pressures (43 cm^3(STP)/cm^3 at 25 bar vs a measured value of 56 cm^3(STP)/cm^3). On the other hand, the solubility of carbon dioxide in AF1600 is correctly evaluated in the whole range of pressures. In both cases, the model is used with no adjustable parameters. As a conclusion, we may say that, for these light gases, the NELF model works satisfactorily in predicting “a priori” the solubility in the fluorinated copolymers under study.

Sorption and Dilation of Hydrocarbons and Fluorocarbons. The solubilities of a series of normal alkanes (CH_4, C_2H_6, C_3H_8, n-C_4H_{10}) and perfluoroalkanes (CF_4, C_2F_6) in AF2400 and AF1600, presented in the work of Merkel et al.,[14] have been compared with the predictions of the NELF model. The amount of dilation induced during sorption was measured for two representative elements of the homologous series, ethane and perfluoroethane. First of all, one may notice that in both perfluorinated copolymers the sorption level for a perfluorocarbon compound is systematically higher than for the homologous hydrocarbon with the same number of carbon atoms. Such behavior is clearly shown in Figure 4, where the experimental sorption isotherms of methane and ethane in AF2400 at 35 °C are compared with those of the corresponding perfluorocarbons. The solubility at 25 bar is about 20 cm^3(STP)/(cm^3 of polymer) for methane while it is 32 cm^3(STP)/(cm^3 of polymer) for CF_4 in AF2400; for ethane and perfluoroethane, the respective solubilities at the same pressure are 52 and 57 cm^3(STP)/(cm^3 of polymer). An analogous difference between fluorinated and nonfluorinated compounds is demonstrated by the solubility isotherms in AF1600. In comparing the behavior of the two polymers, we observe that all penetrants are more soluble in AF2400 than in AF1600, which is consistent with the higher free volume characterizing the AF2400 matrix. On the basis of the dilation measurements, the swelling induced by the fluorocarbons in both copolymers is greater than the swelling induced by their hydrocarbon analogues. In addition, for each penetrant the volume dilation induced in AF1600 is systematically larger than in AF2400, consistent with the behavior of the light gases. The dilation isotherms of C_2H_6 and C_2F_6 are shown in Figure 5, from which we can see that the amount of volume change for AF1600 at 25 bar is about 6% when C_2H_6 is the penetrant and about 12% for C_2F_6. At the same penetrant pressure, the relative volume change for AF2400 is 5% with C_2H_6 and 9.4% with C_2F_6. For the remaining penetrants, no dilation data were collected, and thus the model can only be used in the low-pressure range for which the approximation of constant density of the matrix is reasonable. For swelling compounds, such as propane and n-butane, we will compare the NELF predictions with experimental sorption data in the low-pressure range, i.e., up to 5 bar. On the other hand, for methane and perfluoromethane

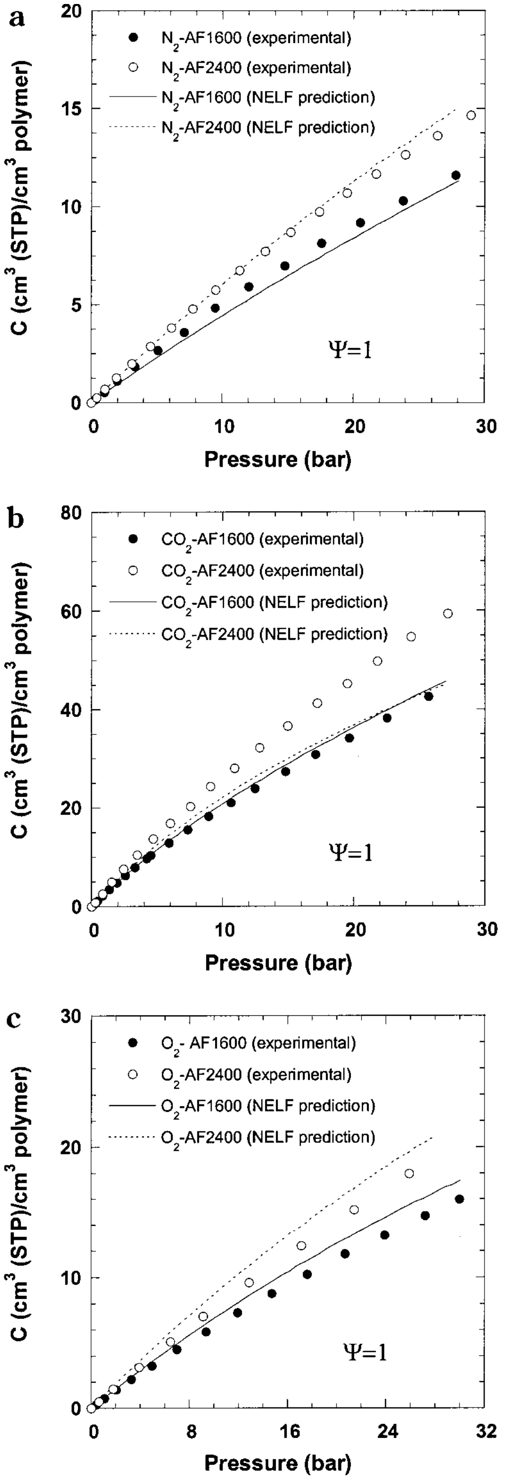

Figure 3. Solubility isotherms in AF1600 and AF2400 for N_2 (a), CO_2 (b), and O_2 (c) at 35 °C: experimental data (taken from ref 14) and NELF model predictions ($\Psi = 1$).

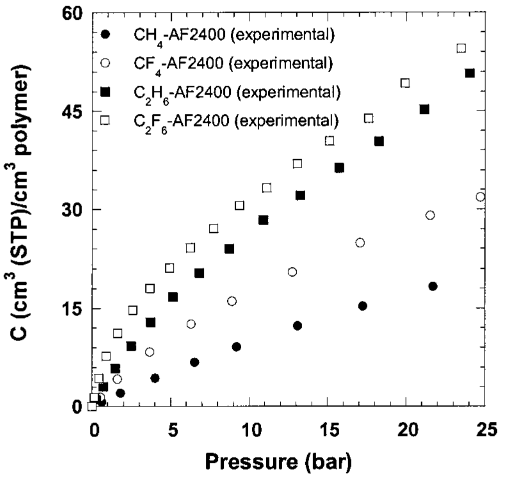

Figure 4. Solubility isotherms at 35 °C of CH_4 and CF_4 and of C_2H_6 and C_2F_6 in AF2400 from ref 14

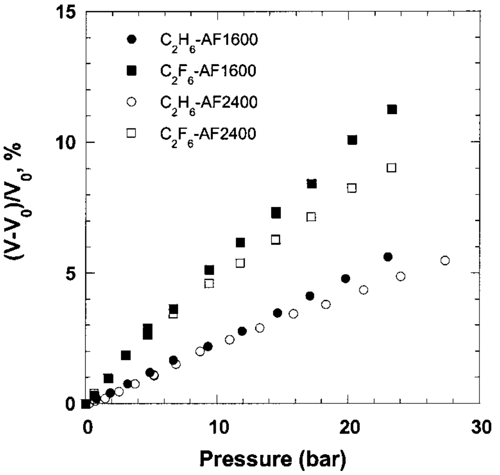

Figure 5. Volume dilation due to the sorption of C_2H_6 and C_2F_6 in AF1600 and AF2400 as measured in this work at 35 °C.

the density can be assumed to be constant, and thus the comparison will be performed over the entire pressure range inspected in the sorption measurements.

The solubility trend experimentally observed for hydrocarbons and fluorocarbons in AF1600 and AF2400 is consistent with the different energetic interactions between penetrants and polymeric matrix, which are favorable to the dissolution of a compound in a chemically similar environment. The same general qualitative idea was indeed found to hold in PDMS;[9] in this case of course, hydrocarbons are more soluble than fluorocarbons since this polymer has no fluorine nor any halogen group and provides for an aliphatic-like environment. In the case of the amorphous Teflons, however, the solubility ratios between homologous hydrocarbons and perfluorocarbons are small as compared to PDMS in which the sorption levels of alkanes are up to 10 times higher than those of the corresponding perfluoroalkanes. This difference is reasonable since the exceptionally high free volume of glassy AF1600 and AF2400 allows for somewhat indiscriminate sorption, in contrast to rubbery PDMS where penetrant and polymer are more likely to be in close proximity.

We will now compare the experimental sorption of hydrocarbons and fluorocarbons in the amorphous Teflons to the predictions based on the NELF model. As illustrated in Figure 6a, methane sorption isotherms are correctly predicted by the NELF model when a nondefault binary interaction parameter (Ψ), equal to 0.95 for both polymeric solutions, is introduced. For CF_4 (Figure 6b), the predicted isotherm exactly reproduces the experimental shape in AF1600 for pressures up to 15 bar; while for AF2400 the model properly represents the low-pressure behavior and tends to underestimate solubility with increasing pressure (the error equals 25% at 24 bar). It should be noted that both the predicted isotherms for CF_4 were calculated with no adjustable parameters, i.e., with Ψ equal to unity, which is

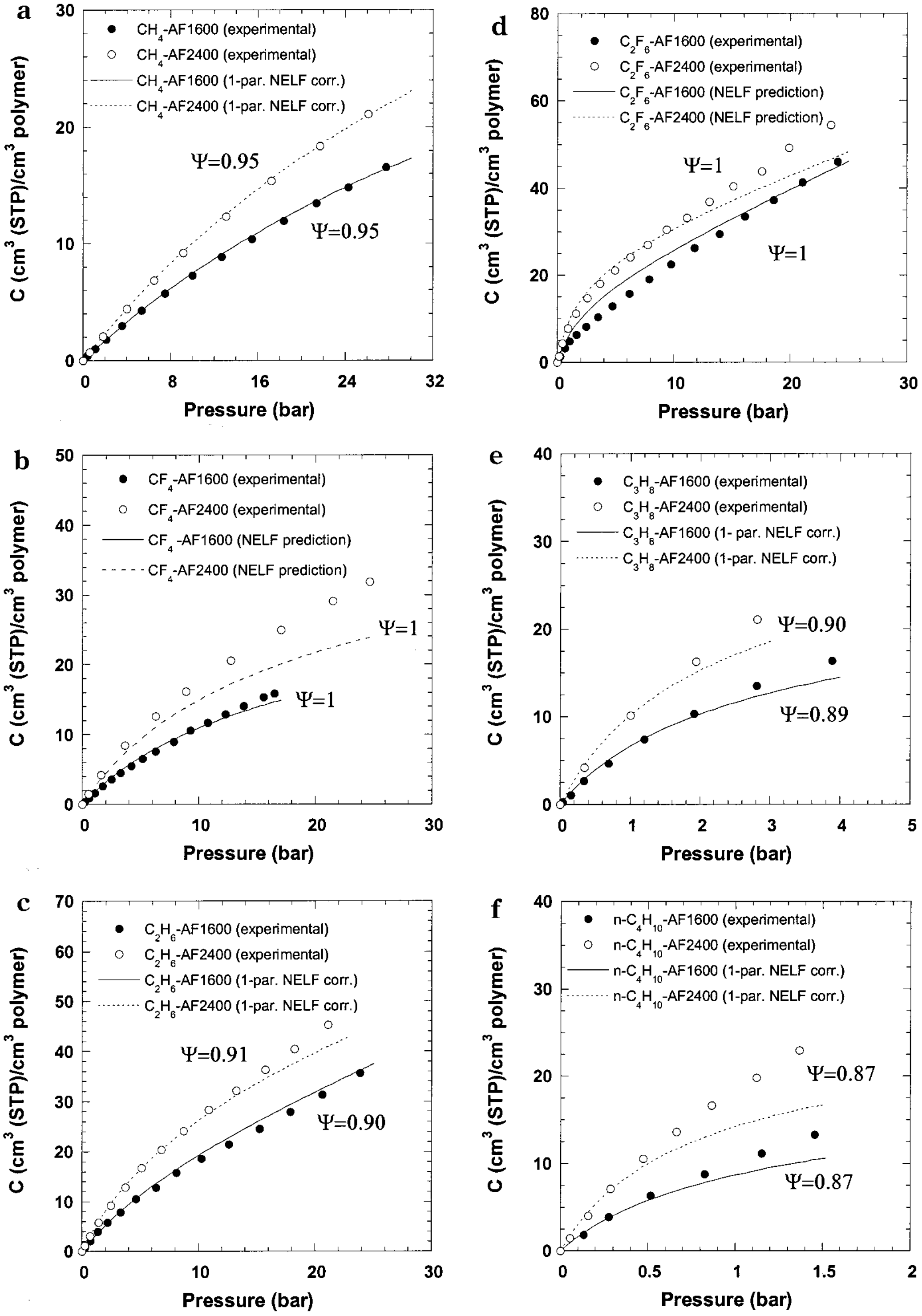

Figure 6. Solubility isotherms of different *n*-alkanes and perfluorocarbons in AF1600 and AF2400 at 35 °C. Comparison of experimental data (taken from ref 14) and NELF model predictions ($\Psi = 1$) or one-parameter NELF model correlations ($\Psi \neq 1$): (a) data and correlations for CH_4; (b) data and predictions for CF_4; (c) data and correlations for C_2H_6; (d) data and predictions for C_2F_6; (e) data and correlations for C_3H_8; (f) data and correlations for *n*-C_4H_{10}.

otherwise consistent with the fact that we have a perfluorinated penetrant in a highly fluorinated matrix.

In the case of ethane, for which we incorporated the dilation data collected during sorption in the expression of the mixture chemical potential, we obtained a correct prediction for the solubility over the entire range of pressures after introducing a value of Ψ equal to 0.90 for AF1600 and 0.91 for AF2400 (Figure 6c). For perfluoroethane (Figure 6d), the solubility is correctly predicted by the NELF model in AF2400 with no adjustable parameter for pressures up to 15 bar, while an underestimation is obtained at higher pressures; in the case of AF1600, the sorption values are moderately overestimated in the low-pressure range. For propane sorption (Figure 6e), the comparison between predicted and experimental isotherms is performed in the range 0−4 atm, where the dilation may be expected to be small. The adjustable parameter Ψ needed to fit the sorption isotherm of propane in this range is 0.89 for AF1600 and 0.90 for AF2400. The deviation between experi-

Table 3. Infinite Dilution Solubility Coefficients (Experimental Data from Ref 14)

		AF1600 S_0 [cm^3 (STP)/(cm^3 of polymer atm)]						AF2400 S_0 [cm^3 (STP)/(cm^3 of polymer atm)]					
		NELF model			experimental			NELF model			experimental		
penetrant	T_c (K)	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
N_2	126.2	0.56	0.48	0.42	0.78	0.58	0.62	0.76	0.65	0.57	0.76	0.68	0.64
O_2	154.6	0.99	0.81	0.68	0.87	0.73	0.64	1.0	0.88	0.77	0.90	0.87	0.81
CO_2	304.1	3.6	2.7	2.0	3.4	2.7	2.5	3.9	3.0	2.3	4.1	3.5	3.0
CH_4	190.4	1.1	0.87	0.73	1.2	0.99	0.95	1.4	1.2	1.0	1.3	1.2	1.0
C_2H_6	305.4	4.2	3.2	2.4	4.5	3.4	2.8	6.3	4.8	3.7	6.2	5	3.8
C_3H_8	369.8	14	9.6	6.9	16	9	7.2	21	15	11	16	14	11
CF_4	227.6	2.6	2.0	1.5	2.9	1.7	2.0	3. 7	2.8	2.2	3.5	2.7	2.2
C_2F_6	293	14	9.5	6.7	10	6	5.0	24	17	12	11	11	7.2

	AF1600						AF2400					
	NELF model			experimental			NELF model			experimental		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
$S_0(CF_4)/S_0(CH_4)$	2.4	2.3	2.1	2.4	1.7	2.1	2.6	2.3	2.2	2.7	2.2	2.2
$S_0(C_2F_6)/S_0(C_2H_6)$	3.3	3.0	2.8	2.2	1.8	1.8	3.8	3.5	3.2	1.8	2.2	1.9

mental and calculated isotherms increases at higher pressures, consistent with the approximation made regarding dilation. In the case of *n*-butane, reported in Figure 6f, the solubility is correctly represented in the range 0−2 atm when introducing a binary parameter of 0.87 in both AF2400 and AF1600.

From the above discussion one may observe that while the sorption of fluorocarbons is satisfactorily predicted by the NELF model using no adjustable interaction parameters, i.e., by considering $\Psi = 1$, the calculated isotherms for hydrocarbons need to be corrected by adjusting the value of Ψ using the experimental solubility. The more Ψ deviates from unity, the more the binary characteristic pressure p^*_{12} accounting for interactions between unlike molecules (*1*−*2*) in a unit volume deviates from the geometric mean between the pure component's characteristic pressures (p^*_1 and p^*_2) as indicated in eq 10. In particular, when the empirical value of Ψ is smaller than unity, as is the case for hydrocarbons in perfluorinated AF1600 and AF2400, the geometric mean overestimates the actual interaction energy per unit volume between gas and polymer molecules. In our observations, the NELF model with a unit value for Ψ correctly fits the sorption isotherms of fluoroalkanes in the amorphous Teflon copolymers, while for the case of hydrocarbons the first-order approximation offered by the geometric mean rule is no longer appropriate. The values of the binary parameter Ψ which best fit the sorption isotherms of alkanes in AF1600 and AF2400 are rather close to one another in all cases and range from 0.87 to 0.95. Analogously, in the aliphatic polymer PDMS, a constant value of the adjustable parameter Ψ was obtained for homologous penetrants. For example, to fit experimental sorption data in PDMS, Ψ was found equal to 0.96 for hydrocarbons and 0.87 for fluorocarbons.[9] Both observations for the equilibrium solubility in a nonhalogenated rubber (PDMS) and for the pseudoequilibrium solubility in glassy perfluorinated polymers are consistent with the physical meaning of the binary parameter and the geometric mean rule of the energy interaction parameters. That is, when penetrant and polymer are chemically similar, Ψ is close to unity, while with increasing chemical differences the deviation of Ψ from unity increases. Indeed the values of Ψ which were obtained for perfluorinated penetrants in an aliphatic matrix are similar to those needed for describing the dissolution of aliphatic hydrocarbons in perfluorinated matrixes.

Infinite Dilution Solubility Coefficients at Various Temperatures. Another useful way to compare NELF model predictions with experimental sorption data is based on infinite dilution solubility coefficients S_0. By definition we have:

$$S_0 = \lim_{p\to 0}\left(\frac{c}{p}\right) \tag{16}$$

where c is the concentration of gas in the polymer expressed in cm^3(STP)/(cm^3 of polymer) and S_0 is the slope of the tangent to the sorption isotherm in the limit of low pressure. In this limit of infinite dilution, a comparison between experimental data and NELF predictions is immediately possible for those penetrant−polymer pairs for which no dilation data are available during sorption, since dilation is of no importance in the zero pressure limit. For both copolymers a comprehensive list of the solubility properties is reported in Table 3. The solubility coefficients at infinite dilution are listed for all the penetrants considered at three different temperatures (25, 35, and 45 °C), along with the ratios between solubilities of homologous penetrants (CH_4:CF_4, C_2H_6:C_2F_6) at 35 °C. For the sake of comparison, the same table also reports the values calculated using the NELF model for the solubility coefficients, S_0, as well as for the solubility ratios of hydrocarbons vs homologous fluorocarbons.

Typically, the infinite dilution solubility coefficient increases with increasing measures of penetrant condensability such as critical temperature, T_C.[35] Indeed, it was observed that the logarithm of S_0 increases linearly with T_C. For this reason, the comparison between measured and calculated solubility coefficients in AF1600 is reported vs penetrant critical temperature in Figure 7, parts a−c, at 25, 35, and 45 °C, respectively. It is worth pointing out that the NELF model calculations were performed by considering the parameter Ψ constant with temperature according to the original formulation of the Sanchez−Lacombe lattice fluid theory, although there are cases (e.g. CH_4−PS, C_2H_4-LDPE, and CO_2−PMMA) in which the experimental sorption isotherms are better described by the SL model when Ψ is allowed to vary with temperature.[36] In an analogous way the solubility coefficients in AF2400 are shown in

Table 4.. Sorption Enthalpies at Infinite Dilution (Experimental Data from Ref 14)

	$\Delta H_{S,\infty}$ (kJ/mol)			
	AF2400		AF1600	
	exptl	NELF model	exptl	NELF model
N_2	−8.6	−11.1	−11.1	−12.1
O_2	−12.0	−4.1	−12.1	−14.8
CO_2	−11.3	−20.7	−16.2	−23.4
CH_4	−10.6	−15.7	−15	−15.5
C_2H_6	−12.8	−23.3	−17.6	−22.3
C_3H_8	−16.8	−26.8	−31.4	−29.4
n-C_4H_{10}	−31.2	−26.2	−25.9	−26.7

Figure 8, parts a−c at the three different temperatures studied. It is apparent from the figures that there is no significant error in considering the binary interaction parameter constant with temperature within the range investigated, although a moderate improvement would obviously be obtained when optimizing Ψ for each temperature.

Finally, solubility coefficients at the three temperatures inspected allow us to obtain the sorption enthalpies at infinite dilution for the gas−polymer systems under study. The sorption enthalpies were evaluated from the van't Hoff equation

$$\ln(S(T)) = \ln(S(T_0)) - \frac{\Delta H_S}{RT} \qquad (17)$$

and then compared with the values calculated by the NELF model. The results of the comparison are shown in Table 4. The value for CF_4 was not displayed because the experimental data at 25 °C were not consistent with the values at other temperatures. The prediction of mixing enthalpies is a much more stringent test for the NELF model than the calculation of solubility coefficients alone, since temperature dependence is involved. Nonetheless, the comparison is quite satisfactory in the case of AF1600, for which the average percentage error between experimental and predicted values is 14.5%, while for AF2400, if we hold the parameter Ψ constant, the average error is 48%.

NELF as a Two-Parameter Correlation Model. In this section, we will show that the NELF model can also be used to correlate solubility data in the absence of experimental dilation information. When no adjustable interaction parameter (Ψ*)* is needed to fit low pressure solubility, only one sorption datum is sufficient to draw the entire solubility isotherm by the NELF model.[8] Considering as input in eq 14 the experimental solubility datum ω_1 at p and T, and solving the equation as a function of the polymeric density, ρ_2, one can calculate the polymer dilation at pressure p. Since it is frequently found that dilation isotherms are linear with pressure, one can obtain a straight line representing the volumetric isotherm vs pressure based only on the matrix volume at a single pressure and the density at zero pressure (i.e., the density of the dry polymer). This volumetric data is then readily used by the NELF model to calculate a sorption isotherm in the usual manner.

For the case of hydrocarbon sorption in AF1600 and AF2400, and for all penetrants for which it is necessary to adjust the binary interaction parameter (Ψ*)* to experimental data in the range of low pressures, the NELF model contains a single adjustable parameter (Ψ*)* if the volume dilation is known. Otherwise, in the absence of dilation information, the model becomes a two-parameter correlation. In this case, the two model parameters are obtained from the polymeric density at a certain penetrant pressure (used to estimate dilation) and from the infinite dilution solubility coefficient, S_0 (which gives Ψ).

Table 5. Parameters of the NELF Correlation

	AF 1600		AF 2400	
	Ψ	$(\Delta V/V_0\%)/p$ (bar^{-1})	Ψ	$(\Delta V/V_0\%)/p$ (bar^{-1})
CH_4	0.95	≅0	0.95	≅0
C_2H_6	0.90	0.25[a]	0.91	0.20[a]
C_3H_8	0.89	0.55	0.90	0.67
n-C_4H_{10}	0.87	1.5	0.87	3.3

[a] Experimental value.

In this work, we have studied the sorption properties of CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}, while direct dilation measurements were carried out only for ethane. All of these penetrants, with the exception of methane, may yield significant swelling of the polymer. Consequently, we will consider the dilation curves, which are unknown in the case of methane, propane, and *n*-butane, as straight lines whose slope is obtained from the pure polymer density and from the density calculated by the NELF model at a certain pressure using the solubility at that pressure as input in eq 14. At all the other pressures, the polymer density will be obtained from this straight line; the corresponding solubility isotherm is then calculated from eq 14 using the estimated density as input.

The comparisons between experimental sorption data and the NELF model correlation obtained according to the above two-parameter procedure are presented in parts a−c of Figure 9. The correlation fits the shape of the experimental curves perfectly. In Table 5, we listed the values of the parameters used for the correlation: the energetic binary interaction parameter Ψ and the slope of the linear dilation isotherm, expressed as the ratio between the percentage volume change and the penetrant pressure. The values of the dilation slopes thus calculated increase with increasing penetrant molecular weight, consistent with expectations based on solubility values. This method is useful when it is necessary to extrapolate a solubility isotherm over a wide range of pressures in the absence of experimental swelling data, and it forms a powerful and interesting alternative to other correlation equations, such as the dual-mode model, for which three parameters are needed. The dilation values calculated in this way also provide an estimate of the swelling when only solubility data are available. In Table 5, the slopes of the dilation isotherms calculated for the sorption of propane and *n*-butane are larger for AF2400 than for AF1600. This result is opposite to expectations based on the experimental dilation isotherms for C_2H_6 shown in Figure 5. This difference in behavior between the penetrants is the natural result of the underprediction of the sorption isotherm of ethane, observed at high pressures in AF2400 (Figure 6c), when the NELF model calculations are performed based on the experimental dilation data. In turn, this may be associated with the fact that for AF2400 the pure polymer parameters appear to be somewhat less reliable than for AF1600 (Figure 1), as we already indicated.

Partial Molar Volumes. By combining the sorption and dilation data collected in AF2400 and AF1600 one can calculate penetrant partial molar volumes, which are defined as usual by

$$\bar{v}_1 \equiv \left(\frac{\partial V}{\partial n_1}\right)_{T,p,n_2} \tag{18}$$

where V is the total mixture volume. In a solution formed by a low molecular weight penetrant and a polymer, the partial molar volume is calculated in the following manner:

$$\bar{v}_1 = v_{\mathrm{STP}}\left[\frac{\mathrm{d}}{\mathrm{d}p}\left(\frac{\Delta V}{V_0}\right) + \beta\right]\frac{\mathrm{d}p}{\mathrm{d}c} \tag{19}$$

where β is the isothermal compressibility of the polymer and c is the penetrant concentration expressed as standard gas volume contained per unit polymer volume.

Figure 10 reports the partial molar volumes of N_2, CO_2, C_2H_6, and C_2F_6 in AF1600 and AF2400 and compares these values to those reported in the literature for mixtures with liquids and rubbery polymers. The partial molar volumes at infinite dilution have extremely low values if compared to those in liquids, and they increase with increasing concentration. Small variations of the total system volume at low concentration (resulting in low values of partial molar volumes) are consistent with the sorption of gas molecules into the excess free volume of a glassy polymer. At higher penetrant concentrations this excess volume becomes progressively filled causing the polymeric matrix to ultimately swell more and more markedly with additional penetrant sorption. The experimental results also suggest that above a certain value of concentration the excess free volume ceases to contribute to sorption and causes the swelling to vary linearly with composition and, consequently, the partial molar volumes to approach a constant value. This behavior is in total agreement with that observed by Koros et al. during dilation measurements of CO_2 in other glassy polymers such as polycarbonate and PTMSP.[37-39] In PTMSP, in particular, which is characterized by a free volume comparable to that of the amorphous Teflon copolymers, they reported a value of partial molar volume of CO_2 at infinite dilution of 5 cm^3/mol, and a plateau value at high concentrations of 30 cm^3/mol. In this work, we calculated the partial molar volume at infinite dilution of CO_2 at 35 °C to be 5.5 cm^3/mol in AF2400 and 6.0 cm^3/mol in AF1600, while for concentrations greater than 30 cm^3(STP)/(cm^3 of polymer), it approaches a constant value of 15 and 35 cm^3/mol in AF2400 and AF1600, respectively. For comparison, the partial molar volume of CO_2 in silicone rubber is about 48 cm^3/mol.[9] Analogous trends are observed during sorption of nitrogen, C_2H_6, and C_2F_6, whose values of partial molar volume are reported in Table 6.

Conclusions

Polymer dilation during sorption, which is essential physical information for the predictive use of the NELF model, has been measured for selected penetrants (N_2, CO_2, C_2H_6, and C_2F_6) in Teflon AF1600 and AF2400. Nitrogen induces a small volume dilation, equal to about 0.5% at 30 bar, in both polymers, while more appreciable swelling is obtained upon exposure to CO_2, C_2H_6, and C_2F_6. In both perfluorinated polymers, C_2F_6 induces more dilation than its hydrocarbon analogue, consistent with its higher solubility and larger size. For the swelling penetrants, higher solubilities and smaller volume dilations were observed in AF2400 than in AF1600, consistent with the former polymer's larger fractional free volume.

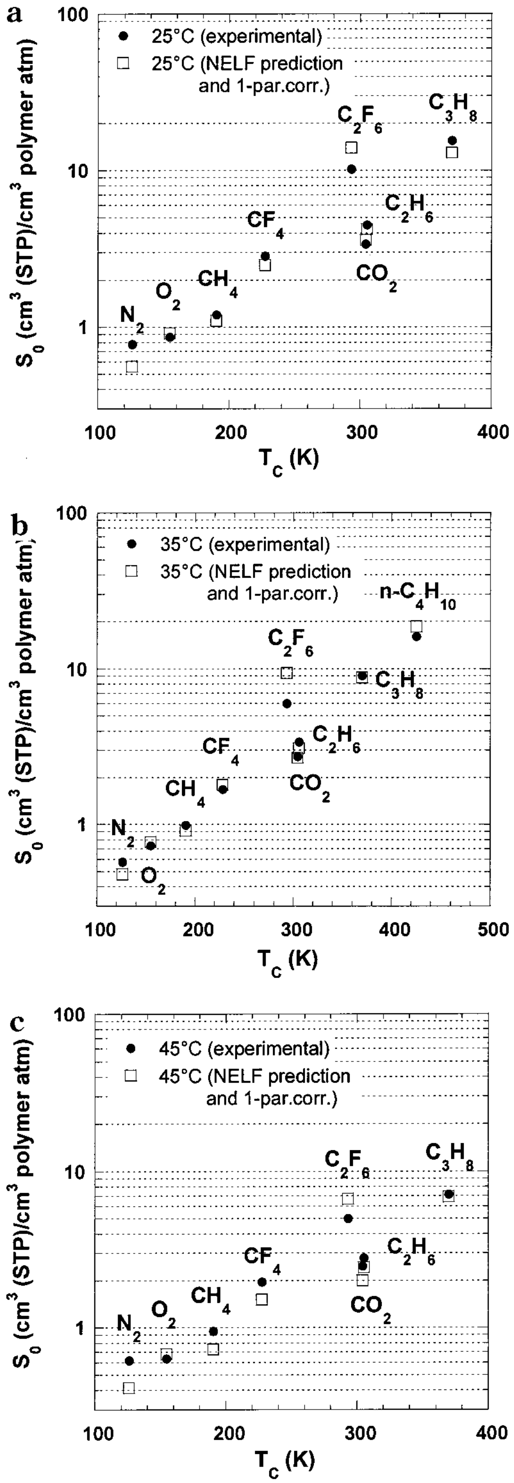

Figure 7. Infinite dilution solubility coefficients of different penetrants in AF1600, at 25 (a), 35 (b), and 45 °C (c). For the light gases and fluorocarbons the NELF model calculations are predictive at all temperatures; for hydrocarbons the NELF model calculations are predictive at 25 and 45 °C. Experimental sorption data were taken from ref 14.

The experimental sorption data have been compared with the calculations of the NELF model. On the basis of the first-order approximation for the binary mixing parameter ($\Psi = 1$) the NELF predictions are in good agreement with experimental data for nitrogen and

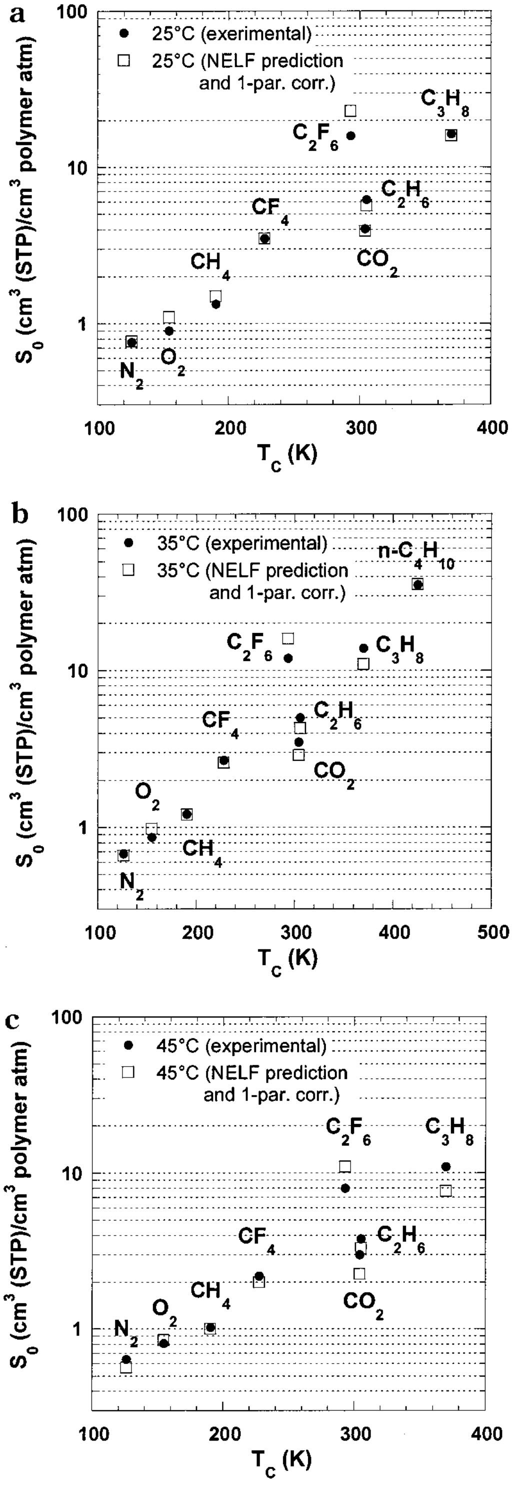

Figure 8. Infinite dilution solubility coefficients of different penetrants in AF2400, at 25 (a), 35 (b), and 45 °C (c). For the light gases and fluorocarbons the NELF model calculations are predictive at all temperatures; for hydrocarbons the NELF model calculations are predictive at 25 and 45 °C. Experimental sorption data were taken from ref 14.

oxygen sorption in both copolymers. For carbon dioxide the predictions are good for both polymers in the low pressure range, while at higher pressures a rather good agreement is obtained only for AF1600. CO_2 solubility in AF2400 is underestimated by the model at higher pressures, with a deviation in all cases smaller than 30%. For perfluorocarbon solubility, satisfactory agreement is observed between NELF and experimental data

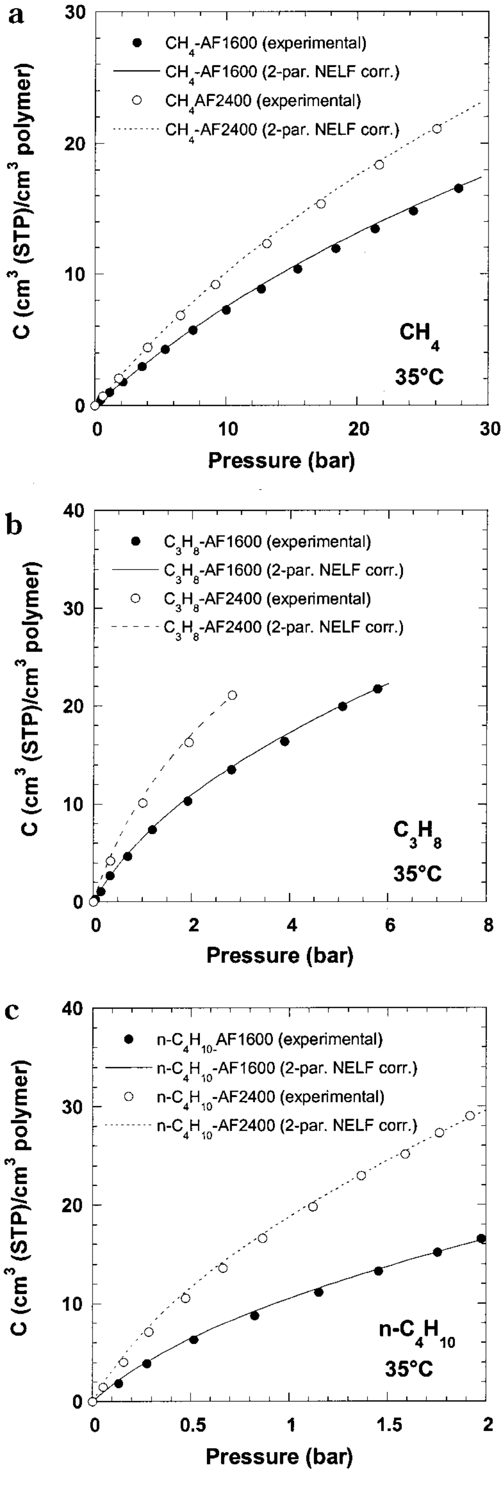

Figure 9. Comparison between experimental solubility isotherms (ref 14) and two-parameter NELF model correlation for CH_4 (a), C_3H_8 (b), and n-C_4H_{10} (c), in AF1600 and AF 2400 at 35 °C. The correlation parameters are shown in Table 6.

in AF1600 over the entire pressure range. For AF2400 good agreement is obtained up to moderate pressures, around 10 bar, while at higher pressures the model somewhat underestimates the observed perfluorocarbon solubility. Finally, for the hydrocarbons inspected (CH_4, C_2H_6, C_3H_8 and n-C_4H_{10}) the first-order approximation for Ψ is no longer appropriate and its value must be adjusted to the experimental data to obtain good estimates via NELF. In AF1600 the proper value of the

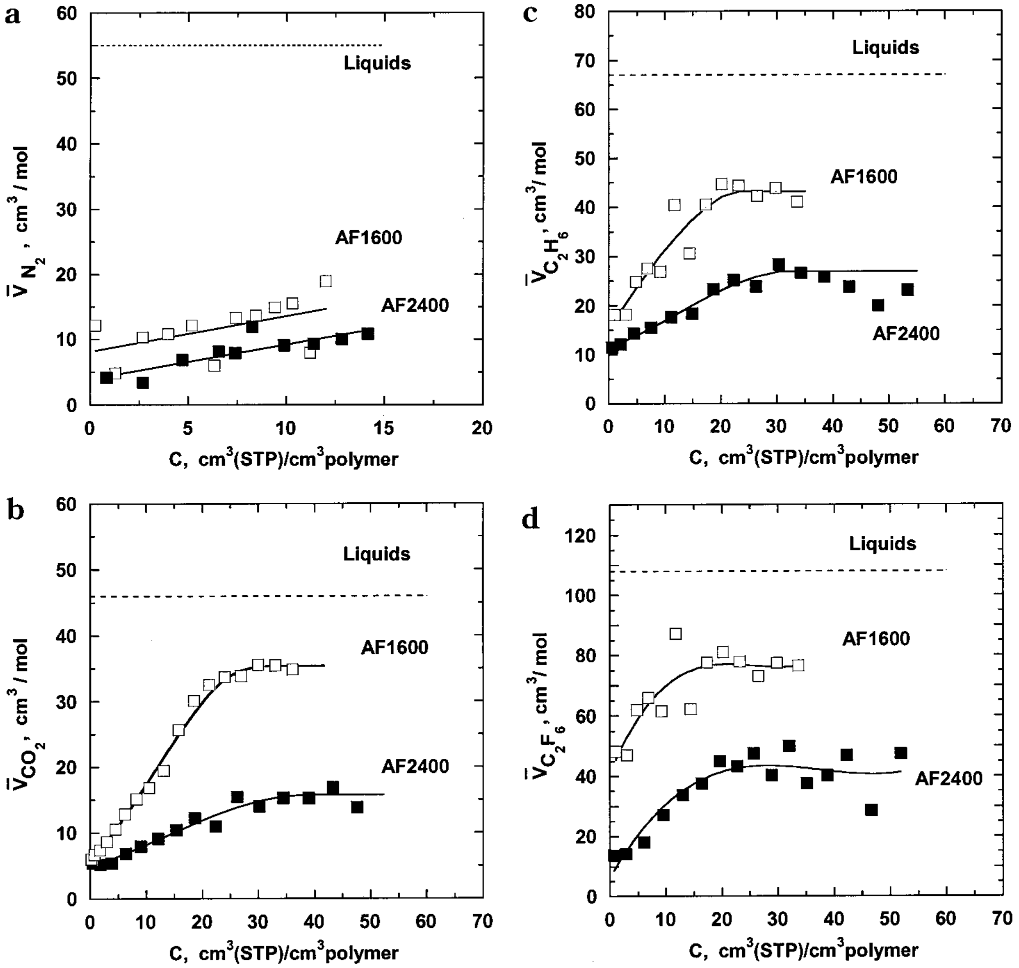

Figure 10. Experimental partial molar volumes of N_2 (a), CO_2 (b), C_2H_6 (c), and C_2F_6 (d), in AF1600 and AF2400 at 35 °C. The solid lines are curve fits of the experimental data.

Table 6. Infinite Dilution Partial Molar Volumes of Penetrants at 35 °C

	molar vol of penetrant			
	N_2	CO_2	C_2H_6	C_2F_6
AF1600[a]	11	6	18	48
AF2400[a]	5	5.5	11.5	14
PTMSP[39]		5		
PC[37]		17.9		
PDMS, rubber[9]	64	48	73	139
liquids at 25 °C[42b]	55	53	67	
cyclohexane at 25 °C[33]				108

[a] Partial molar volumes estimated using Equation 19. [b] Averaged values for five organic liquids.

binary interaction parameter is 0.95 for CH_4, 0.90 for ethane and propane, and 0.87 for *n*-butane, while for solubility in AF2400 the corresponding values are 0.95, 0.91, 0.89, and 0.87, respectively. These values are very close to those obtained for perfluorinated penetrants in PDMS,[9] consistent with the fact that Ψ embodies the deviation from the geometric mean of the energetic interactions between unlike species in a mixture. In both ref 9 and this study the binary interaction parameter (Ψ) has almost the same value for all the homologous components, it decreases slightly with increasing molecular weight, and it is independent of temperature.

Use of the NELF model to calculate infinite dilution solubility coefficients was found to be satisfactory for all penetrants, at each temperature inspected, so that even the infinite dilution enthalpy of mixing can be reasonably predicted by the NELF model.

A method was proposed for correlating solubility isotherms of swelling penetrants over a wide range of pressures by introducing an additional parameter into the NELF model which corresponds to the value of dilation at fixed penetrant pressure. This parameter can be calculated based on one experimental solubility datum at fixed pressure. In this way, the model contains at the most two adjustable parameters. Results of a comparison with experimental solubility isotherms of *n*-alkanes in both copolymers are extremely good over the entire range of pressures inspected.

Finally, we calculated the partial molar volumes of N_2, CO_2, C_2H_6, and C_2F_6 in AF1600 and AF2400. Their values are much lower than the corresponding values measured in liquids and increase with increasing concentration. Both these results are consistent with the high free volume structure of the amorphous Teflons and with previous results in glassy polymers.

Acknowledgment. This work has been partially supported by the Italian Ministry of University and Scientific and Technological Research, Funds ex 40%. Partial financial support provided by the National Science Foundation (CTS 98-03225) is gratefully acknowledged.

References and Notes

(1) Barrer, R. M.; Barrie, J. A.; Slater, J. *J. Polym. Sci.* **1958**, *27*, 177.

(2) Michaels, A. S.; Vieth, W. R.; Barrie, J. A. *J. Appl. Phys.* **1963**, *34*, 1
(3) Bondar, V. I.; Kamiya, Y.; Yampol'skii, Y. P. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 369.
(4) Doghieri, F.; Sarti, G. C. *Macromolecules* **1996**, *29*, 7885−7896.
(5) Sarti, G. C.; Doghieri, F. *Chem. Eng. Sci.* **1998**, *53*, 3435−3447.
(6) Doghieri, F.; Sarti, G. C. *J. Membr. Sci.* **1998**, *147*, 73−86.
(7) Doghieri, F.; Canova, M.; Sarti, G. C. In *Polymer Membranes for Gas and Vapor Separation*; ACS Symposium Series 733; Freeman, B. D., Pinnau I., Eds.; American Chemical Society: Washington, DC, 1999; Chapter 13.
(8) Giacinti, M.; Doghieri, F.; Sarti, G. C., *Ind. Eng. Chem. Res.* **2001**, *40*, 3027.
(9) De Angelis, M. G.; Merkel, T. C.; Bondar, V. I.; Freeman, B. D.; Doghieri, F.; Sarti, G. C. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 3011−3026.
(10) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 415−434.
(11) Kamiya, Y.; Naito, Y.; Terada, K.; Mizoguchi, K.; Tsuboi, A. *Macromolecules* **2000**, *33*, 3111−3119.
(12) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 273−296.
(13) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D. *Macromolecules* **1999**, *32*, 370−374.
(14) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Yampol'skii, Y. P. *Macromolecules* **1999**, *32*, 8427−8440.
(15) Resnick, P. R., US Pat. 3 978 030, 1976.
(16) Nemser, S. M.; Roman, I. C., US Pat. 5 051 114, 1991.
(17) Buck, W. H.; Resnick, P. R. Properties of Amorphous Fluoropolymers based on 2,2-Bistrifluoromethyl-4,5-Difluoro-1,3-Dioxole. Presented at the 183rd Meeting of the Electrochemical Society, Honolulu, HI, 1993.
(18) Pinnau, I.; Toy, L. G. *J. Membr. Sci.* **1996**, *109*, 125−133.
(19) Alentiev, A. Y.; Yampol'skii, Y. P.; Shantarovich, V. P.; Nemser, S. M.; Platé, N. A. *J. Membr. Sci.* **1997**, *126*, 123−132.
(20) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352−2362.
(21) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568−2580.
(22) Sanchez, I. C.; Lacombe, R. H. *J. Polym. Sci.: Polym. Lett. Ed.* **1977**, *15*, 71−75.
(23) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145−1156.
(24) Panayiotou, C.; Vera, J. H. *Can. J. Chem. Eng.* **1981**, *59*, 501.
(25) Panayiotou, C.; Vera, J. H. *Polym. J.* **1982**, *14*, 681.
(26) Boudouris, D.; Panayiotou, C. *Macromolecules* **1998**, *31*, 7915−7920.
(27) Astarita, G. *Thermodynamics*; Plenum Press: New York, 1989.
(28) Dee, G. T. Private communication.
(29) Pottiger, M. T.; Laurence, R. L. *J. Polym. Sci.: Polym. Phys. Ed.* **1984**, *22*, 903.
(30) Hariharan, R.; Freeman, B. D.; Carbonell, R. G.; Sarti, G. C. *J. Appl. Polym. Sci.* **1993**, *50*, 1781−1795.
(31) Walsh, D. J.; Buck, W. H. The unusual pressure−volume−temperature properties of copolymers of tetrafluoroethylene with bis-2,2-trifluoromethyl-4,5-difluoro-1,3-dioxole. Technical Report.
(32) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *48*, 1061−1080.
(33) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold Company: New York, 1970.
(34) Sanchez, I. C.; Panayiotou, C. G. In *Models for Thermodynamic and Phase Equilibria Calculations*; Sandler, S. I., Ed.; Dekker: New York, 1994.
(35) Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1997.
(36) Kiszka, M. B.; Meilchen, M. A.; McHugh, M. A. *J. Appl. Polym. Sci.* **1988**, *36*, 583.
(37) Fleming, G. K.; Koros, W. J. *Macromolecules* **1986**, *19*, 2285−2291.
(38) Fleming, G. K.; Koros, W. J. *J. Polym. Sci.: Polym. Phys. Ed.* **1990**, *28*, 1137−1152.
(39) Pope, D. S.; Koros, W. J.; Hopfenberg, H. B. *Macromolecules* **1994**, *27*, 5839−5844.
(40) Vargaftik, N. B. *Handbook of Physical Properties of Liquids and Gases*, 2nd ed.; Hemisphere Publ., Washington, DC, 1975.
(41) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*; Hemisphere Publ., New York, 1989.
(42) Kamiya, Y.; Terada, K.; Mizoguchi, K.; Naito, Y. *Macromolecules* **1992**, *25*, 4321.
(43) Of course eq 12 derives from the definition of mass fraction, according to which $\omega_2 = (\rho_2/\rho)$ and thus it is by no means an assumption of the theory, as was erroneously interpreted by Boudoris and Panayiotou;[26] its violation compromises the validity of the corresponding results, as is the case for the model presented in ref 26.

MA0106090