# On the Solubility of Gas Molecules in Glassy Polymers and the Nonequilibrium Approach

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ABSTRACT: The recent nonequilibrium approach of Doghieri and Sarti for the solubility of gases in glassy polymers is reexamined. Analytical expressions for the equilibrium and nonequilibrium contributions to the chemical potential of the penetrant are presented. Volume dilation of the glassy matrix is explicitly taken into consideration. The role of the apparent partial molar or specific volume of the sorbed gas is also examined. The model is tested against the experimental data of Fleming and Koros for the solubility of $CO_2$ in Bisphenol A polycarbonate.

## Introduction

The sorption of gases and the concomitant dilation of polymers below and above the glass transition temperature are very different in their behavior. This difference is, essentially, arising from the fundamental difference of the thermodynamic state of the amorphous polymer below and above the glass transition, namely, the nonequilibrium glassy state and the equilibrium liquidlike rubbery state, respectively. The sorption phenomena above the glass transition are rather well understood and, in general, are easily amenable to a clear thermodynamic interpretation. The picture is not as clear in the glassy state and there is a continuing effort toward the development of a relevant physically sound framework.

In the area of atomistic modeling, numerous Monte Carlo or molecular dynamics simulations have been carried out in recent years for the calculation of gas solubilities in rubbery matrixes. Very few such simulations have appeared, however, for glassy matrixes. Gusev and Suter[1] studied dynamics of light gases in rubbery polyisobutylene and glassy Bisphenol A polycarbonate, reproducing accurately the experimental diffusion coefficients. The calculated Henry's constants, however, were of limited accuracy. Sunderrajan et al.[2] used grand canonical Monte Carlo simulations to study penetrant solubility in glassy and rubbery polymeric matrixes. They studied the effect of reservoir penetrant pressure on the partition coefficient of a penetrant in a polymer without using specific gases or polymers. Hofmann et al.[3] used the transition state Monte Carlo method of Gusev and Suter[1] for the calculation of diffusivities and solubilities of light gases, such as $H_2$, $N_2$, and $O_2$, in polysiloxanes and polyimides. The gas solubilities in the glassy matrixes were described satisfactorily. We are not aware of any published atomistic modeling results for the solubility of $CO_2$ or common vapors in glassy polymers. Semiempirical statistical thermodynamic approaches with minimal demands in computer time remain, of course, useful alternatives.

Apart from the classical, very successful but, essentially, empirical dual-mode sorption model,[4,5] statistical thermodynamic developments, which make use of an appropriate order parameter,[6] have been the focus of much interest in recent years.[7−10] Doghieri and Sarti[10] have recently proposed a very successful predictive model for the solubility in glassy polymers in which the polymer species density in the solid mixture is considered as an order parameter and it is thermodynamically treated as an internal state variable. The way, however, the model has been developed does not allow for the matrix dilation to be accounted for explicitly. We consider their approach as a very promising one and the objective of this article is to reexamine it and introduce explicitly the polymer matrix dilation upon gas sorption. A better insight into the sorption phenomena by glassy polymers could be gained in this way.

## The Sorption Model

The developments in this section will heavily be based upon the formalism presented earlier[11,12] for the solubility of gases in rubbery polymers and polymer melts. As previously, we will use for simplicity the lattice−fluid (LF) model of Sanchez and Lacombe.[13,14] Extension to other more general models[15] is quite straightforward. Only the essentials will be given here. Details of the LF formalism can be found in refs 11−14. The gas solubility will be treated as a quasi-equilibrium problem and the amount of gas sorbed into the polymer matrix will be found by requiring that the chemical potentials of the penetrant gas in the gas and glass phases be equal. In this section we will derive the needed expression for the chemical potential of the penetrant.

Let us consider a system of $N_1$ and $N_2$ molecules of components 1 (gas) and 2 (polymer), respectively, at temperature $T$ and external pressure $P$. According to the LF model, each molecule is characterized by the scaling constants $T^*_i$, $P^*_i$, and $\rho^*_i$ for the temperature, pressure, and density of component $i$ ($i = 1, 2$), respectively. An equivalent set of scaling constants is $\epsilon^*_i$, $v^*_i$, and $r_i$ for the average potential energy per segment, the hard-core volume per segment, and the number of segments of component $i$, respectively. They are interrelated as follows:

$$\epsilon^*_i = RT^*_i = P^*_i v^*_i \tag{1}$$

and

$$M_i/\rho^*_i = r_i v^*_i \tag{2}$$

where $R$ is the gas constant and $M_i$ is the molecular weight of component $i$.

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The mixture is also characterized by the corresponding scaling constants $T^*$, $P^*$, and $\rho^*$, and alternatively, the constants $\epsilon^*$, $v^*$, and $r$. Some mixing and combining rules are needed for the case of mixtures. As previously,[11,12] the following rules will be adopted here:

$$\epsilon^* = \phi_1\epsilon_1^* + \phi_2\epsilon_2^* - \phi_1\phi_2X_{12} \tag{3}$$

where the volume fractions $\phi_i$ are defined by the equation

$$\phi_i = \frac{r_iN_i}{r_1N_1 + r_2N_2} = \frac{r_iN_i}{rN} \qquad i = 1, 2 \tag{4}$$

$N$ being the total number of molecules in the mixture ($N = N_1 + N_2$). The interchange energy parameter $X_{12}$ in eq 3 is given by the equation

$$X_{12} = \frac{\epsilon_1^* + \epsilon_2^* - 2\sqrt{\epsilon_1^*\,\epsilon_2^*}}{RT} \tag{5}$$

The following combining rule is adopted here for the segmental hard-core volume $v^*$ in the mixture

$$v^* = \phi_1v_1^* + \phi_2v_2^* \tag{6}$$

A direct consequence of eq 6 is the following mixing rule:

$$\frac{1}{\rho^*} = \frac{w_1}{\rho_1^*} + \frac{w_2}{\rho_2^*} \tag{7}$$

where $w_1$ and $w_2$ are the mass fractions of penetrant and polymer, respectively.

The reduced temperature, pressure, and volume (density) are given by the following equations, respectively:

$$\tilde{T} = \frac{T}{T^*} \qquad \tilde{P} = \frac{P}{P^*} \qquad \tilde{v} = \frac{1}{\tilde{\rho}} = \frac{V}{V^*} = \frac{\rho^*}{\rho} \tag{8}$$

$V$ and $V^*$ being the total volume and the total hard-core volume of the system, respectively.

In equilibrium conditions the reduced density may be obtained directly from the LF equation of state:[12]

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} + \left[\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\tilde{\rho}}{\tilde{T}} + 1\right] - \frac{1}{r} = 0 \tag{9}$$

The key difference with the earlier formalism[11,12] is that, now, the density of the glassy phase will not be obtained from the equation of state of the model itself (eq 9), but it will be introduced externally as an order parameter. In contrast with Doghieri and Sarti,[10] we will assume that the density $\rho$ of the mixture is given by the equation:

$$\rho = \frac{M}{V} = \frac{\rho_2 + m_1}{1 + m_1V_1} = \frac{\rho_2}{w_2 + \rho_2w_1V_1} \tag{10}$$

where $\rho_2$ is the density of the pure polymer, $m_1$ is the mass of the sorbed penetrant per cm$^3$ of the polymer, and $V_1$ is the apparent partial specific volume of the penetrant. The corresponding assumption made by Doghieri and Sarti[10] is

$$\rho = \frac{\rho_2}{w_2} \tag{11}$$

but $\rho_2$ is not a property of the pure polymer or a constant. This assumption requires that the density $\rho_2$ be specified at each composition.

With the above definitions, the LF equation for the Gibbs free energy of the mixture may be written as[12]

$$G = rNRT^*\left\{\frac{\tilde{T}}{\tilde{\rho}}\left[(1-\tilde{\rho})\ln(1-\tilde{\rho}) + \frac{\tilde{\rho}}{r}\ln\tilde{\rho}\right] + \frac{\tilde{P}}{\tilde{\rho}} - \tilde{\rho} - \tilde{T}\left[\frac{\phi_1}{r_1}\ln\frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{\omega_2}\right]\right\} \tag{12}$$

$\omega_i$ being a constant characteristic of component $i$, which will be canceled in all applications of our interest. The chemical potential will be obtained, now, from this equation as

$$\frac{\mu_1}{RT} = \frac{1}{RT}\left(\frac{\partial G}{\partial N_1}\right)_{T,P,N_2,\rho_2} \tag{13}$$

It is essential to point out that in the above derivation it is $\rho_2$ and not $\tilde{\rho}$ that is kept constant. By performing the indicated derivation we obtain the following equation for the chemical potential of the penetrant:

$$\frac{\mu_1}{RT} = \ln\phi_1 + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + r_1\tilde{\rho}{\phi_2}^2X_{12} + r_1(\tilde{v} - 1)\ln(1-\tilde{\rho}) + \ln\frac{\tilde{\rho}}{\omega_1} - \frac{r_1\tilde{\rho}}{\tilde{T}_1} + r_1\frac{v_1^*}{v^*}\frac{\tilde{P}\tilde{v}}{\tilde{T}} - \mathrm{EOS} \tag{14}$$

Equation 14 is identical to the corresponding equation obtained previously[11,12] for the penetrant−polymer systems at equilibrium except for the last term. This term arises from the fact that the equation of state (eq 9) is not valid in the nonequilibrium case and is

$$\mathrm{EOS} = \mathrm{DR}\left\{\frac{\tilde{P}\tilde{v}}{\tilde{T}} + \left[\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\tilde{\rho}}{\tilde{T}} + 1\right] - \frac{1}{r}\right\} \tag{15}$$

If eq 9 were valid, EOS would be equal to zero. The term DR in front of the bracket in eq 15 arises from the derivative of $\tilde{\rho}$ with respect to $N_1$. By combining eqs 7, 8, and 10, we obtain for DR

$$\mathrm{DR} = r_1\frac{w_1}{\phi_1}\frac{w_2\rho^*}{\rho_2^*}\left[\frac{\tilde{\rho}}{\tilde{\rho}_2}(1 - V_1\rho_2) + \frac{\rho_2^*}{\rho_1^*} - 1\right] \tag{16}$$

Obviously, the expression for DR depends on the assumption for $\rho$. If eq 11 were adopted, eq 16 would become

$$\mathrm{DR} = r_1\frac{v_1^*}{v^*} \tag{17}$$

To perform the solubility calculations we need the expression for the chemical potential of the pure penetrant in the gas phase. The LF equation for the chemical potential of pure fluid 1 is[13,14]

$$\frac{\mu_1^G}{RT} = r_1(\tilde{v}_1 - 1)\ln(1 - \tilde{\rho}_1) + \ln\frac{\tilde{\rho}_1}{\omega_1} - \frac{r_1\tilde{\rho}_1}{\tilde{T}_1} + r_1\frac{\tilde{P}_1\tilde{v}_1}{\tilde{T}_1} \tag{18}$$

The amount of gas sorbed in the glassy state is obtained by equating the chemical potentials as given by eqs 14 and 18.

## Application

Fleming and Koros[16] have conducted a systematic study on the conditioning effects of carbon dioxide on sorption and dilation behavior for Bisphenol A polycarbonate (PC) at 35 °C. They, thus, provide experimental data on both solubility and volume dilation upon gas sorption. These data were used by Doghieri and Sarti[10] for testing their model and are very well suited for testing the model of the previous section. The only problem is that the temperature of 35 °C is close to the critical temperature of $CO_2$: In the proximity of the critical point the LF model fails to properly reproduce the fluid density.[13,14] We are not aiming, however, at a quantitative description of the gas solubility, and thus, the accuracy of the evaluated densities in the gas phase by the LF equation of state (eq 9) is sufficient for the purposes of this article. Better results could be obtained by using other equations, such as the Peng–Robinson[17] or the Soave–Redlich–Kwong[18] equation of state, for evaluating the penetrant densities at 35 °C, which are needed in eq 18 for the chemical potential. This is not, however, a thermodynamically consistent procedure and it has not been used here.

The used LF scaling constants for PC and $CO_2$ are reported in Table 1. The scaling constants for PC are identical to those used by Doghieri and Sarti.[10] Use, however, of their scaling constants for $CO_2$ would demand a rather drastic correction of the simple combining rule of eq 5. To preserve the simplicity of the model without sacrificing significantly its performance, we have set the hard core volume per segment of the penetrant, $v_1^*$, equal to the corresponding volume of the polymer, $v_2^*$, as is the practice in the PV model.[15] We then adjusted the other two scaling constants, $T_1^*$ and $\rho_1^*$ so that they describe adequately the penetrant densities over extended ranges of temperature and pressure. In Figure 1 are compared the experimental[19] and calculated densities of carbon dioxide by using the scaling constants of Table 1.

For the solubility calculations the model does not have any binary adjustable parameters. Two types of calculations have been done: In the first, the concentration of sorbed $CO_2$ into the polymer was considered known and the volume dilation of the polymer was calculated. In the second, the volume dilation was considered known and the amount of gas sorbed was calculated. During these calculations the partial specific volume $V_1$ of the penetrant was determined from the known volume dilation or the concentration of the sorbed penetrant. The density $\rho_2$ of pure PC was fixed equal to 1.200 g/cm$^3$ for the "as received" or "unconditioned" sample.[16] For the sample conditioned at 900 psi, which had shown[16] a residual excess volume $\Delta V/V_0 = 0.008$, the density $\rho_2$ was fixed equal to 1.200/1.008 = 1.190 g/cm$^3$. Doghieri and Sarti present an extensive discussion about their use of $\rho_2$ as an order parameter or an internal state variable. The essential point is that at each pressure they considered the density of the glassy matrix known and, on the basis of it, they have calculated the gas solubility. In this respect, their approach is similar to the second type of the above calculations.

**Table 1. Pure Component LF Scaling Constants**

| component | $\rho^*$ (kg/L) | $T^*$ (K) | $v^*$ (cm$^3$) |
|---|---|---|---|
| $CO_2$ | 1.210 | 405 | 11.75 |
| PC[7] | 1.275 | 755 | 11.75 |

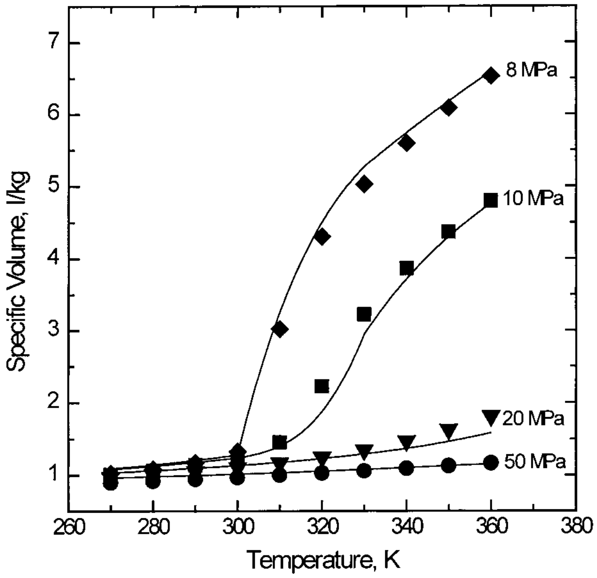

**Figure 1.** Experimental[19] (symbols) and calculated (solid line) specific volume of $CO_2$. The calculations have been made by eq 9 with the scaling constants reported in Table 1.

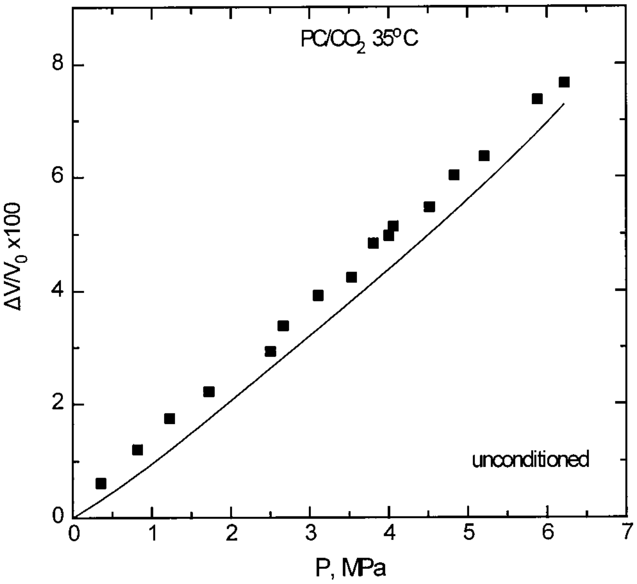

**Figure 2.** Calculated and experimental[16] excess volumes of the $CO_2$–"as received" PC system by considering the amount of gas sorbed (gas solubility) known.

In Figures 2 and 3 are compared the experimental[16] and calculated excess volumes for the unconditioned and the $CO_2$-conditioned PC sample, respectively, by considering the amount of sorbed gas known. These experimental data correspond to sorption tests for increasing pressure. The corresponding partial specific volumes of the penetrant $V_1$, as calculated by the model, are shown in Figure 4. In Figures 5 and 6 are compared the experimental[16] and calculated gas solubilities in the glassy matrix for the unconditioned and the $CO_2$-

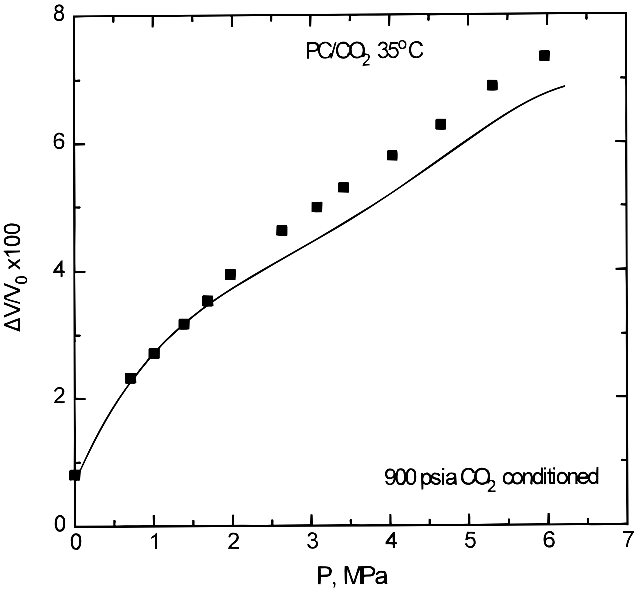

**Figure 3.** Calculated and experimental[16] excess volumes of the $CO_2$–"$CO_2$ conditioned at 900 psi" PC system by considering the amount of gas sorbed (gas solubility) known.

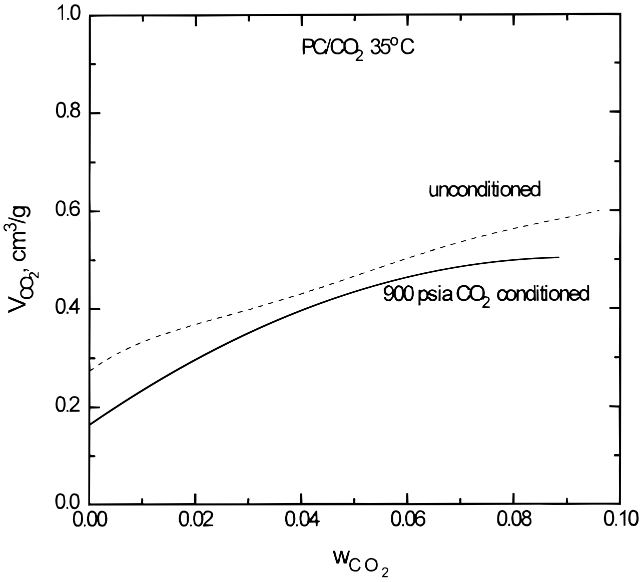

**Figure 4.** Calculated apparent partial specific volume of $CO_2$ for "as received" (dotted line) and "$CO_2$ conditioned at 900 psi" PC sample by considering the amount of gas sorbed known.

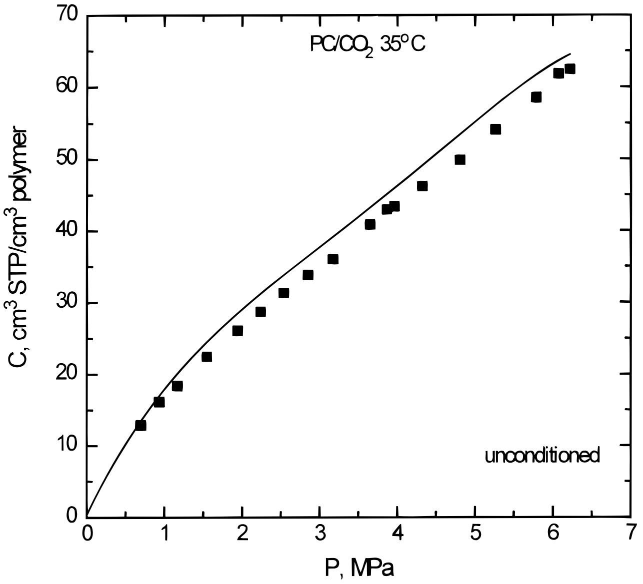

**Figure 5.** Calculated and experimental[16] gas solubilities of the $CO_2$–"as received" PC system by considering the excess volume (volume dilation) known.

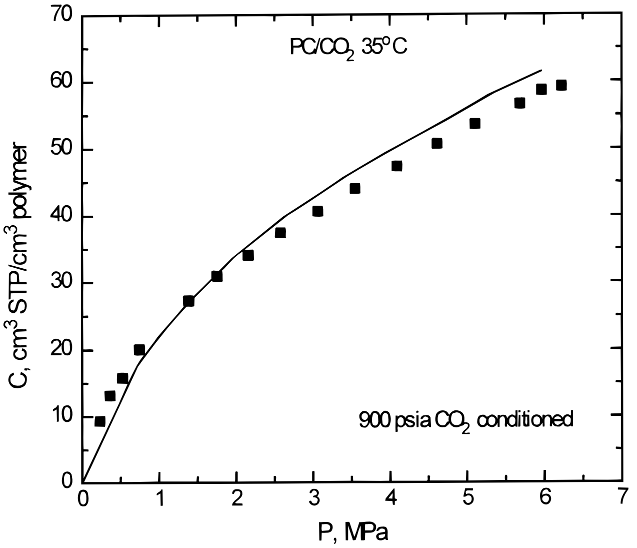

**Figure 6.** Calculated and experimental[16] gas solubilities of the $CO_2$–"$CO_2$ conditioned at 900 psi " PC system by considering the excess volume (volume dilation) known.

conditioned PC sample, respectively, by considering the volume dilation (excess volumes) known. As observed, the experimental data are reasonably well reproduced.

Part of the observed deviation between experimental and calculated data could be attributed to the definition of the residual excess volume $\Delta V/V_0$. We adopted the simple definition: the observed volume dilation per (initial) cm$^3$. Thus, if an initial polymer sample of 1 cm$^3$ weighs 1.200 g and after conditioning and removal of $CO_2$ shows a volume equal to 1.008 cm$^3$, its density becomes equal to $1.200/1.008 = 1.190$ g/cm$^3$. The corresponding estimation by Fleming and Koros[16] is 1.194 g/cm$^3$. We have also assumed that all reported densities are for 35 °C.

In a second set of experiments, Fleming and Koros[16] have conducted desorption and volume consolidation measurements for conditioned samples at three pressures. The observation was that the desorption values for solubility and volume dilation were significantly greater than the corresponding previous conditioned sorption response. The model of the previous section can be used for correlating these types of measurements as well. In Figure 7 are compared the experimental and calculated excess volumes for conditioned and unconditioned samples by considering the amount of (de)-sorbed gas known. The corresponding calculated partial specific volumes of the penetrant are shown in Figure 8. In Figure 9 are compared the experimental and calculated gas solubilities upon pressure decrease by considering the volume dilation known. As observed, the experimental data are again reasonably well reproduced.

It is worth observing in Figures 4 and 8 that the calculated partial specific volume of the penetrant, $V_{CO_2}$, exhibits a variation with $CO_2$ concentration, in qualitative agreement with the experimental data.[16] In Figure 8, in particular, the experimentally observed maximum

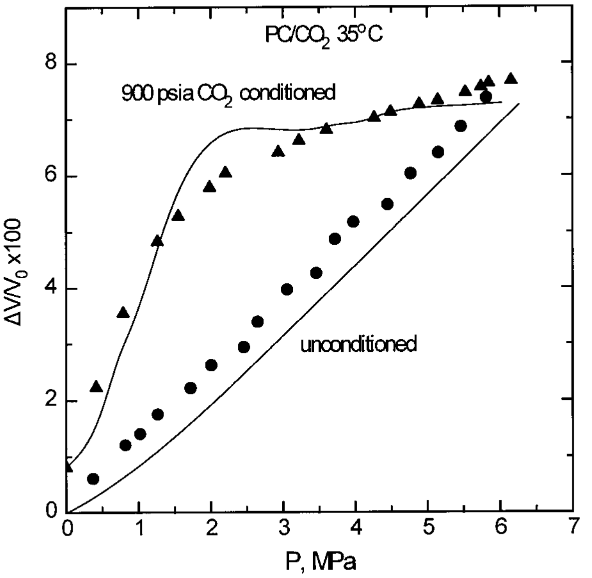

**Figure 7.** Calculated and experimental[16] excess volumes of the $CO_2$–"as received" and the "$CO_2$ conditioned at 900 psi" PC system upon desorption by considering the amount of gas sorbed (gas solubility) known.

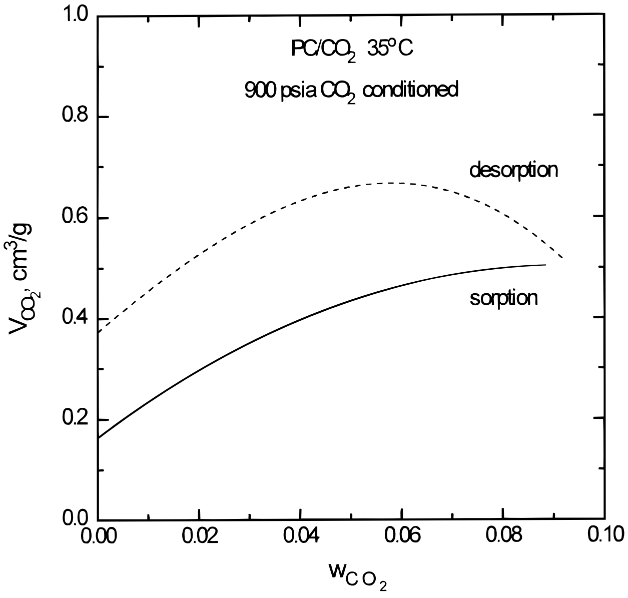

**Figure 8.** Calculated apparent partial specific volume of $CO_2$ for "$CO_2$ conditioned at 900 psi" PC sample upon sorption (solid line) and "$CO_2$ conditioned at 900 psi" PC sample upon desorption (dotted line) by considering the amount of gas (de)sorbed known.

in the variation of $V_{CO_2}$ with concentration upon desorption can be reproduced by the model calculations.

## Discussion and Conclusions

The formal difference of the model of this work with the classical LF model of polymer solutions[11–14] resides on the extra EOS term in eq 14 for the chemical potential of the penetrant in the polymer phase. This term in turn arises from the fact that, when the system is not in equilibrium, the equation of state (eq 9) is not valid and is, of course, absent in the classical LF model. In the calculations of the previous section the contribution of this extra term varies between 0 and ca. 10%, depending on the external pressure. It would be interesting to examine the variation of this contribution with the temperature and annealing conditions as well.

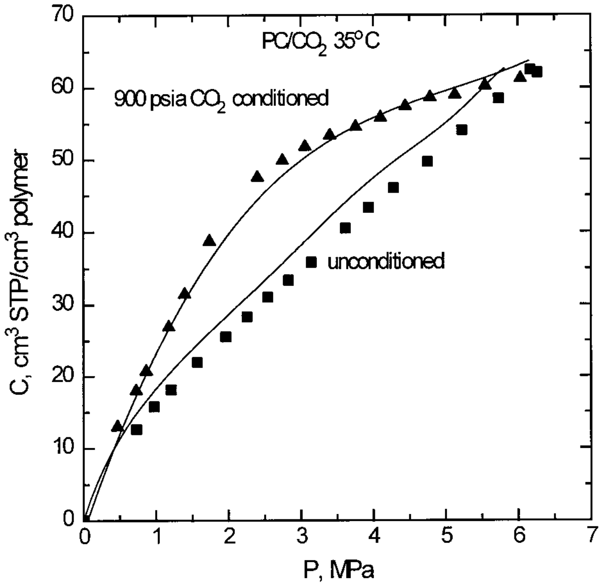

**Figure 9.** Calculated and experimental[16] gas solubilities of the $CO_2$–"as received" and the "$CO_2$ conditioned at 900 psi" PC system upon desorption by considering the excess volume known.

The model can be used in different ways, depending on whether the gas solubility or the volume dilation are known. In either case, the intermediate step is the evaluation of the apparent partial specific volume of the penetrant. If this quantity is known or can be calculated from other considerations, then the model is entirely predictive.

The study presented in this work should be considered as rather preliminary. Extensive data over larger ranges of temperature, pressure, and type of penetrant and polymer are needed for fully testing the model and for extracting more solid conclusions. From such studies a deeper understanding of the variation of the key quantity, namely, the apparent partial specific volume of penetrants, may be obtained. The advantage of the present model is that it can be directly integrated to a scheme for the evaluation of the glass transition temperature and its variation with penetrant concentration.[20,21] Above this temperature the solubility can be studied with the corresponding equilibrium equations of the very same model, as indicated previously.[11,12]

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