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Predictive Model for the Solubility of Fluid Mixtures in Glassy Polymers

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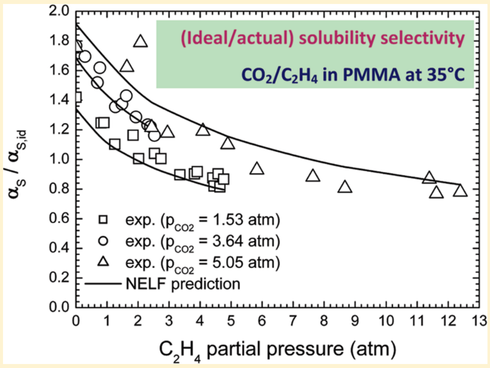
ABSTRACT: The estimation of the solubility of fluid mixtures in polymeric phases is an essential prerequisite for membrane separations and in the design of several devices, such as chemical sensors: the presence of swelling and strongly interacting components in the fluid mixture can often cause rather large deviations from the pure component sorption behavior. For rubbery polymers, the usual equilibrium tools such as the multicomponent versions of the equation of state (EoS) models can be adopted, while for the case of glassy polymers, which are not at equilibrium, such an approach cannot be followed. The general model called nonequilibrium thermodynamics of glassy polymers (NET-GP) has proved to be a successful tool for predicting the solubility of pure gases, vapors and liquids in glassy polymers, and it is here applied to the prediction of multicomponent fluid solubility. In particular, three gas—gas—polymer systems, which show significant deviations from the ideal behavior, are examined at room temperature and various pressures: CH_4/CO_2 in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), C_2H_4/CO_2, and N_2O/CO_2 in poly(methyl methacrylate) (PMMA). The maximum deviation between experimental data and the model predictions is equal to 10%, using as input only the pure component parameters and the binary parameters evaluated from pure gas sorption data. The model thus proves to be a reliable tool to estimate the mixed gas solubility in glassy polymers, in the common case in which such data are not experimentally available for the system of interest.



INTRODUCTION

The solubility of pure and mixed low molecular weight species in glassy polymers is an essential information in applications such as chemical sensors,[1,2] packaging,[3,4] and membrane separations.[5,6] While the experimental evaluation of the solubility of pure gases in solid polymers relies on several, well-established procedures[7] and many data exist in the literature for a wide variety of polymers of industrial interest,[8] very few and delicate time-consuming experimental procedures have been established to measure the solubility of mixed gases or vapors in a polymeric material[9−13] and only a few data are available for glassy polymers.[14−22] Therefore, it is important to develop mathematical models that permit the calculation of the solubility of multicomponent gas mixtures in glassy polymers on the basis of pure components properties and possibly of pure gas solubility only.

Several thermodynamic models have been developed to evaluate the solubility of gases and gaseous mixtures in rubbery polymers. Such models are based on the activity coefficient approach[23−26] or proper equations of state (EoS).[27−40] Vice versa, in the common practice that is presently encountered, the description of solubility in glassy polymers is still performed with empirical and semiempirical models. The most used is the multicomponent version of the dual mode sorption model,[41] while other semiempirical approaches have been proposed, using group contribution methods,[42] a modified activity coefficient approach,[43] or suggestions derived from molecular thermodynamic considerations.[44] Unfortunately, all of them do not allow any reliable predictive evaluation. Another approach, which proved more successful to model multicomponent gas solubility in glassy polymers,[45,46] is based on the idea that the glassy polymer is an elastic solid deformed by the penetrant, and the penetrant chemical potential in the polymer phase must be the sum of two contributions, one associated with the deformation of the solid to accommodate the penetrant and another to the mixing of the penetrant in the deformed solid. The analysis of pure penetrant sorption data gives the estimate of the required material parameters, which are then used to predict the sorption of gaseous mixtures. This approach, however, fails at high pressures of penetrant because the glassy polymer cannot be considered any longer as an elastic solid, when the plasticization induced by the gases is relevant.

Computer simulations on the molecular scale can also be applied, in principle, to model the solubility of gaseous mixtures in glassy phases.[47] However, only few examples of that kind are available in the open literature because these calculations are very time-consuming and often are not accurate, due to the nonequilibrium structure of the polymer, whose relaxation times are much longer than those reachable with a reasonable CPU time.

Not only does the solute content in a glassy material depend on temperature and pressure, as is the case for equilibrium rubbery amorphous polymers, but also it changes according to the history of the solid sample. A thermodynamic description of

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the properties of glassy mixtures must, therefore, take into account the nonequilibrium state of the system.

In the past decade, a general thermodynamic model, the nonequilibrium thermodynamics for glassy polymers (NET-GP) approach,[48−51] was proposed to calculate the solubility of small molecules in glassy polymers. According to that theory, the density of the polymer matrix is considered as an order parameter for the nonequilibrium state of the system, and the glassy phase is described using expressions for the free energy from existing EoS models, obtaining the respective nonequilibrium versions. Several different cases were inspected with that approach, mainly by using the lattice fluid (LF) EoS model[30−33] and the corresponding nonequilibrium version (NELF), first presented in 1996 as a tool to predict the gas solubility in homogeneous glassy phases.[52−54] Later the NELF model was applied successfully to represent different phenomena, such as pure gas sorption in glassy polymeric blends[55] and in composite (mixed matrix) membranes,[56,57] to study the effect of aging[58] and of swelling[59] on the sorption process in glassy polymers, and to interpret the correlations between the infinite dilution solubility in glassy polymers and the penetrant parameters.[60,61] Also, the NELF model allowed one to represent the anomalous interactions between alkane penetrants and glassy fluoropolymers,[62−64] and the solubility of liquids in glassy polymers.[65] The NET-GP model has also been implemented with more recent EoS models, such as the statistical associating fluid theory (SAFT) and related versions[34−37] and the perturbed hard chain sphere (PHSC) model,[38−40] obtaining the corresponding NE-SAFT and NE-PHSC models.[48−51,66]

The NET-GP procedure has been only marginally applied to mixed gases so far, confining the attention to the case of the solubility of CO_2/C_2H_4 mixtures in poly(methyl methacrylate) (PMMA) at a pressure of about 2 bar at 35 °C,[67] for which experimental data were available.[14]

The present work is focused explicitly on the application of the NET-GP approach to the case of multicomponent mixtures, and on its ability to predict the solubility of gas mixtures in glassy polymers based only on pure component equilibrium properties, on the knowledge of the pure polymer density in the glassy state and on pure gas solubility data. In particular, we will use the NELF model, which adopts the Lattice Fluid representation of pure substances and their mixtures.[30−33]

Most of the works on mixed gas transport studies are found in the membrane science publications, motivated by the necessity to investigate realistically the gas separation performance of polymeric membrane materials. However, most often those works are focused on the determination of mixed gas permeability coefficients rather than on the single contributions of diffusivity and solubility, which are more difficult to determine, at least in mixed gas conditions. The mixed gas permeation can be monitored by coupling a dynamic permeation apparatus to an analytical instrument that measures the composition of the permeate stream;[68] depending on the sensitivity of such instrument, one can also monitor the permeate composition in the transient stage, allowing to determine the mixed gas diffusivity of the various penetrants.[21,69] The determination of mixed gas solubility, on the other hand, normally requires to evaluate the composition of the head space in a chamber where the polymer sample has reached equilibrium with a gaseous mixture.[9] The quantities of gas absorbed in the polymer can be evaluated as the difference between the initial and final amount of gas present in the fluid mixture. Such a procedure is often associated with a significant error which can be minimized by suitably reducing the difference between the mass of penetrant in the gaseous phase and that absorbed in the solid, i.e. by using very small chambers and/or large amounts of polymer.[9] Moreover, the withdrawal of a certain amount of gas phase for the analysis alters, to some extent, the equilibrium condition reached at the end of the experiment and has to be properly taken into account.

In this work, we consider the data from the pioneering works by Sanders and Koros[9,14,17] on the solubility of C_2H_4/CO_2 and N_2O/CO_2 mixtures in PMMA and by Story and Koros[19,20] on the solubility of CO_2/CH_4 mixtures in PPO. For such common glassy polymers, the pure component parameters entering the lattice fluid model are readily available, and moreover, the NELF procedure for the pure gas solubility has already been applied successfully.[53,54]

■ THEORETICAL BACKGROUND

As discussed above, the determination *a priori* of the solubility of mixed gases and vapors in a glassy polymer is attractive for many applications, in particular in the membrane field. In membrane separation processes, indeed, the membrane performance is characterized by the permeability and selectivity values, that correspond to the productivity and efficiency of the membrane separation stage, respectively. The selectivity α_{ij} between two penetrants i and j, if the downstream pressure is significantly lower than the upstream value, is expressed as

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i}{D_j}\cdot\frac{S_i}{S_j} = \alpha_D\cdot\alpha_S \tag{1}$$

where the permeability, P_i, of the i^{th} penetrant can be calculated from its diffusivity, D_i, and solubility coefficient, S_i, on the basis of the solution−diffusion model and of Fick's law for the diffusive mass flux. Therefore, selectivity is the product of a diffusivity-based contribution, α_D, and of a solubility-based contribution α_S, defined respectively as $\alpha_D \equiv (D_i)/(D_j)$ and $\alpha_S \equiv (S_i)/(S_j)$. Normally, the diffusivity-based factor is the most significant one: however, the solubility factor can also play a significant role and even be larger than the diffusivity factor, as in the presence of penetrants highly soluble in the glassy polymer, such as CO_2, or in the case of high free volume glassy polymers such as poly(trimethylsilyl propyne),[70,71] addition-type poly(trimethylsilyl norbornene)[72,73] and poly(bis(trimethylsilyl) tricyclo nonene).[74]

A first approximation for the value of α_{ij} can be obtained by considering the pure gas values of solubility and diffusivity coefficients; the value of α_{ij} estimated in this way is commonly referred to as "ideal". However, many authors observed that the presence of other gases affects, often significantly, the solubility and/or the diffusivity of a gas in the polymer: in such cases, the actual selectivity may deviate largely from the value of ideal selectivity.[15,18,75]

It is therefore important to have a predictive tool for the estimation of the actual solubility-selectivity, α_S, accounting for the deviation from the pure gas case: in this work we propose the use of the NELF model, based on the more general results of the NET-GP approach,[48−51] whose main features will be briefly recalled hereafter.

In the NET-GP framework the glassy polymer−penetrant phases are assumed homogeneous and amorphous, and their state is characterized by the classical macroscopic variables, i.e., temperature T, pressure p and composition, with the addition of order parameters accounting for the departure from equilibrium.

In isotropic conditions, the density of the polymer species, ρ_{pol}, is sufficient to determine the departure from equilibrium and is chosen as the proper order parameter. The hindered mobility of the glassy polymer chains freezes the material into a nonequilibrium state that can be labeled by the difference between actual polymer density, ρ_{pol}, and its equilibrium value, ρ_{pol}^{Eq}, at the given T, p and mixture composition considered. All thermodynamic functions, as for instance the Helmholtz free energy density a^{NE}, are thus given by an equation of the following type:

$$a^{NE} = a^{NE}(T, p, \mathbf{\Omega}, \rho_{pol}) \tag{2}$$

Here $\mathbf{\Omega}$ is the vector whose components are the mass ratios between solute i ($i = 1, 2, ..., N_p$) and polymer: $\mathbf{\Omega} \equiv (\Omega_1, \Omega_2, ..., \Omega_{Np})$.

Considering the order parameter ρ_{pol} as an internal state variable for the system and applying the theory of materials endowed with internal state variables, it was shown that the nonequilibrium Helmholtz free energy density of the glassy phase, a^{NE}, depends only on temperature, polymer mass density and composition, and its value is independent of pressure:[48]

$$\left(\frac{\partial a^{NE}}{\partial p}\right)_{T, \rho_i, \rho_{pol}} = 0 \tag{3}$$

The chemical potential per unit mass of the penetrant i dissolved in the glassy phase is given by the following expression:[48]

$$\mu_i^{NE} = \left(\frac{\partial G^{NE}}{\partial m_i}\right)_{T, p, m_{j\neq i}, m_{pol}} = \left(\frac{\partial a^{NE}}{\partial \rho_i}\right)_{T, \rho_{j\neq i}, \rho_{pol}} \tag{4}$$

Here G^{NE} is the total Gibbs free energy of the mixture, m_{pol} and m_i are the masses of polymer and of penetrant i, respectively, and ρ_i is the density of the i^{th} penetrant.

As a direct consequence of eq 3, in a general nonequilibrium state the Helmholtz free energy density, a^{NE}, coincides with the corresponding property a^{Eq} evaluated on the equilibrium curve at the same T, ρ_{pol}, and $\mathbf{\Omega}$:

$$a^{NE}(T, p, \mathbf{\Omega}, \rho_{pol}) = a^{Eq}(T, \mathbf{\Omega}, \rho_{pol}) \tag{5}$$

Similarly, the chemical potential per unit mass of solute i in the glassy phase is given by:

$$\mu_i^{NE}(T, p, \mathbf{\Omega}, \rho_{pol}) = \mu_i^{Eq}(T, \mathbf{\Omega}, \rho_{pol}) \tag{6}$$

Such results are derived in general terms and are independent of the particular EoS model used for the free energy.[48] Therefore, once an expression for the Helmholtz free energy equation is selected for the polymer-penetrant mixture, the corresponding pseudoequilibrium equation between the equilibrium gas phase (g) and the nonequilibrium solid phase (s) is readily obtained as:

$$\mu_i^{Eq(g)}(T, p, \mathbf{y}) = \mu_i^{NE(s)}(T, \mathbf{\Omega}, \rho_{pol}) \tag{7}$$

where $\mathbf{y}$ is the vector whose components are the molar fractions y_i of the penetrants in the gas phase. The quantity $\mu_i^{Eq(g)}$ may be calculated through any appropriate equilibrium equation of state. In order to avoid possible misunderstandings about eqs 5 and 6, it is important to point out that the independent variables used in the expression for a^{NE} and a^{Eq} are not T, p and composition but rather temperature, composition, and polymer density, the latter being related to the mixture density ρ (or specific volume v) through the following relationship:

$$\rho_{pol} = \omega_{pol}\rho = \frac{\omega_{pol}}{v} = \frac{\rho}{1 + \sum_{i=1}^{N_p} \Omega_i} \tag{8}$$

Here ω_{pol} is the polymer mass fraction. The typical values of T, $\mathbf{\Omega}$, and ρ_{pol} encountered for glassy polymers do not represent any real equilibrium state for the polymer mixtures, indeed the value of ρ_{pol} entering eqs 5–7 is assigned from separate independent information on the nonequilibrium properties and is not calculated from an equation of state.

To calculate solubility isotherms in glassy phases, one thus needs to use the values of the characteristic parameters of the pure components, that may be found in specific collections, together with the density of the glassy polymer ρ_{pol}, which depends on the experimental conditions and on the history of the samples. For non swelling penetrants, the density of the membrane at every pressure can be considered equal to its initial value, ρ_{pol}^0; in the case of swelling agents, information on the density of the membrane at every pressure condition can be retrieved from dilation experiments conducted in parallel to sorption experiments. Dilation isotherms are not so commonly available or measured; however, it has been seen[76−78] that in most cases of pure gas sorption in common glassy polymers there is a linear dependence of the polymer density on the partial pressure of the swelling penetrant, and therefore a single swelling coefficient, k_{sw}, can be used to account for the volume dilation induced by a pure penetrant in a glassy polymer:[59]

$$\rho_{pol}(p) = \rho_{pol}^0(1 - k_{sw}p) \tag{9}$$

Therefore, in the absence of specific dilation data, the parameter k_{sw} can be adjusted virtually on one only solubility datum at high pressure, and the correlation represented by eq 9 provides an estimate of the polymer swelling at any other pressure.

For gaseous mixtures, no extensive experimental indication exists about the swelling that they induce in glassy polymers. For the sake of simplicity, the natural extension of eq 9 is here considered by assuming that the global volume dilation induced by the gaseous mixture in the glassy polymer is the sum of the swelling that each penetrant would induce if they were pure at a pressure equal to their partial pressure in the mixture, therefore:

$$\begin{aligned}\rho_{pol}(p) &= \rho_{pol}^0(1 - k_{sw,1}p_1 - k_{sw,2}p_2 - ...) \\ &= \rho_{pol}^0\left(1 - \sum_{i=1}^{N_p} k_{sw,i}p_i\right)\end{aligned} \tag{10}$$

where p_i is the partial pressure of penetrant i. Using eqs 7 and 10, the phase equilibrium condition between an external gas mixture and the glassy polymer contains the pure polymer density ρ_{pol}^0 and the swelling coefficient vector $\mathbf{k_{sw}} \equiv (k_{sw,1}, k_{sw,2}, ..., k_{sw,Np})$, and is thus of the following type:

$$\mu_i^{Eq(g)}(T, p, \mathbf{y}) = \mu_i^{NE(s)}(T, p, \mathbf{\Omega}, \rho_{pol}^0, \mathbf{k_{sw}}) \tag{11}$$

Equilibrium free energy functions a^{Eq} used for the nonequilibrium chemical potential calculation may be given by different equations of state models as the lattice fluid,[30−33] SAFT,[34−37] or the PHSC one,[38−40] with the nonequilibrium information represented by the value of ρ_{pol}. For every particular mixture, one will select the EoS model that is most appropriate and exclude the ones which are not suitable. It is for instance known that the LF theory is not accurate in predicting the behavior of solutions between polar and non polar substances, and to represent self-associating and interassociating compounds: for that purpose, one can use the NE-SAFT model which relies on the statistical associating fluid theory representation of associating fluids.

The NELF model[52−54] used in this work to predict the mixed gas solubility in glassy polymers adopts the representation of pure substances and their mixtures of the LF theory,[30−33] according to which each species i is characterized by three pure component parameters: the close-packed characteristic density, ρ_i^*, (or the molar volume of the lattice cell, $v_i^* = M_i/(\rho_i^* r_i^0)$, in which M_i is the molecular weight), the characteristic temperature T_i^* and the characteristic pressure p_i^*. The number of cells occupied by a molecule of species i in the pure state, r_i^0, can be expressed as

$$r_i^0 = \frac{M_i p_i^*}{\rho_i^* R T_i^*} = \frac{M_i}{\rho_i^* v_i^*} \tag{12}$$

and differs from the number of cells occupied by the same molecule i in the mixture, r_i. The latter quantity is given by a mixing rule of the LF model, which postulates the conservation of the close-packed molecular volume of the i^{th} component upon mixing[31]

$$r_i v^* = r_i^0 v_i^* \tag{13}$$

where v^* is the average close-packed volume of a mer in the mixture. The concentration of each component i in the mixture is conveniently expressed in terms of its close-packed volume fraction, ϕ_i, which is defined as the fraction of lattice sites occupied by the N_i molecules of species i in the mixture.[31]

$$\phi_i \overset{def}{=} \frac{r_i N_i}{\sum_{i=1}^{N_p+1} r_i N_i} \equiv \frac{\omega_i/\rho_i^*}{\sum_{i=1}^{N_p+1} \omega_i/\rho_i^*} \tag{14}$$

Here the last identity derives from eqs 12 and 13 and from to the definition of mass fraction ω_i.

On the basis of statistical thermodynamic arguments and the mean field approximation, the lattice fluid theory provides the following dimensionless expression for the equilibrium total Helmholtz free energy of the mixture A^{Eq}, in the limit of infinite coordination number:[31]

$$\frac{A^{Eq}}{rNRT^*} = -\tilde{\rho} + T\left[\left(\frac{1}{\tilde{\rho}} - 1\right)\ln(1-\tilde{\rho}) + \frac{1}{r}\ln(\tilde{\rho}) + \sum_{i=1}^{N_p+1}\frac{\phi_i}{r_i}\ln(\phi_i)\right] \tag{15}$$

In the above equation, r is the molar average number of lattice sites occupied by a molecule in the mixture, and is thus given by $r = \Sigma_i x_i r_i$. The dimensionless temperature $\tilde{T}$, density $\tilde{\rho}$, and pressure $\tilde{p}$ are defined as follows:

$$\tilde{T} = \frac{T}{T^*} \tag{16}$$

$$\tilde{\rho} = \frac{\rho}{\rho^*} \tag{17}$$

$$\tilde{p} = \frac{p}{p^*} \tag{18}$$

where the LF characteristic parameters of the mixture, ρ^*, p^*, and T^*, depend on the composition of the mixture according to the following mixing rules:[32]

$$\frac{1}{\rho^*} = \sum_{i=1}^{N_p+1}\frac{\omega_i}{\rho_i^*} \tag{19}$$

$$p^* = \sum_{i=1}^{N_p+1}\phi_i p_i^* - \frac{1}{2}\sum_{i=1}^{N_p+1}\phi_i\sum_{j\neq i}\phi_j\cdot\Delta p_{ij}^* \tag{20}$$

$$T^* = \frac{p^*}{r}\sum_{i=1}^{N_p+1} x_i r_i^0 \frac{T_i^*}{p_i^*} = \frac{p^* v^*}{R} \tag{21}$$

In eq 20 the quantity Δp_{ij}^* characterizes the interaction energy between species i and j and is expressed as follows:[32]

$$\Delta p_{ij}^* = p_i^* + p_j^* - 2(1-k_{ij})\sqrt{p_i^*\cdot p_j^*} \tag{22}$$

where each quantity k_{ij} represents the only binary parameter associated with each i−j pair of the mixture.

From eq 15, the equilibrium Helmholtz free energy for a mixture can be calculated as a function of temperature, density and composition, as long as the pure component parameters, ρ_i^*, p_i^*, and T_i^* are known, together with the binary parameters, k_{ij}.

Alternatively, the equilibrium Helmholtz free energy of the polymeric mixture may be calculated at a given temperature, pressure and composition from eq 15 after calculating the corresponding equilibrium density from the equilibrium Sanchez−Lacombe equation of state[31]

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}\left(1 - \sum_{i=1}^{N_p+1}\frac{\phi_i}{r_i}\right)\right] = 0 \tag{23}$$

which was obtained minimizing the mixture Gibbs free energy with respect to the volume.

The pure components characteristic parameters p^*, T^* and ρ^*, can be obtained by fitting the pure component equation of state (eq 23 with $\phi_i = 1$) to experimental equilibrium data, such as the pressure-volume-temperature properties above T_g for the polymers and the liquid−vapor equilibrium properties for the penetrants.[30,32] It has often been observed, in the case of polymers, that the LF equation of state cannot fit with high accuracy the volumetric data in the rubbery region in wide ranges of temperatures and pressures:[79] for this reason, the fitting procedure is normally restricted to ranges of T and p close to the experimental conditions of the sorption experiments. In the present work, the LF parameters for most compounds have been taken from previous works, as it will be described in the following.

By applying eq 4 to the expression of the Helmholtz free energy of the polymer mixture given by eq 15 the expression for the nonequilibrium chemical potential μ_i of species i in the glassy mixture is finally obtained as follows:[67]

$$\frac{\mu_i^{NE}}{RT} = \ln(\tilde{\rho}\phi_i) - \ln(1-\tilde{\rho})\left[r_i^0 + \frac{r_i - r_i^0}{\tilde{\rho}}\right] - r_i - \tilde{\rho}\,\frac{r_i^0 v_i^*}{RT}\left[p_i^* + \sum_{j=1}^{N_p+1}\phi_j(p_j^* - \Delta p_{i,j}^*)\right] \tag{24}$$

Equation 24 represents the basic equation for the NELF model which provides the explicit dependence of the chemical potential

Table 1. Values of Pure Component Parameters

	T^* (K)	p^* (MPa)	ρ^* (g/cm^3)	ref	ρ^0_{pol} at 35 °C (g/cm^3)
PMMA	695	560	1.270	54	1.172 (series I) 1.181 (series II)
PPO	739	479	1.177	79	1.0669[19,82]
CO_2	300	630	1.515	52	-
N_2O	325	500	1.402	this work, data from ref 80	-
C_2H_4	295	345	0.680	61	-
CH_4	215	250	0.500	54	-

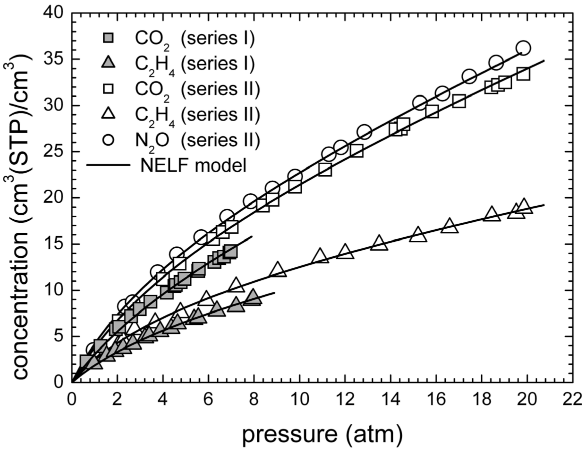

Figure 1. Solubility isotherms of pure CO_2 and C_2H_4 (series I from ref 14 and series II from ref 17) and of pure N_2O (series II) in PMMA at 35 °C: experimental data and NELF predictions.

Table 2. Values of the Binary Interaction Parameters and of the Swelling Coefficients

		k_{ij}	$k_{sw,i} \times 10^4$ bar^{-1}
PMMA	CO_2	0.005	15.4
	N_2O	0.023	17.1
	C_2H_4	0.015	8.90
PPO	CO_2	0.001	9.36
	CH_4	−0.062	0.00

of each penetrant of a multicomponent glassy mixture on temperature, composition and density.

For the evaluation of the solubility of all penetrants i of a mixture, a set of i pseudoequilibrium equations has to be solved to retrieve the mass fraction of all penetrants in the polymer. Each pseudoequilibrium equation is given by eq 7. At each iteration on the value of the mixture composition vector, the dimensionless glassy mixture density $\tilde{\rho}$ is updated since from eqs 8 and 17 one has:

$$\tilde{\rho} = \frac{\rho}{\rho^*} = \frac{\rho_{pol}}{\omega_{pol}\rho^*} \qquad (25)$$

The above procedure is actually simpler than that followed for the calculation of multicomponent solubility in a rubbery polymer using an EoS, since the phase density is not calculated from the same EoS but is given by eq 25, in which ρ_{pol} is independent of the solid mixture composition and is evaluated from eq 10 or from experimental mixed gas dilation data when available.

RESULTS

Pure Gas Solubility: Predictions and Comparison with Experimental Data. The sorption isotherm of each pure component in the polymer is considered first, before evaluating the solubility of a gaseous mixture in a glassy polymer matrix. That procedure allows us to determine the binary interaction parameters k_{ij} between each pure penetrant and the polymer, as well as the swelling coefficients $k_{sw,i}$ of every penetrant i in the polymer, according to eq 9. The values of the LF parameters needed for the calculation of the solubility isotherms of the pure gases are taken from previous works and are reported in Table 1.

For PMMA, the set of parameters comes from ref 54 and the fitting was focused in the range 0−800 bar and between T_g and 160 °C. In the case of PPO, the LF parameters were obtained from the work of Rodgers,[79] that performed the fitting in the range 0−500 bar and 203−320 °C. Standard fitting procedures, based on the data of saturated liquid density and vapor pressure at various temperatures, have been used to retrieve the LF parameters for the penetrants listed in Table 1, which are taken from previous works, with the exception of N_2O, whose parameters were not published before.

Figure 1 reports the experimental sorption isotherms from refs 14 and 17 relative to the solubility of CO_2, C_2H_4, and N_2O at 35 °C in PMMA, together with the predictions obtained from application of the NELF model.

It can be noticed that, for the same system of CO_2 and C_2H_4 sorption in PMMA, different solubility isotherms were reported at the same temperature, by the same authors in refs 14 and 17, respectively. That behavior is likely due to the fact that the PMMA samples used have a different initial density, as a consequence of different pretreatments, as mentioned by the authors. However, such density value was not reported in those papers and it was estimated with the procedure hereafter explained. First, the k_{ij} parameter for the CO_2−PMMA couple was estimated in a range in which k_{ij} is the only fitting parameter, i.e., in the rubbery region. In such interval indeed the pure polymer density and swelling coefficient are known from the equilibrium density of the pure polymer and of the gas−polymer mixture, respectively, according to the LF EoS. For this purpose experimental sorption data of CO_2 at high pressure in rubbery PMMA from ref 81 were fitted to the LF equation of state, obtaining the value of k_{ij} of 0.005. The NELF model was then employed to evaluate the two values of PMMA glassy density, ρ^0_{pol}, by best fitting the CO_2 sorption isotherms in the two glassy samples in the low pressure range, obtaining the values of 1.181 g/cm^3 for the first PMMA sample[14] and of 1.172 g/cm^3 for the second one.[17] Such values were used in the NELF model to estimate the solubility of CO_2 and C_2H_4 in the pure gas state: remarkably, both series of data are described by the NELF model with the same values of the binary interaction coefficients, k_{ij}, and also the same swelling coefficients $k_{sw,i}$ (Table 2). Such result indicates that the model interpretation is consistent with the hypothesis, made also by the authors of the experimental measurements, that the different solubility in the two PMMA samples is due only to different initial nonequilibrium states of PMMA.

In Figure 2, the experimental[19] and NELF-calculated solubility of pure CH_4 and CO_2 in glassy PPO at 35 °C are reported. The

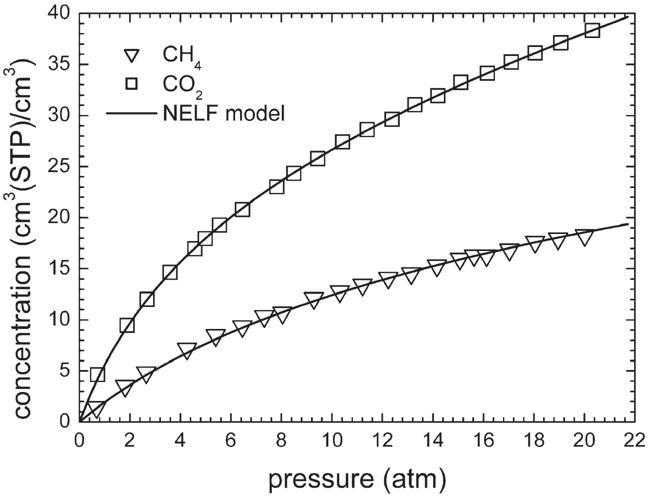

Figure 2. Solubility isotherms of pure CO_2 and CH_4 in PPO at 35 °C. Experimental data were taken from refs 19 and 20.

value of ρ_{pol}^0 equal to 1.0699 g/cm^3 for PPO is obtained from the experimental density reported in ref 19 at 30 °C and the thermal expansion coefficient calculated from Zoller.[82]

In both cases of PMMA and PPO, the parameters of the model are adjusted with a two-step procedure. First the low pressure portion is analyzed, and the value of k_{ij} are fitted to the solubility data with $k_{sw,i} = 0$ (indeed at low pressure, according to eq 9, the density and, thus, the solubility are practically unaffected by the value of $k_{sw,i}$). Then, a fit of the entire data set with the previously determined values of k_{ij} is performed with $k_{sw,i}$ as adjustable parameter. The maximum pressure at which the swelling is negligible cannot be defined a priori but depends on the penetrant and polymer considered, as well as on the temperature. The parameter values thus obtained are reported in Table 2. As illustrated in Figures 1 and 2, the NELF model is able to describe the experimental sorption isotherms with small values of the binary interaction parameters (in the order of a few percent) and reasonable values of swelling coefficients. Dilation data of CO_2 in glassy PMMA at 35 °C are indeed available from the work by Kamiya et al.[81] and the resulting experimental dilation isotherm is described by a linear trend with $k_{sw,i} = 15.4 \times 10^{-4}$ bar^{-1}, just equal to the value obtained in this work. Unfortunately, no experimental data have been published for the swelling of the other systems here considered, so no direct comparison for the other $k_{sw,i}$ values used is possible.

Mixed Gas Solubility: Predictions and Comparison with Experimental Data. For the evaluation of the solubility of a gaseous mixture in a glassy polymer, the parameters (ρ_{pol}^0, k_{ij}, $\boldsymbol{k_{sw}}$) calculated from pure gas sorption were used, whereas the parameters k_{ij} relative to penetrant-penetrant interactions were taken equal to zero (Table 2). Indeed, it has been noticed in all the gas−polymer solutions here considered that the k_{ij} values for the penetrant−penetrant pairs have a very limited effect on the calculated solubility. Such a result is reasonably due to the fact that rather dilute gas−polymer systems are inspected, so that the probability of having a penetrant−penetrant interaction is much lower than the probability of penetrant−polymer interaction.

PMMA−CO_2/C_2H_4 and PMMA−CO_2/N_2O. In Figures 3 and 4, the first series of mixed gas solubility data for the PMMA - CO_2/C_2H_4 mixtures has been considered (from ref 14). In particular, parts a and b of Figure 3 report the equilibrium content of CO_2 and C_2H_4 as a function of CO_2 partial pressure at the fixed C_2H_4 pressure of 2.09 and 3.93 atm, respectively, while parts a and b of Figure 4 show the solubility of CO_2 and C_2H_4 versus C_2H_4 partial pressure, at the constant CO_2 pressure of 1.53 and 3.64 atm, respectively.

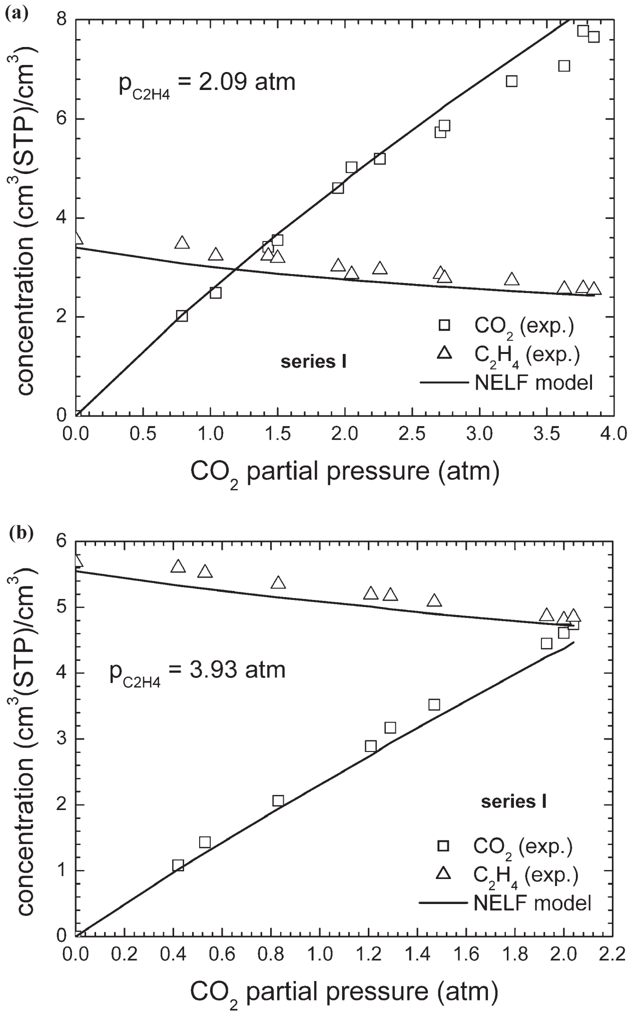

Figure 3. Solubility of CO_2 and C_2H_4 in PMMA at 35 °C; dependence on CO_2 partial pressure at the fixed C_2H_4 partial pressure of (a) 2.09 atm and (b) 3.93 atm. Experimental data were taken from ref 14.

It can be seen experimentally that the increase of CO_2 partial pressure lowers the C_2H_4 content in the membrane at given partial pressures of C_2H_4 (Figure 3); the same effect is observed for the CO_2 content as the partial pressure of C_2H_4 increases (Figure 4). Correspondingly, the solubility isotherm of C_2H_4 in the presence of CO_2 is lower than that measured in the pure gas state at the same pressure, as well as it happens for the solubility isotherm of CO_2. Therefore, the sorption of both penetrants is inhibited by the presence of the second penetrant. Noticeably, the NELF model predictions, reported as solid lines in Figures 3 and 4, reproduce well the experimental behavior observed for mixed gas solubility. As mentioned above, no adjustable parameters were introduced in the prediction of the mixed gas behavior of such systems.

In the first series of solubility data in PMMA, the pressure range explored in the experiments is below 4 atm and the volume dilation induced by the two gases in the PMMA matrix is

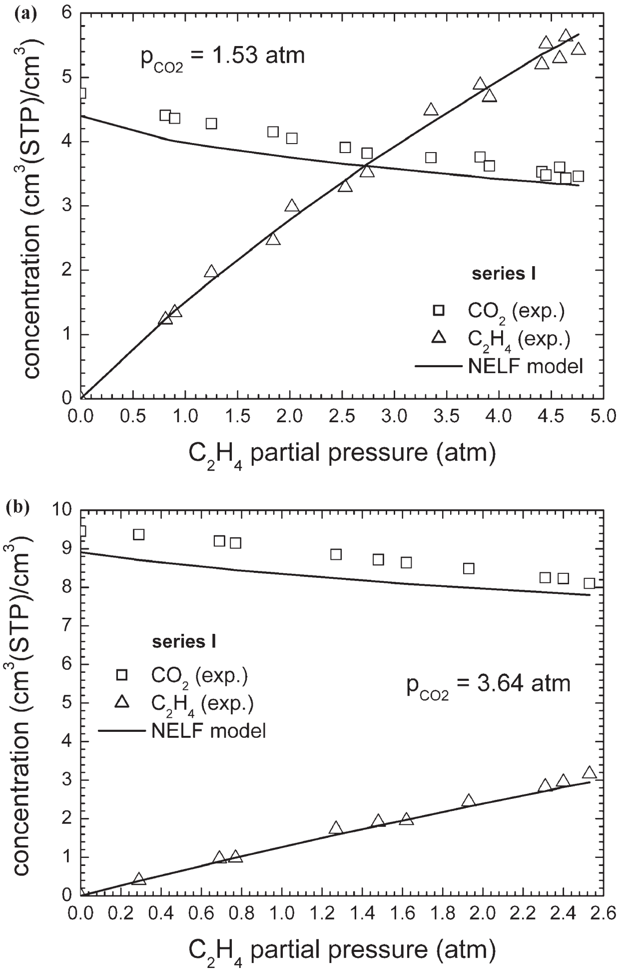

Figure 4. Solubility of CO_2 and C_2H_4 in PMMA at 35 °C; dependence on C_2H_4 partial pressure at the fixed CO_2 partial pressure of (a) 1.53 atm and (b) 3.64 atm. Experimental data were taken from ref 14.

small: according to eq 10, dilation was estimated to be less than 0.5% in all cases. Therefore, any difference between the mixed gas and the pure gas case has to be attributed to other effects, such as the competition between penetrants for sorption into the polymer.

In the second series of data relative to the same gas mixture in PMMA, taken from ref 17, higher pressure values were investigated (up to 14 atm) and the experimental data are reported in Figure 5, parts a and b. Also in this case, the NELF model is able to predict accurately the solubility of CO_2 and C_2H_4 in glassy PMMA in the whole pressure range inspected, with no additional adjustable parameters with respect to the case of pure gases. A slight deviation from experimental data can be noticed in some cases; however, it is always in the range of the expected experimental error of about 10%. In this second sorption data series, the higher gas concentration reached at higher pressures produces a non negligible dilation of the glassy volume up to 2−3% of the dry value. The simple mixing rule for the swelling, introduced in eq 10, seems to be rather accurate in describing this phenomenon and the related gas sorption.

In the same type of PMMA used for the data of Figure 5, a second gas mixture was considered, formed by N_2O and CO_2;[17] in Figure 6, the solubility of N_2O and CO_2 is reported versus CO_2 partial pressure, at a fixed N_2O pressure of 5.05 atm. In this case, both penetrants are strong swelling agents for the glassy

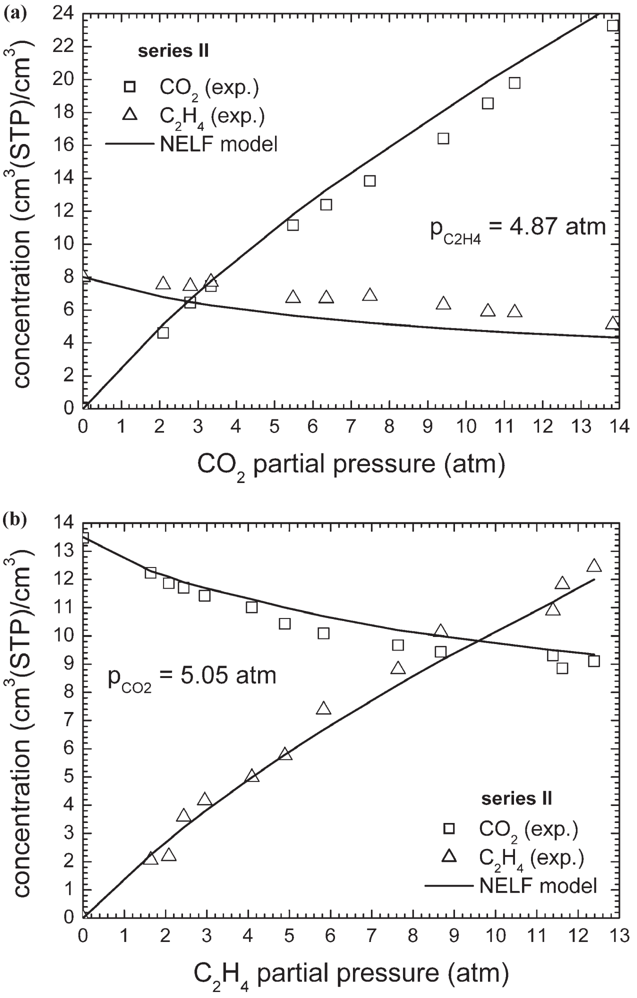

Figure 5. Solubility of CO_2 and C_2H_4 in PMMA at 35 °C versus: (a) CO_2 partial pressure at the fixed C_2H_4 partial pressure of 4.87 atm and (b) C_2H_4 partial pressure at the fixed CO_2 partial pressure of 5.05 atm. Experimental data were taken from ref 17.

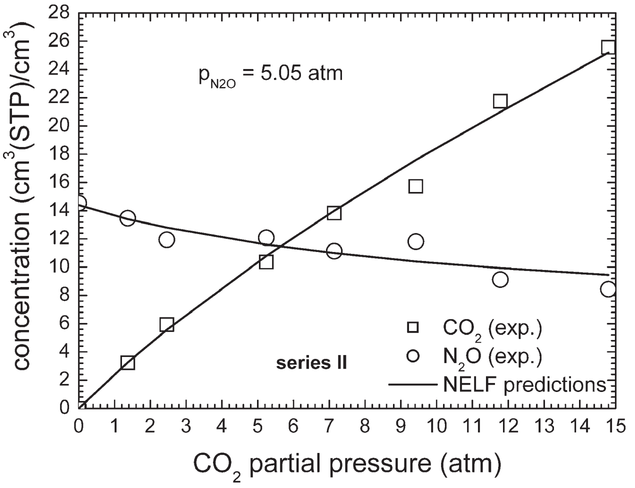

Figure 6. Solubility of CO_2 and N_2O in PMMA at 35 °C; dependence on CO_2 partial pressure at the fixed N_2O partial pressure of 5.05 atm. Experimental data were taken from ref 17.

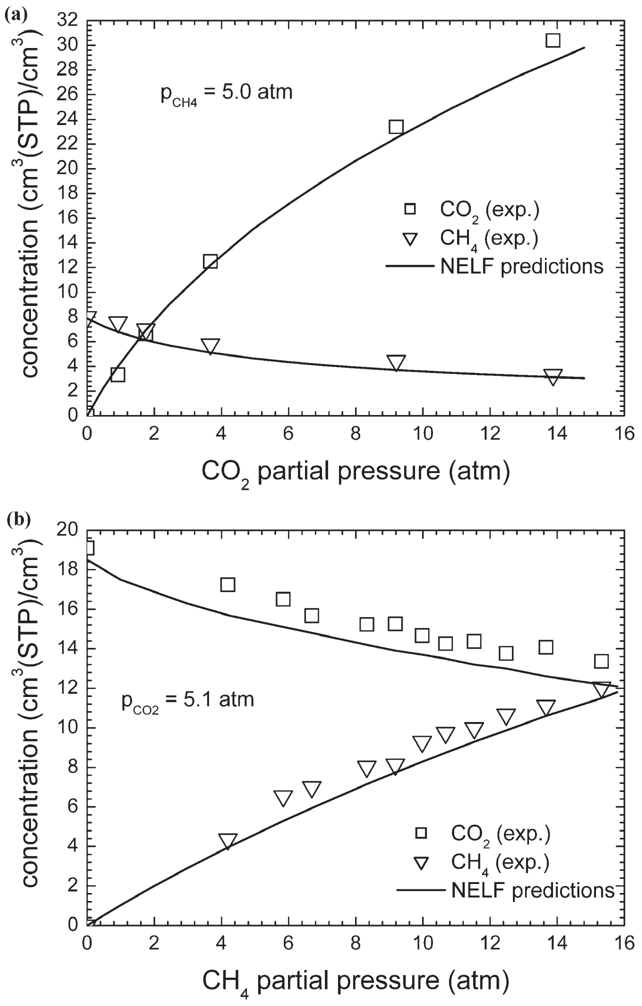

Figure 7. Solubility of CO_2 and CH_4 in PPO at 35 °C versus: (a) CO_2 partial pressure at the fixed CH_4 partial pressure of 5.0 atm and (b) CH_4 partial pressure at the fixed CO_2 partial pressure of 5.1 atm. Experimental data were taken from ref 19.

matrix and, therefore, a remarkable volume dilation is expected, especially at high partial pressures of CO_2. However, the presence of a second component does not favor the sorption of any penetrant because, for both CO_2 and N_2O, the solubility measured in mixed gas conditions is lower than the corresponding value measured in the pure state. The model is able to predict, qualitatively and quantitatively, the gas solubility behavior of both gases.

PPO–CO_2/CH_4. In parts a and b of Figure 7, the gas solubility of CO_2/CH_4 mixtures in PPO is reported for two different experimental conditions, respectively: in the first one, the methane pressure is fixed to 5 atm and the partial pressure of CO_2 is increased; in the second case, the carbon dioxide pressure is 5.1 atm and the CH_4 partial pressure is raised in differential steps.[19] Trends similar to the ones already observed for mixed gas sorption in PMMA are observed in Figure 7; in both cases, the NELF model is able to predict the solubility isotherms rather accurately. In Figure 7b, the deviation between the experimental values and the predictions of the NELF model is larger than in the previous cases, but still within the limit of 10%. However, such a deviation is associated with an inconsistency of the experimental data rather than to a poor performance of the model, because the experimental CO_2 solubility value at about 5 atm of CO_2 reported for the mixed gas state, in the limit of zero CH_4 pressure, is slightly higher than that reported for pure CO_2 sorption (19.1 versus 18.5 cm^3(STP)/cm^3 pol). Also in this case the solubility of both penetrants is depressed by the presence of the other gas.

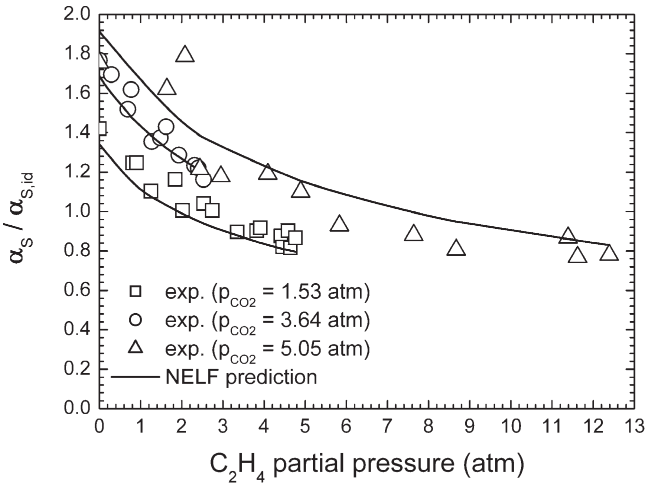

Figure 8. Solubility selectivity of CO_2 versus C_2H_4: ratio between actual and ideal values at different fixed CO_2 partial pressures, for CO_2/C_2H_4 gaseous mixtures in glassy PMMA at 35 °C (experimental data calculated from refs 14 and 17).

Solubility–Selectivity Prediction. The NELF model proved able to predict accurately the solubility of gaseous mixtures in the glassy polymers inspected, on the basis of the pure component parameters and using the binary parameters obtained from the solubility of pure gases. The same model can thus be used to determine the actual values of the solubility selectivity factor α_S, which, on the contrary, is often estimated from the pure component data alone, leading to an "ideal" solubility selectivity ratio, $\alpha_{S,id}$. In Figure 8 we report the values of the ratio between the actual and the ideal solubility selectivity, $\alpha_S/\alpha_{S,id}$, for CO_2 over C_2H_4 in PMMA at 35 °C, at various fixed values of CO_2 partial pressure, as a function of C_2H_4 partial pressure. The quantities, evaluated from experimental data, are compared with the NELF model predictions, represented as solid lines.

Experimentally, it can be seen that, in the whole pressure range inspected, the solubility coefficients of both CO_2 and ethylene decrease. However, in the low ethylene pressure range, the actual CO_2/C_2H_4 selectivity is higher than the value measured in pure gas conditions, indicating that the solubility of ethylene is depressed more significantly than that of carbon dioxide by the presence of the other gas. This behavior is reasonable since in this pressure range the CO_2 content in the membrane is much larger than that of ethylene. When the partial pressure of ethylene becomes sufficiently high, the trend changes and the solubility selectivity becomes higher than the ideal value (i.e., $\alpha_S/\alpha_{S,id} > 1$). Interestingly, such inversion occurs at a point in which the ethylene molar content in the matrix equals that of CO_2, a condition that is reached at about 2.7 atm of ethylene and 1.53 atm of CO_2 (Figure 4a) and at 9.5 atm of ethylene and 5.05 of CO_2 (Figure 5b). Above this point, the presence of a second gas becomes more unfavorable for the sorption of CO_2 (the less abundant penetrant in the matrix), than for that of ethylene. The behavior is qualitatively similar at all CO_2 pressures considered.

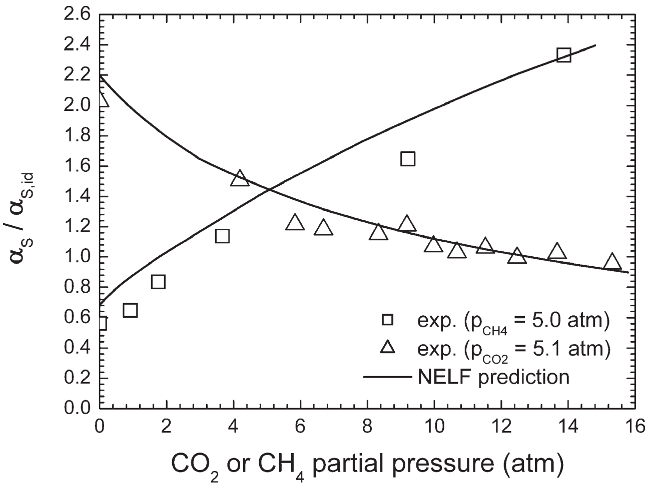

Figure 9. Solubility selectivity of CO_2 versus CH_4: ratio between actual and ideal values, for CO_2/CH_4 gaseous mixtures in glassy PPO at 35 °C (experimental data calculated from ref 19).

The NELF model is clearly able to describe properly the deviations from the ideal behavior in the entire pressure range, and to represent the particular point where ideal and real selectivity values coincide.

For the CO_2/CH_4 selectivity in PPO, the values of $\alpha_S/\alpha_{S,id}$ are plotted in Figure 9 for the two cases of fixed CO_2 partial pressure (5.1 atm) and of fixed CH_4 partial pressure (5 atm). In the first case, the data are represented by open triangles: it can be seen that, as in the previous case of PMMA, the presence of CO_2 in the membrane somehow inhibits the sorption of CH_4 in the low methane pressure range, which is lower than that observed in the case of pure methane, and results in a value of solubility selectivity higher than the ideal one ($\alpha_S/\alpha_{S,id} > 1$). The solubility selectivity then decreases and seems to approach the ideal value for a partial pressure of CH_4 equal to about 16 bar, a value at which the molar content of CH_4 in the membrane equals that of CO_2, as it is visible from Figure 7b. The same ratio is also reported in the same Figure 9, evaluated at fixed CH_4 partial pressure versus CO_2 partial pressure: remarkably, in this case an increase in CO_2 partial pressure leads to a significant increase in the real solubility selectivity. This behavior is perfectly symmetrical to the previous one, because it indicates that the sorption of CO_2 in the glassy matrix is unfavored, with respect to the pure CO_2 sorption case, when a certain amount of CH_4 is already absorbed in the polymer: the curve approaches the unity value at a pressure of CO_2 equal to about 2 atm, that, as it can be seen in Figure 7a, is close to the point of intersection between CO_2 and CH_4 sorption isotherms (1.6 atm of CO_2).

Such experimental behaviors are exactly identical to those observed in the case of C_2H_4/CO_2 sorption in PMMA and seem to indicate that the ideal solubility selectivity can only be retrieved when the number of gas molecules of the two species present in the glassy polymer is similar. When the polymer is more abundant in molecules of penetrant species i, the solubility selectivity α_{ij} is higher than the ideal value, and *vice versa*. Such behavior could be driven by energetic aspects and/or by entropic effects, and it seems not to be related to swelling effects. Interestingly, this trend can be well reproduced by the NELF model, and will be further investigated in the future on a larger number of systems.

The results discussed in this paragraph indicate that there can be a rather remarkable difference between the "ideal" solubility selectivity $\alpha_{S,id}$ and the actual value α_S because, even in relatively narrow pressure range (up to about 15 atm), the factor $\alpha_S/\alpha_{S,id}$ varied between 0.6 and 2.4. That observation indicates the necessity to estimate with accuracy the actual solubility selectivity, in order to avoid rather large errors in the design of membrane separation modules and in any other application. Such estimation can be performed with good reliability by using the NELF model and knowing the pure gas sorption behavior.

■ CONCLUSIONS

The NELF model has been applied to evaluate the mixed gas solubility and solubility selectivity in glassy polymers. The predictive procedure presented requires the following: (i) LF characteristic parameters for the pure gases and pure polymers; (ii) pure gas solubility data in the desired polymer, to retrieve the energetic binary parameter and swelling coefficient values for the penetrant-polymer couples. In modeling the ternary mixture (gas−gas−polymer), the gas−polymer interaction parameters are taken equal to those obtained from the pure gas sorption isotherm, and the gas−gas interaction parameters are taken equal to zero. The swelling induced by the gas mixture in the glassy polymer is considered to follow an additive rule, based on the partial pressure of each component in the gaseous mixture and on the pure gas swelling coefficient in the polymer.

Reliable and rather satisfactory representations have been obtained for the solubility of CH_4/CO_2 mixtures in PPO and of the C_2H_4/CO_2 and N_2O/CO_2 mixtures in PMMA, at room temperature, at various pressures. The mixed gas solubility differs significantly from the corresponding pure gas value, in particular in all the cases inspected the equilibrium content of a gas sorbed in a polymer is lowered by the presence of a second gas. The relative decrease of solubility with respect to the pure gas state is not equal for the two components, but is more significant for the component that is less abundant in the matrix, making the solubility selectivity in general deviate from the ideal value. An exception is apparently observed when the molar content of the two gases in the matrix is similar: in such a case the solubility of both gases is lowered to a similar extent with respect to the pure gas case, and the solubility selectivity coincides with the ideal value. This trend is correctly predicted, both qualitatively and quantitatively, by the model, whose use will allow us to avoid large errors in the design of membrane separation modules and other devices.

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