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Nonequilibrium Lattice Fluids: A Predictive Model for the Solubility in Glassy Polymers

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ABSTRACT: The calculation of sorption isotherms for gases and vapors in glassy polymers is approached through a nonequilibrium equation of state procedure. The basic peculiar feature of the system, represented by the nonequilibrium structure of the mixture, is accounted for by introducing an order parameter for an isotropic glass. By revisiting the lattice fluid model by Sanchez and Lacombe (*Macromolecules* **1978**, *11*, 1145.), an expression for the Gibbs free energy of nonequilibrium lattice fluids is obtained 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 absence of adjustable parameters makes the resulting model entirely predictive for the solubility, once the pseudoequilibrium volumetric data are available. The comparison of the predicted isotherms with the data for CO_2−poly(carbonate) systems at 35 °C, obtained by Fleming and Koros (*Macromolecules* **1990**, *23*, 1353.) under different polymer prehistories, points out the remarkably good ability of the model to represent the sorption/desorption behavior and hysteresis experimentally observed.

1. Introduction

Sorption and desorption of low molecular weight species in or from glassy polymers has attracted considerable attention in recent years in view of the various different applications in which they play a crucial role, such as in membrane separations, in the extraction of solvents and of contaminants, and in the preparation of packaging materials.

In addition, a stimulating conceptual challenge is present, associated with the nonequilibrium nature of the glassy systems, which, at a given temperature, pressure and external penetrant activity, exhibit significantly different pseudosolubilities as well as transport kinetics as a consequence of different concentration or thermomechanical prehistories.[2−5] Correspondingly, all the usual well-established and powerful tools based on equilibrium thermostatics become inappropriate to describe the behavior of such systems.

For rubbery phases and polymer melts the thermodynamic properties, including the solubility of low molecular weight species, can be described properly through reliable expressions based on the equation of state (EOS) approach[1,6−8] or on the activity coefficient procedure;[9−12] the latter method can suitably be applied as long as the operating pressure is below the critical pressure of the penetrants, while the EOS approach is to be preferred at higher pressures, in order to avoid the use of hypothetical states far apart from the actually measurable physical states of the dissolved species.

For the solubility of gases and vapors in glassy polymers, on the other hand, the more successful description is represented thus far by the dual-mode sorption model;[13,14] the extensive use in correlating solubility data for different systems,[15−17] the excellent success, and the simplicity of its application render the model very attractive and apparently insuperable.

Yet, the heuristic way in which it is introduced originated several research efforts aiming to obtain a more fundamental background for the parameters entering the model itself.[18−20] Actually, dual-mode sorp-

tion was introduced on a phenomenological basis, assuming that two populations of penetrant molecules are present in the polymeric solid: one is dissolved in the bulk polymer matrix and has a partial concentration (c_D) expressed as a function of pressure through Henry's law; the second is considered as adsorbed into the surface of the microvoids which are supposed to be present into the polymer, essentially as a consequence of the excess free volume frozen into the glassy matrix. The concentration of the adsorbed molecules (c_H) is described by a Langmuir adsorption isotherm. The resulting overall concentration of the dissolved gas is thus expressed as the sum of c_D and c_H as follows:

$$c = c_D + c_H = k_D p + \frac{c'_H b p}{1 + b p} \quad (1.1)$$

and its variation as a function of pressure may be calculated on the basis of the model parameters k_D, c'_H and b.

As already mentioned, the model can rather accurately correlate the concentration of gases in glassy polymers in most of the known cases and provides a successful conceptual framework for gas sorption; the idea of the coexistence of "equilibrium" and "nonequilibrium" contributions to the overall concentration of the penetrant species, described by the first and the second term of eq 1.1, respectively, appears to be physically sound. Indeed, it has been shown that the parameter c'_H can be related to the initial volume of the polymer matrix,[19] while the "equilibrium" parameter k_D can be related to the dilation of the polymer due to the sorption process.[18] As has been shown very recently,[20] the "equilibrium" term can also be calculated by an EOS procedure, while the c_H contribution can be correlated to the nonequilibrium properties of the mixture through the excess free volume sites distribution.

Nonetheless, the dual-mode sorption shows the typical limitations of substantially empirical models: the parameters must be evaluated for each polymer penetrant system at each temperature independently and, moreover, in desorption the three parameters must be given values different from the ones used in the sorption

process, in order to describe sorption/desorption hysteresis behaviors.

Moreover, the idea of two separate populations for the sorbed molecules is not supported, to our knowledge, by any direct experimental evidence and, most of all, its introduction is not necessary to describe the solubility in other physical phases containing an appreciable concentration of vacancies. From a more fundamental point of view, the separation of the penetrant species in two different populations appears to be a somewhat crude physical picture.

Further alternative studies on sorption modeling are based on a more fundamental approach, considering the glassy mixture as a nonequilibrium phase in which a single population of the sorbant molecules is present;[21-25] the properties of the mixture, as well as of its constituents, are obtained through suitable statistical thermodynamic expressions for the Gibbs free energy. The nonequilibrium properties of the glassy state are accounted for by making use of an appropriate order parameter.

To that aim, Wissinger and Paulaitis[22] introduce the fractional free volume at the glass transition temperature of the mixture, as the order parameter, and consider its value as frozen into the system for all temperatures below T_g. On the basis of two binary adjustable parameters and the knowledge of the glass transition concentration at the fixed temperature, the model allows for a reasonable fitting of the sorption data of CO_2 in poly(methyl methacrylate) or poly(styrene) over a wide range of pressures across the glass transition. The predictive evaluation of the glass transition temperature as a function of the amount of gas sorbed by the polymer was then addressed by Kalospiros and Paulaitis,[26] based on the same lattice fluid theory endowed with the proper order parameter.

Conforti *et al.*[21] consider instead the actual fractional number of holes per polymer mass present in the mixture as an alternate order parameter; its changes can be monitored by the volumetric variations in the mixture. The model can be used for the correlation of sorption data when volume dilation during the same sorption process is known. Good results have been obtained by Barbari and Conforti[27] in fitting the solubility of several penetrants in poly(carbonate) (PC) by using one adjustable parameter, characteristic of the polymer, and a second fitting parameter which needs to be evaluated specifically for each solubility isotherm. The drawback embodied by the demand of dilation data in order to correlate solubility isotherms is compensated by the ability of the model to describe sorption–desorption hysteresis behavior.[28] The latter result, indeed, is based on the different volumetric behavior of the system under sorption or desorption process conditions.

The models by Wissinger and Paulaitis and by Conforti and Barbari originate from the idea of an order parameter for the representation of solubility in glassy polymers and account for the lattice compressibility by means of the evaluation of fractional free volume of the polymer penetrant mixture. Both of these subjects are in focus in this work; thus, a deeper insight into these models is in order.

The model by Wissinger and Paulaitis represents a special application of the thermodynamics of systems endowed with internal state variables,[29] insofar as the order parameter is considered as "frozen in" at a given fixed value; thus, the first model is intrinsically unable

to represent the significant solubility variations and hysteresis associated with sorption–desorption cycles. In order to accommodate such behaviors, further improvements are thus demanded which allow for an appropriate time evolution in the order parameter.

On the other side, the model by Barbari and Conforti is based on statistical thermodynamic developments which neglect the entropic contributions of the polymeric species, as a simplification associated with the hindered mobility experienced by the polymeric chains below T_g. Although that assumption may appear reasonably justified, we notice that it does not allow for the existence of an equilibrium fractional free volume in the limit of vanishing penetrant concentration, and thus the model does not lead to any equilibrium expression for the pure polymer. That point appears to be a serious internal inconsistency of the model and may become a serious drawback in deriving expressions for the thermodynamic properties of the mixture, even if the gas solubility may remain unaffected by that assumption, whenever the fractional free volume is determined directly from the experimental value of the mixture density, as it is suggested in ref 27.

In this work we introduce a new model for the calculation of sorption isotherms for gases and vapors in glassy polymers which is obtained by modifying the lattice fluid theory for polymer solutions developed by Sanchez and Lacombe[1] through the introduction of an order parameter which describes the nonequilibrium state of the glass. We assume here that the density of the polymeric species in the penetrant–polymer solid mixture is a suitable order parameter measuring the nonequilibrium swelling of the polymer matrix; we treat that quantity as the kinetically driven internal state variable of the model. Since the order parameter here considered is a macroscopic and measurable quantity, comparison between the solubility data predicted by the model and the experimental values are possible and straightforward whenever the swelling of the polymer matrix is directly measured during sorption. In those cases, the model is entirely predictive and does not contain any adjustable parameter.

Unlike the model by Barbari and Conforti (the glassy polymer lattice sorption model, GPLSM), in the work here considered the solubility may be predicted simply on the basis of the polymer density rather then on the dilation data. That is not a trivial distinction as in the present approach the value of the solubility coefficient at low pressure may be obtained by using the value of the initial polymer density while the same is not possible within the frame of GPLSM.

The direct comparison of the model predictions with the experimental data obtained by Fleming and Koros[18] for CO_2–PC systems satisfactorily validates the model expression, as will be discussed in section 5. For the sake of simplicity, we leave to a later work a more thorough and detailed analysis of the model predictions for several different polymer–penetrant pairs.

2. Polymer Density as an Order Parameter

Order parameters were introduced to describe nonequilibrium conditions in quite different thermodynamic systems[30] (e.g. systems with chemical reactions, with phase or structural changes) and soon were applied to the analysis of the glass transition[26,31-33] in polymeric systems.

It is worthwhile to distinguish between the use of order parameters as additional variables labeling the

states of the system and the use of order parameters as true internal state variables.

In the first case, as it is in the model by Barbari and Conforti,[27] the dependence of thermodynamic properties of the system on the state variables is considered by accounting also for their dependence on the order parameters; the latter quantities are used as intermediate variables useful in the theoretical development, the values of which are a function of the thermodynamic state, possibly taken from experimental data directly.

A different procedure is used when the order parameter is treated as an internal state variable, as for example in the model by Wissinger and Paulaitis,[22] and then its time rate of change is in general assumed to depend on the state of the system itself. In that case, by confining our attention to the case of a mixture with a single internal state variable Z (although the generalization to multiple internal state variables is straightforward), we have

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = F(T,p,\omega_j,Z) \quad j = 1, 2, ..., N_c - 1 \quad (2.1)$$

In eq 2.1, ω_j represents the mass fraction of species j in the mixture containing N_c components. Thus the time rate of change of the internal state variable is itself a material property, insofar as it depends upon the state variables, i.e. temperature, T, pressure, p, composition, ω_j, and Z, which are needed to describe the mixture properties under nonequilibrium conditions.

The latter approach is used also in the present work; then, hereafter we consider the following expression for the molar Gibbs free energy of the mixture:

$$\tilde{G} = \tilde{G}(T,p,\omega_j,Z) \quad (2.2)$$

where Z is so far an unspecified internal state variable the rate of change of which is described by a kinetic expression such as eq 2.1.

We point out that, contrary to what is assumed in previous model descriptions of the glassy state, and in particular in the model by Wissinger and Paulaitis,[22] we do not take here the order parameter as "frozen in" at its glass transition value, but we rather follow the approach by Coleman and Gurtin[29] and consider the order parameter as a separate state variable. For the total Gibbs free energy function the thermodynamic analysis leads to

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_{i=1}^{N_c} \mu_i \, \mathrm{d}n_i + A \, \mathrm{d}Z \quad (2.3)$$

where

$$A = \left(\frac{\partial G}{\partial Z}\right)_{T,p,n_i} \quad (2.4)$$

is called the affinity to the order parameter Z, and S, V, and μ_i are the nonequilibrium entropy, volume, and chemical potential of species i, respectively. We observe in particular that the expression for the term μ_i resulting from eq 2.3 is

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,Z,n_{j\neq i}} \quad (2.5)$$

and its value is in general different from the chemical

potential prevailing at equilibrium conditions for the same temperature, pressure and composition.

The equilibrium value of the order parameter is a function of the state variables of the system, T, p, and ω_j and represents the Z value at which the function $F(T,p,\omega_j,Z)$ in eq 2.1, i.e. the time rate of change $\mathrm{d}Z/\mathrm{d}t$, vanishes. Its value can be obtained from the results of the thermodynamic analysis for systems endowed with internal state variables,[29] which requires that at equilibrium the affinity value A, defined in eq 2.4, vanishes to zero:

$$A = 0 \quad \text{at equilibrium} \quad (2.6)$$

We observe now that several recent models for the description of equilibrium properties of polymers and polymer solutions[1,6] are based on free energy expressions in which an order parameter is present. In those cases, however, the nature of the order parameter has no separate specific role in the expressions for the thermodynamic properties resulting from the models; indeed only equilibrium states are considered in refs 1 and 6, so that the order parameter is related to the equilibrium state variables through the use of the equilibrium condition and the chemical potential of the ith species, μ_i, is obtained from the set of eqs 2.5 and 2.6.

On the contrary, the nonequilibrium characteristic of the order parameter is an essential feature for our present purposes, and a proper release of the condition in eq 2.6 is in order for the evaluation of the chemical potential of penetrant components in nonequilibrium mixtures.

Indeed, a simple thermodynamic treatment of the glassy state may be conceived for those cases in which the relaxation of the order parameter is kinetically hindered so that after an initial transient its value can be assumed as constant in time, even if not equal to its equilibrium value. Under those conditions, eq 2.1 becomes

$$F(T,p,\omega_j,Z) \approx 0 \quad (2.7)$$

while, on the other side, the equilibrium equation, eq 2.6, does not hold true. Indeed eq 2.7 does not label a single precise value of the nonequilibrium internal state variable, at any T, p, and ω_j, but rather an entire range; the Z value characterizing pseudoequilibrium conditions varies with T, p, and ω_j and with the path followed in the prehistory experienced.

The related phase equilibria—or rather pseudoequilibria—calculations are performed through the minimization of the Gibbs free energy of the system, under the constraint of fixed value for the order parameter.

That is a major point for the purpose of the present work; it is worthwhile to notice that, as it is indicated by eq 2.3 or 2.5, the specific choice of the order parameter is particularly important for the calculation of the chemical potential under nonequilibrium conditions, and thus for the calculations of the pseudoequilibrium composition. Vice versa, for true equilibrium calculations, the particular choice of the order parameter is immaterial, in view of the equilibrium condition, eq 2.6.

In order to consider a suitable order parameter for the description of the glassy state of polymeric materials, we observe that the latter is characterized by an excess free volume with respect to the equilibrium value. Indeed, different thermal, mechanical, or sorption his-

tories may result in different excess free volumes for the glass at the same present value of temperature, pressure, and composition.

We can thus recognize the existence of several different variables which mark the excess free volume and then the out of equilibrium degree of the glassy structure; within the frame of statistical thermodynamics, the number of holes per polymer mass or the fractional free volume as used by Barbari and Conforti[27] and by Wissinger and Paulaitis,[22] respectively, are just two examples.

As long as the order parameter is used as a yardstick for the out of equilibrium degree in the polymeric structure, different possible choices may be regarded as equivalent and, with reference to a precise Gibbs free energy function, interchangeable with each other. On the contrary, when the order parameter is used as an internal state variable, a kinetic equation as eq 2.1 holds and, accordingly, the rate of variation of the order parameter is assumed to depend only on the state of the system. As is evident, the kinetic equations of the type (2.1) associated with the different variables which can be considered as order parameters are not interchangeable at all with each other and thus represent different alternatives. The problem of the most appropriate choice of an internal state variable can appropriately be addressed by considering the physical meaning of the kinetic equation (2.1).

In the present work, the choice of the internal state variable is made after considering a possible expression for the swelling kinetics of the polymer matrix under sorption conditions. From a general point of view many different aspects should be carefully considered when the problem of coupling between sorption and deformation processes of polymeric materials is addressed. However, it is well beyond the scope of this work to discuss the most general thermodynamically consistent form of the constitutive equations for the diffusive mass flux and stress tensor which should be used in those cases, and the reader is referred to some remarkable papers recently published by several authors on this subject.[35-37]

We here simply remind that, after considering a reference state for the polymer solid, a proper description of the deformation may be obtained through the use of the displacement gradient tensor $\mathbf{F}$:

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \xi} \qquad (2.8)$$

where vectors $\mathbf{x}$ and ξ label the same polymer element in current and reference configurations, respectively.

In the case of isotropic materials, a viscoelastic equation for the stress−strain relationship may be written in the form

$$\frac{\mathrm{d}J}{\mathrm{d}t} = f(J, T, P, \omega_j) \qquad (2.9)$$

where J is the determinant of the displacement gradient tensor $\mathbf{F}$ and the time derivative on the left-hand side is made on a material reference basis.

Equation 2.9 is a special case of a rate-type viscoelastic constitutive equation for the mechanical properties. Although what follows could be easily extended to more general constitutive equations, the restriction to the stress−strain relation of the form given in eq 2.9 allows us to use directly the results for the thermodynamic of systems endowed with internal state variables,

in particular eqs 2.3−2.6, by simply stating that for the glassy materials we identify the determinant J, or equivalently the partial polymer density, ρ_2, as an internal state variable.

It is worthwhile to point out here that, as a result of the assumption of the constitutive equation (2.9) for the stress strain relationship, a jump in the applied stress results in a discontinuity in the time rate of change of the polymer volume. We also notice that, when pure materials are considered, the incompressible material case is obtained when the function f in eq 2.9 is constant and equal to zero. We here consider the case in which function f in eq 2.9 changes according to the value of all its arguments and results in values negligible also for density values which do not correspond to the true equilibrium state. The pseudoequilibrium conditions are obtained when the swelling of the polymer matrix is inhibited, i.e. when the partial polymer density has reached values which result in negligible f in the kinetic equation (2.1) even if the condition of vanishing affinity, eq 2.6, does not hold true. According to that stated above, under pseudoequilibrium conditions the expression for μ_i in eq 2.5 thus represents the chemical potential of the species i to be used in phase-equilibria calculations.

Unlike the equilibrium value, which is identified by the condition in which eq 2.6 holds, densities which make the rate function f in eq 2.9 negligibly small for given values of temperature, pressure, and composition may be not determined on a purely thermodynamic basis, and further considerations on the viscosity and elastic modulus for the swelling process are necessary for their evaluation.

A special case, which is of interest in the present work, is obtained when the experimental values of the polymer densities under pseudoequilibrium conditions are available. In that case, the kinetic equation eq 2.9 may be disregarded. By using the experimental ρ_2 values in the expressions for μ_i, the nonequilibrium chemical potential reduces to a function of temperature, pressure, and composition, and then a solubility calculation may be performed in a straightforward way.

3. Equilibrium and Pseudoequilibrium Solubilities

In order to study the solubility of penetrant species into solid polymers, we first consider the equilibrium condition between the solid polymer−penetrant mixture (S) and a gaseous external phase containing pure penetrant (G) at temperature T and pressure p. In terms of species fugacities, f_i, the equilibrium condition for the penetrant is

$$f_1^{(S)}(T, p, \omega_1) = f_1^{(G)}(T, p) \qquad (3.1)$$

where ω indicates the weight fraction and the subscript 1 labels the penetrant species properties.

Under equilibrium conditions (3.1), instead of the absolute fugacities, we can consider the activities with respect to the pure penetrant component at the same temperature T of the mixture and at the reference pressure p^0, which may be arbitrarily chosen:

$$\frac{f_1^{(S)}(T, p, \omega_1)}{f_1^0(T, p^0)} = \frac{f_1^{(G)}(T, p)}{f_1^0(T, p^0)} \qquad (3.2)$$

As usual, the fugacity ratios in eq 3.2 are expressed in terms of chemical potential μ_1 for the penetrant species as follows:

$$\frac{f_1}{f_1^{\,0}} = \exp\left\{\frac{\mu_1 - \mu_1^{\,0}}{RT}\right\} \qquad (3.3)$$

where $\mu_1^{\,0}$ is the penetrant chemical potential for the pure component at the temperature T and at the reference pressure p^0.

The introduction of the reference pressure p^0 may be useful since it results in more reliable calculations when the equations of state used hold true with satisfactory accuracy only in a limited range of pressure, rather than in the entire interval needed for a proper evaluation of the absolute fugacity, from vanishing p all the way to the actual pressure.

The latter case may be of interest not only when the thermodynamic models used for the solid polymeric phase are intrinsically unable to describe properties of vapor phases but also for those cases in which the EOS parameters for the pure component have been obtained by regression of data pertinent to a limited pressure range. In those cases two different equations of state can be used to evaluate the left- and right-hand side in eq 3.2, where the reference pressure p^0 is conveniently chosen in order to obtain reliable expressions for the penetrant activity in the solid and in the vapor phases.

Thus we can study the pseudoequilibrium conditions for the sorption in glassy polymers through the use of eqs 3.2 and 3.3 when, for the solid phase, the chemical potential μ_1 is obtained from eq 2.5, in which the polymer density ρ_2 is taken as the only internal state variable describing the lack of equilibrium existing within the glassy matrix. Then one has

$$\mu_1^{(S)} = \left(\frac{\partial G^{(S)}}{\partial n_1}\right)_{T,p,n_2,\rho_2} = \mu_1^{(S)}(T,p,\rho_2,\omega_1) \qquad (3.4)$$

The chemical potential $\mu_1^{(S)}$ of the penetrant species in the solid mixture, calculated from eq 3.4, depends explicitly upon the polymer density ρ_2, in addition to temperature, pressure, and composition.

Vice versa, the calculations of the chemical potentials $\mu_1^{(G)}$ and μ_1^{0} of the penetrant species in the gaseous phase and in the reference state, respectively, are performed through the usual equilibrium chemical potentials defined as

$$\mu_1^{(G)} = \left(\frac{\partial G^{(G)}}{\partial n_1}\right)_{T,p} \qquad (3.5)$$

Therefore, the pseudoequilibrium conditions written by coupling eq 3.2 with eqs 3.4 and 3.5 give rise to different values of the penetrant concentration in the polymer, ω_1, for different values of the polymer density ρ_2, at any given T and p.

The above framework is, thus far, qualitatively consistent with the experimental indication that different values for the penetrant pseudosolubility are indeed obtained for different initial values of the polymer densities.[38] A corresponding quantitative formulation rests upon the use of an adequate expression for the Gibbs free energy, G, of the penetrant–polymer solid mixture, as a function of penetrant concentration and polymer density ρ_2, as well as of temperature and pressure.

The above procedure becomes effective once an explicit expression for $\tilde{G}$ is available. Several literature models may be considered for that purpose; a complete review of them is well beyond the scope of this work and in that regard we can simply refer to the recent review by Petropoulos.[39] Some useful expressions for the Gibbs free energy as a function of concentration and mixture volume are developed through the lattice model approach; one of the earliest attempts to model polymer–solvent systems considering the solid volume as an independent variable was made by Hildebrand.[40] An expression for the entropy of mixing as a function of the total volume and of the number of polymer and penetrant molecules was obtained which is very similar to that by Flory–Huggins[9,10] when the volume additivity assumption is made.

More recently, valuable expressions for the free energy of mixing for polymer–penetrant systems have been obtained considering "lattice fluid" theories. In that framework, Sanchez and Lacombe[1,41,42] (SL) and Panayiotou and Vera[6] (PV) developed two among the most popular models. In the first case, a lattice is considered as formed by occupied and unoccupied sites (holes), while in the PV model, variations of the nearest-neighbor contacts between polymer segments on individual lattice sites are also taken into account.

As already considered in the previous section, however, in such models only equilibrium expressions for the chemical potential are derived, after the corresponding equations of state for pure fluids or for mixtures are obtained through the use of the equilibrium condition, eq 2.6. The resulting expressions may thus be used properly to predict solubility of gases and liquids in polymers, only under "true thermodynamic equilibrium" conditions.

In this work the internal state variable approach is introduced within the lattice fluid model developed by Sanchez and Lacombe after recognizing the partial polymer density as a convenient order parameter in representing out-of-equilibrium states of the polymeric mixture. Although an analogous approach could be equally developed within other theories, we presently confine our attention to the SL lattice fluid model in view of its simplicity and of the remarkable results which can be obtained from the use of the corresponding equilibrium EOS in predicting solubility data for polymer–solvent systems above the glass transition temperature. In addition, we observe that the nonequilibrium lattice fluid properties are rather straightforward to be obtained from the SL approach. Indeed, the only order parameter of the SL model, i.e. the fraction of holes in the lattice, is directly related to the polymer density which, in the present work, is considered as the only internal state variable necessary to account for the nonequilibrium properties.

4. Chemical Potentials under Pseudoequilibrium Conditions. Nonequilibrium Lattice Fluids (NELF)

Pure Components. In order to obtain suitable expressions for the solubility of low molecular weight species in nonequilibrium lattice fluids (NELF), it is convenient to recall some of the relevant results obtained by Sanchez and Lacombe.[1] Their expression for the Gibbs free energy for a pure component fluid containing n moles at given values of temperature, pressure, and polymer density is[1]

$$G = rnRT^* \left\{ -\tilde{\rho} + \frac{\tilde{p}}{\tilde{\rho}} + \frac{\tilde{T}}{\tilde{\rho}} \left[(1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r} \ln(\tilde{\rho}) \right] \right\} \quad (4.1)$$

where r is the number of lattice sites occupied by a single molecule, R is the gas constant; the reduced density, pressure and temperature, respectively, are defined as follows:

$$\tilde{\rho} = \rho/\rho^* \qquad \tilde{p} = p/p^* \qquad \tilde{T} = T/T^* \quad (4.2)$$

The quantities ρ^*, p^*, and T^* are the model parameters for the pure component and the number r is related to them through the molar volume of the sites, v^*:

$$r = \frac{M}{\rho^* v^*} \quad (4.3)$$

$$v^* = \frac{RT^*}{p^*} \quad (4.4)$$

In eq 4.3, the quantity M is the molar mass of the pure component. It is crucial to point out that eq 4.1 was derived for a lattice fluid generally not under equilibrium conditions at reduced density, pressure, and temperature, $\tilde{\rho}$, $\tilde{p}$, and $\tilde{T}$, respectively. Indeed the equilibrium density is then obtained from eq 4.1 as the $\tilde{\rho}$ value which minimizes the Gibbs free energy of the system, and the original SL equation of state is calculated from the following equilibrium condition:

$$\left(\frac{\partial G}{\partial \rho} \right)_{T,p,n} = 0 \quad \text{at equilibrium} \quad (4.5)$$

Correspondingly, in the SL equilibrium lattice fluid model, the equilibrium chemical potential of the pure component is calculated at any temperature and pressure from eq 4.1, using the density values satisfying the equilibrium condition eq 4.5.

Mixtures. The above lattice fluid theory was then extended to the case of mixtures by introducing proper combination rules for the model parameters. We here consider the mixing rules proposed by Sanchez and Lacombe[1] which, for the case of binary mixtures, can be summarized as follows.

(a) For the molar volume of lattice sites, v^*,

$$v^* = \phi_1^0 v_1^* + \phi_2^0 v_2^* \quad (4.6)$$

where the concentration variable ϕ_1^0 is defined as follows in terms of the number of moles, n_1 and n_2, of components 1 and 2, respectively:

$$\phi_1^0 = \frac{r_1^0 n_1}{r_1^0 n_1 + r_2^0 n_2} \quad (4.7)$$

(b) For the ratio between the number of sites occupied by a molecule of species 1 in the mixture (r_1) and the number of sites occupied by the same molecule in the pure state (r_1^0), the following assumption is made:

$$\frac{r_1}{r_1^0} = \frac{v_1^*}{v^*} \quad (4.8)$$

(c) For the characteristic pressure, p^*,

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1 \phi_2 \Delta p^* \quad (4.9)$$

where ϕ_1 is the volume fraction of penetrant species defined by the equation:

$$\phi_1 = \phi_1^0 \frac{v_1^*}{v^*} \quad (4.10)$$

Only one binary parameter is thus contained in the above reported mixing rules, i.e. Δp^* appearing in eq 4.9.

As a result of the reported set of mixing rules, the following relation holds for the characteristic density ρ^* as a function of the mixture composition:

$$\frac{1}{\rho^*} = \frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*} \quad (4.11)$$

Finally, the characteristic temperature T^* may be obtained for the mixture from the corresponding values v^* and p^*, through the same relation used for pure fluids, eq 4.4.

For a lattice fluid binary mixture, containing n_1 moles of the low molecular weight fluid and n_2 moles of polymer, the Gibbs free energy expression is obtained from the following equation:[1]

$$G = RT^*(r_1 n_1 + r_2 n_2) \left\{ -\tilde{\rho} + \frac{\tilde{p}}{\tilde{\rho}} + \frac{\tilde{T}}{\tilde{\rho}} \left[(1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\phi_1}{r_1} \tilde{\rho} \ln(\phi_1 \tilde{\rho}) \right] \right\} \quad (4.12)$$

In eq 4.12 the dimensionless density, temperature, and pressure, $\tilde{\rho}$, $\tilde{T}$, and $\tilde{p}$, are again defined by eqs 4.2, and the characteristic properties ρ^*, p^* and T^* are given by eqs 4.6–4.11 and 4.4. As for the case of pure components, also for mixtures the lattice fluid Gibbs free energy expression, eq 4.12, generally refers to the nonequilibrium conditions existing at the prevailing values of the variables T, p, ω_1, and ρ. The equilibrium density at a given temperature, pressure, and composition is calculated from eq 4.12 as the value which minimizes the Gibbs free energy, and is thus calculated from the following expression:

$$\left(\frac{\partial G}{\partial \rho} \right)_{T,p,n_1,n_2} = 0 \quad \text{at equilibrium} \quad (4.13)$$

The equilibrium Gibbs free energy and the equilibrium chemical potential expressions are consequently obtained from eq 4.12 when the density is taken as the equilibrium value reached at the prevailing temperature, pressure, and composition.

Vice versa, in the present work we are interested in nonequilibrium lattice fluids with the polymer density as the internal state variable. Therefore the Gibbs free energy expression for the model is embodied by eq 4.12 directly, as a function of temperature, pressure, and concentration and of the internal state variable ρ_2, which is related to the reduced mixture density $\tilde{\rho}$ through the following relationship:

$$\tilde{\rho} = \frac{\rho_2}{\omega_2} \frac{1}{\rho^*} \quad (4.14)$$

From eq 4.12, the chemical potential for the penetrant species in a NELF mixture, $\mu_1^{(S)}$, is obtained by using eqs 3.4 and 4.14. After some algebra, the following expression is thus obtained:

$$\frac{\mu_1^{(S)}}{RT} = \ln(\tilde{\rho}\phi_1) - [r_1^0 + (r_1 - r_1^0)/\tilde{\rho}] \ln(1 - \tilde{\rho}) - r_1 -$$
$$\tilde{\rho}[r_1^0 v_1{}^*(p_1{}^* + p^* - \phi_2{}^2\Delta p^*)]/(RT) \quad (4.15)$$

Equation 4.15 represents the most important result in order to describe the solubility in NELF mixtures. In eq 4.15 the last term represents an energetic contribution to μ_1, while the first three terms originate from the entropy contributions. Both terms are affected by the polymer density value and, typically, the ρ_2 variations encountered result in significant changes in the entropic contribution and only in minor changes in the energetic term. In particular, when the polymer prehistory gives rise to larger matrix volumes, smaller values for the chemical potential $\mu_1^{(S)}$ or, equivalently, larger solubility values are obtained from eq 4.15. That trend qualitatively parallels the commonly accepted picture underlying the dual-mode model, in which larger matrix volumes are associated with larger "microholes" in the polymer and consequently to a larger capacity of the nonequilibrium Langmuir mode.

Through eq 4.15 the phase equilibrium conditions prevailing at a given value of temperature, pressure, and composition and of the order parameter ρ_2 can be calculated through eqs 3.2 and 3.3, simultaneously accounting for eq 4.14.

In the general case, in order to evaluate the pseudo-equilibrium solubility in a specific polymer from a vapor phase of pure component 1, at given temperature and pressure, we should couple the above mentioned phase equilibrium condition with the evolution equation for the order parameter, which is expressed in general terms as

$$\frac{d\rho_2}{dt} = f(T, p, \omega_1, \rho_2) \quad (4.16)$$

The evolution equation (4.16) should be introduced together with the corresponding initial condition to evaluate the order parameter ρ_2 in pseudoequilibrium states. It is beyond the aim of the present work, however, to inspect what expressions are feasible for the kinetic function $f(T, p, \omega_1, \rho_2)$; it is sufficient here to point out that the NELF model allows for the calculation of the pseudoequilibrium sorption isotherms in nonequilibrium glassy structures through eq 4.15, in which the order parameter ρ_2 has the value obtained from the evolution equation (4.16).

Of course, eq 4.16 can alternatively be substituted by directly measured values of the polymer densities, if available. In the latter case, which will be the only one examined hereafter, the present model does not contain any adjustable parameters for the description of the nonequilibrium state; more precisely, the only parameter which may possibly be considered is associated with the quantity Δp^* entering eq 4.6, which represents the mixing rule for the characteristic pressure p^*. However, one can consider for Δp^* its first approximation written only in terms of pure components parameters in the following form:

$$\Delta p^* = (\sqrt{p_1{}^*} - \sqrt{p_2{}^*})^2 \quad (4.17)$$

Thus no adjustable parameter is actually left into the model. Of course, instead of using eq 4.17, Δp^* could alternatively be obtained through some direct equilibrium measurements for the binary mixture. Nonetheless, this point is of really minor importance to our present aim; indeed, while changes in Δp^* result in significant changes in the equilibrium solubilities, we found that the values of Δp^* only slightly affect the pseudosolubilities in nonequilibrium glassy polymers, as will be discussed later.

5. Comparison with Experimental Data

As already mentioned in the previous section, from eqs 4.15 and 4.16 we have the explicit expressions for the chemical potential of the penetrant species dissolved in the solid polymer, in terms of concentration, polymer density, temperature, and pressure, that is used to predict the pseudosolubility of gases and vapors in a glassy polymer with an isotropic nonequilibrium structure. In the present work we do not investigate or speculate on the possible reasonable forms of the kinetic equation eq 4.16; indeed, there are very little published data for mixtures, if any, which can be useful to that aim. However, since the role of eq 4.16 is essentially to provide for the value of the nonequilibrium polymer density to be used in the expression for the penetrant chemical potential, eq 4.15, we realize that a direct comparison between the gas solubility predicted by the NELF model and the experimental values is equally possible if the polymer density is available, together with the penetrant solubility, from direct independent measurements.

Several remarkable works have been published in recent years in which both solubility and dilation experimental data are reported for the sorption of gases in glassy polymers as a function of the external gas pressure.[2,18,43−45] In some cases both sorption and desorption experiments were considered, and usually two different values are observed for the corresponding pseudoequilibrium penetrant contents in the polymer; typically the pseudosolubility observed during desorption is larger than the value obtained in the sorption case at the same temperature and gas pressure. In addition, two different dilations in the solid matrix are observed during sorption and desorption, the latter case showing larger matrix volumes. The above situations are particularly interesting for our present purpose to test the NELF model, in which the mixture volume per polymer mass is the order parameter for the glassy structure.

For the sake of simplicity and clarity, in the present work we confine our attention to a single penetrant−polymer system, i.e. carbon dioxide in PC, which was experimentally characterized by Fleming and Koros[2,18] in careful and complete detail, as far as the relevant model quantities are concerned. Fleming and Koros presented one sorption isotherm at 35 °C up to 900 psia, as well as three desorption isotherms starting from three different pressures, 300, 600, and 900 psia, respectively. Correspondingly, the volume dilation of the matrix, obtained from the measurements of both thickness and area of the polymeric film, were also reported as a function of pressure, for all the mentioned isotherms. Therefore the above sets of data are suitable to test the ability of the NELF model to estimate the pseudoequilibrium solubilities in a glass.

To that extent eq 3.2 is considered; the fugacity ratio in the polymer phase, $f_1^{(S)}/f_1^0$, is obtained from eq 3.3

Table 1. Pure Component Sanchez–Lacombe Parameters

component	ref	ρ^* (kg/L)	T^* (K)	p^* (MPa)
PC	this work	**1.275**	**755**	**534**
PC	20	1.2743	768.2	539.5
PC	49	1.276	802	496
CO_2	this work	**1.515**	**300**	**630**
CO_2	20	1.505	309	574.1
CO_2	51	1.62	283	659.6

by making use of eq 4.15, for the chemical potential of the low molecular weight species dissolved into the nonequilibrium glass, and the chemical potential $\mu_1{}^0$ in the reference state is calculated from the equilibrium SL equation. The fugacity ratio of the penetrant in the external phase, $f_1{}^{(G)}/f_1{}^0$, appearing on the right-hand side of eq 3.2, is calculated from the Peng–Robinson (PR) equation of state[46] which usually appears more appropriate for that aim, although other EOS approaches may be equally successful.[47]

The above calculation procedure is motivated by the expectation of a good description of the thermodynamic properties for condensed or for highly dense phases from the use of a lattice fluid model, whereas more accurate results are expected from the PR model for the fugacity in the gas phase. The use of eq 3.2, containing the fugacity ratios, instead of eq 3.1, containing the absolute fugacity values in each phase, allows consideration of a reference state for the chemical potential at a pressure conveniently high so that the activity in both solid and vapor phase could be satisfactorily evaluated from the respective models. In the following calculations a reference pressure as high as twice the critical pressure for the penetrant component was considered.

The prediction of solubility data can now be obtained for the same system from the NELF model, based on the pure component Sanchez–Lacombe parameters ρ^*, T^*, and p^* for PC and CO_2, once the binary interaction parameter Δp^* is known. The Sanchez–Lacombe pure component parameters are reported in the literature[1,41] for a number of polymers and simple fluids. Their validity, however, is usually confined to a specific temperature range; for polymers, typically the data refer to temperatures much higher then the glass transition temperature and hold for a limited pressure range, while for low molecular weight fluids the parameters are obtained at values significantly below the critical temperature. Since the temperature considered in Fleming and Koros experiments ($T = 35$ °C) is lower than the glass transition temperature of PC ($T_g = 151$ °C) and slightly higher than the critical temperature of the penetrant ($T_c = 34$ °C), we feel it is not appropriate to simply use the Sanchez Lacombe parameters reported in the literature for both pure components and need first of all to obtain them directly from PVT (pressure–volume–temperature) data in a range close to the operating conditions here of interest.

The experimental PVT data for PC in the temperature range from 170 to 330 °C and for the pressure range from 1 to 1770 bar, which were used for the regression, are due to Zoller.[48] Thus the pure component PC parameters ρ^*, p^*, and T^* for the SL EOS were obtained only from data above the glass transition temperature, but we limited our analysis to a relatively narrow temperature range close to T_g, in order to optimize the description of the thermodynamic properties of PC at the temperature used in the sorption experiment. The pure component Sanchez–Lacombe parameters for PC as obtained from the regression procedure are reported in Table 1, and the fitting results are shown for
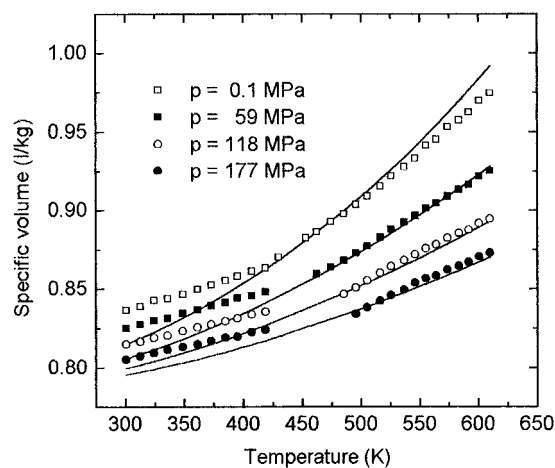

Figure 1. Comparison between calculated and experimental density of poly(carbonate): experimental data by Zoller[48] and calculated data from the Sanchez–Lacombe EOS; the values of SL model parameters used for the fitting are reported in Table 1.
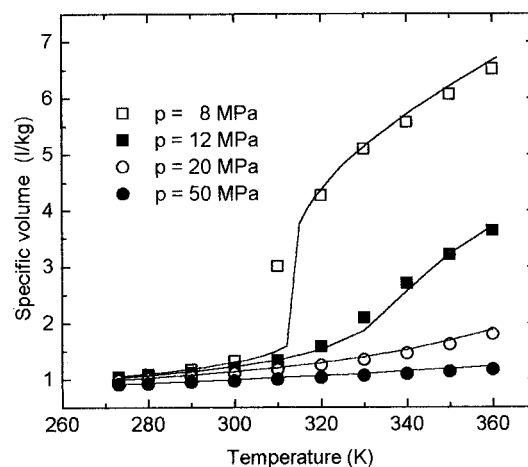

Figure 2. Comparison between calculated and experimental density of carbon dioxide: experimental data by Vargaftik[50] and calculated data from the Sanchez–Lacombe EOS; the values of SL model parameters used for the fitting are reported in Table 1.

comparison in Figure 1. For the sake of comparison, in Table 1 are also reported the values of SL EOS parameters directly taken from the literature.[20,49]

For the determination of pure CO_2 parameters, we considered the liquid density as a function of temperature in a range around its critical value, for different pressures; the experimental data used are taken from the work of Vargaftik.[50] The characteristic temperature, pressure, and density obtained from the comparison of experimental data and SL EOS predictions are reported in Table 1, and the results of the fitting procedure, shown in Figure 2, are quite satisfactory. Also for the case of CO_2 the values of SL parameters obtained in the present work are compared with literature data[20,51] in Table 1. The values of CO_2 critical pressure, critical temperature, and acentric factor, needed for the calculation of the fugacity ratio in the gaseous phase from PR EOS, have been obtained from ref 52.

The pseudosolubility of carbon dioxide in poly(carbonate) can now be calculated on the basis of the pseudoequilibrium conditions and the calculation procedure described in the previous sections. The order parameter ρ_2 needed for the calculations was obtained
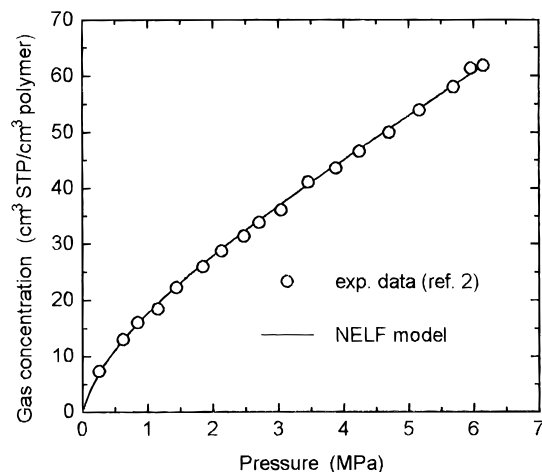
Figure 3. Comparison between calculated and experimental apparent solubility of carbon dioxide in poly(carbonate) at 35 °C: experimental data by Fleming and Koros[2] and calculated data from the model presented in this work; the values used for SL model parameters are reported in Table 1.

Figure 4. Comparison between calculated and experimental apparent solubility of carbon dioxide in poly(carbonate) at 35 °C: experimental data by Fleming and Koros[2] and calculated data from the model presented in this work; the values used for SL model parameters are reported in Table 1.

from the experiments on the dilation of the PC matrix, at each sorption/desorption data point reported by Fleming and Koros,[18] and was calculated with reference to the initial polymer density value of 1.200 kg/L.

In the absence of specific precise information for the CO_2–PC mixture, the binary parameter Δp^* entering the SL mixing rules is considered given by eq 4.17, as usually suggested as a first approximation. We have to notice however that, contrary to what usually occurs in liquid–vapor equilibria (see e.g. Prausnitz et al.[53]), in the present case the solubility results obtained are rather insensitive to the energetic binary parameter, and essentially the same values are obtained even if Δp^* is taken as equal to zero.

The corresponding solubility results calculated through the NELF model, using the pure component parameters reported in Table 1, are shown in Figure 3, together with the experimental data of Fleming and Koros. The agreement between calculated and experimental results is actually very satisfactory; the ability of the model to represent the data is to be particularly appreciated since it is used in an entirely predictive way, based on PVT data of pure components and on the solid mixture dilation only, with no adjustable parameters.

The latter result can be compared with the correlation which was obtained for the same experimental data on the basis of nonpredictive models. Indeed, in a recent review by Barbari and Conforti,[54] a comparison is performed among the ability of six different literature models to correlate the same experimental data here considered. A minimum of two adjustable parameters was used for the data correlation in any of the models considered by Barbari and Conforti, and only for the cases of the three parameters dual mode and the GPLSM were the results of the fitting comparable with the prediction obtained in the present work.

The desorption isotherms data obtained by Fleming and Koros[18] were also considered here and compared with the NELF model predictions. Again, the pure polymer and penetrant parameters reported in Table 1 were used for the prediction, as well as the binary interaction parameter given by eq 4.17. The comparison between experimental and calculated pseudosolubility is shown in Figure 4, where also the predicted curve for the sorption isotherm is reported as a reference. The agreement is good for all three isotherms and we stress
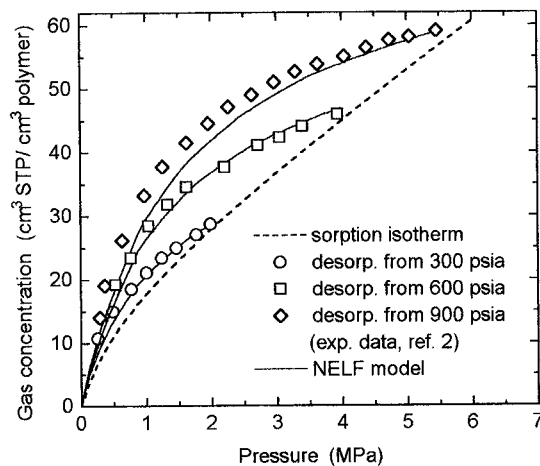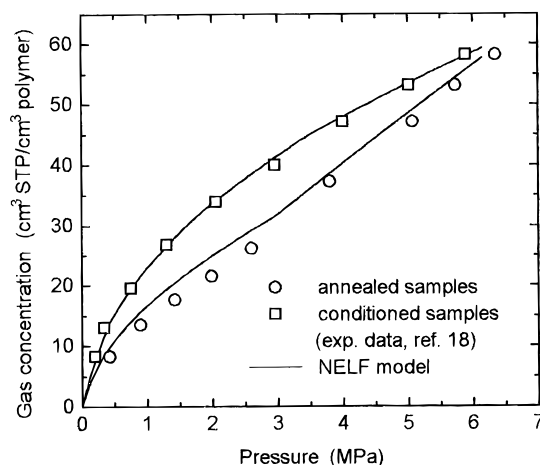

Figure 5. Comparison between calculated and experimental apparent solubility of carbon dioxide in poly(carbonate) at 35 °C: experimental data by Fleming and Koros[18] and calculated data from the model presented in this work; the values used for SL model parameters are reported in Table 1.

again the fact that no adjustable parameters have been used for these predictions, as was the case for the sorption data shown in Figure 3.

As it is clearly indicated in Figure 4, significant differences for the penetrant sorbed into the polymer matrix may be predicted through the use of the NELF model for the same temperature and pressure, as a consequence of the different actual polymer density associated with different out-of-equilibrium isotropic structures.

Finally, two further sorption isotherms for carbon dioxide in poly(carbonate) samples were considered, as obtained by Fleming and Koros, for the cases of conditioning and annealing treatments.[18] Both the samples conditioned under 900 psia CO_2 and the samples annealed at 135 °C for 3 weeks, after the conditioning treatment, were used in ref 18 and the volume dilation of the samples were also measured in both cases. The pseudoequilibrium concentration of CO_2 in PC at 35 °C, predicted by the NELF model as a function of pressure, are compared with the experimental data in Figure 5. The values of Sanchez–Lacombe parameters reported in Table 1 for both CO_2 and PC were used for the predictions also in this case, as well as the dilation data
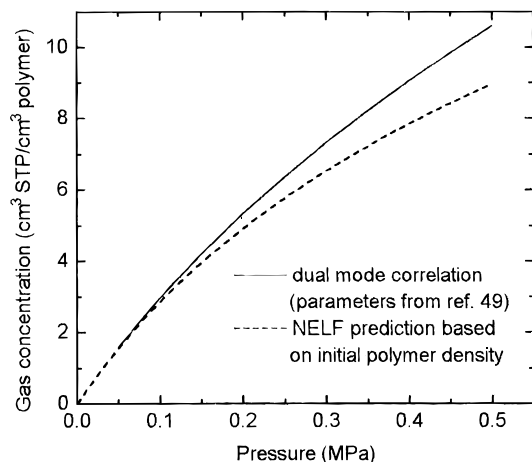
Figure 6. Comparison between calculated and experimental apparent solubility of carbon dioxide in poly(carbonate) at 35 °C in the low-pressure range: experimental data by Fleming and Koros[18] correlated through the dual-mode model by Barbari and Conforti;[54] calculated data from the NELF model, on the basis of the dry polymer density of the samples; the values used for SL model parameters are reported in Table 1.

for the corresponding sorption isotherms reported in ref 18.

The appreciable differences observed for CO_2 solubility in the samples exposed to different pretreatments are well described by the prediction of the model. The calculated CO_2 concentrations in annealed samples appear somewhat overestimated by the NELF model, although its predictive ability is still definitely quite satisfactory.

While taking into account the effect of the polymer density on the solubility allows the NELF model to represent the different solubilities obtained under different histories of the polymer samples, the necessity of volumetric data for the mixture under nonequilibrium conditions may appear as a serious drawback for the model application. To correctly address this point it is important to notice that, for the NELF model, the value of the polymer density, rather than its variations, is necessary in order to predict the solubility coefficient for a given temperature and pressure. In any case, when the dilation data are not available, the NELF model allows for the predictive calculation of the solubility coefficient in the limit of low pressures, simply based on the value of the pure polymer density.

A reasonable example of that has been obtained again for the case of sorption data of CO_2 in PC as presented by Fleming and Koros. Solubility calculations have been performed according to the NELF model neglecting, this time, dilation data and considering the polymer density as fixed for all pressures to the value measured by Fleming and Koros for the dry polymer. In Figure 6 the results for this calculation are compared with the dual-mode correlation obtained by Barbari and Conforti[54] for the mentioned experimental data.

As it is evident from the plot, the solubility coefficient obtained from the dry polymer density in the limit of low pressures exactly recovers the value obtained by the dual-mode correlation, while obviously the prediction fails to represent the experimental data at high pressure. That is a particularly interesting result and we stress here that it is obtained by a completely predictive use of the model presented here, based only on the value of the dry polymer density.

Some comments are now due on the results shown in this section. First of all we note that, for the sake of

generality, we left the phase equilibrium equation in the form of eq 3.2; nonetheless, the use of a thermodynamic model for the vapor phase different from that of the condensed one, proved to be inessential in the calculation performed here. Indeed, the results of gas solubility presented in this section can be obtained with negligible variations also by using the SL model for the pure penetrant vapor phase with the same pure component parameters considered for the NELF calculations.

Secondly, we observe that the solubility data obtained from the model are more sensitive to the value of pure component parameters than the volumetric data used for their regression; then, in order to obtain better predictive results for the solubility, an accurate evaluation of the pure component parameters should be considered, in a temperature range as close as possible to the value of interest. However, when the NELF solubility predictions are performed on the basis of any other set of the literature values listed in Table 1 for SL parameters of pure components, variations may be obtained limited to a maximum value of 10% with respect to the results shown in Figures 3–6.

Finally, the solubility data in glassy polymers obtained by the NELF model proved to be substantially insensitive to the value of the binary energetic parameter Δp^*. That is a major difference with respect to the application of the original equilibrium SL lattice fluid model to the solubility in polymer-penetrant systems above T_g; in the NELF model, ρ_2 is an order parameter, the value of which is independently given, irrespective of Δp^*, while in the equilibrium SL model the equilibrium density, and hence the solubility, varies also with Δp^*. Indeed, for the NELF model the solubility is dominated by the entropic term, which is essentially associated with the polymer density and is unaffected by the energetic interaction parameter Δp^*.

The above mentioned crucial role played by the polymer density of a glassy matrix is also in qualitative agreement with the well-accepted idea that the excess free volume in the glassy structure is the main parameter responsible for the nonequilibrium solubility and with the corresponding picture of the hole-filling process depicted by the dual-mode model.

6. Comparison with Previous Models

A comparison is now in order between the NELF model and two other models previously recalled and recently proposed by Conforti and Barbari[21] and by Wissinger and Paulaitis,[22] respectively.

The glassy polymer lattice sorption model[21] (GPLSM) is based on an expression for the Gibbs free energy of mixing derived for a lattice with occupied sites and holes. The number of holes in the lattice is the most important parameter in the model and its variation with the penetrant concentration is determined on the basis of experimental dilation data versus pressure at the operating conditions prevailing during the sorption experiment. Thus, just as for the case of the NELF model, dilation data for the sorption conditions are necessary in order to predict the amount of penetrant sorbed into the polymer for given values of pressure and temperature.

A major difference with respect to the NELF approach is represented by the fact that within GPLSM the number of holes is not considered as an internal state variable, but is rather treated as an additional param-

eter which in turn depends on the state variables. Unlike the case of the equilibrium solubility calculations, however, the dependence of the number of vacancies on penetrant concentration is not determined from the equilibrium condition represented by eq 2.6 but from the experimental volume dilation value.

In addition, in the case of GPLSM, two different adjustable parameters are present: one is the interaction energy for the pure polymer, which can be possibly evaluated from the sorption data of different penetrants in the polymer under consideration, and the other is the Henry's law constant, which comes into play when the activity coefficient expression, appropriate for the gas species, is introduced into the equilibrium equation.

With the two adjustable parameters, or possibly one only if the polymer interaction energy parameter is evaluated from different sorption data, the model can accurately describe some sorption isotherms and in particular those obtained by Fleming and Koros[18] for the CO_2−PC system already examined in the previous section. By considering the volume dilation of the solid as an independent variable, just as we did in this work, the GPLSM also accounts for different gas solubilities in the polymer and for sorption and desorption isotherms. Indeed, gas sorption−desorption hysteresis has been addressed by Conforti and Barbari,[28] offering a GPLSM analysis of the same data by Fleming and Koros also considered in this work. Even after considering the Henry's law constant as an adjustable parameter, however, only qualitative prediction of the solubility of CO_2 in poly(carbonate) can be obtained in that case, the polymer energy parameter being fixed to the value obtained from the fitting of the sorption isotherm data.

In contrast, Wissinger and Paulaitis[22] suggested a model aimed to describe the sorption in glassy polymers based on an existing polymer solution theory and the concept of order parameters. They used the PV model for the thermodynamic properties of penetrant−polymer systems, considering two order parameters, the fraction of holes, and the number of nearest-neighbor contacts between polymer segments in the individual lattice sites. At temperatures below the glass transition temperature, Wissinger and Paulaitis consider the two order parameters as "frozen in" at the same values existing at T_g; while that assumption appears in many respects reasonable and consistent with previous descriptions of the glassy state by means of internal state variables,[33] it makes the model intrinsically unable to differentiate among the solubilities obtained under different histories of the polymeric samples.

The solubility of CO_2 in glassy poly(methyl methacrylate) and poly(styrene) was considered by Wissinger and Paulaitis as predicted from PV EOS with model parameters evaluated from the fitting of sorption data in liquid polymers. For the cases in which only the hole fraction was "frozen in" through the glass transition, good agreement with the experimental solubility results was obtained for those systems in which even the equilibrium model, with parameters adjusted from the sorption data in the melt, gives qualitatively good predictions.

With respect to the model presented in this work, the approach proposed by Wissinger and Paulaitis allows for the calculation of the volume dilation of the system. On the other hand, however, as it considers a unique value of dilation and solubility for given values of temperature and pressure, the model cannot account for sorption−desorption hysteresis effects.

7. Conclusions

The NELF model is presented for the prediction of gas and vapor solubilities in nonequilibrium glassy polymers. The model is essentially based on the idea that an isotropic glassy mixture can be represented by considering the partial polymer density as the order parameter which labels the nonequilibrium structure resulting from the matrix prehistory.

The order parameter is considered as an internal state variable and the corresponding relevant thermodynamic relationships have been coherently used, including the expression for the chemical potential of the low molecular weight species dissolved into the nonequilibrium glass.

The use of polymer density as an internal state variable is consistent with the use of a rate-type viscoelastic law for the stress−strain relationship for isotropic materials.

Contrary to what is obtained for the thermodynamic equilibrium conditions, different expressions of the nonequilibrium chemical potentials are derived from the same Gibbs free energy expression for the mixture, when different parameters are considered as internal state variable. That makes the choice of the order parameter crucial, for the calculation of solubility under nonequilibrium conditions.

An expression for the chemical potential of the penetrant species in isotropic glassy polymers was then obtained from the well known SL lattice fluid model, by releasing the equilibrium condition, in accordance with the assumption that the polymer density is an internal state variable. The solubility calculations under defined conditions of temperature and pressure may be performed in general if a suitable evolution equation of the internal state variable is available.

In the present work, however, the specific form of the evolution equation for the internal state variable was not investigated. On the other hand, by simply observing that its main role is to provide for the polymer density value to be used in the fugacity expressions, a procedure was indicated to calculate the pseudosolubility of the gas in the polymer for those cases in which the volume of the solid matrix has been independently measured. In such cases the model is entirely predictive and does not contain any adjustable parameters; the NELF model for the solubility in glassy polymers is in fact based on the knowledge of the pure components PVT data and on the measurement of the solid matrix volume.

The model allows consideration of different gas solubilities for different dilations of the matrix, as observed for the sorption/desorption hysteresis phenomenon.

The solubility calculated from the NELF procedure shows very good agreement with the experimental data obtained by Fleming and Koros for CO_2−PC system at 35 °C. The sorption−desorption hysteresis behavior proved to be described in a satisfactory way in that case. A more thorough comparison with experimental data for different polymer penetrant pairs is left to a subsequent work.

While in the absence of reliable time evolution equations for the internal state variable the need of the volume dilation data limits the actual predictive capability of the model, we observe that all the quantities entering the NELF model have precise physical meaning and can be directly measured independently. On the basis of only the experimental value of the density of the dry polymer, the model allows for the pure

prediction of the solubility coefficient in the limit of very low pressures; the results obtained in that pressure range for the pair CO_2–PC show good agreement with the data and support that conclusion.

Following a procedure which appears to be both simple and quite satisfactory from a fundamental point of view, the model thus accounts for the relevant features observed for the solubility of low molecular weight species into glassy polymers.

We observe in closure that, while the SL lattice fluid model was here chosen for the nonequilibrium Gibbs free energy, obviously a procedure analogous to the above may be developed by choosing a different model for the nonequilibrium Gibbs free energy.

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