Calculation of the Solubility of Liquid Solutes in Glassy Polymers

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The solubility of liquid molecules in glassy polymers has been considered by using the general results of the Non-Equilibrium Thermodynamics of Glassy Polymers (NET-GP), which proved successful to calculate solubility isotherms of gases in glassy polymers for rather different situations, including polymer blends, mixed gases, and mixed matrices. It is shown that the existing model is suitable also for liquid penetrants in a glassy phase: water and ethanol sorption in polycarbonate (PC) and water sorption in polysulfone (PSf) have been examined as examples. The model's ability to predict the solubility from both liquid and vapor phases was tested successfully, using the same values of the parameters for both phases. In the case of PC, the model was also applied to calculate successfully the solubility of liquid water at different temperatures from 25 to 130°C, with a single value of the energetic binary parameter. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 292–301, 2012

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Introduction

The use of glassy polymers is widely spread in a great variety of different technical applications, and they are commonly encountered in our daily life. Their interaction with the external environment is of great importance either for the direct application they are used for, for example in the packaging of food and pharmaceuticals, protective barriers, membrane separation processes, and for increasing the life time of the products whose interactions with the chemicals present in the environment may affect the mechanical properties and long-term resistance. The main physical properties which allow to characterize the interactions between polymer and environment, are the solubility of the different penetrants and their diffusivity, possibly with the addition of the swelling effects caused by the penetrants and by the stress distribution associated to mass transport. The same properties are also of major importance in relevant membrane separation processes as for instance in pervaporation.

For rubbery or gel-like phases, the solubility of liquids can be calculated successfully by using well-established models either for the excess Gibbs free energy or equations of state (EoS). One of the most popular and applied is Flory–Huggins theory[1] for which expressions of the interaction parameter χ and modifications required to account for the presence of crosslinks in the polymer network have been proposed[2]; successful use has also been made of UNIQUAC,[3,4] UNIQUAC free volume,[5] and UNIFAC free volume models,[6,7] which were applied for a number of polymeric solutions. The solubility of gases and vapors in polymer rubbers has also been properly calculated by using EoS with models appropriate for condensed phases as the lattice fluid (LF) theory of Sanchez and Laçombe,[8–10] perturbed hard sphere chain (PHSC) theory,[11–13] and statistical associating fluid theory (SAFT) models, both in the presence and in the absence of hydrogen bonding groups.[14–17]

For glassy polymer phases, on the other hand, the situation is different and not equally studied or established as the case

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of rubbery polymers; the main reason of course is found in the fact that glasses are nonequilibrium phases, for which the usual equilibrium thermodynamic conditions and the models recalled above do not apply; their properties in general depend not only on temperature, pressure, and composition but also on the prehistory that they have experienced for temperature, stress, deformation, and composition.

The problem has been tackled by introducing ad hoc models, based on a simplified heuristic schematization of the physical behavior, the most successful of which is the well-known dual mode sorption (DMS) model widely applied to correlate empirically the solubility of gases and vapors in glassy polymers.[18]

More recently, the solubility of gases and vapors in glassy polymers has been described by using the extension to glassy phases of the EoS approach, on the basis of the nonequilibrium thermodynamics of glassy polymers (NET-GP)[19–22]; that procedure proved rather useful and also successful to predict the solubility isotherms of gases and vapors in pure glasses or in glassy polymer blends, based on the usual mixing rules associated to the EoS selected and on the pure component parameters, which are determined from separate independent information. The different nonequilibrium models thus derived and associated to different EoS's offer explicit expressions for the chemical potential of the penetrants dissolved in the glassy phase from which the solubility can be calculated. In particular, many different cases were inspected and represented with the LF model and the corresponding nonequilibrium LF (NELF) version, first presented in 1996.[23–25] The NELF model was later successfully applied to the prediction of gas solubility in many different situations: (i) mixed gases in glassy polymers,[26] (ii) single gases in glassy polymeric blends,[27] and (iii) single gases in composite (mixed matrix) membranes.[28,29] Moreover, the NELF model was applied to represent the effect of ageing on the sorption process in glassy polymers,[30] to establish correlations between the infinite dilution solubility in glassy polymers and the penetrant parameters,[31,32] to estimate the swelling of a glassy polymer on the basis of sorption data,[33] and to elucidate the interactions between alkane penetrants and fluorinated glassy polymers.[34–36]

The solubility calculations based on nonequilibrium models use expression mathematically not as easy as the DMS model. However, the latter is used to correlate existing solubility data, whereas, on the contrary, the nonequilibrium thermodynamic models have a reasonable predictive ability and, on the other side, executable programs to perform the isotherm calculations are freely available online,[37] together with the model parameters of common polymers and penetrants. Such nonequilibrium models have been applied thus far to calculate the solubility of gases and vapors in glassy polymers even though the expressions of the chemical potential are not associated to a specific state of aggregation of the external phase and should apply equally well in general also for penetrants deriving from a liquid-phase.

As an alternative to the macroscopic models mentioned above, other options, which have been investigated and applied, are represented by methods based on molecular dynamics or Montecarlo techniques, which use intermolecular potential expressions rapidly developed and investigated in the recent decade.[38] The latter approaches and the multiscale methods developed[39,40] appear very promising, even though at present their application for the routine calculation of solubility isotherms appears too long and costly to be applied as the only standard tool for general use.

Very recently, the solubility of liquids in glassy polymers has been considered by Arnold[41,42] who developed a new specific ad hoc model based on the free-volume hole filling idea. That model considers the presence of pre-existing sites in the glassy matrix, endowed with a frozen-in distribution of hole sizes; the variation of Gibbs free energy associated to hole filling with liquid molecules is calculated considering detailed contributions due to elastic energy, interactions between polymer and penetrant, and to less immediate contributions as interactions energies across a hole; hole loss and the entropy change of liquid molecules have also been considered through an ad hoc expression, hard to test; no polymer contribution to entropy changes has been considered. Overall, the hole-filling model presented in Refs. 41 and 42 contains a series of parameters to be determined or adjusted, which offer predictions not fully reliable, often leading even to orders of magnitude for the solubility difference from the value experimentally measured. The sensitivity analysis performed for different model parameters indicates that the errors of the solubility calculated can actually be rather high.[42]

Therefore, we found it worthwhile and interesting to inspect the applicability to the solubility of liquids of the nonequilibrium EoS models, which appear rather promising on the basis of our experience in their use for the solubility of gases and vapors in glassy matrices. The aim of this work is to examine how the NET-GP theory can be used to calculate the solubility of liquids in glassy polymers and to discuss the procedures to determine the relevant model parameters from independent sources.

Theoretical Background

The NET-GP results

Thermodynamic analysis of the phase equilibrium conditions involving a polymeric glass represents an application of the NET-GP, which ultimately leads to the relationships existing in general between the thermodynamic properties above the glass transition temperature and those prevailing below T_g under pseudo-equilibrium conditions. The latter are asymptotically attained by the glassy phase when the external relevant boundary conditions of temperature, pressure, and stress are kept constant together with the fugacity of all the components in the external environment; they represent of course the physical conditions under which the phase equilibrium, or rather pseudo-equilibrium, solubility of the external penetrants are reached. In view of the departure from true equilibrium, which is frozen into the glassy phase, the pseudo-equilibrium conditions depend on the thermomechanical prehistory of the material.

In the NET-GP analysis, the glassy polymer-penetrant phases are considered homogeneous and amorphous, and their state is characterized by the classical variables of macroscopic thermodynamics, that is, temperature, pressure, and composition, with the addition of order parameters accounting for the departure from equilibrium. The possible presence of anisotropic elongations or other nonuniformities frozen into the glass have been neglected thus far confining the attention to the basic case of isotropic conditions, for which the specific volume of the polymer matrix, or, equivalently the density of the polymer species, ρ_{pol}, is sufficient to determine the departure from equilibrium and is thus chosen as the only proper order parameter. In other words, 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 at the given temperature, pressure and mixture composition, $\rho_{\text{pol}}^{\text{EQ}}$. All material properties, as for instance, the Helmholtz free energy per unit volume a^{NE}, will thus be given by an equation of the following type:

$$a^{\text{NE}} = a^{\text{NE}}\left(T, p, \rho_i, \rho_{\text{pol}}\right) \tag{1}$$

where T, p, and ρ_i are temperature, pressure, and density of the ith penetrant, whereas ρ_{pol} is the polymer mass per unit volume; it is also rather common to substitute in Eq. 1 the ρ_i values with the mass ratio between solute i and polymer $\Omega_i = \rho_{i/}\rho_{\text{pol}}$.

Considering the order parameter ρ_{pol} as an internal state variable for the system, and applying well-established thermodynamics for materials endowed with internal state variables, it was shown that[19–22]:

1. the nonequilibrium Helmholtz free energy per unit volume of the glassy phase, a^{NE}, depends only on temperature, polymer mass density, and composition, and its value is independent of pressure:

$$\left(\frac{\partial a^{\text{NE}}}{\partial p}\right)_{T,\rho_i,\rho_{\text{pol}}} = 0 \tag{2}$$

2. the chemical potential per unit mass of penetrant i dissolved in the glassy phase is given by the following expression:

$$\mu_i^{\text{NE}} = \left(\frac{\partial G^{\text{NE}}}{\partial m_i}\right)_{T,p,m_{j\neq i},m_{\text{pol}}} = \left(\frac{\partial a^{\text{NE}}}{\partial \rho_i}\right)_{T,\rho_{j\neq i},\rho_{\text{pol}}} \tag{3}$$

where 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;

3. the nonequilibrium Helmholtz free energy, a^{NE}, is the extension to nonequilibrium states obtained as a cylindrical function from the equilibrium Helmholtz free energy at all pressures; in other words, in a general nonequilibrium state a^{NE} coincides with the corresponding property a^{EQ} evaluated on the true equilibrium curve at the same temperature, composition, and density of the polymer species:

$$a^{\text{NE}}\left(T, p, \rho_i, \rho_{\text{pol}}\right) = a^{\text{EQ}}\left(T, \rho_i, \rho_{\text{pol}}\right) \tag{4}$$

4. similarly, the chemical potential of solute i in the glassy phase is given by:

$$\mu_i^{\text{NE}}\left(T, p, \rho_i, \rho_{\text{pol}}\right) = \mu_i^{\text{EQ}}\left(T, \rho_i, \rho_{\text{pol}}\right) = \left(\frac{\partial a^{\text{EQ}}}{\partial \rho_i}\right)_{T,\rho_{j\neq i},\rho_{\text{pol}}} \tag{5}$$

To avoid possible misunderstandings about Eq. 5, it is important to point out its physical meaning: the expression of the chemical potential of the penetrant in the glassy polymer at the prevailing temperature, pressure, and composition is found to be calculated by an expression of the chemical potential formally identical to the equilibrium one converted in terms of temperature, composition, and polymer density, in which, however, the nonequilibrium value of the polymer density is used; the latter is given from separate experimental information for the glassy phase.

Therefore, once an expression for the equilibrium free energy a^{EQ} is selected as appropriate for the equilibrium polymer-penetrant mixture, the corresponding nonequilibrium equation is readily obtained through the simple relationships represented by Eqs. 4 and 5. Such results have been derived in general and are independent of the particular EoS model used to describe the Helmholtz free energy or the penetrant chemical potential under equilibrium conditions: the NET-GP results hold for any thermodynamic model suitable for the polymer-penetrant mixture under examination and are not restricted to any particular equation of state.

Nonequilibrium free energy functions can thus be obtained starting from different EoS as LF, SAFT, and PHSC, just to mention the relevant models, which have been considered in recent work,[19–35,43] and give rise to the corresponding nonequilibrium models denoted by NELF, NE-SAFT, and NE-PHSC, respectively. The nonequilibrium information entering Eqs. 4 and 5 is represented by the actual value of polymer density in the glassy phase, which must be known from a separate source of information as, for instance, direct experimental data, correlations, volume rheology models, and of course cannot be calculated from the equilibrium EoS.

Determination of the model parameters

The pure component parameters of the models can be retrieved following different procedures for the solute species and for the polymer; for the latter case use of volumetric data as a function of temperature and pressure above the glass transition temperature represents the main option, applicable in general for the cases in which the rubbery phase can be reached before thermal degradation; volumetric and/or vapor pressure values are frequently available and rather useful data to obtain pure component parameters for the penetrants. All mixture models for free energy have also one binary interaction parameter, k_{ij}, associated to each couple of chemical species, which can be obtained separately, for example, from gas-polymer equilibrium data in the rubbery phase, when available. In the absence of any direct experimental information, the first-order approximation can be used for k_{ij} ($k_{ij} = 0$) or alternatively, it can be treated as adjustable parameter as is often done in the thermodynamic literature.

Equilibrium and pseudo-equilibrium solubility calculation

In the case of true thermodynamic phase equilibrium, in which the absolute minimum is attained for the system Gibbs free energy at given T and p, the solubility calculation is performed following the classical thermodynamic result, which imposes the equality between the equilibrium chemical potential of the *j*th penetrant in the polymeric solid ($\mu_{\mathrm{j}}^{\mathrm{EQ(s)}}$) and in the external fluid phase ($\mu_{\mathrm{j}}^{\mathrm{EQ(f)}}$)), together with the equilibrium value of the polymer density. The equilibrium solute content, $\Omega_i^{\mathrm{EQ}} = \rho_i^{\mathrm{EQ}}/\rho_{\mathrm{pol}}^{\mathrm{EQ}}$, and polymer density, $\rho_{\mathrm{pol}}^{\mathrm{EQ}}$, can be calculated from the following usual conditions:

$$\begin{cases} \left(\frac{\partial g^{(s)}}{\partial \rho_{\mathrm{pol}}}\right)_{T,p,\Omega_i} = 0 \\ \mu_j^{\mathrm{EQ}(s)}\left(T, \Omega_i^{\mathrm{EQ}}, \rho_{\mathrm{pol}}^{\mathrm{EQ}}\right) = \mu_j^{\mathrm{EQ}(f)}(T,p) \end{cases} \tag{6}$$

The symbol $g^{(s)}$ represents the Gibbs free energy of the polymeric mixture per unit polymer mass. Equations 6 hold true of course in both cases of liquid or vapor external phase.

For the solubility in glassy phases, the situation is substantially different, because the polymer density does not match its equilibrium value $\rho_{\mathrm{pol}}^{\mathrm{EQ}}$, but it finally reaches an asymptotic value determined by the kinetic constraints acting on the glassy matrix and substantially depending on the past history of the polymer sample. Correspondingly, also the penetrant solubility in the polymeric phase reflects the pseudo-equilibrium state reached by the system. In view of the NET-GP results such pseudo-equilibrium condition corresponds to the minimum Gibbs free energy for the system, at T and p, under the constraint of a fixed value (the pseudo-equilibrium value) of the polymer density in the condensed phase:

$$\mu_j^{\mathrm{NE}(s)}\left(T, p, \Omega_j, \rho_{\mathrm{pol}}\right) = \mu_j^{\mathrm{EQ}(f)}(T,p) \tag{7}$$

In Eq. 7, the nonequilibrium solute chemical potential is calculated through Eq. 5 after an appropriate equation of state model for the polymer-penetrant system has been selected.

The pseudo-equilibrium content of penetrant j in the polymer, Ω_j, can be calculated whenever the value of the pseudo-equilibrium polymer density, ρ_{pol}, is known. That value represents a crucial input for the nonequilibrium approach, characterizing the departure from equilibrium, and usually all nonequilibrium models are rather sensitive to the polymer density value; ρ_{pol} must be assigned as a separate independent information, and in general cannot be calculated simply from temperature and pressure because it depends also on the mechanical, thermal, and sorption history of the sample.

The polymer density value during sorption is normally not available at all penetrant activities, and that is a constraint for the application of the NET-GP approach as a completely predictive tool. However, the knowledge of the polymer density value appears much simpler and less problematic than the knowledge of the entire hole size distribution in the glass, as it is required by the hole filling model,[41,42] the comparison with which is one of the motivations of the present work. In several cases of practical interest, indeed, the pseudo-equilibrium density of the polymer can be easily known with negligible errors: that is the case when the pseudo-solubility of the penetrant is very small as, for instance, in the presence of penetrants at low activity (i.e., ratio between penetrant pressure and its vapor pressure), when the polymeric mixture is infinitely dilute and the volume of the polymer is not significantly affected by the presence of very small solute fractions; that is also the case of liquid solutes with very low solubility. The density of the pure unpenetrated glass, ρ_{pol}^0, thus provides a very good estimate of the actual polymer density, ρ_{pol}, and the NET-GP approach can be applied in a straightforward and predictive way. Similar consideration holds true also in the case of nonswelling penetrants, for which the pseudo-equilibrium calculation can also be reduced to the following low-activity approximation:

$$\mu_j^{\mathrm{NE}(s)}\left(T, p, \Omega_i, \rho_{\mathrm{pol}}^0\right) = \mu_j^{\mathrm{EQ}(f)}(T,p) \tag{8}$$

When swelling agents or higher gas pressures are used, practical application of the NET-GP approach needs some further consideration. In particular, for the gaseous phases it can be noticed[44–46] that, generally, the polymer mass density during sorption practically varies linearly with penetrant pressure, in a relatively wide pressure range, at least for temperatures sufficiently below glass transition, so that the following relationship is followed by polymer density[33]:

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

where the swelling coefficient, k_{sw}, represents the effect of gas pressure on pseudo-equilibrium polymer density and is itself a nonequilibrium parameter, depending on thermomechanical and sorption history of the specific polymer sample. In view of Eq. 9, in the case of gas sorption at high pressure, the pseudo-equilibrium condition, Eq. 7, becomes:

$$\mu_{\mathrm{sol}}^{\mathrm{NE(s)}}\left(T, p, \Omega_{\mathrm{sol}}, \rho_{\mathrm{pol}}^0(1 - k_{sw}p)\right) = \mu_{\mathrm{sol}}^{\mathrm{EQ}(g)}(T,p) \tag{10}$$

Through Eq. 10, the pseudo-equilibrium solubility can be evaluated also for the case of swelling penetrants, even in the cases in which polymer dilation is not known from direct experimental evidence. Indeed, the swelling coefficient, k_{sw}, can be treated as the only adjustable parameter in Eq. 10, and its value can be determined, for example, from virtually a single experimental solubility datum at high pressure for the system under consideration.[33]

The procedures reviewed above have been successfully applied for the calculations of solubility isotherms of gases and vapors also in a relatively broad pressure range and in many different systems, as already mentioned. The procedure is completely predictive when the swelling coefficient k_{sw} and the binary parameter k_{ij} are known for the polymer penetrant pair under examination; in the case of nonswelling penetrants, the binary parameter alone is required, which can be inferred from the knowledge of the mixture behavior above T_{g} or, in the absence of that information, can be given by its first-order approximation ($k_{ij} = 0$)[10] or else used as a fitting parameter to be adjusted to the entire solubility isotherm. In the case of swelling penetrants, we may have situations in which both k_{sw} and the binary parameter are used as two fitting parameters for the entire isotherm below the glass transition, or cases in which only k_{sw} is an adjustable parameter if the binary parameter is known from separate equilibrium information for the mixture.

On the other hand, when only the solubility of one pure liquid at one temperature is considered, as it is apparently the case analyzed by Arnold,[41,42] the aim is to calculate one single solubility data point using a model which in all cases may contain more than one adjustable parameter; consequently, it will not make much sense to try to best fit the adjustable parameters to the single data point given by the solubility of the pure liquid at one temperature.

On the contrary, the approach to follow is to check whether the same parameter values allow to describe a relatively large number of experimental data as for instance a solubility isotherm from vapor phase, with the extension to the pure liquid at the solute vapor pressure at the temperature under consideration. Therefore, to test the ability of the nonequilibrium EoS models cited above to calculate the solubility of liquids in glassy polymers we will consider polymer-penetrant pairs for which solubility data are available both for the pure vapors at different pressures and for the liquid phase. The predictive ability of the model to evaluate liquid solubility is tested in a straightforward way for the cases in which volume swelling is negligible, for example, for water solubility in polycarbonate (PC) and in polysulfone (PSf): in such cases, the unpenetrated polymer density is commonly available, whereas the binary interaction parameter can be retrieved from experimental data for the vapor solubility; then the solubility of the liquid solute is predicted with no further adjustable parameters.

The situations in which the liquid penetrants give rise to a swollen glassy phase are less simple, insofar as information on volume dilation is required, which on the contrary is rarely available from independent data; for such cases, an example of which is given by ethanol in PC, one can consider the following alternative procedures:

i. Obtain the binary interaction parameter from the vapor solubility data in the infinite dilution limit, if available, where the swelling plays no effect, then derive the swelling coefficient from vapor solubility data in the higher-pressure range; alternatively, if the infinite dilution data are not available, use the solubility data at low activity to retrieve both binary interaction parameter and swelling coefficient. From k_{ij} and k_{sw}, one then calculates the solubility of the liquid solute. This procedure relies on the hypothesis that polymer density varies linearly with pressure; that may not be accurate in the entire activity range and may lead to an underestimation of polymer volume at unit activity and thus to an underestimation of liquid solubility.

ii. Obtain the binary interaction parameter from vapor solubility data, using the low-activity range of the sorption isotherm as before, then use this parameter to calculate the solubility of the liquid phase, considering volume dilation estimated from the assumption of volume additivity between pure glassy polymer and pure liquid penetrant; the final volume is thus a function of the final liquid solubility and is calculated iteratively. Usually, the penetrant partial molar volume in glassy polymers is lower than its pure liquid value; therefore, an overestimation of the solubility of liquid solutes is expected from this method.

iii. Use the experimental value of the liquid solubility together with the volume additivity assumption to retrieve the energetic binary parameter and the swelling coefficient (or equivalently the final polymer density), and then check if the same values hold true to describe properly also the solubility isotherm from the vapor-phase.

Of course, procedures (i) and (ii) can be used to predict the liquid solubility, reasonably offering a lower and an upper estimation of its value, respectively; procedure (iii) instead may be used to check the overall consistency of the approach to calculate the solubility of solutes in the entire activity range from zero to unity.

Results and Discussion

Estimation of $\mathbf{T}_g$ *depression*

Before affording the calculation of the solubility of liquid solutes in glassy polymers, one has to determine whether the final state of aggregation is glassy or rubbery. Indeed, considering solubility data collected in the entire range of penetrant activity, from zero to unity, in a polymer, which is initially well below its T_{g}, two types of experimental behaviors can be observed: (i) the polymer remains glassy at all activities, even in presence of the liquid penetrant, as it is usually the case of penetrants with a limited solubility in the polymer phase; (ii) the penetrant is highly soluble in the polymer and induces a glass transition at some point of the solubility isotherm. In the latter case, the low-molecular weight solute decreases the polymer glass transition temperature, so that after penetrant sorption one might also find that the initially glassy polymer has turned rubbery. This important point was apparently not taken into consideration in developing the hole-filling model proposed in Refs. 41 and 42. Of course, the procedures to follow for the solubility calculation depend on the final state of the polymer mixture and are different when the final state is rubbery, which requires the use of equilibrium EoS, from the case in which the final state is still glassy, which requires the use of the nonequilibrium approach. The same value of the binary parameter has to be used above and below T_{g}, in the absence of an uncommon temperature dependence.

The consistency of the latter procedure was shown in Ref. 21 where infinite dilution solubility coefficient of CO_2 in PC was examined, above and below the glass transition temperature, showing that the same value of the binary coefficient $k_{ij} = 0.05$ applies to the equilibrium behavior above T_{g}, with the SAFT EoS in the version by Huang and Radosz,[16] as well as below T_{g} with the NE-SAFT model. Similarly, the same conclusion is drawn from Figure 1,[21] reporting the comparison between infinite dilution solubility coefficients of CO_2 in PSf and the results obtained with SAFT EoS above T_{g}, as well as with NE-SAFT model below T_{g}[21]; clearly consistent results for both the glassy and rubbery states are obtained using the same value of the binary parameter $k_{ij} = 0.045$. For reference, the same Figure 1 also contains the results obtained by using in the whole temperature range the equilibrium SAFT EoS with the default value for the binary parameter ($k_{ij} = 0$), which overestimates the experimental equilibrium data. The above results show clearly that the energetic interactions between the penetrant and the polymer remain constant across the glass transition, consistently with the NET-GP theory, and the difference is due only to the polymer structure, which below T_{g} requires the use of the glass density value as an internal state variable and use of the nonequilibrium approach.

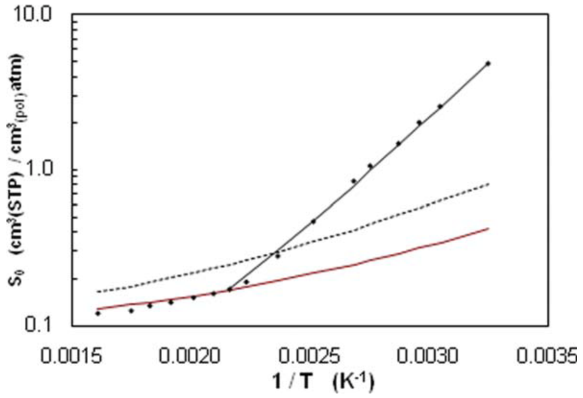

Figure 1. Solubility coefficient of CO_2 in PSf at infinite dilution reported as a function of reciprocal temperature.

The correlation with SAFT EoS in the equilibrium range and with NE-SAFT model in nonequilibrium conditions are reported using the same binary interaction parameter k_{ij} = 0.045; the dotted line indicates equilibrium SAFT EoS calculations with k_{ij} = 0.[21] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conversely, to model the sorption isotherm in the presence of a penetrant-induced glass transition in the polymer one has to apply the nonequilibrium approach only in the activity range lying below T_g, whereas at higher activities, above T_g, the equilibrium expressions apply. Examples of this more complex behavior will be considered in a subsequent work. In the present analysis, we will confine our attention only to the cases in which the polymer remains glassy in the entire range of penetrant activity up to the liquid state. Therefore, the final solvent content in the polymer does not alter the glassy state, and the glass transition temperature remains always well above the experimental temperature. This condition may be verified by using one of the relationships commonly applied to calculate T_g in polymeric mixtures, such as the Kelley–Bueche equation[47]:

$$T_g = \left[\Delta\alpha_P T_{g,P}(1 - V_S) + \alpha_S T_{g,S} V_S\right] / [\Delta\alpha_P(1 - V_S) + \alpha_S V_S] \tag{11}$$

where the thermal expansion coefficient of the solvent is taken to be $\alpha_S = 1.2 \times 10^{-3}$ K^{-1}, the change in the thermal expansion coefficient of the polymer at T_g is $\Delta\alpha_p = 3.8 \times 10^{-4}$ K^{-1}, and $T_{g,S}$ =135 K for water and 100 K for ethanol. With the assumption of volume additivity, the volume fraction of the diluents, V_S, can be estimated directly from the penetrant-to-polymer mass ratio under phase equilibrium conditions.

Table 1. Lattice Fluid EoS Parameters for the Penetrants and Polymers Considered

	LF EoS				
	ρ^* (kg/L)	T^* (K)	p^* (MPa)	Source	ρ_2^0 (kg/L)
PC	1.275	755	534	23	1.200
PSf	1.31	830	600	25	1.236
H_2O	1.05	670	2400	32	
C_2H_5OH	0.915	470	880	32	

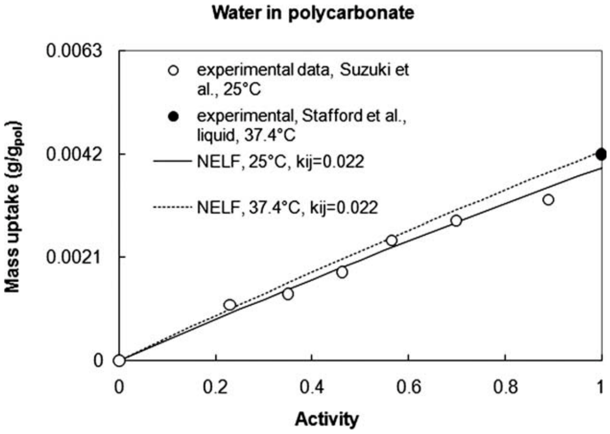

Figure 2. Solubility of water in PC; open circles are for vapor phase, filled symbol is for liquid.

Experimental data at 25°C are from Ref. 49 and the value at 37.4°C is from Ref. 50.

Using Eq. 11 to evaluate the T_g depression induced by liquid absorption at 25°C in PC, with the solubility data given by Kambour et al.,[48] one obtains that for PC T_g decreases from 159 to 154°C in the presence of water and to 50°C in the presence of ethanol. For PSf, in the presence of water at 25°C, T_g varies from 185 to 174 °C. In all the above cases, therefore, the polymer matrices remain glassy and the nonequilibrium approach must be adopted in the entire penetrant activity range to describe the solubility of water in PC and in PSf and of ethanol in PC.

Solubility calculations

The applicability of the method illustrated above to the calculation of the solubility of liquids in glassy polymers is now tested by considering some examples for which the solubility from both the liquid and the vapor phases are available for the penetrants of interest, as it is required for an independent parameter estimation. In very few cases, for the same penetrant, solubility data in glassy polymers have been presented for unsaturated vapors and for the saturated vapor or liquid state; therefore, data from different sources had to be used for our present aim.

Water Sorption in PC at 25°C. For the PC–water pair, the solubility isotherm from the vapor-phase is available at 25°C from Suzuki et al. for PC samples, which were synthesized in-house[49]: the data were obtained with a Cahn electrobalance in the activity range 0–0.80. Application of the NELF model, based on the pure component parameters available from the literature and reported in Table 1, gives a good representation of the observed behavior (Figure 2), with a swelling coefficient equal to zero, consistently with the rather limited solubilities, using a binary interaction parameter k_{ij} = 0.022, that is a standard value when limited deviations from the usual first-order approximation are encountered. The densities of the glassy PC samples were not reported in Ref. 49; so that we used the common value for pure glassy PC density of 1.200 g/cm^3. The NELF model prediction can be calculated up to the pure liquid conditions using the same parameters and the binary coefficient required to fit the low pressure vapor solubility isotherm. Experimental data for liquid solubility were taken from the work by Stafford et al.,[50] which were obtained at 37.4°C: indeed other values for liquid water absorption in PC, such as the one given by Arnold,[42] are lower than the values measured for the vapor-phase in Ref. 49, thus they were not considered because they clearly refer to much different samples. The liquid solubility value observed by Stafford et al. at 37.4°C is equal to 0.0042 g/g_{pol}.[50] The variation of PC density in the thermal range between 25 and 37.4°C was considered negligible, and the density value was taken equal to 1.200 g/cm^3 for both cases. The same binary parameter $k_{ij} = 0.022$ was used for the NELF prediction at both temperatures and one correspondingly found that the model is able to capture both the solubility data from the vapor-phase at 25°C and those from the liquid-phase at 37.4°C, as it is clearly shown in Figure 2, where the lines represent of the NELF model calculations at the two temperatures considered.

Water Sorption in PC at Different Temperatures (25–130°C). Using the same model parameters as above, we can now calculate in a completely predictive way the temperature dependence of the solubility of liquid water in PC in the temperature range from 25 to 130°C and compare the results with the values reported by Bair et al.[51]; to that end the variation with temperature of the pure polymer density is accounted for using the volume thermal expansion coefficient of PC obtained as three times the linear expansion coefficient of 6.5×10^{-5} K^{-1}.[52] Indeed, Bair et al.[51] actually used a different PC (Lexan 141), the density of which was not reported in their work; in the manufacturer data sheet one finds values around 1.20 with some oscillation for the density at room-temperature, and we know that the solubility in the glass is highly sensitive to the pure polymer density. In the absence of more precise information regarding the pure polymer density in both references, we simply show in Figures 3a and b the results of NELF model calculation obtained by using for the pure polymer density at 25 °C the values 1.20 and 1.21 g/cm^3, respectively, and $k_{ij} = 0.022$. With no further comment or speculation about the actual density value, which was not reported with the solubility data, it is relevant to notice that in any case the predictive use of the NELF model offers a rather satisfactory estimation of the trend of the temperature dependence of liquid water solubility in PC, in a rather broad temperature range.

Ethanol sorption in PC at 30°C. This case is somewhat different from that of water sorption considered above, insofar as ethanol induces an appreciable volume swelling in the glassy matrix, especially at high-activity values, and consequently, in estimating the solubility with the NELF model the polymer density cannot be considered equal to that the of the unpenetrated glassy polymer. The problem is therefore to fit simultaneously two adjustable parameters, namely the swelling coefficient k_{sw} and the interaction binary parameter k_{ij}, to the solubility data available. For ethanol in PC, we have experimental information provided by Kambour et al.[48] for the liquid solubility (0.078 g/g_{pol} at 24°C), and by Hwang et al.[53] for the vapor solubility isotherm at 30°C in the entire activity range from zero to unity, with a saturated vapor solubility of 0.083 g/g_{pol}; both sources indicate solubilities for the liquid phase much higher than the value assumed by Arnold[42] for the uptake of liquid ethanol in PC, equal to 0.009 g/g_{pol}, which is even smaller than the solubility from the low-activity vapor-phase, and thus it was not considered for our present comparison.

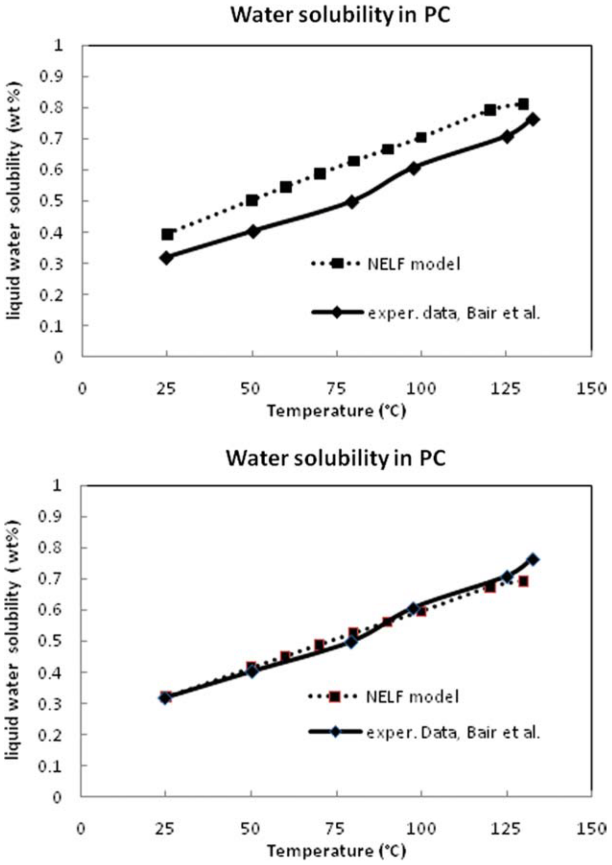

Figure 3. Solubility of liquid water in PC vs. temperature.

Comparison between experimental data by Bair et al.[51] and NELF model predictions based on the binary parameter obtained at 25°C from the data by Suzuki et al.[49] (**a**) the pure polymer density at 25°C was taken as 1.20 g/cm^3 and (**b**) the pure polymer density at 25°C was taken as 1.21 g/cm^3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As already pointed out previously, in the absence of direct experimental data for polymer volume dilation, we may consider the following alternative procedures for swelling penetrants in polymers which remain glassy.

(a) Retrieve the parameter values from the low-activity solubility isotherm.

In this case, we have used the first four points of the vapor solubility isotherm provided by Hwang et al.,[53] up to the activity of 0.287; the best fit of the NELF model to such data leads to a binary interaction parameter $k_{ij} = 0.03$ and to a swelling coefficient $k_{sw} = 7$ MPa^{-1}; the corresponding solubility isotherm is extrapolated up to unit activity (liquid penetrant), as shown in Figure 4a, offering an estimation of the liquid penetrant solubility of 0.060 g/g_{pol}, with a deviation of −28% from the experimental value reported in Ref. 53; such a deviation is essentially due to the underestimation of the volume dilation at higher activities due to the use of the swelling coefficient obtained at low activities.

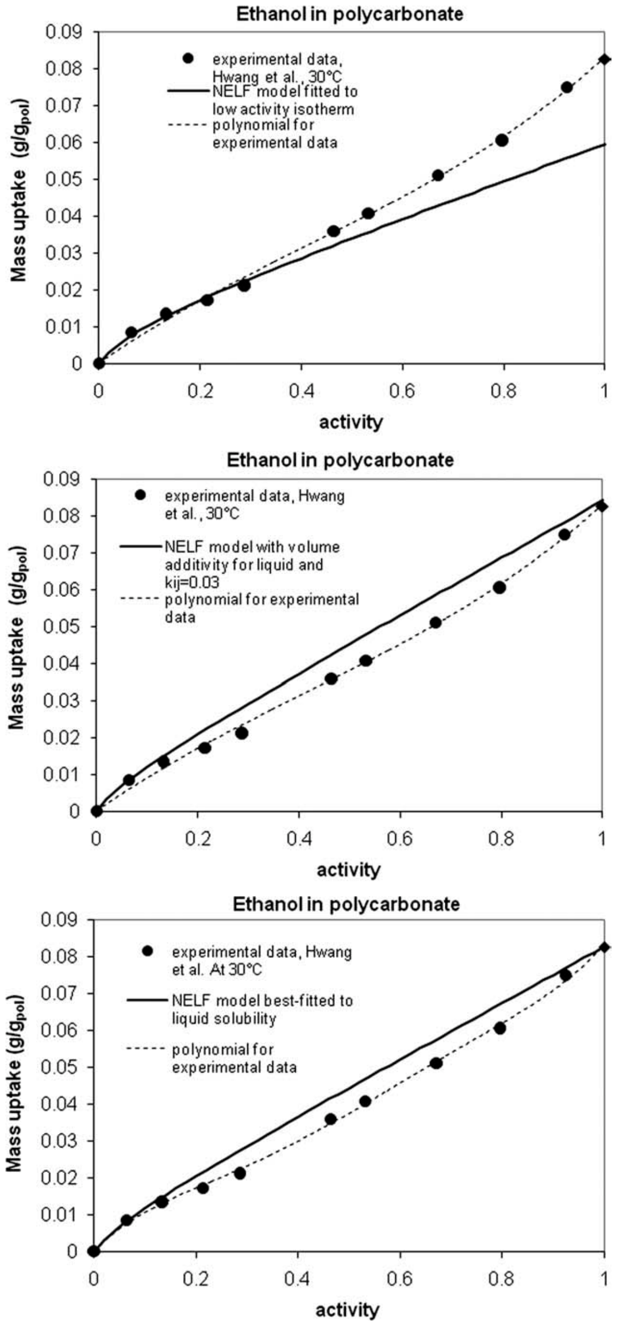

Figure 4. Solubility of ethanol in PC at 30°C.

Experimental data are from Ref. 53, plain circles are vapors, plain diamond is liquid; calculations consider unpenetrated polymer density of 1.200 g/cm^3; (**a**) parameters retrieved from low-activity range: $k_{ij} = 0.03$ and $k_{sw} = 7$ MPa^{-1}; (**b**) binary parameter is retrieved from low-activity range: $k_{ij} = 0.03$ and volume additivity is considered for the polymer in equilibrium with the liquid (average $k_{sw} = 11.0$ MPa^{-1}); (**c**) parameters retrieved from the solubility of the liquid: $k_{ij} = 0.032$ and average $k_{sw} = 10.83$ MPa^{-1}.

(b) Use the binary interaction parameter retrieved from vapor solubility, together with the volume additivity assumption to estimate the swelling due to the liquid.

In this case, the binary interaction parameter is again $k_{ij} = 0.03$ as in case (a), whereas the polymer density ρ_{pol} and the final solute-to-polymer mass ratio Ω_{sol} are found as the solution of the following set of equations:

$$\frac{1}{\rho_{\text{pol}}} = \frac{1}{\rho^0_{\text{pol}}} + \frac{\Omega_{\text{sol}}}{\rho_{\text{sol}}} \tag{12}$$

$$\mu_{\text{sol}}^{\text{NE(s)}}\left(T, P_{V,\text{sat}}, \Omega_{\text{sol}}, \rho_{\text{pol}}, k_{ij}\right) = \mu_{\text{sol}}^{\text{EQ(g)}}\left(T, P_{V,\text{sat}}\right) \tag{13}$$

In Eq. 13, $P_{V,\text{sat}}$ indicates the vapor pressure of the solute at the temperature T, which is 0.010332 MPa for ethanol at 30°C. Use of the NELF model with $k_{ij} = 0.03$ and the parameter values listed in Table 1 leads to the following solution:

$$\Omega_{\text{sol}} = 0.084\text{g}/\text{g}_{\text{pol}}$$
$$\rho_{\text{pol}} = 1.0636\text{g}/\text{cm}^3$$

The solubility of liquid ethanol is thus calculated within 2.0% deviation with respect to the experimental value, which is actually very satisfactory; using Eq. 9, the average swelling coefficient associated to the polymer density calculated is $k_{sw} = 11.0$ MPa^{-1}, which is about 60% larger than the one retrieved in case (a) from the low-activity branch of the solubility isotherm; Figure 4b shows that the parameters found in this case can also be reasonably well applied to describe the solubility isotherm in the entire activity range.

(c) Retrieve the parameter values using the experimental liquid solubility and the volume additivity assumption.

In this case, we use again Eqs. 12 and 13 considering that now Ω_{sol} is known and equal to 0.0827 g/g$_{\text{pol}}$, whereas the binary interaction parameter k_{ij} and the final polymer density ρ_{pol} are unknown. The solution gives now:

$$k_{ij} = 0.032$$
$$\rho_{\text{pol}} = 1.0636\,\text{g}/\text{cm}^3$$

Correspondingly, the average swelling coefficient over the entire activity range is $k_{sw} = 10.83$ MPa^{-1}; the values obtained are very close to those obtained for case (b) above. Use of such values enables us to calculate the entire solubility isotherm through the NELF model, which describes reasonably well the experimental data available at all activities, as it is shown in Figure 4c.

In summary, we can see that for a swelling penetrant like ethanol in PC, the solubility of the liquid can be reasonably calculated by using the binary coefficient retrieved from the low-pressure vapor isotherm and the assumption of volume additivity to estimate the volume dilation due to the liquid penetrant; that procedure is quite satisfactory for the case examined (2% error). The use of the liquid solubility value together with volume additivity gives rise to model parameter estimation (binary interaction parameter and average swelling coefficient), which leads to an overall solubility isotherm very close to the experimental data, thus confirming the robustness of the nonequilibrium approach considered. The use of the model parameters retrieved from the low-pressure solubility isotherm alone leads to less precise but still acceptable predictions of the liquid solubility value. That is due to the fact that the density variation with penetrant pressure is not actually linear in the entire activity range, as it is clearly indicated in Figure 5, which shows the

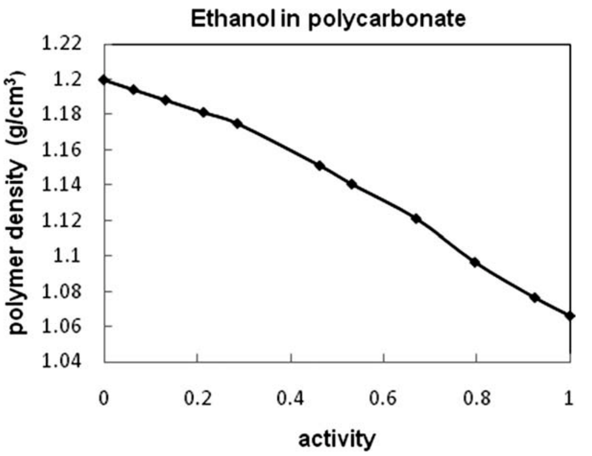

Figure 5. Polymer density of PC vs. ethanol activity at 30°C, calculated from the experimental solubility isotherm and the NELF model, with k_{ij} = 0.03.

PC density variation vs. ethanol activity at 30°C; the values of polymer density with sorption have been calculated with the NELF model equation using as input the experimental solubility data available[53] and the binary parameter $k_{ij} = 0.03$, following the procedure already tested for the same aim.[33]

Water Sorption in PSf. For the solubility of water in bisphenol-A PSf, detailed experimental data were reported at 40°C by Schult and Paul[54] who used the product commercially available as Udel 1700, without indicating explicitly the pure polymer density; however, the latter value can be obtained from the manufacturer data sheet[55] as 1.24 g/cm^3 at ambient temperature, changing with temperature with a volume thermal expansion coefficient of 56×10^{-6} K^{-1}, so that the density at 40 °C can be estimated as 1.236 g/cm^3. Using that value, the experimental data for the vapor solubility isotherm can be well described by the NELF model with no need of a swelling coefficient ($k_{sw} = 0$), consistently with the rather limited solubility. By using a binary parameter $k_{ij} = 0.020$, one can best fit the NELF model to the low-activity solubility isotherm, obtaining a liquid solubility value of 0.0078 g/g$_{\text{pol}}$ with a deviation of −10% with respect to the experimental value of 0.0087 g/g$_{\text{pol}}$[54]; conversely, the actual liquid solubility may be obtained with $k_{ij} = 0.011$, which in turn still describes reasonably well also the solubility isotherm for the vapor phase, as it is apparent from Figure 6.

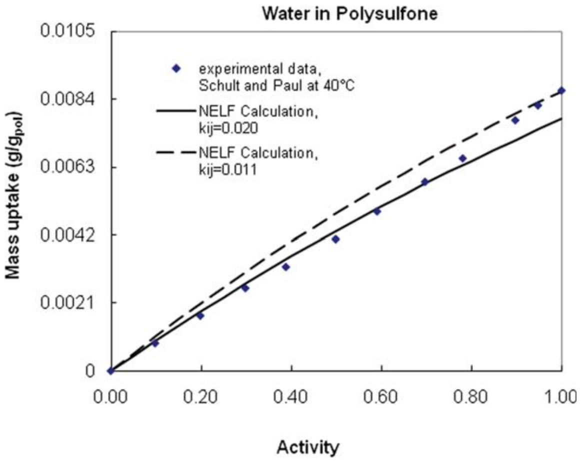

Figure 6. Solubility of water in PSf at 40°C.

Data points from Schult and Paul;[54] continuous line is fitted to the low-activity isotherm, with $k_{ij} = 0.020$; dotted line is fitted to liquid solubility, with $k_{ij} = 0.011$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

The solubility of liquid solutes in glassy polymers can be described by using the NET-GP approach and the NELF model in particular. It is shown that the NELF model, widely applied to predict gas and vapor solubility in glassy polymers, is suitable also for liquid penetrants in a glassy matrix, using model parameters obtained from independent experimental information.

As examples of nonswelling solutes, the cases of water sorption in PC at room-temperature and in the temperature range from 25 to 130°C have been considered and properly described by using a single value of the binary interaction parameter estimated independently, from low-pressure vapor sorption isotherm; similarly, water solubility in PSf at 40°C is successfully described following the same procedure.

As example of swelling solute, the case of ethanol solubility in PC at 30°C has been examined using the binary interaction parameter obtained from low-pressure solubility data; in the absence of direct experimental data on volume dilation, the volume additivity assumption proved to be rather effective to calculate liquid solubility, whereas only a more approximate estimate can be obtained using the swelling coefficient retrieved from the low-pressure vapor sorption isotherm.

In the cases inspected, the inferred values of the binary interaction parameters k_{ij} are typical of those reported for the mixtures of interest.

The attention has been limited to cases in which penetrant solubility does not turn the polymer into a rubbery phase; the latter case will be examined in a forthcoming work.

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