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Permeability and solubility of carbon dioxide in different glassy polymer systems with and without plasticization

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ABSTRACT

The description of permeability and solubility of CO_2 in different complex polymer matrices in the glassy state is analyzed by considering the diffusion coefficient as the product of a kinetic factor, mobility, and a thermodynamic factor associated to the concentration dependence of the chemical potential of the diffusing species, according to what recently presented for different pure polymers [Minelli and Sarti, J. Membr. Sci. 435 (2013) 176–185]. The thermodynamic factor is calculated in a predictive way by using the nonequilibrium lattice fluid model (NELF) or is obtained directly from experimental solubility isotherms, when pure component parameters for the NELF model are not available. The mobility factor is considered to depend exponentially from penetrant concentration, following the usual trend commonly found experimentally, and its expression contains only two adjustable parameters. The permeability model is used to describe steady state permeation of CO_2 in a series of complex glassy phases, formed by polysulfone (PSf) and polyphenylene oxide (PPO) with different plasticizers, glassy polymer blends, glassy random copolymers and crosslinked polyimides. The analysis shows that in all the cases examined, the model used is able to describe the experimental trends in a simple and effective way, accounting for all the different behaviors observed, in which permeability is either decreasing or increasing with upstream pressure and even when permeability is non-monotonous and presents a minimum value due to the so-called plasticization effect. A general correlation is also found for both model parameters: the infinite dilution mobility correlates well with the reciprocal fractional free volume, according to the FFV theory, while the plasticization factor is associated to the swelling coefficient of the polymer matrix.

1. Introduction

Permeability of gases and vapors in glassy polymers is a fundamental property for gas separations with membranes, since in most the applications the peculiar features of glassy polymers are exploited [1–3]. Steady state permeability of species i, P_i, is defined as

$$P_i = \frac{\dot{N}_i l}{p_i^u - p_i^d} \qquad (1)$$

where $\dot{N}_i$ is the steady state molar flux of species i, l is the membrane thickness and $p_i^u - p_i^d$ is the partial pressure difference between upstream and downstream phases. Permeabilities of various gases in different membranes are widely studied to inspect both membrane productivity as well as the separation performance represented by the separation factor α_{ij} between gases i and j. Indeed, whenever $p^d \ll p^u$, as it is usually the case in gas separations, one has

$$\alpha_{i,j} \equiv \frac{y_i^d / y_j^d}{y_i^u / y_j^u} = \frac{P_i}{P_j} \qquad (2)$$

Permeabilities must be measured under the real mixed gas conditions of composition, pressure and temperature, which require rather demanding and time-consuming experimentations. Often the separation factor is reported for simplicity through its ideal value, $\alpha_{i,j}^{id}$, as evaluated from the permeabilities of the pure penetrants, as

$$\alpha_{i,j}^{id} = \frac{P_{i,pure}}{P_{j,pure}} \qquad (3)$$

A proper model description is thus required to complement adequately the experimental activity and to be able to account, possibly in a simple way, for the different behaviors observed. In fact, it is known that for glassy polymers the permeability

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dependence on upstream pressure can follow different general trends:

i) permeability can be constant, as it is common for light gases, and for penetrants scarcely soluble in the polymer;
ii) permeability can decrease with p^u, as it is frequently the case for many gases;
iii) permeability can increase with p^u, as it is often the case of highly soluble penetrants, which induce a significant swelling of the polymer matrix;
iv) permeability can also initially decrease, then increase after going through a minimum value, according to what is commonly attributed to a plasticization effect.

Recently, a simple and effective model has been proposed to calculate the permeability of gases in glassy polymers, able to describe all the different behaviors observed, simply based on only two adjustable parameters [4]. The model calculates separately the average diffusivity $D_{i,ave}$, valid over the molar concentration range $c_i \in (0, c_i^u)$, and the solubility coefficient S_i defined as

$$S_i = \frac{c_i}{p_i} \tag{4}$$

From such values, one obtains readily the steady state permeability when the downstream pressure is negligibly small with respect to the upstream value, since the following relationship holds true:

$$\lim_{p_i^d \to 0} D_{i,ave} = \lim_{p_i^d \to 0} \frac{\dot{N}_i l}{c_i^u} = \frac{P_i p_i^u}{c_i^u} = \frac{P_i}{S_i} \tag{5}$$

The model presented in Ref. [4] is based on the following main steps or assumptions:

a. the solubility isotherm of the penetrant in the glassy polymer matrix is described through the nonequilibrium thermodynamic theory for glassy polymers (NET-GP), after selecting the appropriate equation of state; in the absence of strong polar interactions or hydrogen bonding, the nonequilibrium lattice fluid model (NELF) is considered, otherwise other models are required, as for instance nonequilibrium statistical associating fluid theory (NE-SAFT);
b. diffusivity is given as the product of a kinetic mobility coefficient and a thermodynamic factor. The latter is calculated directly from the solubility isotherm, either through the NELF model or through the experimental data. For the mobility coefficient, an exponential dependence on penetrant concentration is considered.

Overall, the model contains only two adjustable parameters, namely the pre-exponential factor of mobility and the plasticization factor for its concentration dependence, while no adjustable parameters are associated to the solubility isotherm and the thermodynamic factor.

The model is rather simple, straightforward to use, and already proved very satisfactory to describe the dependence on pressure of CO_2 permeability in a series of pure polymers showing either a decreasing dependence on pressure, or an increasing dependence, or also an initial decrease followed by a subsequent increase due to the so-called plasticization [4]. In addition, the same mobility coefficient was found to apply equally well to steady state permeability with plasticization as well as to the transient diffusion observed in mass uptake experiments.

In the present work, the same permeability model already presented in Ref. [4] is applied to describe the permeability of CO_2 in a series of more complex glassy polymer systems. The cases of polysulfone (PSf) and poly(phenylene oxide) (PPO) added with various amounts of different plasticizers are considered, as well as different BCPC/PMMA polymer blends, different PMMA/PS random copolymers, and polyimides with different degrees of crosslinking. The model contains only two adjustable parameters, based on which it is able to describe well the observed features of CO_2 permeability in all the systems analyzed.

For the sake of convenience, the theoretical background is briefly summarized in the next section.

2. Theoretical background

2.1. Solubility

It has been shown that the thermodynamic properties of glassy polymers are well described by the nonequilibrium thermodynamics for glassy polymers (NET-GP) [5,6], which indicates how the equilibrium expression of the Helmholtz free energy can be extended to represent the nonequilibrium state of the glass. Several equations of state are appropriate for polymer mixtures, and can be used to that aim. Explicit examples have been successfully studied in detail, considering several equations of state (EoS) as the lattice fluid (LF) EoS developed by Sanchez–Lacombe [7,8], the statistical associating fluid theory (SAFT) [9–11], the perturbed hard sphere chain theory (PHSC) [12], and lattice fluid model with hydrogen bonding (NRHB) [13]. The corresponding nonequilibrium models are indicated as NELF [5,14–16], NE-SAFT [17], NE-PHSC [18] and NE-NRBH [19], respectively. Among the above models, NELF has been widely used and its pure component parameters are already available for a large series of polymers and penetrants. Hence, it is rather natural to consider the NELF model for the calculation of the solubility isotherms for the systems examined in this work.

The main features of the NELF model are hereafter briefly summarized, whereas the main quantities and equations used in the NELF model are systematically reported in Table 1. Polymers and penetrants are characterized by the pure component parameters (p_i^*, ρ_i^*, T_i^*) of the equilibrium Sanchez and Lacombe theory, and the mixture properties (p^*, ρ^*, T^*) are obtained through the mixing rules introduced by the same model [7,8]. The pure component characteristic parameters are generally obtained by best fitting the LF EoS to pressure–volume–temperature (pVT) data above T_g for the polymers, and to either pVT or vapor–liquid equilibrium data for the penetrants. The values of such characteristic parameters may be found in specific data collections [20,21].

The departure from equilibrium of the glassy phases is accounted for by the use of an additional state variable, represented by the actual value of the nonequilibrium polymer density, ρ_p^{NE}, which describes the thermodynamic state of the system together with the usual set of state variables (temperature, pressure and composition) [5]. Therefore, the phase equilibrium conditions are obtained, at all penetrant mass fractions ω_i, when the chemical potential of each penetrant i has the same value both in the external gas phase, with mole fraction y_i, and in the mixture with the glassy polymer:

$$\mu_i^{NE(s)}(T, p, \omega_i, \rho_p^{NE}) = \mu_i^{Eq(g)}(T, p, y_i) \tag{6}$$

The density of the glassy polymer, ρ_p^{NE}, depends on the experimental conditions and on the history of the samples. For non-swelling penetrants, the density of the polymer phase at every pressure can be considered equal to the value of the pure unpenetrated polymer. In the case of swelling agents, as is usually the case of CO_2, the density of the polymer at every sorption pressure value is required; that can be retrieved from parallel dilation experiments. In their absence, the dependence of polymer density on penetrant pressure must be accounted for. In the usual