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Thermodynamic basis for vapor solubility in ethyl cellulose

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ABSTRACT

The solubility of several gases and vapors in glassy ethyl cellulose (EC) over wide ranges of temperature and pressure is described by means of a thermodynamic model, which specifically accounts for the nonequilibrium volumetric properties of EC. The behaviors of polymer/penetrant mixtures are represented by the well-established nonequilibrium lattice fluid model (NELF) in its latest development, suitable to be used in a pure predictive fashion for the representation of the volume swelling of the polymer matrix, as induced by penetrant sorption. The analysis reveals the ability of the model to describe all the experimental trends, and a sole binary parameter for each polymer/penetrant couple is considered. The NELF model allows the satisfactory prediction of the thermodynamic properties of all polymer/solute systems examined, in the entire range considered for temperature and vapor fugacity.

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1. Introduction

The solubility and diffusivity of low molecular weight species in polymeric systems are material properties of crucial importance for the performance of a variety of polymer based industrial processes. The transport of gases and vapors, indeed, is relevant in the field of gas separation membranes, painting and oil piping, as well as in packaging, fuel cells and sensor applications [1–6]. The study of the mechanisms of penetrant solubility and diffusion is thus of fundamental importance, and numerous experimental and modeling efforts are indeed devoted to this subject [7].

Several models are currently employed for the description of the solubility of low molecular weight species in rubbery polymers, based on activity coefficients [8,9] or proper equations of states (EoS) [10–13]. Unfortunately, these approaches are not directly applicable to nonequilibrium systems, such as glassy polymers, and only a limited number of studies are devoted to this theoretical analysis [14–16]. Hence, the use of empirical tools is often encountered, as the dual mode sorption (DMS) model [17,18], which counts on adjustable parameters depending on the penetrant/polymer couple, as well as on temperature, pressure and history of the glassy polymer [19]. These limitations have been overcome by the development of the nonequilibrium thermodynamic theory for glassy polymers (NET-GP) by Doghieri and Sarti [20]. The model provides the description of the penetrant

solubility in polymeric glasses within a thermodynamic framework, in which the out-of-the-equilibrium density of the system is treated as an additional state variable.

On the other hand, the most widely used correlation to describe the permeability behavior of gases and vapors in polymeric glasses is given by the DMS model [21]. In this framework, the two populations of penetrant molecules, dissolved and adsorbed onto free volume hole surfaces, are described by two separate diffusion coefficients, and are combined following the so-called total or partial immobilization schemes [22,23]. However, the main limitations of DMS are due to the fact that it cannot be used in a pure predictive manner, and that, in addition, it can hardly describe complex behaviors. Indeed, the description of the plasticization region, as well as the increasing trend in permeability with pressure, is out of reach for the DMS model in its simplest formulation with two transport parameters only. Subsequent modifications of the model have been proposed to account for the strong dependence of diffusion coefficients on penetrant concentration, with the consequent introduction of further adjustable parameters [24,25].

Recently, Minelli and Sarti have proposed a simple and effective model to evaluate the permeability of gases in glassy polymers, considering the diffusion coefficient as the product of a kinetic factor, the mobility, and a thermodynamic factor accounting for dependence of the chemical potential of the diffusing species on its concentration in the membrane: this approach utilizes only two adjustable parameters used to describe the concentration dependence of the mobility coefficient [26]. The model has been successfully employed to describe the permeability behaviors of

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CO₂ in many different glassy polymers [26], polymer blends and copolymers [27], and it was also able to represent the temperature dependence of the transport parameters of CO₂ in semicrystalline PET, below and above polymer T_g [28].

Among glassy polymers, ethyl cellulose offers interesting properties for separation purposes, as good filmability, medium gas separation and pervaporation performances, good flexibility and stability, and also low cost [29–32]. Indeed, asymmetric hollow fibers of ethyl cellulose (as well as of cellulose acetate and derivatives) are being utilized for the separation of air [33]. Although a relevant number of papers has been devoted to the characterization of cellulose acetate (see e.g. [34–37]), only a limited amount of experimental works have been reported in the literature on the solubility and transport of gases and vapors in ethyl cellulose [38–43].

In the present work, the experimental characterization of gases and vapors solubility in glassy ethyl cellulose (ethoxy content 49%) at different temperatures carried out by Barrer et al. [44,45] has been investigated thoroughly.

Although not focused on a polymer material (ethyl cellulose) with remarkable separative performances for membrane application, the experimental sorption data after Barrer and coworkers [44,45] are of great interest, spanning over a wide range of temperatures and solute activities, and several penetrants were also investigated. Hence, these experimental results are definitely suitable for the complete modeling analysis given by the NELF approach, which, if coupled with the rheological tool recently introduced for the a priori evaluation of the solute induced polymer swelling, provides the description of solubility isotherms of the different penetrants in a predictive fashion.

In a subsequent work, the permeability data, also provided by Barrer et al. [44,45], will be considered, and the transport model developed by Minelli and Sarti [26] will be applied to represent the dependence of permeability on upstream penetrant activity by means of two parameters only.

2. Theoretical background

In the present work, the description of penetrant solubility is carried out by means of a thermodynamic based model, the NELF, already presented in details in a previous work [20], which contains the complete illustration of the model; however, the main features are here briefly recalled for the sake of clarity.

2.1. NELF model

The nonequilibrium thermodynamics for glassy polymers (NET-GP) [20,46,47] is a well established modeling approach for the thermodynamic description of glassy polymeric phases that, when coupled with the lattice fluid equation of state proposed by Sanchez and Lacombe [10,48,49], results in the nonequilibrium lattice fluid model (NELF). The model provides the extension of expressions for the Helmholtz free energy density to represent the nonequilibrium state of the glass, by accounting for the polymer density as an additional state variable. The Sanchez–Lacombe EoS gives explicit relationships for Helmholtz free energy density and chemical potential of the different species, which are then used to describe nonequilibrium properties.

The NET-GP approach has been successfully applied to describe the solubility of gases and vapors in a variety of different polymer systems [50–57], as well as blends and copolymers [58] or composites [59]. Furthermore, the model proved its ability in the determination of solubility of liquids and gaseous mixtures in glassy polymers [60,61].

The main equations of the NELF model, for the evaluation of solute fugacity in a glassy polymer/penetrant mixture, are schematically reported in Table 1.

For the description of thermodynamic properties of glassy polymer/solute systems, the NELF model relies on the analysis of specific volumetric behavior of the pure polymeric species below

Table 1
Definition of the different properties as well as main correlations for the Sanchez–Lacombe/NELF framework.

Symbol	Name	Notes
<i>State variables</i>		
ω_i	Mass fraction of solute i	$(1 \leq i \leq N_c - 1)$
T	Temperature	
p	Pressure	
ρ_{pol}	Polymer mass density	
<i>Model parameters</i>		
ρ_i^*	Characteristic density of pure component i	$(1 \leq i \leq N_c)$
p_i^*	Characteristic pressure of pure component i	$(1 \leq i \leq N_c)$
T_i^*	Characteristic temperature of pure component i	$(1 \leq i \leq N_c)$
M_i	Molar mass component i	$(1 \leq i \leq N_c)$
k_{ij}	Binary interaction parameter for (i,j) components pair	$k_{ij} = k_{ji}; k_{ii} = 0 \ (1 \leq i \leq N_c; 1 \leq j \leq N_c)$
<i>Model variables</i>		
v_i^*	Lattice site molar volume for pure component i	Eq. I
ρ^*	Characteristic density of the mixture	Eq. II
$\tilde{\rho}$	Reduced mixture density	Eq. III
ϕ_i	Volume fraction of component i in the mixture	Eq. IV
v^*	Average close-packed mer molar volume in the mixture	Eq. V
Δp_{ij}^*	Interaction characteristic pressure for (i,j) pair in the mixture	Eq. VI
$\mu_i^{NE,res}$	Residual chemical potential of solute i in the glassy polymeric mixture	Eq. VII
		Calculation
		$v_i^* = \frac{RT_i^*}{p_i^*}$
		$\frac{1}{\rho^*} = \sum_{i=1}^{N_c} \frac{\omega_i}{\rho_i^*}$
		$\tilde{\rho} = \left(1 - \sum_{i=1}^{N_c-1} \omega_i\right) \frac{\rho_{pol}}{\rho^*}$
		$\phi_i = \omega_i \frac{\rho_i^*}{\rho^*}$
		$\frac{1}{v^*} = \sum_i \frac{\phi_i}{v_i^*}$
		$\Delta p_{ij}^* = p_i^* + p_j^* - 2(1 - k_{ij}) \sqrt{p_i^* p_j^*}$
		$\frac{\mu_i^{NE,res}}{RT} = \frac{M_i}{\rho_i^* v^*} \left\{ 1 - \frac{v_i^*}{v^*} - \ln(1 - \tilde{\rho}) \left[1 - \frac{1 - (v_i^*/v^*)}{\tilde{\rho}} \right] - \rho^* v_i^* \left[p_i^* + \sum_{j=1}^{N_c-1} \phi_j (p_j^* - \Delta p_{ij}^*) \right] \right\}$ $(1 \leq i \leq N_c - 1)$

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