

# Modeling Solubility Isotherms and Sorption Kinetics of Supercritical Carbon Dioxide in Initially Glassy Polymers Using Non-Equilibrium Thermodynamics

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**ABSTRACT:** Solubility and swelling isotherms for CO<sub>2</sub> in PMMA have been measured at two different temperatures and over a wide pressure range, using ellipsometry and QCM techniques. Results have been successfully interpreted in terms of NET-GP approach modified for high pressures. Mass uptake kinetics for differential sorption experiments in the same systems have been also measured using high-pressure QCM in order to test the transport model for sorption and dilation kinetics developed coupling non-equilibrium thermodynamic theory with a simple rheological model for volume relaxation. Indeed, NET-GP model makes use of the volume of polymer network as out-of-equilibrium order parameter which has to be evaluated using a meaningful equation for the evolution of polymer network volume representing the relaxation phenomenon of the glassy mixture toward the equilibrium state.

Reliability of the overall model is here discussed by comparing model results with sorption kinetics measured in differential sorption experiments in glassy and rubbery films.

## INTRODUCTION

Carbon dioxide in its liquid and supercritical state is a very attractive replacement for traditional aqueous and organic solvents in a number of industrial applications, primarily due to its tuneable solvent properties, low cost, low toxicity, non-flammability, and because it is an excellent plasticizing agent for many polymers. In most of its potential applications a key element for success in controlling final product quality relies on the ability to correctly predict sorption and consequent dilation of the polymeric matrix at different temperatures and pressures. Indeed, a reliable thermodynamic model, capable of describing swelling of glassy polymers starting from dry polymeric matrices up to fully plasticized materials, is an essential pre-requisite for any transport model aimed at predicting concentration profiles as well as sorption, desorption and even dissolution kinetics of polymeric films. A model for sorption kinetics is presented in this work, which can account for initial glassy condition of dry polymer and is able to represent polymer relaxation induced by sorption of swelling agent.

The model here discussed relies on a thermodynamic approach to the description of properties of glassy polymeric mixtures which proved to be reliable in representing features of gas and vapour solubility isotherms in glassy polymers. On the other hand, direct application of original thermodynamic model was limited to those cases in which polymer

density in pseudo-equilibrium condition was known from independent information. The thermodynamic model is here combined with a simple model for bulk rheology of polymeric species which ultimately allows describing kinetics of polymer swelling induced by solute diffusion and corresponding mass uptake.

## I – THERMODYNAMIC AND TRANSPORT MODELS

Formulation of a mass transport model for the isothermal diffusion process of a mobile solute species into a polymeric film can be obtained, in terms of polymer and solute mass densities ( $\rho_s$  and  $\rho_p$  respectively), through the following set of species mass balances

$$\begin{aligned}\frac{\partial \rho_s}{\partial t} &= \nabla \cdot (\rho_s \underline{v}_p + \underline{j}_s) \\ \frac{\partial \rho_p}{\partial t} &= \nabla \cdot (\rho_p \underline{v}_p)\end{aligned}\quad (1)$$

Where  $\underline{v}_p$  and  $\underline{j}_s$  are polymer velocity and solute diffusive flux. The latter, in turn, can be expressed with reference to solute chemical potential field in polymer-solute mixture ( $\mu_s$ ) using a generalized fickian constitutive equation where species densities dependent diffusion coefficient  $D^*$  appear:

$$\underline{j}_s = -\rho_s D^* \underline{\nabla}(\mu_s/RT) \quad (2)$$

In order to be able to represent both the case of rubbery and glassy state, a constitutive equation is here considered for the volume dilation process of polymer matrix induced by solute sorption. A simple two Voigt elements model is here assumed for the polymer network which can be stated as detailed hereafter, where labels A and B are used for the two Voigt elements:

$$\begin{aligned}\frac{1}{\rho_p} &= \chi \frac{1}{\rho_p^A} + (1-\chi) \frac{1}{\rho_p^B} \\ \frac{1}{\rho_p^A} \frac{\partial \rho_p^A}{\partial t} &= \frac{p - p^{eq}(T, \rho_p^A, \mu_s)}{\eta_A} \\ \frac{1}{\rho_p^B} \frac{\partial \rho_p^B}{\partial t} &= \frac{p - p^{eq}(T, \rho_p^B, \mu_s)}{\eta_B}\end{aligned}\quad (3)$$

In the above equation  $\chi$  represents the weight of Voigt element A in the set and  $\eta_A$  and  $\eta_B$  are the two solute concentration dependent bulk viscosities, characteristic of element A and B respectively. In the same equations difference between actual pressure  $p$  in the polymer mixture and equilibrium pressure  $p^{eq}$  expected for the thermodynamic state of polymer element is considered as the driving force for the swelling process. To account for a rough but meaningful representation of rubbery and glassy state characteristic rheological behaviour, the following assumptions are stated in the model here discussed:

$$\eta_A = \begin{cases} \eta_A^G(\omega_s) & \omega_s \leq \omega_{sg} \\ \rightarrow 0 & \omega_s > \omega_{sg} \end{cases} \quad (4)$$

$$\eta_B = \begin{cases} \rightarrow \infty & \omega_s \leq \omega_{sg} \\ \rightarrow 0 & \omega_s > \omega_{sg} \end{cases}$$

where  $\omega_{sg}$  indicates the threshold values of solute concentration for glass-rubber transition at system temperature.

Proper initial conditions for polymer and solute densities and appropriate boundary conditions for solute chemical potential must be added to the above balance and constitutive equations to obtain a model representation of a given sorption process. Specific expression for thermodynamic and transport properties must be finally considered to complete the model set of equations. In the model calculations discussed below, the free energy expression for solute-polymer mixture is considered as derived within the approach of Non Equilibrium Lattice Fluid [1, 2]. The latter allows for the calculation of expressions for both solute chemical potential  $\mu_s$  and equilibrium pressure  $p^{eq}$  appearing in Eqs.(2) and (3). The Chow's theory [3] is used to derive an expression for the solute concentration at glass transition and free volume theory [4] is used to express the dependence of diffusion coefficient on polymer and solute mass densities. The bulk viscosity for the element A of Voigt model is finally assumed to change with solute concentration according to the relation proposed by Royer et al.[5].

## II –EXPERIMENTAL RESULTS AND COMPARISON WITH MODEL CALCULATIONS

Sequences of isothermal differential CO<sub>2</sub> sorption experiments in supported PMMA films were performed on a high pressure QCM apparatus, where mass uptake over time was measured. Experiments were then repeated in a high pressure ellipsometer, where volume dilation of the sample was evaluated. Both types of experiments were extended up to 120 bar, well inside the supercritical region for carbon dioxide. Supported PMMA films for QCM and ellipsometric experiments were prepared according to different protocols, whose details are given elsewhere [6]. Protocols were defined in order to assure similar thickness, in the range 1.2 – 1.5  $\mu\text{m}$  and similar mass density at room temperature, close to 1.187 kg/L, was obtained for films used in the two kind of experiments. Results for CO<sub>2</sub> solubility measured in a sorption-desorption cycle at 50 °C are reported in figure 1 and corresponding values for volume dilation measured are indicated in figure 2 (plots in solid and open symbols, respectively). Solubility and dilation measurements show similar results in sorption and desorption runs for solute content above the glass transition value  $\omega_{sg}$ , while clearly higher solubility and volume swelling were measured for desorption run, with respect to sorption, below  $\omega_{sg}$ . Sorption kinetics also exhibited quite different features in steps below the glass transition solute concentration with respect to those performed above the same limit. Indeed, while the latter case was characterized by well known fickian kinetics, sorption steps below  $\omega_{sg}$  exhibited the so called “two stage” sorption behaviour. An example of mass uptake measured for low pressure differential sorption step is shown in figure 3 (plot in symbols). In those cases, a first stage in sorption process is observed in which solute component diffuses into the polymeric sample which is substantially non deformed with respect to initial conditions. An apparent equilibrium value for the mass uptake is reached at the end of the first stage and a second sorption stage follows with a different kinetics order and rate which

ultimately brings to a higher value of pseudo-equilibrium solute concentration in the sample. Second stage in sorption process can be easily associated, in generic terms, to structural relaxations in polymer network. A representation of solubility, volume dilation and sorption kinetics can then be obtained through the use of the above model. By means of NELF model, correlation of solubility and dilation data can be obtained after pure component lattice fluid parameter are retrieved from pure component PVT data for both solute and polymeric species (see parameters values in table 1). Results of the fitting procedure on both solubility and volume swelling in the entire pressure range are binary parameters for energy interaction and mixing volume. Binary parameters for PMMA/CO<sub>2</sub>, retrieved from fitting procedure on data shown in figures 1 and 2 are reported in table 1. Correlation results for solubility and volume swelling obtained from the model are shown in figures 1 and 2 (plots in lines). In model calculations, threshold value of solute concentration for glass transition was calculated equal to 9.6% of CO<sub>2</sub> by weight, after PMMA parameters for Chow's model indicated in table 1.

Analysis of mass uptake kinetics in sorption process below the glass transition can be performed, by means of the model described in the previous section, once values for free volume parameters, weight factor  $\chi$ , and characteristic viscosity  $\eta_A^0$  in Royer's expressions for  $\eta_A^G$  are estimated. Pertinent solute and polymer segment jump volumes, as well as overlapping factor  $\gamma$  in free volume model, are indeed available from technical literature and their values are reported in table 1. Fitting procedure for mass uptake kinetics can thus be attempted using  $\chi$ ,  $\eta_A^0$  and pre-exponential factor  $D_0$  in free volume model as adjustable parameters. Example of results from this kind of fitting procedure is given in figure 3 (plots in lines). It must be first observed that the model interprets the apparent equilibrium mass uptake reached after the first sorption stage as the pseudo equilibrium solute content in the sample corresponding to the case of polymer mass density constrained to its initial value. The latter can be calculated after the expression of mixture free energy, once the value of initial density of the polymer sample is known, and the result is clearly independent on all adjustable parameters considered in this discussion. It is thus a remarkable result that a quite good estimate for the apparent equilibrium solute content at the completion of the first diffusive step in sorption process is obtained from model prediction. On the other hand, it clearly appears that the model can only give account of the characteristic time of the first diffusive step of the sorption process, by means of a suitable value for  $D_0$  (indicated in table 1). In fact, order kinetics experimentally observed for the first stage is significantly higher than that predicted by fickian constitutive equation used in the model here considered. It is then to observe that setting weight factor  $\chi$  to 0.68 a correct representation of final solute content in the sample is obtained. Finally, tuning the characteristic viscosity value allow to satisfactorily describe the kinetics of relaxation stage in sorption process, as shown by lines pertinent to different parameter values in figure 3.

## CONCLUSIONS

A model for the relaxation in polymer induced by sorption of swelling agents is here presented and discussed. Model features and capability to represent essential features of pseudo equilibrium solubility and volume dilation, as well as sorption kinetics at solute concentration below the glass transition was discussed in this work by means of comparison of model calculations with experimental results for CO<sub>2</sub> sorption in PMMA films. Significance of specific model parameters, and thus applicability of the model in predictive procedures, can only be discussed through the comparison of results of analysis of several different systems.

Figure 1 Solubility isotherm for sorption-desorption cycle of CO<sub>2</sub> in PMMA at 50°C: comparison between experimental data and results from NELF theory

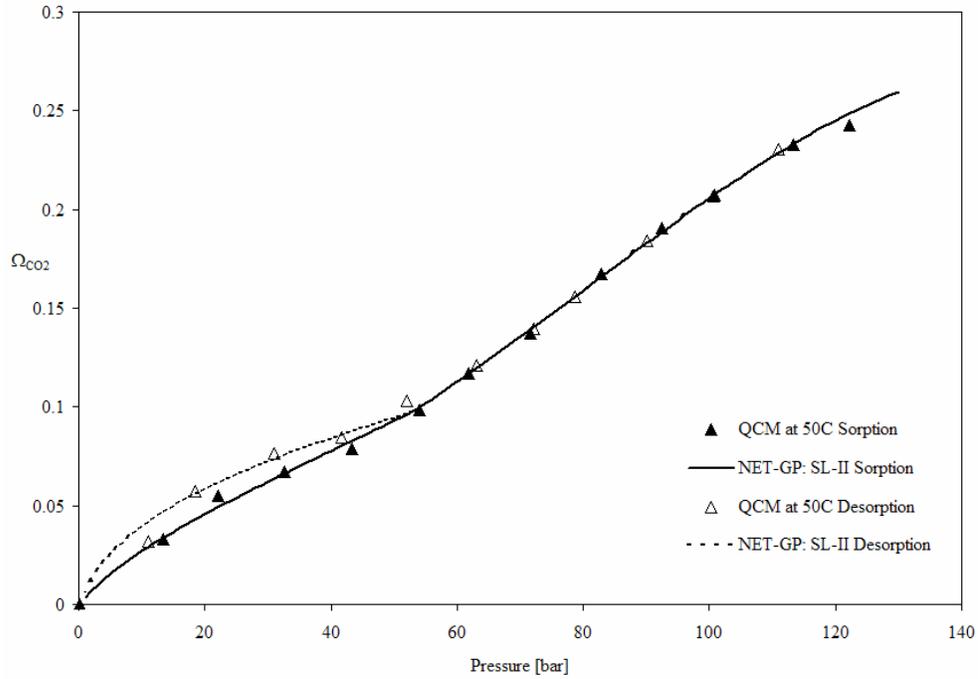


Figure 2 Volume swelling isotherms for sorption - desorption cycle of CO<sub>2</sub> in PMMA at 50°C: prediction using the NELF theory

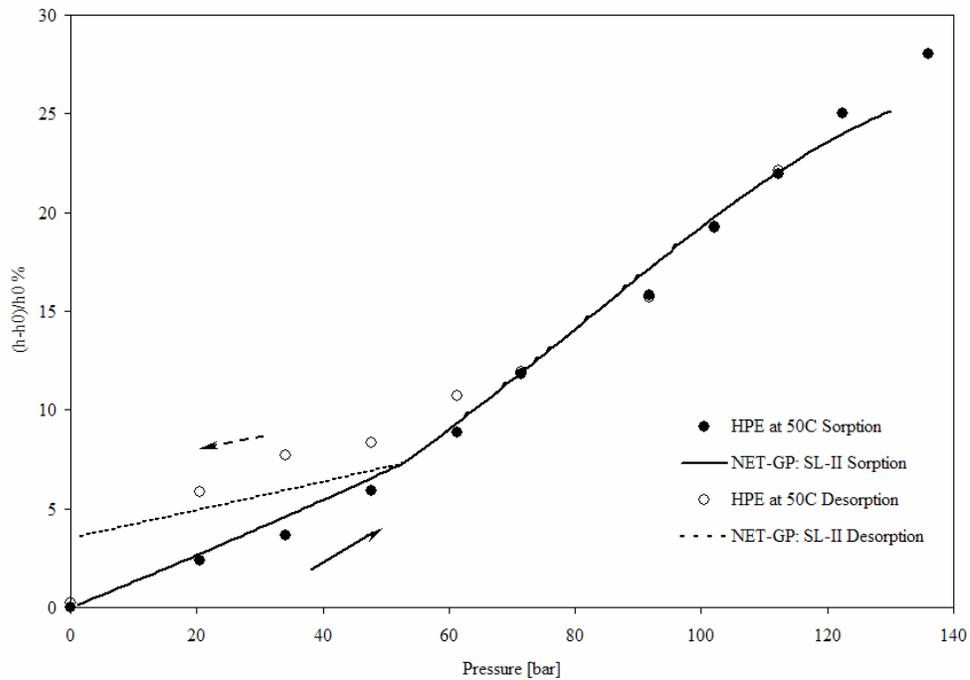
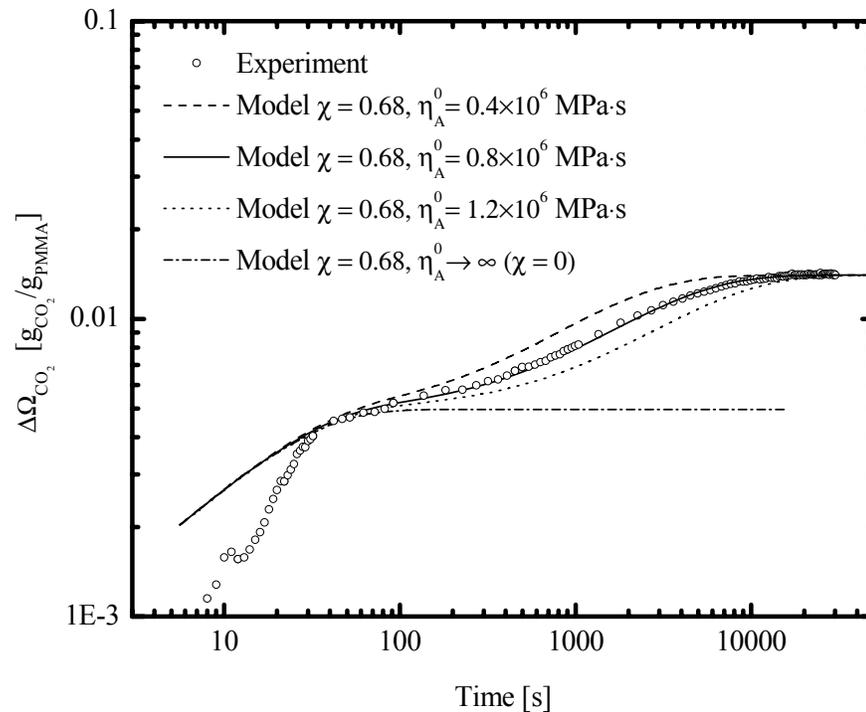


Table 1 Model parameters

Lattice Fluid parameters							
	T* (K)	P* (MPa)	$\rho^*$ (g/cm <sup>3</sup> )	M (g/mol)			
PMMA	696	503	1.269	100000	PMMA/CO <sub>2</sub>	k = 0.12	$\eta = -0.015$
CO <sub>2</sub>	283	659	1.62	44			
Additional parameters for Chow's model							
$\Delta C_p = 32.72$ J/mol K				$T_g = 105$ °C			
Free volume model parameters							
$D_0 = 6.7 \cdot 10^{-11}$ cm <sup>2</sup> /s		$\gamma = 0.53$		$\zeta V_p^* = 0.121$ cm <sup>3</sup> /g		$V_s^* = 0.77$ cm <sup>3</sup> /g	

Figure 3 Solute mass uptake for CO<sub>2</sub> in PMMA film for sorption step from 370 to 450 *psi* at 50 °C, experimental data and model results



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