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Predictive calculation of hydrogen and helium solubility in glassy and rubbery polymers

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ABSTRACT

Hydrogen sorption isotherms in selected glassy and rubbery polymers, available over a wide range of temperatures (−20 to 70 °C) and pressures (0–60 atm) have been modeled and correlated using equilibrium and non-equilibrium thermodynamic models based on the lattice fluid theory. A good representation of the experimental data can be obtained for the systems considered over the whole range of pressures and temperatures inspected by using just one fitting parameter, under the fundamental assumption that hydrogen behaves as a non-swelling penetrant. The theoretical estimates of infinite dilution solubility coefficients are in excellent agreement with the experimental data. Remarkably, the model analysis allows a reliable estimate of the isosteric heat of sorption and its dependence on the hydrogen concentration over the whole range of pressures considered. A similar theoretical analysis has been performed by considering the helium sorption data available at 35 °C for a series of polymers considered for membrane-based gas separations. Finally, He/H_2 solubility–selectivity at 35 °C has been correctly predicted: as expected, the glassy Teflon® AF-series perfluorinated copolymers display a higher He/H_2 solubility selectivity compared to the hydrocarbon-based polymers.

1. Introduction

Hydrogen and helium sorption in polymers has attracted interest because of the importance of these gases in membrane-based separation processes [1,2]. In many industrial processes, hydrogen needs to be recovered from purge gas streams or have its composition adjusted for syngas feeds [3]. Similarly, helium can be recovered from natural gas [4,5,6]. The issue of hydrogen sorption in polymers is of interest for the optimization of energetic devices, such as fuel cells and batteries [7]. Despite the relevance of this subject, a systematic and comprehensive analysis of hydrogen and helium sorption and transport in membrane materials is still lacking in the literature. Recently, a consistent set of experimental data was reported by Smith et al. [1,8]

The analysis of separation processes based on dense membranes is grounded in the general assumption that the permeability of gases and liquids can be expressed as the product of a solubility coefficient and a diffusion coefficient, as described by the *solution-diffusion model* [9]. Consequently, the separation factor or membrane selectivity displays a solubility contribution and a diffusivity contribution. Perfluorinated polymers, such as Nafion N117, first reported by Chiou et al. in 1988 [10], display permeability and selectivity levels that surpass the He/H_2 upper bound defined by Robeson in 1991 [11]. More recently, other authors [12–15] reported that perfluoropolymers, such as amorphous Teflon® AF2400 and AF1600 and Hyflon AD60 also readily exceed this limit. Remarkably, at fixed helium permeability, the He/H_2 selectivity displayed by perfluorinated polymers is roughly 2.5 times higher compared to hydrocarbon-based polymers. The good performance of fluorinated materials in He/H_2 separation arises from the relatively high values of solubility selectivity compared to hydrocarbon-based polymers [8]. Therefore, predicting the solubility separation factor would represent a great advantage, thus allowing an a priori evaluation of polymer membrane performance.

In this study we employ the Non-equilibrium Lattice Fluid (NELF) Model [16] and the Sanchez–Lacombe equation of state [17,18] to predict hydrogen and helium solubility in a series of glassy and rubbery polymers often considered for membrane-based gas separations. Both the NELF and Sanchez–Lacombe models have been developed within the framework of Lattice Fluid Theory [17,18] and are grounded on rigorous thermodynamic principles.

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Their ability to predict pure and mixed fluids solubility in neat rubbery or glassy polymers, polymer blends and mixed-matrix membranes has been evaluated in a number of papers [16,19–23].

Recently, Smith et al. [1,8] reported a consistent set of hydrogen and helium sorption data in different glassy and rubbery polymers suitable for membrane-based gas separations, namely amorphous Teflon® AF1600 and AF2400, Matrimid® polyimide, polysulfone (PSF) and polydimethylsiloxane (PDMS). In this contribution, these experimental data have been analyzed in the framework of the Lattice Fluid Theory. In particular, the hydrogen and helium solubility in rubbery PDMS has been calculated with the Sanchez–Lacombe equation of state, while the Non Equilibrium Lattice Fluid Model (NELF) has been used for the other polymers, which are glassy at the experimental conditions. The modeling of hydrogen and helium sorption in polymers is relatively simple compared to the case of carbon dioxide or higher hydrocarbon sorption, since the former can be safely considered as non-swelling penetrants, i.e., they can be accommodated in the polymer matrix without inducing appreciable dilation. Consequently, the calculation of hydrogen and helium solubility in polymers with Lattice Fluid Theories can be performed by using just one fitting parameter, i.e. the mean field interaction parameter. In some cases, first approximation estimates of hydrogen and helium solubility isotherms can be obtained also by using the Lattice Fluid Models in a completely predictive fashion, i.e., by setting the mean field interaction parameter equal to unity, under the assumption that the polymer–penetrant system behaves as a regular mixture [16,22]. This modeling approach also provides an estimate of the isosteric heat of sorption for hydrogen in the different polymers considered. Remarkably, the dependence of the isosteric heat on the penetrant concentration can be correctly described, thus making possible a structure-property correlation for all the systems considered.

In recent years, other approaches such as molecular modeling have emerged as possible tools to investigate the mass transport properties of glassy and rubbery polymers [24]. However, in many cases the cost/benefit ratio offered by these techniques is not fully satisfactory, owing to the enormous requirement of computational power and the fairly low reliability of the results, which do not always agree with the experimental data [24]. These limitations are especially true in the case of glassy systems, for which the characteristic relaxation times are too long to be properly simulated even with modern computers. For this reason, macroscopic modeling remains the most reliable tool to describe the thermodynamic and transport properties of complex systems, such as glassy polymers.

The importance of theoretical modeling arises also from the fact that the hydrogen and helium solubility in polymers is very low and, consequently, very difficult to measure. For example, when considering the *pressure decay* technique, uncertainty associated with volume calibrations does not allow an accurate measurement of very low values of gas solubility; moreover, the accuracy of pressure transducers is often not high enough [1,8].

For these reasons, predictive calculations of hydrogen and helium solubility are sought to reduce measurements that are experimentally intensive and to guarantee a time saving and accurate evaluation of membrane performance. Some of the polymers considered in this work, such as polysulfone and Matrimid®, are currently employed in hydrogen purification [25,26]. AF-series amorphous Teflons® have also been considered for hydrogen removal from hydrocarbons in refinery applications [27].

2. Theoretical background

2.1. Gas transport in polymers

Within the framework of the solution-diffusion model, the gas permeability in polymers is expressed as the product of the solubility coefficient S and the concentration-averaged effective diffusion coefficient $\overline{D}$ [9]. This model applies for dense rubbery and glassy polymers, such as the ones considered in this work.

The ideal membrane selectivity of component i, in a mixture with a second component j, is equal to the ratio of the pure gas permeabilities under the hypothesis of negligible downstream pressure. On the basis of the solution-diffusion model, the ideal selectivity displays a solubility contribution and a diffusivity or size sieving contribution, i.e.

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{S_i}{S_j}\right) \times \left(\frac{\overline{D}_i}{\overline{D}_j}\right) \tag{1}$$

In some cases, when considering mixtures of light gases and highly permeable polymers, such as rubbery PDMS or high free volume glassy polymers, the diffusivity selectivity can be close to one, so the ideal selectivity is driven by the solubility–selectivity contribution.

Gas solubility in polymers typically depends on temperature according to the exponential law [28,29]

$$S = S_{\infty} \exp\left(-\frac{\Delta H_s}{RT}\right) \tag{2}$$

where ΔH_S is the enthalpy of sorption, R is the ideal gas constant, and $S_{\infty}$is the pre-exponential factor. As reported by Gee [30], gas sorption in polymers can be envisioned as a two-step process, involving penetrant condensation and the subsequent mixing of the penetrant with the polymer phase. As a consequence, the enthalpy of sorption can be expressed as the sum of the enthalpy of condensation and the enthalpy of mixing [28,29]

$$\Delta H_s = \Delta H_{cond} + \Delta H_{mix} \tag{3}$$

The condensation term is almost always negative, while the mixing term can be either positive or negative, depending on the nature of polymer–penetrant pair.

2.2. Sanchez–Lacombe equation of state

In the Lattice Fluid Theory proposed by Sanchez and Lacombe [17,18], the polymer chain can be envisioned as a sequence of beads in a three dimensional lattice. When considering the polymer in a mixture with a low molecular weight solvent, the two species are randomly mixed on the lattice. The compressibility of the system is guaranteed by the existence of empty cells in the lattice: from this point of view, the Sanchez–Lacombe equation of state overcomes a limitation of the Flory–Huggins theory [31] which does not envisage the existence of empty cells. The Sanchez–Lacombe equation of state (EoS) has been successfully used to predict gas solubility in rubbery polymers and in polymer melts [23,32,33]. In the Sanchez–Lacombe model, the chemical–physical properties of each substance are completely characterized by three characteristic parameters, p^*, ρ^* and T^*, which can be estimated from experimental pVT data. The parameter p^* is a characteristic pressure and provides an estimate of the cohesive energy density at close-packed conditions, i.e. at 0 K. The parameter ρ^* is the characteristic density at close-packed conditions and represents the highest value of density that one can expect for each substance. Finally, T^* is related to the interaction energy between two segments occupying adjacent positions in the lattice. The Lattice Fluid Theory [17,18] is able to describe the thermodynamic properties of pure fluids and their mixtures and also allows a straightforward calculation of the chemical potential of each species. More specifically, at any given temperature and pressure, the solubility of a gas or vapor in a rubbery polymer can be calculated by invoking the validity of the EoS for the pure penetrant in the external gas/vapor phase (Eq. (4)S, see *Supporting*