**Filled symbols:
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13 **Predictive calculation of hydrogen and helium solubility in glassy and rubbery**
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Graphical abstract

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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 to 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/H₂ solubility-selectivity at 35°C has been correctly predicted: as expected, the glassy Teflon® AF-series perfluorinated copolymers display a higher He/H₂ solubility selectivity compared to the hydrocarbon-based polymers.

Keywords: Membrane-based gas separations; Lattice Fluid theory; solubility selectivity.

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/H₂ 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/H₂ selectivity displayed by perfluorinated polymers is roughly 2.5 times higher compared to hydrocarbon-based polymers. The good performance of fluorinated materials in He/H₂ 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. 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].

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

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

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57 The importance of theoretical modeling arises also from the fact that the hydrogen and helium
58 solubility in polymers is very low and, consequently, very difficult to measure. For example,
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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 $\bar{D}$ [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.:

$$\alpha_{ij} = \frac{P_i}{P_j} = \left(\frac{S_i}{S_j} \right) \times \left(\frac{\bar{D}_i}{\bar{D}_j} \right) \quad (\text{eq.1})$$

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]:

$$S = S_{\infty} \exp \left(-\frac{\Delta H_s}{RT} \right) \quad (\text{eq.2})$$

where ΔH_s is the enthalpy of sorption, R is the ideal gas constant, and S_∞ 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]:

$$\Delta H_s = \Delta H_{cond} + \Delta H_{mix} \quad (\text{eq.3})$$

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. 4S, see *Supporting Information*) and for the polymer-penetrant

mixture (Eq. 5S, see *Supporting Information*), and by equating the chemical potentials of the penetrant in the external gas/vapor phase and in the mixture (Eqs. 6S-7S, see *Supporting Information*). In this way, at any given pressure and temperature, the following variables can be determined: *i*) the pure penetrant density, *ii*) the polymer-penetrant mixture density and *iii*) the penetrant mass fraction in the mixture.

For the sake of clarity, the model equations, the main parameters and the mixing rules used to express the mixture properties are compiled in the *Supporting Information*, where the subscripts 1 and 2 denote the properties of penetrant and of polymer, respectively. For detailed insight into the model, we refer to literature sources [17,18]. Here it is useful to recall that the parameter Ψ appearing in the mixing rule for p^* quantifies the deviation of the polymer-penetrant mean field interaction from the geometrical mean rule (Eq. 2S, see *Supporting Information*). When the penetrant-polymer mixture follows Hildebrand's regular solution theory [34] Ψ is equal to unity, but in many cases it can be greater or less than unity if departure from regular solution theory occurs. In our modeling approach the binary parameter Ψ is treated as a fitting parameter, and it is adjusted to the experimental sorption isotherms over the whole range of pressures inspected.

2.3 NELF Model. The equation of state-based approach, which has been widely employed to describe the gas/vapor sorption in rubbery polymers and in polymer melts, cannot be applied directly in the case of glassy polymers, since at any given pressure and temperature below T_g , the polymer density is a non-equilibrium value, which depends on the history of the sample, including the preparation protocol.

Different models have been proposed over the years to represent or predict the gas solubility in glassy polymers. Among them, we recall the Dual Mode Sorption Model [35], the Wissinger-Paulaitis model [36] and the NELF model [16, 19-22]. The Dual Mode Model [35], despite its ability to correctly describe the pure and mixed gas sorption isotherms in glassy polymers, does not show any predictive power, since the estimation of its parameters requires the availability of experimental sorption data. The model proposed by Wissinger et al. [36] fails in predicting the hysteresis phenomena observed in glassy polymers during desorption experiments. Conversely, the NELF model [16, 19-22] has proven to be very effective in predicting pure and mixed gas sorption and desorption isotherms in glassy matrices. The effectiveness of this model

relies on the choice of the polymer density as an order parameter to quantify the degree to which the system is out of equilibrium: owing to this assumption, the thermodynamic state of the glassy polymer-penetrant mixture can be completely defined by the three classical equilibrium variables, i.e., temperature, pressure and composition, plus the polymer density, which needs to be accurately measured experimentally. Thus, the NELF model extends the Sanchez-Lacombe Lattice Fluid Theory, which holds for polymers above the glass transition temperature, to the non-equilibrium domain of glassy polymers. The advantage of this model is the possibility to describe the thermodynamic behavior of glassy polymer/penetrant mixtures by using the same characteristic parameters and the same mixing rules valid for the Sanchez-Lacombe model (see *Supporting Information*, eqs. 1S, 2S and 3S). To predict the gas solubility isotherm, the NELF model requires as an input parameter the value of the glassy polymer density, ρ_2 , at the actual temperature and pressure, as well as the three Lattice Fluid parameters for the polymer and penetrants. When considering non-swelling penetrants, such as hydrogen and helium, the polymer density can be safely considered to be constant over the whole range of penetrant pressures inspected, since essentially no dilation is expected. Such an assumption relies on the small molecular size of hydrogen and helium, as well on their very low solubility in all the polymers considered. The model also works well in the case of bulky swelling penetrants, whose dissolution in a glassy polymer matrix may cause a significant decrease in polymer density as long as sorption proceeds [20-22].

A detailed description of the model is reported elsewhere [16,19-22]: for the sake of clarity, we summarize only the most relevant equations in the *Supporting Information*. The gas solubility in polymers below T_g can be calculated by solving the phase equilibrium condition between the pure external penetrant (Eq. 6S) and the solid glassy mixture (Eq. 8S) and by invoking the validity of the corresponding equilibrium EoS for the pure penetrant in the external gas phase (Eq. 4S). The characteristic LF parameters for the penetrants and for the polymers considered in this study were taken from literature sources and are reported in Table 1, together with the experimental density at 25°C and the thermal expansion coefficient α_v for each polymer. Different sets of LF parameters are available in literature for PDMS [32]. In this study, we will use the set retrieved by Sanchez and Lacombe [17] by fitting the polymer pVT data in a wide range of temperature (up to 343 K) and pressure (up to 100MPa). Other sets of LF parameters for PDMS were estimated by fitting to the Sanchez-Lacombe EoS the experimental density, thermal expansion coefficient and isothermal compressibility at the fixed temperature of 308 K [32, 37].

Table 1. Relevant physical properties and Lattice Fluid parameters for the polymers and the penetrants considered.

	density at 25°C (kg/L) [1,8]	$\alpha_v (10^{-4} K^{-1})$ [38–41]	T_g (°C) [1,8]	T^* (K)	p^* (MPa)	ρ^* (kg/L)	source
Teflon® AF1600	1.836	2.6	160	575	280	2.160	[20]
Teflon® AF2400	1.744	3.0	240	624	250	2.130	[20]
Matrimid®	1.231	0.84	305	880	450	1.350	[42]
PSF	1.215	1.68	186	830	600	1.310	[43]
PDMS	0.980	9.1	-123	476	302	1.104	[23]
H_2				46	37	0.078	[43]
He				9.3	4	0.148	[43]

3. Experimental

Hydrogen and helium solubility in glassy and rubbery polymers was measured using a Rubotherm® Magnetic Suspension Balance. Full details about the materials and the experimental methods have been reported by Smith et al. [1,8]. For each polymer, the density was measured at room conditions by using a measurement kit (Mettler-Toledo, Greifensee, Switzerland) and *n*-heptane as the buoyant fluid [1,8]. Some of the most relevant physical properties of these polymers (density, volumetric thermal expansion coefficient and glass transition temperature) are recorded in Table 1.

4. Modeling results

4.1 Hydrogen sorption isotherms. The hydrogen sorption isotherms in rubbery PDMS, available at temperatures ranging from -20 to 70°C [1], are reported in Fig. 1: in all cases, they are essentially linear with penetrant pressure and display a fairly weak dependence on temperature. A good agreement is found, over the whole range of pressures and at all the temperatures considered, between the experimental and theoretical isotherms calculated using the Sanchez-Lacombe Equation of State (SLEoS), with a maximum deviation less than 9%. Remarkably, the model is

able to reproduce the slight increase in hydrogen solubility observed in PDMS with increasing temperature, according to the typical behavior of rubbery polymers. In our approach, according to the original theory developed by Sanchez and Lacombe [17,18], the binary mean field interaction parameter Ψ has been considered constant with temperature and equal to the optimal value found by a least squared fitting procedure of the model to the experimental sorption isotherm at 35°C. Moreover, the optimal value of the Ψ parameter (1.25) is greater than unity, thus indicating that the energetic mean field interactions are stronger than one would expect for regular mixtures. This favorable interaction is not surprising, since we are considering the sorption of hydrogen in a hydrogenated polymer.

Fig. 1: H_2 solubility isotherms in PDMS. Filled and open circles stand for experimental data at different temperatures. A) $\bullet$: -20°C; $\bullet$: -10°C; $\bullet$: 0°C; $\bullet$: 10°C; B) $\circ$: 20°C; $\circ$: 35°C; $\circ$: 50°C; $\circ$: 70°C. Continuous lines: Sanchez-Lacombe EoS calculations at different temperatures.

The hydrogen solubility isotherms in glassy Teflon® AF, Matrimid® and PSF, collected at temperatures ranging from -20 to 70°C, are reported in Figs. 2: they display a slightly downward concavity to the pressure axis, according to the typical behavior of glassy polymers. Moreover, the solubility displays a much more pronounced dependence on temperature relative to rubbery PDMS. The NELF model has been used to describe the hydrogen solubility in these polymers, since they are glasses within the experimental range of temperatures considered. To properly account for the effect of temperature, the polymer density was estimated at each experimental temperature by using the thermal expansion coefficients and the density values measured experimentally at 25°C, which are recorded in Table 1. As expected,

the density change with temperature is much more pronounced for PDMS relative to the glassy polymers. In particular, from -20 to 70 °C, the density of PDMS decreases by about 8.5%, while for the other polymers the observed change does not exceed 2.7%.

Since hydrogen can be safely considered to be a non-swelling penetrant, the polymer density has been assumed to be constant over the entire range of pressures considered and equal to the pure polymer value at the actual experimental temperature. Such an assumption relies on the very small amount of hydrogen sorbed in all of the polymers considered (less than 20 cm³(STP)/cm³(polymer) at -20°C and 60 atm in the case of AF2400), as well as on the small size of a hydrogen molecule, whose diameter has been estimated to be 2.77Å [44]. The absence of dilation considerably simplifies the modeling efforts, since separate experimental information on the polymer density during sorption are no longer needed, and Ψ is the sole fitting parameter.

As reported in Figs. 2, the NELF model calculations are in very good agreement with the experimental data for all systems considered, with a maximum deviation of 18% in the case of Matrimid at 70°C and 60 atm.

Interestingly, the model is able to reproduce the marked decrease of gas solubility with temperature observed experimentally. Therefore, the possibility of correctly describing the experimental sorption isotherms by using just Ψ as a fitting parameter seems to confirm that the extent of volume dilation induced by hydrogen sorption in these glassy polymers is negligible. The latter is a crucial issue for membrane gas separations, since swelling phenomena occurring during gas sorption may result in a dramatic loss of selectivity. One of the advantages of this modeling approach is the possibility to estimate the extent of matrix dilation without direct experiments: this analysis is particularly relevant when the dilation is too small to be measured experimentally.

Fig. 2: H_2 solubility isotherms in: A) AF2400; B) Matrimid®; C) PSF; D) AF1600. Filled and open circles stand for experimental data at different temperatures. $\bullet$: -20°C ; $\bullet$: -10°C ; $\bullet$: 0°C ; $\bullet$: 10°C ; $\circ$: 20°C ; $\circ$: 35°C ; $\circ$: 50°C ; $\circ$: 70°C . Continuous lines: NELF model calculations at different temperatures.

As for the case of PDMS, when considering hydrogen sorption in glassy Teflon® AF, Matrimid® and PSF, the binary parameter Ψ was considered constant with temperature and equal to the optimal value found by a best fitting procedure of NELF model to the sorption isotherm at 35°C . This result is relevant, as the procedure proposed in this study allows a completely predictive estimation of hydrogen solubility at -20 , -10 , 0 , 10 , 20 , 50 and 70°C , once the sole fitting parameter Ψ has been optimized on the experimental sorption data at 35°C . Remarkably,

as we will see later, this modelling approach allows an accurate prediction of He/H₂ solubility selectivity with one adjustable parameter only.

Interestingly, at each temperature, the mean field polymer-penetrant interaction is weaker in perfluorinated Teflon® AF2400 ($\Psi \sim 0.97$) that, due to the presence of bulky perfluorinated moieties, displays a high free volume and, in turn, a low cohesive energy density (CED). Moreover, the optimal value of the binary parameter Ψ in the case of hydrogen sorption in Teflon® AF2400 is able to correctly describe the hydrogen solubility isotherm in AF1600, as it was also observed for the case of methane and light hydrocarbons [20, 21]. This finding is not surprising, since the two copolymers contain the same monomers, but in different proportions. Consequently, they display a slightly different fractional free volume. Moreover, in both of the perfluorinated matrices the binary parameter is slightly less than unity, thus, indicating that the energetic interactions are weaker than those one would expect in a regular mixture. This behavior has been observed also in the case of hydrocarbon sorption in amorphous Teflons® AF [20, 21, 45] and can be generally ascribed to the low affinity between perfluoropolymers and non-fluorinated gases [46]. Similarly, the hydrocarbon sorption in perfluorinated liquids also deviates from Hildebrand's regular solution theory [34]. Hildebrand's theory states that compounds with similar values of CED are mutually soluble: in particular, perfluorocarbons display a very low value of CED compared to the analogous hydrocarbons. Thus, perfluoropolymers also display a low value of CED compared to hydrocarbon based polymers; this fact can be verified by noting that the characteristic Lattice Fluid pressure p^* , which provides an indirect estimation of the polymer's CED, has an average value of 250 MPa for amorphous Teflons® AF, while for the other polymers, it is much higher (i.e. 450 MPa for Matrimid®, 600 MPa for PSF).

When considering the other matrices, namely PSF and Matrimid®, the interaction parameter assumes higher values, indicating stronger polymer-penetrant mean field interactions. Both PSF and Matrimid® display a lower fractional free volume and a higher cohesive energy density relative to the Teflon® AF-series copolymers. In particular, in the case of the hydrogen-Matrimid® pair, the optimal value of Ψ is 1.09, while, when considering the hydrogen-PSF pair in the same temperatures range, Ψ is 1.3. In both of these pairs, Ψ is greater than unity, indicating that the binary interaction is stronger than would occur in a regular mixture. This result can be explained, at least from a qualitative point of view, by considering that Matrimid® and PSF are hydrocarbon-based polymers, so their energetic interactions with hydrogen are

expected to be stronger as compared to the case of Teflon® perfluoropolymers. The values of binary parameter obtained for different hydrogen-polymer pairs are recorded later in Table 4.

In the Lattice Fluid theory, the fractional free volume f with respect to the close packed state can be calculated as follows:

$$f = \frac{\rho_2^* - \rho_2}{\rho_2^*} \quad (\text{eq.4})$$

where ρ_2^* is the polymer characteristic Lattice Fluid density, and ρ_2 is the actual polymer density at the experimental temperature. The values of f at 35°C for each polymer are recorded in Table 2. The fractional free volume calculated *via* the Lattice fluid theory is quite different from that estimated using Bondi's rule [47]: both methods are self-consistent, although they are based on different assumptions. In particular, Eq. 4 provides an estimation of the polymer fractional free volume assuming as reference the specific volume under close packed conditions, i.e. at 0 K. By plotting f as a function of FFV a good linear correlation is obtained, thus confirming that the two approaches used to estimate the amount of free volume are consistent with each other.

Finally, the modeling procedure described above for rubbery and glassy polymers allows a reliable prediction of hydrogen sorption isotherms in a wide range of temperatures with just a fitting parameter, which is adjusted on the experimental sorption data available at 35°C. In this way it is possible to mitigate the experimental effort required to measure the hydrogen solubility in polymers.

Table 2. Fractional free volume of different polymers at 35°C as calculated from Lattice Fluid Theory (f) and from Bondi's rule (FFV).

	f (LF Theory)	FFV (Bondi's method)
Teflon® AF1600	0.148 [this study]	0.310 [8]
Teflon® AF2400	0.181 [this study]	0.330 [1]
Matrimid®	0.088 [this study]	0.170 [1]
PSF	0.072 [this study]	0.144 [1]
PDMS	0.112 [this study]	0.180 [1]

4.2 *Infinite dilution solubility coefficient.* Another parameter of interest is the infinite dilution solubility coefficient, defined as:

$$S_0 = \lim_{p \rightarrow 0} \frac{C}{p} \quad (\text{eq.5})$$

where C is the solubility expressed in $\text{cm}^3(\text{STP})/\text{cm}^3(\text{polymer})$, and p is the penetrant gas phase pressure. The importance of S_0 arises from the fact that it correlates with properties of both the polymer and the penetrant, such as the polymer fractional free volume or penetrant condensability. In this section, experimental values of S_0 will be compared to theoretical estimates provided by the Sanchez-Lacombe EoS and by the NELF model. For hydrogen sorption in PDMS, the theoretical values of the infinite dilution solubility coefficient can be evaluated at each temperature from the slope of the tangent to the theoretical sorption isotherm calculated from the Sanchez-Lacombe EoS in the limit of vanishing pressure.

Conversely, in the case of glassy polymers (Teflon® AF-series copolymers, Matrimid® and PSF), the NELF theory provides an analytical expression for the infinite dilution solubility coefficient [22, 43]:

$$\ln(S_0) = \ln\left(\frac{T_{STP}}{p_{STP}T}\right) + r_1^0 \left\{ \left[1 + \left(\frac{v_1^*}{v_2^*} - 1 \right) \frac{\rho_2^*}{\rho_2^0} \right] \ln\left(1 - \frac{\rho_2^0}{\rho_2^*} \right) + \left(\frac{v_1^*}{v_2^*} - 1 \right) + \frac{\rho_2^0}{\rho_2^*} \frac{T_1^*}{T} \frac{2}{p_1^*} \Psi \sqrt{p_1^* p_2^*} \right\} \quad (\text{eq.6})$$

where T_{STP} and p_{STP} are standard temperature and pressure, respectively (273 K, 1 atm), r_1^0 is the number of lattice sites occupied by a molecule of pure penetrant, and v_1^* and v_2^* are the volume occupied by a mole of lattice sites of pure penetrant and polymer, respectively. In Eq. 6, the binary parameter has been set equal to its optimized value, as obtained by fitting to the NELF model the entire sorption isotherms at 35°C, while ρ_2^0 corresponds to the pure polymer density at each experimental temperature.

In Fig. 3, the values of S_0 for PDMS, Teflon® AF2400, Matrimid® and PSF are reported as a function of reciprocal of absolute temperature. Excellent agreement is found between the experimental and theoretical values for all systems considered. This result is remarkable, since the theoretical predictions are obtained by using just one fitting parameter optimized at 35°C, while the model is used in a completely predictive fashion at the other temperatures. In the case

of rubbery PDMS, the infinite dilution solubility coefficient increases with increasing temperature, as expected on the basis of the general endothermic behavior of light gas sorption in polymers above T_g . Conversely, the glassy matrices usually display exothermic sorption behavior, so the solubility coefficient decreases with increasing temperature. As expected, amorphous Teflon® AF2400 displays higher values of S_0 relative to the other matrices, owing to its very high fractional free volume. Conversely, PSF displays the lowest FFV and the lowest values of infinite dilution solubility coefficients among the glassy polymers considered.

Fig. 3: H_2 infinite dilution solubility coefficient as a function of temperature. Red circles: AF2400; black circles: Matrimid®; blue circles: PSF; green circles: PDMS. Filled symbols: exp. data; open symbols: LF model calculations. The continuous lines represent the best fit to Eq.2.

4.3 Isosteric heat of sorption. To further analyze the energetics of hydrogen sorption in the polymers considered in this study, we calculated the enthalpy of sorption as a function of the penetrant concentration, often called the isosteric heat of sorption [28,29]. The isosteric heat can be estimated, at any fixed penetrant concentration, by using the following relationship [28,29]:

$$\left[\frac{\partial(\ln p)}{\partial\left(\frac{1}{T}\right)} \right]_c = \frac{\Delta H_s}{R} \quad (\text{eq.7})$$

where p is the pressure corresponding to a fixed concentration C at each temperature. As reported in Fig. 4, the NELF model and the Sanchez-Lacombe EoS are able to reproduce with good accuracy the values and the trend of isosteric heat as a function of hydrogen concentration for all polymers considered. As expected, for Teflon® AF2400, Matrimid® and PSF, the enthalpy of sorption is largely negative, owing to the globally exothermic character of gas sorption in glassy polymers. Conversely, in PDMS, the enthalpy of sorption assumes positive values, due to the endothermic nature of sorption process in rubbery polymers. Moreover, for PDMS, the absolute value of the isosteric heat is quite low as compared to the glassy matrices, which is consistent with a weak dependence of hydrogen solubility on temperature.

The dependence of isosteric heat on hydrogen concentration is rather weak for all polymers considered. This result is not surprising, since the same trend of ΔH_s with concentration has been previously observed when considering the sorption of light gases (CH_4, O_2, N_2) in other polymers [28]. Both the experimental data and the theoretical calculations based on the non-equilibrium model used indicate a very slight increase of the enthalpy of sorption as a function of penetrant concentration in glassy matrices. Such a weak increase is also in agreement with the physical picture that light gas sorption in glassy polymers can be envisioned as a void-filling, dual-mode sorption process. In other words, the penetrant molecules are initially accommodated in the non-equilibrium free volume of the glassy matrix (i.e., the Langmuir term for polymer sorption). As sorption increases at higher pressures, the free volume becomes gradually saturated and an increasing amount of gas is absorbed in the equilibrium Henry mode. While sorption in the Langmuir mode is largely exothermic, sorption in the Henry mode is much more endothermic, since it requires the creation of space between polymer chains, similar to the sorption mechanism in rubbery polymers [48]. Based on this argument, it is possible to justify the slight increase of ΔH_s as a function of concentration observed experimentally for the glassy polymers considered, and confirmed by the NELF calculations. Moreover, the increase of isosteric heat with concentration is more marked in Matrimid® and PSF, which display lower free volume fractions compared to Teflon® AF2400. The large negative values of ΔH_s displayed by Matrimid® and PSF relative to AF2400 indicates that the former polymers have more favorable energetic interactions with the absorbed hydrogen molecules: this fact is further confirmed by the modeling outcomes, which give for Matrimid®/H₂ and PSF/H₂ the highest value of the mean field interaction parameter Ψ (1.09 and 1.3, respectively).

Interestingly, many authors report that the ratio of non-equilibrium/equilibrium sorption (i.e., the Langmuir to Henry sorption in the framework of the Dual Mode Model) is much lower for perfluorinated polymers than for hydrocarbon based polymers [1,49]. Such an occurrence is confirmed by the globally less exothermic sorption behavior of AF2400. Moreover, as mentioned before, the Henry's law mode of fluoropolymers displays a very low cohesive energy density as compared to the hydrocarbon-based polymers, so creation of intermolecular spaces to further accommodate penetrant molecules requires less energy in the former than in the latter polymers. Consequently, sorption in the Henry's law mode is expected to be much more endothermic in Matrimid® and PSF than in AF2400. This fact might further justify the more pronounced increase of isosteric heat as a function of the penetrant concentration for Matrimid® and PSF.

In the case of PDMS, the experimental isosteric heat is practically constant versus penetrant concentration: this behavior is confirmed by the theoretical values of ΔH_s obtained from the Sanchez-Lacombe equation of state.

Fig. 4. Experimental (open symbols) and theoretical (continuous lines) isosteric heat of sorption as a function of the hydrogen concentration. Black circles: Matrimid®; red triangles: PSF; blue circles: AF2400; green triangles: PDMS.

The energetics of hydrogen sorption in glassy polymers, which can be only qualitatively analyzed in terms of Dual Mode Model, is on the other hand quantitatively described by the NELF model, which provides an analytical expression for the infinite dilution solubility

coefficient, S_0 (Eq. 6). According to Eq. 2, the enthalpy of sorption in the limit of vanishing concentration, ΔH_{s_0} , can be expressed as:

$$\frac{\partial \ln S_0}{\partial \frac{1}{T}} = -\frac{\Delta H_{s_0}}{R} \quad (\text{eq.8})$$

Thus, the derivative of $\ln(S_0)$ with respect to the reciprocal of absolute temperature provides an explicit expression for ΔH_{s_0} ; by neglecting the minor contributions due to thermal dilation one obtains:

$$\frac{\partial \ln S_0}{\partial \frac{1}{T}} = T + r_1^0 \frac{\rho_2^0}{\rho_2^*} T_1^* \frac{2\Psi}{p_1^*} \sqrt{p_1^* p_2^*} \quad (\text{eq.9})$$

Comparing Eqs. 9 and 4, it results that $\frac{\rho_2^0}{\rho_2^*} = 1 - f$; thus, after some algebra we have:

$$\Delta H_{s_0} = -R \left\{ T + 2r_1^0 (1-f) T_1^* \Psi \sqrt{\frac{p_2^*}{p_1^*}} \right\} \quad (\text{eq. 10})$$

In Eq. 10, r_1^0 , T_1^* and p_1^* refer to the penetrant properties and are constant, since the penetrant is fixed. Conversely, the quantity $(1-f)\Psi\sqrt{p_2^*}$ is related to the specific properties of the polymer and the penetrant-polymer mixture. From this simple analysis based on the NELF model, one immediately recognizes that a higher absolute value of $(1-f)\Psi\sqrt{p_2^*}$ is associated with a more exothermic sorption process. Conversely, the lower absolute value of $(1-f)\Psi\sqrt{p_2^*}$ is associated with a less exothermic (i.e., a more endothermic) sorption process. The conclusions drawn on the basis of the NELF model are in reasonable agreement with the experimental data. Indeed, the term $(1-f)\Psi\sqrt{p_2^*}$ is about $12 \text{ MPa}^{0.5}$ when considering perfluorinated Teflon AF2400, for which the hydrogen sorption is less exothermic relative to hydrocarbon-based polymers. In the case of Matrimid® and PSF, that term is 22 and $29 \text{ MPa}^{0.5}$ respectively; thus, as found experimentally, the model predicts similar values of ΔH_{s_0} for these two polymers (-8.40 and -8.56 kJ/mol, respectively). These results appear remarkable if one considers that the model is used in a predictive fashion.

The values of infinite dilution enthalpy of sorption, ΔH_{s_0} , can be obtained by extrapolating both the experimental and theoretical values of ΔH_s reported in Fig. 4 in the limit of vanishing concentrations. The results, recorded in Table 3, indicate good agreement between the experimental and theoretical values of ΔH_{s_0} .

An alternative but effective method to estimate the infinite dilution sorption enthalpy relies on the analysis of infinite dilution solubility coefficients. Indeed, the data reported in Fig. 3 indicate that S_0 displays a Van't Hoff-type dependence on absolute temperature. Thus, according to Eq. 2, we can estimate the infinite dilution sorption enthalpies as the slope of the linear correlation between $\ln(S_0)$ and $1/T$ for the polymers considered. As reported in Table 3, the values of infinite dilution sorption enthalpies, as calculated from the analysis of the experimental and theoretical infinite dilution solubility coefficients, are in good agreement with each other.

Remarkably, the values of enthalpies of sorption at infinite dilution as estimated from the analysis of S_0 values are fully consistent with those obtained by extrapolating the data reported in Fig. 4 in the limit of vanishing concentration. The consistency of the two approaches used to estimate ΔH_{s_0} can be verified by considering the data reported in Table 3.

Table 3. Experimental and theoretical sorption enthalpy at infinite dilution conditions, as calculated using different methods.

	ΔH_{s_0} (kJ/mol)		ΔH_{s_0} (kJ/mol)	
	(from extrapolation method)		(from S_0 analysis)	
	(exp.)	(calc.)	(exp.)	(calc.)
Teflon® AF2400	-5.40 ± 0.3	-5.27	-5.90	-5.23
Matrimid®	-9.40 ± 0.5	-8.40	-9.50	-8.15
PSF	-7.20 ± 0.2	-8.56	-7.25	-8.64
PDMS	0.82 ± 0.1	1.25	0.95	1.34

4.4 Helium solubility. The major concern when dealing with modeling the helium sorption in polymers is the availability of Lattice Fluid parameters for this gas. The Lattice Fluid parameters

of low molecular weight compounds are often determined by fitting the LV equilibrium data and saturated liquid density to the Sanchez-Lacombe EoS [16,22]. The Lattice Fluid parameters for helium, estimated according to the procedure described above, have been first reported in ref. [43]. These value of T^* , p^* and ρ^* , which are listed in Table 1, have been used in this work to calculate the helium sorption isotherms in Teflon® AF1600, Teflon® AF2400, Matrimid®, PSF and PDMS at 35°C. An alternative estimate of the three scaling parameters can be made by considering that the Lattice Fluid theory provides an analytical expression of the second virial coefficient as a function of temperature [50]. In this way, one could obtain the characteristic parameters by a best fitting procedure of the model to the second virial coefficient data. Nevertheless, to guarantee internal consistency, in this work we use the Lattice Fluid parameters as estimated from LV equilibrium data since a similar procedure has been used to determine the same parameters for hydrogen.

In Fig. 5A-B-C-D, the experimental helium solubility isotherms at 35°C in Teflon® AF1600 and AF2400, Matrimid® and PSF, collected by Smith et al. [8], have been compared to the NELF model calculations. Conversely, the Sanchez-Lacombe EoS has been used to interpret the helium sorption data available for PDMS (Fig. 5E). For all the polymers considered, helium solubility is much lower compared to hydrogen. This fact can be explained by considering that gas solubility in polymers scales with critical temperature, which is 5.2 K for helium *vs* 33 K for hydrogen.

In Fig. 5, the continuous lines represent model calculations when Ψ is optimized over the entire sorption isotherm (one-parameter correlation), while the dashed lines represent the fully predicted sorption isotherm when the binary parameter Ψ is set equal to unity (zero-parameter correlation). For all glassy polymers considered, the model calculations agree more than satisfactorily with the experimental data. Remarkably, for the two perfluorinated matrices, the NELF model provides a very good description of the experimental isotherms also when it is used in a completely predictive fashion, i.e. by setting $\Psi=1$. Also in the case of Matrimid®, PSF and PDMS good agreement is observed between experimental and theoretical sorption isotherms. As we will discuss hereafter, the Lattice Fluid parameters for helium may contain uncertainties beyond those expected for more condensable penetrants (hydrogen, light gases, hydrocarbon vapors). Furthermore, helium solubility in these polymers is very low and, therefore, difficult to measure experimentally, especially in the case of PSF, for which the experimental points are much more scattered as compared to the other matrices. As reported by

Smith et al. [1,8], the uncertainties of gravimetrically-determined sorption isotherms are affected by several potential sources of error. Of particular relevance are the uncertainties of the second and third virial coefficients [51] and the pressure reading in the sorption apparatus, which are required to correct for buoyancy effects. Greater relative uncertainties in the buoyancy correction term would be expected for light gases such as hydrogen and helium. The uncertainty of experimental helium sorption isotherms has been estimated by considering the standard deviation of data points from multiple measurements [8]; however, systematic uncertainties arising from buoyancy corrections could also affect these sorption results.

Nevertheless, the modeling results enable us to perform both a quantitative and qualitative analysis of helium sorption data in the different polymers considered. When considering AF2400 and AF1600, the helium solubility is accurately described by the NELF model with the same values of the binary parameter ($\Psi = 0.92$). Similarly to the case of hydrogen sorption, such an occurrence indicates that the extent of the energetic mean field interactions is comparable in the two helium-polymer pairs. This fact seems quite reasonable since the copolymers AF2400 and AF1600 have similar structures, but a slightly different fractional free volume (see Table 2). Moreover, as discussed in the case of hydrogen sorption, the value of the binary parameter in the case of perfluorinated matrices is less than one, thus indicating a weak energetic interaction with the absorbed helium molecules. When considering Matrimid® polyimide, a good representation of the sorption isotherm over the whole range of pressure considered can be obtained by setting $\Psi = 0.75$. Thus, at least from the theoretical point of view, the helium/Matrimid® energetic interaction is even weaker than for the helium/perfluoropolymer pairs. However, the Lattice Fluid parameters for Matrimid® have been estimated from an approximate procedure due to the inaccessibility of the pVT data of this polymer in the rubbery region [42]. The uncertainty of both the Matrimid® and helium Lattice Fluid parameters will likely affect the value of Ψ . For this reason, we have excluded any fundamental interpretation of these results for Matrimid®. In the case of PSF, the NELF model provides an acceptable estimation of the sorption isotherms with $\Psi = 1.8$. This optimal value of the binary parameter, obtained by fitting the entire sorption isotherm to the NELF model, would indicate, in principle, a strong polymer-penetrant interaction, but we believe that this result is rather a model artifact. In this modeling approach Ψ is the sole fitting parameter, thus uncertainty in experimental data will strongly affect this parameter. Indeed, as reported in Fig. 6D, the helium solubility in PSF is very low (less than $1.5 \text{ cm}^3(\text{STP})/\text{cm}^3\text{polymer}$ at 60 atm), and the sorption isotherm appears quite scattered.

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4 Finally, in the case of PDMS, the Sanchez-Lacombe EoS provides a good representation of the
5 experimental data over the whole range of pressure inspected, with $\Psi=1.8$. Also in this case the
6 value of the binary parameter is quite high. Such an occurrence is likely a model artifact, due to
7 the synergistic effect of the experimental uncertainty and of the relative inaccuracy of the Lattice
8 Fluid parameters for helium.
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14 Frisch and Rogers pointed out the quantum effects displayed by helium [52]. These effects have
15 been invoked to explain the completely different properties of helium as compared to
16 hydrogen. Additionally, we mention the fact that helium stays in the liquid state very close to
17 absolute zero, while at the same conditions hydrogen is solid. This behavior seems to be related
18 to the weaker interactions occurring among the helium atoms as compared to hydrogen.
19 Though a theoretical discussion of this issue is beyond the scope of this work, the helium
20 sorption could be affected by this anomalous behavior to some extent. Such an occurrence could
21 be related to the unusually high values of the binary parameter found when considering helium
22 sorption in PSF and PDMS, as well to the quite low value of Ψ estimated in the case of
23 Matrimid®-He system.
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32 Interestingly, the sorption of hydrogen and helium in the Teflon® AF materials at 35°C can be
33 described with approximately the same value of the binary parameter Ψ . This finding would
34 suggest that hydrogen and helium are able to establish very similar mean field energetic
35 interactions with perfluorinated polymers. Conversely, in the case of Matrimid®, PSF and PDMS
36 the optimal values of Ψ found in the case of hydrogen are quite different than the
37 corresponding value for helium. A detailed discussion of the molecular origin of this difference
38 is beyond the scope of this study, thus we prefer to omit further discussions, which would
39 result quite speculative at this stage. Finally, the values of binary parameter for each penetrant-
40 polymer pair are reported in Table 4.
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Fig. 5: He solubility isotherms at 35 °C in: A) AF1600, B) AF2400, C) Matrimid®, D) PSF, E) PDMS. Open symbols: exp. data. Continuous lines: one-parameter LF model calculations. Dashed lines: zero-parameter LF model calculations.

Table 4. Binary parameter adjusted on the solubility isotherm at 35°C for each penetrant-polymer pair.

	Ψ	
	H_2	He
<i>Teflon</i> ® AF1600	0.97	0.92
<i>Teflon</i> ® AF2400	0.97	0.92
<i>Matrimid</i> ®	1.09	0.75
<i>PSF</i>	1.30	1.80
<i>PDMS</i>	1.25	1.80

By using the same procedure described in the case of hydrogen sorption, the theoretical helium infinite dilution solubility coefficients at 35°C have been estimated for AF1600, AF2400, Matrimid®, PSF and PDMS. In particular, when considering helium sorption in PDMS, the theoretical value of S_0 can be evaluated as the slope of the tangent to the theoretical sorption isotherm calculated from the Sanchez-Lacombe EoS in the limit of vanishing pressure. Conversely, in the case of glassy polymers, we used the explicit expression for S_0 provided by the NELF model (Eq. 6).

In Fig. 6, the helium and hydrogen infinite dilution solubility coefficients at 35°C are shown as a function of fractional free volume, calculated on the basis of the Lattice Fluid theory, according to Eq. 4. Remarkably, also in the case of helium the experimental values of S_0 show good agreement with the predictions of Lattice Fluid theories. Finally, according to the NELF model predictions [43], the logarithm of S_0 , for both penetrants, increases with increasing fractional free volume f . Such an occurrence can be explained by arguing that the higher the free volume available for gas sorption, the higher is the probability to accommodate the penetrant molecules in the polymer phase. Thus, the increase of solubility coefficient with fractional free volume is essentially due to entropic effects [43].

Fig. 6. Experimental (filled symbols) and theoretical (open symbols) values of infinite dilution solubility coefficient for helium (black symbols) and hydrogen (blue symbols) at 35°C, as a function of the polymer fractional free volume as calculated from Eq. 4. The continuous lines represent a guide for the eye.

4.5 Estimation of He/H₂ solubility selectivity. The modeling approach used here allows for a straightforward estimation of He/H₂ solubility selectivity for the different polymers considered. As reported in Figs. 7A-B, the experimental values of helium-to-hydrogen solubility selectivity at 35°C agree quite satisfactorily with the theoretical estimations provided by the SL-EoS and NELF models. Both the experimental data and the model results indicate that the two amorphous copolymers, Teflon® AF2400 and AF1600, are the most solubility-selective materials for helium to hydrogen. The solubility selectivity of rubbery PDMS is slightly lower than that of the glassy perfluoropolymers. Some similarities between gas solubility in PDMS and in fluoropolymers have previously been highlighted in the literature [8, 53-54]. This trend can be rationalized on the basis of the Lattice Fluid theory. As reported by Lou et al. [55], for a given gas pair, the polymer cohesive energy density, namely the characteristic Lattice Fluid pressure p_2^* , is the most important parameter affecting the solubility selectivity. As reported in Table 1, Teflon® AF co-polymers and PDMS have similar values of p_2^* , so one can expect similar values of He/H₂ solubility selectivity for these polymers. PSF and Matrimid® display very close values of He/H₂ solubility selectivity, both of which are lower than those of the Teflon® AF-series perfluoropolymers and PDMS. This result is also consistent with the conclusions drawn by Lou et al. [55]. Based on their analysis, one should expect that as p_2^* increases, the helium to

hydrogen solubility-selectivity decreases. Indeed, PSF and Matrimid have higher values of p^* and lower values of helium to hydrogen solubility-selectivity than either Teflon® AF copolymers or PDMS. Thus, as pointed out by Lou et al. [55], the solubility separation factor is strongly affected by polymer cohesive energy density. This conclusion is further supported by a sensitivity analysis of Lattice Fluid model to the three scaling parameters p_2^* , T_2^* and ρ_2^* , whose results, reported in the *Supporting Information Section*, indicate that T_2^* and ρ_2^* affect the solubility-selectivity to a negligible extent. We believe this aspect merits further study, since it could provide a route to identify new classes of polymer membranes with improved gas separation properties.

The solubility selectivity values reported in Fig. 7 are essentially constant over the whole range of pressures considered: this fact further confirms that the hydrogen and helium sorption does not induce any swelling effect on the polymer matrices. Indeed, the occurrence of swelling phenomena would be accompanied by a significant change in selectivity at high pressures.

Thus, the theoretical analysis proposed in this work can provide some insights regarding the fundamentals of hydrogen and helium sorption in polymers and also reduce the experimental efforts usually needed to evaluate membranes performance.

Fig. 7: *He/H₂ solubility selectivity at 35°C. A) AF2400 (black open circles), AF1600 (blue open circles), Matrimid® (red open circles); B) PSF (blue open squares) and PDMS (black open squares). Continuous lines represent the theoretical estimates provided by LF models.*

In Fig. 8 the He/H_2 solubility selectivity at 35°C is reported as a function of the helium solubility coefficient [44] in the limit of infinite dilution. Remarkably, the model calculations agree very well with the experimental data for the polymers considered.

Both the experimental and theoretical results reported in Fig. 8 confirm the higher He/H_2 solubility selectivity displayed by fluoropolymers as compared to hydrocarbon-based polymers. Remarkably, the model also predicts the similar sorption behavior displayed by rubbery PDMS and glassy Teflon® AF samples [47, 48].

Fig. 8: He/H_2 solubility selectivity vs. He solubility coefficients at infinite dilution and 35°C . Filled symbols: experimental values; open symbols: model calculations.

5. Conclusions

The hydrogen and helium sorption isotherms in a series of rubbery and glassy polymers have been modeled with equilibrium and non-equilibrium Lattice Fluid theories. The theoretical hydrogen sorption isotherms display good agreement with the experimental data for all polymers considered over a broad range of pressures and temperatures. The isosteric heat of sorption and its functional dependence on hydrogen solubility can be correctly predicted for all polymers considered. The model analysis relies on the fundamental assumption that hydrogen

behaves as a non-swelling penetrant, so the binary interaction parameter Ψ is the sole fitting parameter. Remarkably, the value of Ψ for each penetrant-polymer pair was optimized on the experimental sorption data at 35°C and was used to calculate, in a completely predictive fashion, the hydrogen solubility isotherms at the other temperatures considered. In the case of amorphous Teflon® AF materials, the binary parameter is slightly less than unity, indicating that the mean field energetic interaction with hydrogen molecules is less favorable as compared to the ideal case of Hildebrand's regular solution theory. Such a negative deviation from Hildebrand's theory has been already observed in the case of hydrocarbon sorption in perfluoropolymers and in fluorinated liquids. For the hydrocarbon-based polymers, Ψ is greater than unity, thus indicating a more favorable energetic interaction with the absorbed hydrogen molecules. The different behavior observed in the case of fluorinated polymers as compared to the hydrocarbon-based polymers can also be ascribed to the higher fractional free volume (or the lower CED) of the former matrices.

The helium sorption isotherms available for Teflon® AF2400 and AF1600 at 35°C are in good agreement with the NELF calculations. The optimal value of the parameter Ψ , which is the same for the two copolymers, is less than unity, as in the case of hydrogen sorption. The helium solubility in Matrimid® can be correctly described in terms of the NELF model by setting the mean field interaction parameter Ψ equal to 0.75. This value of Ψ is quite low and may indicate a very weak interaction between Matrimid® and helium molecules. In the case of PSF and PDMS, the model calculations agree with the experimental data over the whole range of pressures considered. For both He/PSF and He/PDMS pairs, the interaction parameter is higher than one. A detailed analysis of the mean field interactions has been omitted in the case of helium sorption. Indeed, since in this modeling approach Ψ is the sole fitting parameter, its value could be strongly affected by the uncertainty in experimental data, as well as in the Lattice Fluid parameters for helium. It is worth noting, however, that the sorption of hydrogen and helium in the perfluorinated copolymers at 35°C can be described with approximately the same value of the binary parameter. This finding indicates that the two gases are able to establish very similar mean field interactions with both of perfluorinated copolymers. Conversely, the sorption of hydrogen and helium in Matrimid®, PSF and PDMS can be described with quite different values of Ψ .

The model analysis based on the Lattice Fluid theories enables also an accurate estimation of infinite dilution solubility coefficients for both penetrants considered.

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4 Finally, the He/H₂ solubility selectivity is correctly predicted for all the systems inspected. Both
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6 the experimental and model results indicate that perfluorinated copolymers and PDMS display
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8 higher He/H₂ ideal selectivity compared to PSF and Matrimid®. Remarkably, the similar
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10 sorption behavior displayed by Teflon® AF co-polymers and PDMS can be rationalized in terms
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12 of the Lattice Fluid theory.
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figure 1a

figure1b

figure 2a

figure 2b

figure 2c

figure 2d

figure 3

figure 4

figure 5a

figure 5b

figure 5c

figure 5d

figure 5e

figure 6

figure 7a

figure 7b

figure 8