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Modelling sorption thermodynamics and mass transport of n-hexane in a propylene-ethylene elastomer

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Abstract: Optimization of post-polymerization processing of polyolefin elastomers (POE) is of considerable industrial interest. To this aim, experimental determination and theoretical interpretation of the thermodynamics and mass transport properties of POE-solvent mixtures is relevant. Sorption behaviour of n-hexane vapour in a commercial propylene-ethylene elastomer (V8880 VistamaxxTM from ExxonMobil) is addressed here, determining experimentally the sorption isotherms at temperatures ranging from 115 to 140 °C and pressure values of n-hexane vapour up to 1 atm. Sorption isotherms have been interpreted with the Non-Random-Hydrogen-Bonding Equation of State model retrieving, from data fitting, the value of the binary interaction parameter for the n-hexane/V8880 system. Both the case of temperature-independent and of temperature-dependent binary interaction parameter have been considered. Sorption kinetics was also investigated at different pressures and has been interpreted using a Fick's model determining values of the mutual diffusivity as a function of temperature and of n-hexane/V8880 mixture composition. From these values, n-hexane intra-diffusion coefficient has been calculated interpreting its dependence on mixture concentration and temperature by a semi-empiric model based on free volume arguments.

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1. Introduction

The advancements of metallocene catalyst technology have accelerated the growth and development of polyolefin elastomers (POE) with a finely controlled structure-property characteristics [1]. These elastomers, belonging to the broader class of thermoplastic elastomers (TPE), have been increasingly in use due to their superior mechanical and thermal properties, versatility of use and recyclability [2]. Solution polymerization is one of the key processes to produce polypropylene (PP) based elastomers. The production of propylene-based polyolefins with a variety of properties has continuously grown, since the discovery of Ziegler-Natta catalysts, boosted by a rapid development of catalyst technology combined with polymerization process innovation. Among them, a relevant class is that of propylene-ethylene copolymers, that are semi-crystalline performance polymers with tunable amorphous content, mechanical and optical properties. They are economical, recyclable and can be designed for a specific application (e.g. adhesives, packaging etc.). In view of its industrial relevance, we address here the case of the polymer-solvent system made of propylene-ethylene-based POE and hexane, that is of interest for processing of these POEs.

Understanding thermodynamics of mixtures of long-chain molecules with short, non-polar hydrocarbon molecules, requires sophisticated experiments to provide high quality data and reliable thermodynamic models to explain the complex non-ideal behaviour. Sorption thermodynamics has been the centre of research for many decades, aimed at describing phase equilibria of polyolefins with several small molecules, involved in different polymer processing applications. However, most of the experimental results and theoretical approaches reported in the literature for polyolefin elastomers are restricted to the study of the solubility and transport of gases [3], while investigations focused on sorption of vapours, particularly vapours of alkanes, are quite a few [4].

From a practical viewpoint, the accurate knowledge of the thermodynamics of such polymer-solvent mixtures can be extremely beneficial to optimally model and design polymer plants, control stream compositions going into upstream units and importantly, abide the strict measures on final product quality, thereby creating a significant industrial impact. Furthermore, such analysis can be extended to systems with similar characteristics, providing support to the ongoing research and contribute to the innovation in the field of polymer processing [5, 6].

Elaboration of models for the thermodynamics of polymer containing mixtures, adequate for system description over a wide range of pressure and temperature conditions, is still an active and fascinating research area. To this end, a large number of thermodynamic approaches based on statistical thermodynamics have been built rooted on the lattice models developed by Guggenheim [7] and Flory [8] for complex fluids, including polymers. A relevant example is the lattice fluid (LF) theory of Sanchez and Lacombe (SL) [9-11], successfully adopted to deal with polymer solutions starting from 1976. Since then, other models, still based on a lattice fluid framework, were introduced with improved performances in terms of explicit account of the non-random distribution of molecular species and free volume, as well as of presence of strong specific interactions possibly established between neighbouring molecules, such as hydrogen bonding [12-16]. SL and the following improved LF approaches provide both an expression for the Equation of State of pure fluids and mixtures as well as for the chemical potentials of the components of a mixture and can be applied to fluids over an extended range of external conditions, encompassing liquids, vapors, gases, supercritical fluids, amorphous and glassy polymers, homogeneous as well as inhomogeneous systems, complex aqueous systems, associated polymer mixtures, rubbers, and gels. A relatively recent development of this kind is the Non-Random-Hydrogen-Bonding model (NRHB) proposed by Panayiotou et al. [15, 16], a compressible lattice fluid Equation of State (EoS) theory that, besides the mean-field interactions, accounts also both for the presence of specific interactions (e.g., hydrogen bonding, Lewis acid/Lewis base interactions) and for non-random distribution of components and of free volume in pure compounds [15] as well as in their mixtures [16].

In the present contribution we address the case of n-hexane sorption in a commercial POE made of isotactic propylene repeating units with random ethylene distribution, produced by ExxonMobil under the trade name Vistamaxx 8880 (V8880). Sorption isotherms of n-hexane vapor at several temperatures have been determined by gravimetry and data were interpreted using the NRHB model without the terms accounting for specific interactions, that have been assumed to be absent in view of the chemical structure of the polymer (polyolefin) and of the penetrant (n-hexane). Parameters of NRHB model for the pure components were determined by fitting with the model respectively the experimental PVT behavior of the polymer and the density and vapor pressure data at vapor-liquid equilibrium available in the literature for n-hexane. Experimental sorption isotherms were then fitted through the NRHB model to retrieve the value of the binary interaction parameter for the V8880-n-hexane mixture. Mass transport properties were also investigated determining experimentally the mutual diffusivity of the V8880/n-hexane system at several temperatures and concentrations. From these values, applying a model based on free-volume arguments, was estimated the n-hexane intra-diffusion coefficient in V8880, whose dependence on temperature and mixture composition was interpreted using a semi-empirical model.

2. Theoretical background

2.1. *Modeling sorption thermodynamics by NRHB approach*

An evolution of classical compressible LF theories used to describe the thermodynamics of amorphous rubbery polymer-penetrant mixtures, consisted in introducing modifications to the SL theory by accounting for the for non-random distribution of components and of free volume and for the presence of specific interactions between neighboring molecules. The non-random hydrogen-bonding theory (NRHB) is a model belonging to this class of approaches [15-19]. In the present context, in view of the absence of hydrogen bonding and other specific interactions in the system under investigation, the contribution related to specific interactions has been omitted in the description of the model equations. Moreover, we address here only the specific case of a binary system made of a polymer and a low molecular weight penetrant.

When the NRHB model is used to describe the thermodynamic behavior of a pure component displaying no hydrogen bonding, only three characteristic scaling parameters are needed, i.e., $v^*_{i,sp,0}$, $\varepsilon^*_{i,h}$ and $\varepsilon^*_{i,s}$. The first one, $v^*_{i,sp,0}$, is needed to calculate the specific closed packed specific volume of component *i*, $v^*_{sp,i}$, according to the following equation [20]:

$$v^*_{i,sp} = v^*_{i,sp,0} + \left(T - 298.15\right) v^*_{sp,1}, \tag{1}$$

where $v^*_{sp,1}$ is a constant for a given homologous series [21-27] and it is set equal to $-0.412 \cdot 10^{-3}$ $cm^3 \cdot g^{-1} \cdot K^{-1}$ for non-aromatic hydrocarbons, $-0.310 \cdot 10^{-3}$ $cm^3 \cdot g^{-1} \cdot K^{-1}$ for alcohols, $-0.240 \cdot 10^{-3}$ $cm^3 \cdot g^{-1} \cdot K^{-1}$ for acetates, $-0.300 \cdot 10^{-3}$ $cm^3 \cdot g^{-1} \cdot K^{-1}$ for water and $0.150 \cdot 10^{-3}$ $cm^3 \cdot g^{-1} \cdot K^{-1}$ for all the other fluids [26, 27]. Finally, T represents the temperature (expressed in Kelvin).

In the case of a polymeric compound, equation (1) is modified so that it takes also into account for the pressure dependence, becoming:

$$v^*_{i,sp} = v^*_{i,sp,0} + \left(T - 298.15\right) v^*_{sp,1} - 0.135 \cdot 10^{-3} P \tag{1a}$$

where P represents the pressure (expressed in this equation in MPa).

The other two energy parameters, $\varepsilon^*_{i,h}$ and $\varepsilon^*_{i,s}$, which represent, respectively, the enthalpic and entropic terms, are needed to calculate the average mean field interaction energy per molecule of component *i*, ε^*_i, that is expressed as [15]:

$$\varepsilon^*_i = \varepsilon^*_{i,h} + \left(T - 298.15\right) \varepsilon^*_{i,s} \tag{2}$$

Notably, the volume occupied by a cell of a molecule of species *i*, v^*_i, is assumed to take the universal value of $9.75/N_{AV}$ cm³/molecule, with N_{AV} representing the Avogadro number. Consistently, in the case of a mixture, the molar volume of lattice cells, indicated as v^*, takes the same value, independently of concentration. From this set of parameters, the number of lattice cells occupied by one molecule of species *i*, r_i, can be calculated [16, 20] using the following expression:

$$r_i = \frac{M_{w,i} v^*_{i,sp}}{v^*_i} \tag{3}$$

where M_{wi} is the molecular weight of component *i*.

The values of the three model parameters for the pure component *i*, i.e., $v^*_{i,sp,0}$, $\varepsilon^*_{i,h}$ and $\varepsilon^*_{i,s}$, are generally retrieved from vapor pressure and/or volumetric properties for the case of a pure component with a low molecular weight while, in the case of a polymer, are retrieved from PVT data in the melt state.

An additive parameter is the so-called molecular shape factor s_i, defined as the ratio between the number of lattice external contacts per molecule of component *i*, q_i, and r_i.

This parameter can be either evaluated using the UNIFAC group contribution model [28] or can be retrieved from fitting procedures of experimental data along with the three characteristics scaling parameters. In section 6.1 is reported the procedure to estimate these four parameters for the case of n-hexane and of the V8880 polymer.

Model equations, for pure components are expressed in terms of dimensionless reduced variables, i.e., reduced temperature, $\tilde{T}_i$ reduced pressure $\tilde{P}_i$ and reduced density $\tilde{\rho}_i$:

$$\tilde{T}_i = \frac{T}{T_i^*};\ \tilde{P}_i = \frac{P}{P_i^*};\ \tilde{\rho}_i = \frac{\rho}{\rho_i^*} = \frac{1}{\tilde{v}_i} \tag{4}$$

The corresponding normalizing factors for the temperature T, pressure P and density ρ, i.e., T^*, P^* and ρ^*, are interrelated via the following expressions [15]:

$$\rho_i^* = \frac{M_{w,i}}{r_i v^*} \tag{5}$$

$$\varepsilon_i^* = kT_i^* = P_i^* v^* \tag{6}$$

where k is the Boltzmann constant.

In the following, we will indicate with subscript '1' the quantities referred to the low molecular weight penetrant and with subscript '2 'those related to the polymer. For the case of a binary mixture of components '1' and '2' the average mean field interaction energy per molecule, ε^*, is obtained through the following mixing rule:

$$\varepsilon^* = \theta_1^2 \varepsilon_1^* + 2\theta_1\theta_2\varepsilon_{12}^* + \theta_2^2\varepsilon_2^* \tag{7}$$

where θ_1 and θ_2 are the so-called surface contact fractions [16] which depend on concentration and

$$\varepsilon_{12}^* = \left(1 - k_{12}\right)\sqrt{\varepsilon_1^* \varepsilon_1^*} \tag{8}$$

where the *binary interaction parameter*, k_{12}, measures the departure of mean field interaction energy from the value provided by the geometric mixing rule. Analogously, in a binary mixture, parameters r and q are calculated using the following simple mixing rules:

$$r = r_1 x_1 + r_2 x_2 \tag{9}$$

$$q = q_1 x_1 + q_2 x_2 \tag{10}$$

and so

$$s = {}^{q}\!/_{r} \tag{11}$$

where x_i is the molar fraction of component i.

As for pure components, also for a binary mixture, dimensionless reduced variables, i.e., reduced temperature $\tilde{T}$, reduced pressure $\tilde{P}$ and reduced density $\tilde{\rho}$ [16], can be defined as follows:

$$\tilde{T} = \frac{T}{T^*} = \frac{kT}{\varepsilon^*} \tag{12}$$

$$\tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{kT^*} \tag{13}$$

$$\tilde{\rho}=\frac{1}{\tilde{v}}=\frac{Nrv^*}{V} \tag{14}$$

where V is the volume of the mixture and N is the total number of molecules in the mixture. It is worth noting that, also in the case of a mixture, v^* is assumed to take the universal value of 9.75/N_{AV} cm^3/molecule.

The NRHB model provides expressions for the EoS of both the pure components and their mixtures, that take the same form in terms of reduced variables [15, 16]:

$$\tilde{P}+\tilde{T}\left[\ln\left(1-\tilde{\rho}\right)-\tilde{\rho}\left(\sum_i \varphi_i \frac{l_i}{r_i}\right)-\frac{z}{2}\ln\left(1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right)+\frac{z}{2}\ln\Gamma_{00}\right]=0 \tag{15}$$

where $l_i=\left(z/2\right)\left(r_i-q_i\right)-\left(r_i-1\right)$ and z is the coordination number of the lattice in which the molecules are assumed to be arranged, φ_i represents the "close packed" volumetric fraction of species i, and q, defined by eq.(10), represents the average number of lattice contacts per molecule in the mixture. In the NRHB model, the state variables Γ_{ij}, represent the multiplicative corrective factors accounting for the non-randomness of contacts among molecular sites of species j and molecular sites of species i within the lattice (i,j = 0,1,2; in particular, index equal to 0 stands for the empty cells of lattice). Their values can be obtained by solving a set of equations, obtained by minimizing Gibbs free energy as a function of number of different kinds of lattice fluid contacts and by imposing material balance expressions for the lattice fluid contacts [15, 16]. In particular, Γ_{00} accounts for non-random distribution of free volume.

Occurrence of phase equilibrium between a binary polymer-penetrant mixture and the pure penetrant in a vapour or liquid state implies the equality of the chemical potentials of the penetrant in the two coexisting phases:

$$\mu_1^V=\mu_1^P \tag{16}$$

where μ_1^V represents the molar chemical potential of penetrant in the pure vapor/liquid phase while μ_1^P represents that in the polymer-penetrant mixture. In the case of high molecular weight polymers, as is the case at hand, it is assumed that macromolecules are insoluble in the pure penetrant vapor phase in contact with it. As a consequence no expression equating the chemical potentials of the polymer in the two phases at equilibrium is imposed and only eq. (16) rules the phase equilibrium. In the case of the NRHB model applied to a binary mixture not displaying specific interactions, the expression of the chemical potential of the penetrant within the polymer-penetrant phase takes the following form:

$$\begin{aligned}\frac{\mu_1^P}{RT}=&\ln\frac{\varphi_1}{\omega_1 r_1}-r_1\sum_{j=1}^{2}\frac{\varphi_j l_j}{r_j}+\ln\tilde{\rho}+r_1\left(\tilde{v}-1\right)\ln\left(1-\tilde{\rho}\right)-\frac{z}{2}r_1\left(\tilde{v}-1+\frac{q_1}{r_1}\right)\ln\left(1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right)+\\&\frac{zq_1}{2}\left[\ln\Gamma_{11}+\frac{r_1}{q_1}\left(\tilde{v}-1\right)\ln\Gamma_{00}\right]+r_1\frac{\tilde{P}\tilde{v}}{\tilde{T}}-\frac{q_1}{\tilde{T}}\end{aligned} \tag{17}$$

where R represents the universal constant of gases and, ω_i represents a characteristic quantity that accounts for the flexibility and symmetry of molecule of kind i, and it is defined in ref. [14, 15]. This expression must be coupled with the EoS reported before (eq. 15).

The expressions of the EoS and of the chemical potential for pure penetrant in the vapor or liquid state can be obtained respectively from equations (15) and (17) by setting φ_1 = 1 and the number of components in the summation equal to 1.

The NRHB model described above is suitable to deal with the sorption thermodynamics of low molecular weight penetrants in amorphous rubbery polymers. This theoretical approach has been considered to be the proper choice for the interpretation of sorption isotherms of n-hexane in V8880 since tests have been performed at a temperature of 115°C and higher, at which the polymer can be safely assumed to be amorphous in view of the melting temperature of the neat polymer, 97°C (see Table 1), and of the fact that absorbed n-hexane is expected to promote a decrease of the melting temperature below this value [8].

2.2. Modeling diffusive mass transport of n-hexane

Mass transport of low molecular weight compounds in rubbery polymers is generally ruled by the so-called Fickian constitutive law for diffusion (see the classical reference [29]). In fact, diffusion of gases in rubbery polymers (e.g., oxygen in polyolefins) can be described by a mass balance where the mass diffusive flux is expressed by the Fick's law with a binary (mutual) diffusivity independent of concentration of penetrant. This is the so-called 'Ideal Fickian' behaviour. In the cases of diffusion of vapors in rubbery polymers, still a Fickian constitutive expression could be used to express the mass flux, but, in general, a concentration dependent binary (mutual) diffusion coefficient is needed. This is the so-called 'non-Ideal Fickian' behaviour. In this case the dependence of diffusivity on concentration should be known to interpret sorption kinetics. A way to circumvent this difficulty is to consider sorption step experiments in which a relatively small increment of pressure of vapor is imposed at each step, so that a relatively small change in concentration occurs inside the polymer sample during the sorption experiment. In such a case, the diffusivity can be assumed to take a roughly constant value (i.e., an average value in the range of concentration established within the sample during the sorption step). Additionally, it is to be considered that, if the concentration of penetrant is rather high (in general above 10%), beside the mutual diffusion contribution to the mass flux, one should also consider a mass convection contribution related to the average bulk movement of the polymer-penetrant mixture as a result of interpenetration of the components.

In the case at hand, we have interpreted sorption kinetics data assuming a 'non-Ideal Fickian' behaviour. Since each sorption step was accompanied by a relatively small pressure (and, consequently, small concentration) increase, each sorption step was interpreted using the classical solution of the differential mass balance provided by a 'Ideal Fickian' constitutive expression for mass flux [30]. Obviously, since diffusivity is expected to have some degree of dependence on concentration, one also expects to determine different values of diffusivity at each step. The determined value of binary (mutual) diffusivity can be assumed to be associated to the average value of concentration of n-hexane present within the sample (i.e. the average between the initial and final values of concentration of the step considered). In addition, in view of the relatively small values of n-hexane concentration (mass fraction values < 0.1, i.e., percentage <10%), no mass convection (bulk flow) contribution has been considered in the constitutive expression for n-hexane flux.

In the case of an 'Ideal Fickian' behaviour, experimental sorption kinetics at each pressure step can be expressed for a plane sheet at a uniform initial concentration of n-hexane and equal surface concentrations, by [30]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right] \tag{18}$$

where M_t denotes the total amount of diffusing substance which has entered the sheet at time t, M_∞ is the corresponding quantity after infinite time (i.e., at equilibrium) and $2l$ is the sheet thickness. The mutual binary diffusion coefficient D, that is the fitting parameter, is characteristic of the polymer-penetrant couple considered. It is worth noting that, in view of the geometry adopted in this investigation for the sample, that is placed in a molten state in a cylindrical pan, we can consider that we are testing a plane sheet with only one surface exposed to the penetrant vapor, the other being adherent to the surface of the pan. As a consequence, in using eq. 18, the adopted value of $2l$ is actually twice the real sheet thickness.

To gather information on the intrinsic mobility of each component, one should consider the '*intra*-diffusion' coefficient of each of the two components. In fact, the intrinsic mobility of n-hexane in the polymer-penetrant mixture is represented by the n-hexane *intra*-diffusion coefficient (indicated as D_1 in the present context), that reflects the mobility of n-hexane molecules in the absence of any driving force, in particular that exerted by the gradient of chemical potential. Sometimes this coefficient is also reported as *self*-diffusion coefficient [31] although this term is more appropriate with reference to the case of a pure component (i.e. self-diffusivity of pure n-hexane or of pure polymer, representing the intrinsic mobility of the molecules of a component in a pure state). The *intra*-diffusion coefficient of a penetrant tends to the value of the penetrant *self*-diffusion coefficient as its mass fraction in the mixture tends to 1. The same is true for the polymer, i.e. the *intra*-diffusion coefficient of polymer (indicated as D_2 in the present context) tends to the value of the polymer *self*-diffusion coefficient as the mass fraction of polymer in the mixture tends to 1. While the mutual diffusivity is simple to measure, the *intra*-diffusion (or *self*-diffusion) coefficient is more complex to evaluate experimentally. There are theories, however (as, for example the free volume theory [32, 33]), providing theoretical or semi-empirical expressions for the *intra*-diffusion coefficients. Then, if some simplifying assumption is taken as appropriate, i.e., the penetrant-polymer molecular friction coefficient is the geometric average of the penetrant-penetrant and polymer-polymer molecular friction coefficients [32, 33], one can express the mutual diffusivity in terms of the *intra*-diffusion coefficients of the components of the mixture. In the case of low concentration of the penetrant, a further simplification can be adopted, and D can be expressed only in terms of D_1 [32, 33] (see the following eq. 19).

Based on these premises, we can relate the n-hexane-V8880 mutual diffusion coefficient, D, to the n-hexane *intra*-diffusion coefficient, D_1, according to the following 'free volume theory' expression [32, 33]:

$$D = \frac{D_1 \cdot \rho_2 \cdot \hat{V}_2 \cdot \rho_1}{RT}\left(\frac{\partial \mu_1}{\partial \rho_1}\right)_{T,P} \tag{19}$$

where $\hat{V}_2$ represents the partial specific volume of the polymer, ρ_1 and ρ_2 represent, respectively, the density of n-hexane and of polymer (expressed in grams of n-hexane or polymer per unit volume of polymer-penetrant mixture) and μ_1 represents the equilibrium molar chemical potential of n-hexane within the mixture at the given conditions. The values of $\hat{V}_2$ and of $\left(\partial \mu_1 / \partial \rho_1\right)_{T,P}$ can be evaluated numerically using the NRHB model for mixtures.

3. Materials and Methods

3.1. Materials

The investigated polymer is a commercial semicrystalline polyolefin elastomer (POE) made of isotactic propylene repeating units with random ethylene distribution, produced by ExxonMobil under the trade name Vistamaxx™ 8880. Its physical properties, available from the data sheet provided by the producer [34], are summarized in Table 1. A reagent-grade n-hexane with a purity ≥ 99% was purchased from Sigma Aldrich, Milano, Italy.

Table 1. Physical properties of Vistamaxx™ 8880 [34]

Density [g/cm³]	Glass transition temperature [°C]	Melting temperature [°C]
0.879	-22	97

3.2. Dilatometry

Specific volume of the V8880 elastomer, at equilibrium conditions, has been measured as a function of temperature and pressure in the following ranges: 25-200°C, 10.0-200.0 MPa, to be used for the determination of NRHB model [15] parameters. The apparatus used to this purpose was a high-pressure dilatometer by GNOMIX (Gnomix Inc., Boulder, CO USA - see scheme of the apparatus reported in Figure 1). As received polymer granules, ca. 1g, were included in a nickel cup and in the sample compartment of the cell to be subjected to isothermal tests with pressure step increase of 10.0 MPa and with 20s waiting time before each measurement.

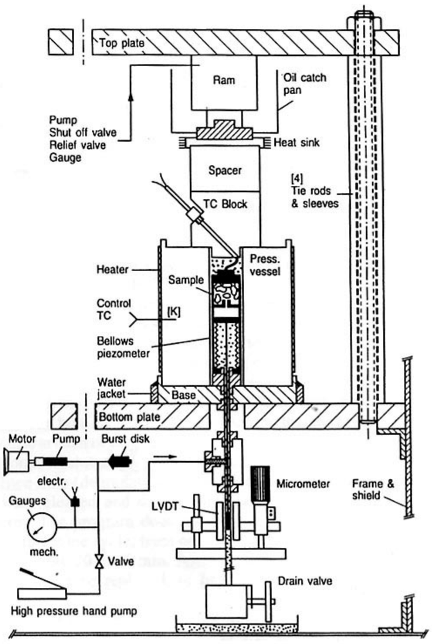


Figure 1. Schematic representation of GNOMIX high pressure dilatometer.

Since the GNOMIX equipment determines only volume changes, a reference absolute density measurement is required at known temperature and pressure conditions. To this aim, a Helium Pycnometer (AccuPyc II 1340, Micromeritics - Alfatest, Italy) was utilized to detrmine the density of the polymer at T = 25°C and at P = 0.1 MPa.

3.2. Gravimetric sorption tests

Vapour sorption experiments of n-hexane in V8880 were performed using a controlled atmosphere McBain micro-balance (see Figure 2), consisting in a quartz spring made of two counter-rotating elements (Ruska Instrument Co., Houston, Texas) located in a jacketed thermostated glass measuring cell . The weight increase of the polymer sample exposed to n-hexane vapor was determined from the measurement of the elongation of a quartz spring at which the sample was hanged. Sample was placed in a cylindrical pan that was suspended to the terminal hook of the spring. The thickness of the sample has been calculated from density data on the basis of the geometrical dimensions of the adopted cylindrical sample pan.

Service lines connect the thermostated measuring cell (accuracy of temperature control of the cell environment ±0.05°C) to a flask, to a pressure transducer (MKS Baratron 121A, with a full-scale of 1000 mbar, a sensitivity of 0.1 Torr, an accuracy of 0.1% of the reading) to the liquid pure n-hexane reservoir, to a turbomolecular vacuum pump and to the exhaust line. The spring was calibrated at three temperatures in the range 110-140°C, to account also for the possible drift of the calibration constant with temperature. The adopted spring had a nominal elongation of 400 mm for 50 mg (with a sensitivity of $1.25 \cdot 10^{-4}$ mg/μm).

Spring elongation was continuously acquired using a travelling camera, with a microscope objective, that was fixed to a high accuracy motorized translation stage (V-817 by Physik Instrumente Karlsruhe, Germany) that was computer controlled, with a positioning accuracy of ± 2.5 µm. The measuring system, considering the characteristics of the adopted quartz spring and the accuracy of the translational stage, featured a minimum detectable weight change equal to $3.12 \cdot 10^{-4}$ mg. The video signal from the camera was continuously acquired and stored at prescribed time intervals in a computer. The whole measuring system (camera, moving stage) was controlled using a *Labview®* acquisition software by National Instruments, Austin (TX).

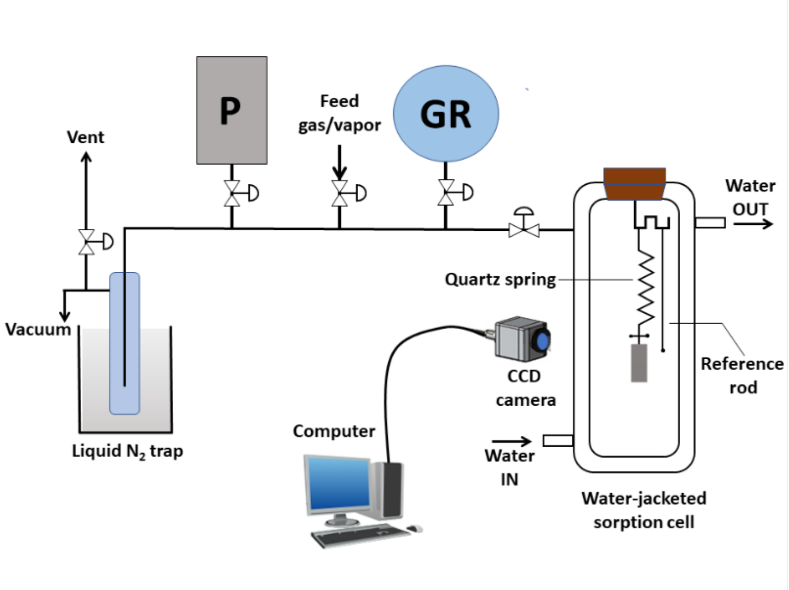


Figure 2. Schematic representation of a McBain quartz spring sorption apparatus. The polymer sample hangs from the quartz spring located in the sorption chamber. (P: pressure transducer; GR: gas/vapor reservoir). Reprinted with permission from [20]. Copyright 2019 Elsevier B.V.

Vapour sorption experiments were performed at 115, 122, 130 and 140 °C, at the pressure values of n-hexane vapor reported in Table 2. The determination of each sorption isotherm was repeated three times. As already mentioned, in this temperature range the polymer is above its melting temperature.

Table 2. Operating pressures [mbar] at the four different temperatures investigated.

T=115 °C	T=122 °C	T=130 °C	T=140 °C
20	80	80	201
79	254	156	597
151	536	251	1058
297	774	414	
405	1047	662	
576		1045	
1001			

As an example of a typical sorption run, it is reported in Figure 3 the sorption step performed from 576 mbar to 1001 mbar at 115°C. The experiment start is at the instant of time at which n-hexane vapor enters the measuring cell. The displacement of the quartz spring end (where the sample is placed inside a quartz pan) is then followed as a function of time and recorded until the sorption equilibrium is attained. A time-independent equilibrium state is assumed to have been attained when the constant asymptotic value was maintained for a time that was at least twice the time needed to reach that value for the first time. In Figure 3 the entire experiment lasts about 5600 s, the time needed to reach the constant spring displacement being about 1800 s and the time waited at the plateau value about 3800 s.

From the spring displacement it was retrieved the increase of sample weight (corresponding to the weight of sorbed n-hexane) by using the spring weight/displacement calibration constant. The weight increase was then transformed in mass fraction of n-hexane absorbed in the polymer-n-hexane mixture (i.e. grams of n-hexane per gram of mixture). Buoyancy effects exerted by the n-hexane vapour have been taken into account by calculating the thrust of the vapour from the weight registered using the spring balance. The thrust has been estimated, for each sorption kinetics test, by extrapolating the weight increase down to the starting time of each test. In addition, a remarkable, but physically sound, assumption that has been made is that no polymer is present in the vapor phase in view of the vanishingly small vapor pressure of the polymer.

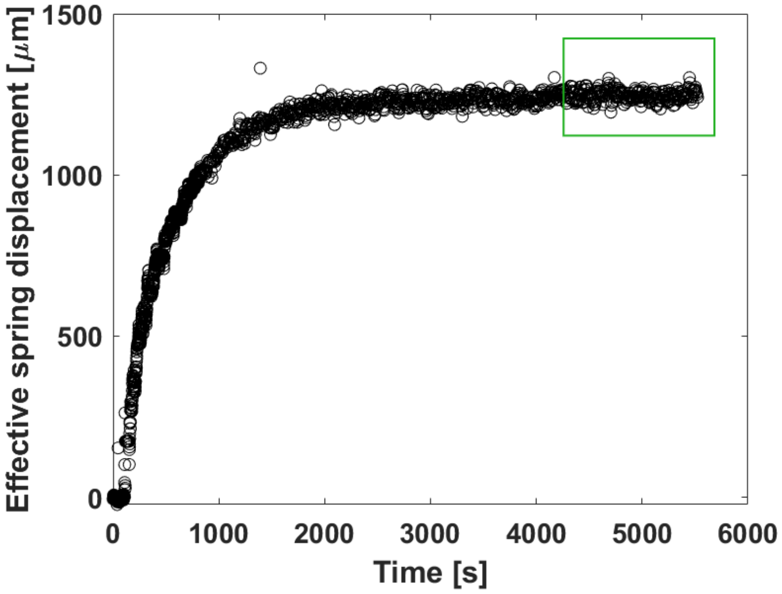


Figure 3. Effective spring displacement during the experiment performed from 575.6 mbar to 1001.2 mbar at 115°C. Equilibrium data are retrieved from the final constant displacement (relevant equilibrium data are highlighted by the green rectangle).

4. Results

4.1. Dilatometric (PVT) behaviour of the V8880 polymer

In Figure 4 are reported the outcomes of the experiments performed with the dilatometer in terms of density vs. pressure at different temperatures. The PVT data are reported in the pressure range 10 – 200 MPa and in the temperature range from 120 to 220 °C, since only data in this range have been used to retrieve the NRHB model parameters for pure V8880. Data fitting of PVT data was performed to determine the three scaling parameters of the model along with the molecular shape factor. Results of data fitting are also reported in Figure 4 and will be discussed in section 5.1.

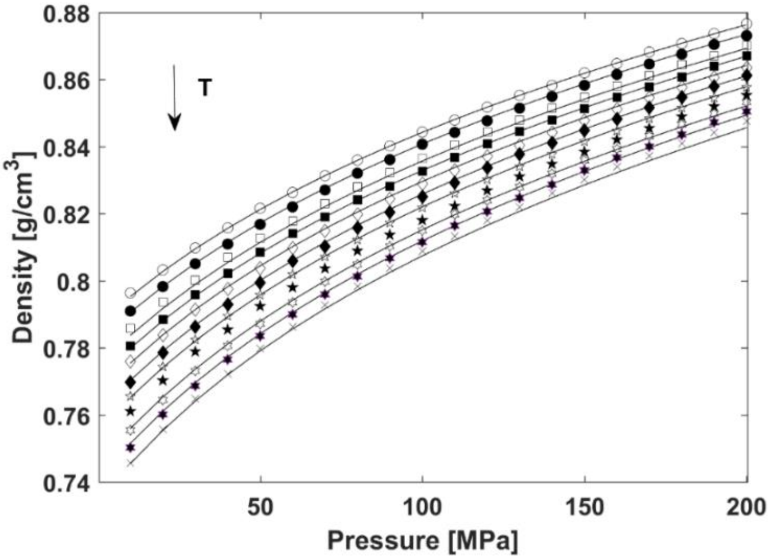
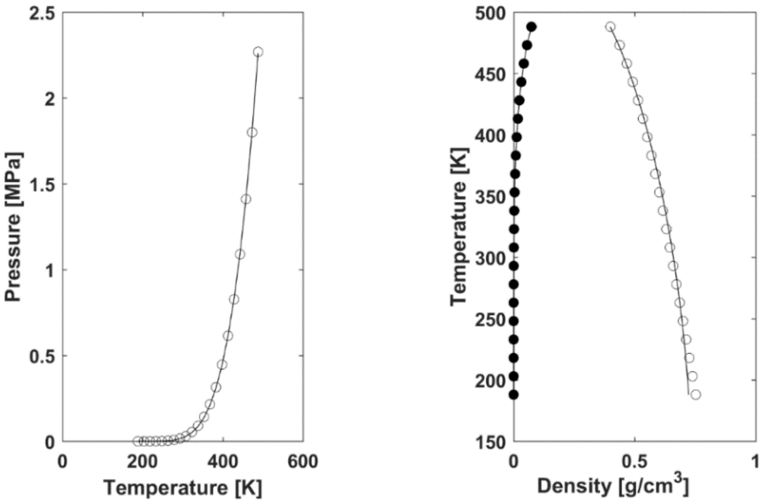


Figure 4. Density vs. pressure isothermal data for V8880. Lines represent the results of simultaneous best fitting of equilibrium dilatometric data using NRHB model. Temperature analyzed are, respectively, from top to bottom: 123.49 °C;132.42°C; 145.50 °C; 152.80°C; 161.31 °C;171.06°C; 180.96°C; 188.84°C; 198.91°C; 207.57°C; 219.39°C.

4.2. *Equilibrium data for ure n-hexane*

Vapour pressure and equilibrium density data at liquid-vapor equilibrium for n-hexane were retrieved from thermodynamics databases (available online at the NIST website: https://webbook.nist.gov/chemistry/, accessed on 2 december, 2020).

In figure 5a are reported the vapor pressure vs temperature data at vapor-liquid equilibrium conditions. In figure 5b are reported temperature vs equilibrium density data for the vapour phase (data on the left) and for the liquid phase (data on the right) at phase equilibrium. Data fitting of these equilibrium data was performed to determine the scaling parameters of NRHB model for pure n-hexane (see continuous lines in Figures 5a, 5b) as it will be discussed in section 5.1.



(**a**) (**b**)

Figure 5. n-hexane equilibrium data: (**a**) Vapour pressure data of n-hexane as a function of temperature; (**b**) temperature vs. density data for n-hexane at vapour-liquid equilibrium (black circles represent liquid density; white circles represent vapour density). Experimental

points were retrieved from 'https://webbook.nist.gov/chemistry/'. Results of simultaneous best fitting of data by using NRHB model are reported as continuous lines.

4.3. Sorption isotherms of n-hexane vapour in V8880

Experimental sorption tests of n-hexane vapour in V8880 have been performed at 115, 122, 130 and 140°C. At each temperature, vapour pressure of n-hexane has been increased stepwise collecting at each step sorption kinetics and the equilibrium sorption value. The range of pressure of pure n-hexane vapour was from 0 up to around 1 atm.

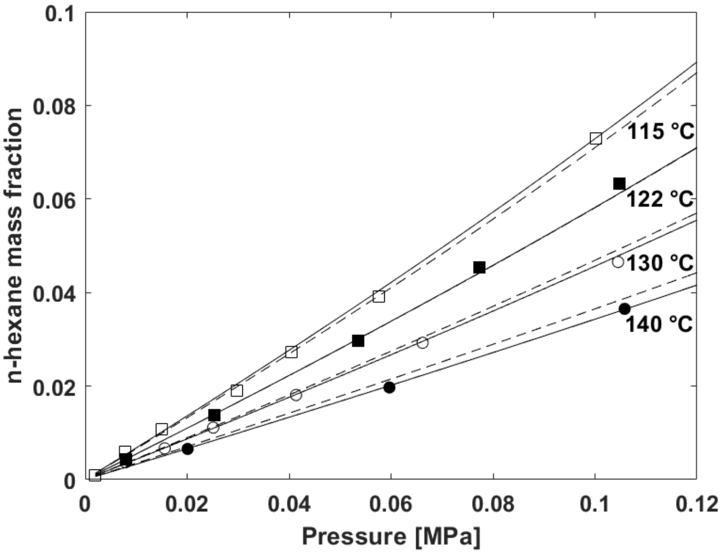


Figure 6. Experimental sorption isotherms of n-hexane vapor in V8880 at 115 °C (white squares), 122 °C (black squares), 130 °C (white circles) and 140 °C (black circles). Results of simultaneous best fitting of data by using NRHB model for mixtures [16] with a temperature-independent binary interaction parameter are reported as dotted lines (best fitting value of k_{12} =- 0.0754). Results of simultaneous best fitting of data by using NRHB model for mixtures [15] using a k_{12} linearly dependent on temperature are reported as continuous lines (best fitting values of the two parameters of eq. (23a) are $k_{12,a}$= - 0.1505 and $k_{12,b}$ =1.90·10^{-4} 1/K).

The results in terms of equilibrium sorption isotherms are reported in Figure 6. Data fitting by NRHB model for mixtures [16] applied to the n-hexane/V8880 system is also reported and will be discussed in section 5.2.

It is worth noting that three runs of 'step-increase of pressure' experiments have been performed at each temperature. After a run made of several steps of increase of pressure of n-hexane vapor a total desorption on n-hexane was performed followed by another set of steps of increase of pressure. The average value of these measurements are reported at each pressure. As expected for rubbery polymer-penetrant mixtures, no hysteresis effect was noticed and all the data of the three runs performed at each temperature accommodate on a single isotherm.

5. Discussion (Modelling)

5.1. Determination of NRHB model parameters for pure components

5.1.1. Fitting of PVT data of V8880 with NRHB EoS

According to the information available on the molecular structure of the polymer, no specific self-interactions are expected to establish among groups on the polymer chains, so that no parameters related to specific interactions need to be determined. The parameters determined by the best fitting procedure of the PVT behavior of pure polymer were only the three scaling parameters and the surface-to volume ratio, s. The fitting procedure performed by using the NRHB model has been applied exclusively to the data acquired above the melting temperature. The results of this procedure are reported in Figure 4 and the best fitting values of model parameters for pure V8880 are reported in Table 3. The molecular weight of the polymer has been assumed to be 80000 g/mol.

Table 3. NRHB parameters calculated by best fitting procedures.

Fluid	ε_h^* $[\mathrm{J \cdot mol^{-1}}]$	ε_s^* $[\mathrm{J \cdot mol^{-}1 \cdot K^{-1}}]$	$v_{sp,0}^*$ $[\mathrm{cm^3 \cdot g^{-1}}]$	s
n-hexane	3986.0	1.5009	1.2771	0.857[1]
V8880	4292.4	2.7679	1.1043	0.631

[1] Taken from [25]. This “surface-to-volume” ratio, *s*, has been estimated in ref. [25] by using the widely adopted UNIFAC group contribution model [28].

5.1.2. Fitting of n-hexane vapor pressure data and density data at vapour-liquid equilibrium.

The values of the three scaling parameters of the NRHB model for the case of pure n-hexane were retrieved by a fitting procedure of data on vapor-liquid equilibrium at several temperatures. Also, in this case, in view of the chemical structure of n-hexane, no specific interaction parameters have been used. The surface to volume ratio, s, in this case was taken from the literature (see Table 3 for details). Results of the best fitting procedure are reported in Figure 6 and the estimated values of model parameters are reported in Table 3.

5.2. Fitting of sorption isotherms

Once the NRHB parameters of the two pure compounds have been retrieved, the NRHB model for mixtures [16] has been implemented to interpret phase equilibrium between pure n-hexane vapor and binary n-hexane/V8880 mixtures. In view of the high molecular weight of the polymer molecules, the assumption that the polymer is not present in the external penetrant vapour phase has been adopted.

In view of the molecular structure of both polymer and n-hexane molecules, no cross hydrogen-bonding or other specific interactions between polymer and penetrant are expected, so that the modelling of the phase equilibrium has been performed disregarding any contribution from specific interactions (both self and cross interactions). So that the model accounts only for mean filed interactions and for non-randomicity of contacts.

To model sorption isotherms, besides the model parameters determined for pure V8880 and pure n-hexane, one additional parameter is still required, i.e. the polymer-penetrant mean field binary interaction parameter k_{12}, which measures the departure of the mean field interaction energy of the binary mixture from the geometric mixing rule. This parameter is related to the couple of compounds involved in the binary mixture considered. In fact, based on the Lorentz–Berthelot combining rule for dispersive cross energy we have that [35]:

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_i \varepsilon_j} \tag{20}$$

Where ε_i and ε_j are the intersegmental interaction energies in the close-packed state for pure components ‘*i*’ and ‘*j*’, while ε_{ij} is the intersegmental interaction energy (cross-interaction energy) in the close-packed state for between a segment of a molecule of component ‘*i*’ and a segment of a molecule of component ‘*j*’ in a mixture. The interaction parameter k_{ij} is introduced to correct for the dispersion energies of unlike molecules. Other mixing rules have been proposed for asymmetric systems or in order to represent better the critical area. The value of the interaction parameter, k_{ij}, is typically retrieved from fitting of experimental sorption isotherms, as we have done in the case at hand. However, some theoretical insight is useful to understand its physical origin. In fact, for relatively simple systems (e.g., mixtures of hydrocarbons or gases with hydrocarbons) the interaction parameter can be estimated from the following equation, derived from the Hudson–McCoubrey theory assuming the validity of Lennard-Jones potential [35]:

$$k_{ij} = 1 - \left[2^7 \left(\frac{\left(I_i I_j\right)^{1/2}}{\left(I_i + I_j\right)} \right) \left(\frac{\sigma_i^3 \sigma_j^3}{\left(\sigma_i + \sigma_j\right)^6} \right) \right] \tag{21}$$

Here I_i and I_j are, respectively, the ionization potentials of compound '*i*' and compound '*j*', expressed in eV. σ_i and σ_j are the diameters of segments of, respectively, molecules of type '*i*' and of type '*j*'. The molecular-size diameters are expressed in Å. The Lennard-Jones value of the exponent in the attractive potential ($n = 6$) has been used in the previous equation. With some degree of approximation, equation (21) can be restated as:

$$k_{ij} = 1 - \left[2 \left(\frac{\left(I_i I_j\right)^{1/2}}{\left(I_i + I_j\right)} \right) \right] \tag{22}$$

Different expressions are obtained in the case of different interaction potentials. Based on these theoretical arguments, one would expect a limited temperature dependence of k_{ij} and a stronger dependence on density (i.e. on mixture concentration). In the literature [36] it is reported that it is important to assume the binary interaction parameter to be at least linearly dependent on temperature to correlate liquid-liquid equilibria for polymers:

$$k_{ij}\left(T\right) = k_{ij,a} + k_{ij,b} T \tag{23}$$

In the following we will interpret experimental sorption isotherms using two approaches:

i) using a temperature independent k_{12} ('athermal' assumption), whose value is obtained by a concurrent fitting of all the four experimental isotherms;

ii) using of a k_{12} that is linearly dependent on temperature, whose value is again obtained by a concurrent fitting of all the four experimental isotherms.

- Using a temperature independent binary interaction parameter

- Using a temperature independent binary interaction parameter;

The value of the temperature independent binary interaction parameter has been retrieved by performing a one parameter concurrent best fitting of the four isothermal data sets for n-hexane sorption in V8880. Based on the fitting procedure, whose results have been already reported in Figure 6, we obtained the value $k_{12} = -0.0754$.

- Using a temperature dependent binary interaction parameter;

The four experimental isotherms were interpreted using the NRHB model for mixtures [16] with a k_{12} assumed to be linearly dependent on temperature:

$$k_{12}\left(T\right) = k_{12,a} + k_{12,b} T \tag{23a}$$

From concurrent fitting of the four sorption isotherms (see Figure 6) we have obtained the following values for the two fitting parameters:

$k_{12,a} = -0.1505$

$k_{12,b} = 1.900 \cdot 10^{-4}$ 1/K

It is noted from Figure 6 that the fitting quality is evidently improved in the case of 130 and 140°C as compared to the case of a temperature independent binary interaction parameter.

Once the values of the interaction parameters have been retrieved by fitting the experimental sorption isotherms at 115, 122, 130 and 140°C, the NRHB model for mixtures with both the temperature independent and temperature dependent k_{12} values has been used to predict the sorption isotherms at 200 and 250°C up to 0.2 MPa (2 atm), which are the conditions of industrial interest, not accessible with the available experimental apparatus. In Figure 7 it is reported the comparison of the model predictions for n-hexane solubility isotherms at T=200°C and T=250°C, carried out respectively assuming k_{12} independent of T (i.e., 'athermal') and assuming k_{12} linearly dependent on T (i.e., 'linear'). The predicted values of n-hexane mass fraction obtained using a linearly dependent binary interaction parameter are lower, at both temperatures, than those predicted by using a temperature independent value.

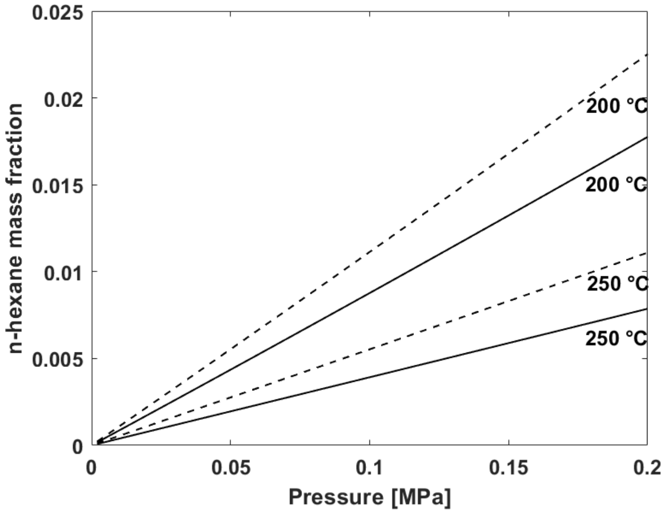


Figure 7. Comparison between the model prediction of n-hexane solubility isotherms in V8880 at T=200°C and T=250°C, carried out respectively assuming k12 independent on T ('athermal', dotted line) and k12 linearly dependent on T ('linear', solid line).

5.3. Modelling n-hexane diffusivity

5.3.1. Fitting sorption kinetics

An example of the results of best fitting of the experimental sorption kinetics data with eq. (18) is reported in Figure 8 for the pressure step from 405 to 576 mbar at 115 °C. It is evident how the sample clearly attains a time-independent equilibrium value in the time frame of the experiment. The very good quality of fitting indicates that the assumption of 'Ideal Fickian behavior' is well suited for the case at hand.

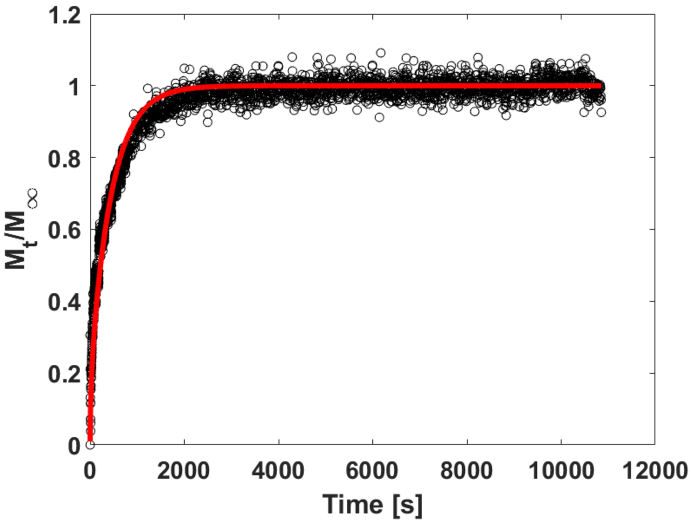


Figure 8. Fitting of sorption kinetics data of n-hexane for the pressure step from 405 to 576 mbar at 115 °C. Red continuous line is the result of data best fitting with eq. (18).

The same fitting method has been applied for every pressure step at all the temperatures. In Figure 9 are reported the calculated values of n-hexane-V8880 Fickian mutual diffusivity (determined at the four investigated temperatures by the fitting procedure of sorption kinetics curves) as a function the average mass fraction of n-hexane during each test.

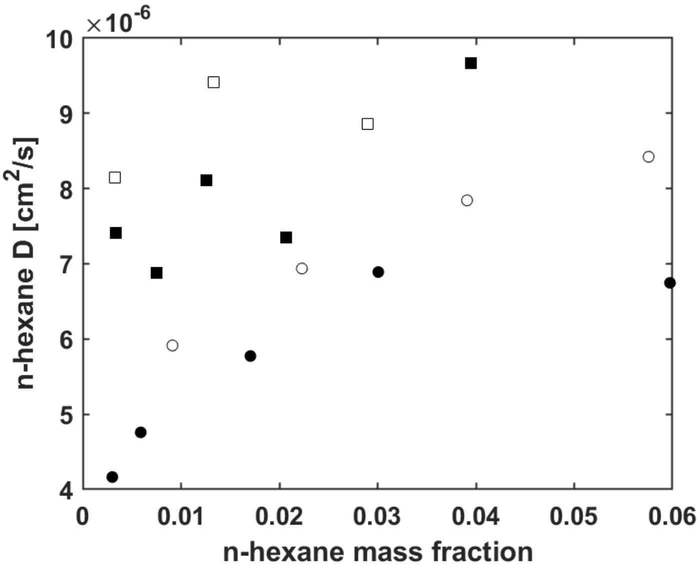


Figure 9. Values of n-hexane-V8880 mutual diffusivity as a function of n-hexane mass fraction in the polymer-penetrant mixture at the four investigated temperatures (115 °C (black circles), 122 °C (white circles), 130 °C (black squares) and 140 °C (white squares)).

The values of mutual diffusivity evaluated at each incremental pressure step has been associated to the average value of n-hexane concentration within the sample during the sorption test, expressed as mass fraction in the polymer-penetrant mixture (the average value of concentration has been calculated as the arithmetic average of the initial and final values of each pressure step). The values of D are affected by an error that is estimated to be around ± $2 \cdot 10^{-7}$ cm²/s.

5.3.1. Fitting sorption kinetics

Using eq. (19), values of D_1 can be readily obtained at the four investigated temperatures from the values of D and are reported in Figure 10. Based on the free volume theory of Duda and Vrentas [32, 33], the following semi-empirical expression, for the penetrant intra-diffusion coefficient can be obtained:

$$D_1 = D_{00} \cdot \exp\left(\frac{E_D}{T}\right) \cdot \exp\left(E_C \omega_1\right) \tag{24}$$

Note that, in formulating eq. (24), explicit account of the effects of pressure has been disregarded due to the low values of pressures investigated. Here D_{00}, E_D and E_C represent the model parameters, which can be retrieved by a concurrent regression of the available values of D_1 reported as a function of ω_1, that represents the n-hexane mass fraction. Results of this best fitting procedure performed on the calculated values of D_1 are reported in Figure 10. The optimized values of the parameters obtained are:

$D_{00} = 5.57 \cdot 10^{-2}$ [cm²/s]

$E_D = -3.653\ 10^3$ [K]

$E_C = 1.220$

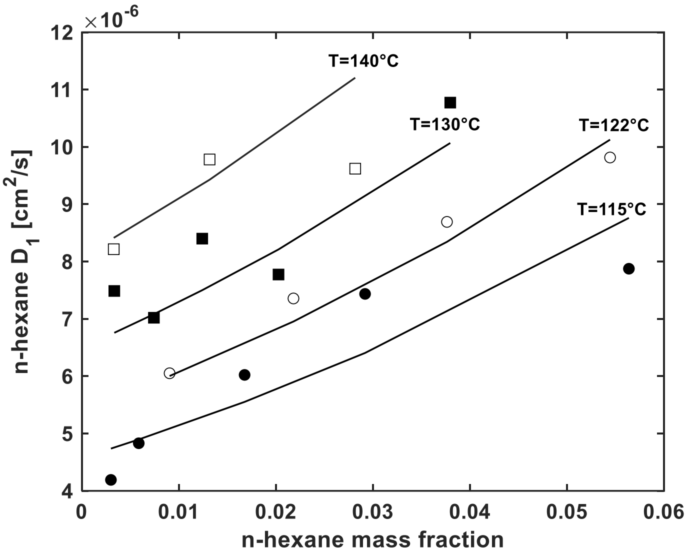


Figure 10. Values of D_1 vs. mass fraction of n-hexane (linear plot) at the four investigated temperatures (115 °C (black circles), 122 °C (white circles), 130 °C (black squares) and 140 °C (white squares)). Continuous lines represent best fitting of data by means of eq. (24).

6. Conclusions

This contribution is focused on the interpretation of mixture thermodynamics and mass transport properties of a POE/n-hexane system, that is of interest to tailor processing operations involving this class of thermoplastic elastomers. Attention has been focused on relatively high temperature conditions and on low hydrocarbon concentrations.

Sorption thermodynamics has been successfully interpreted using the NRHB model, disregarding the terms accounting for specific interactions, that are not expected to be present in the system at hand. An excellent concurrent fitting of n-hexane sorption isotherms at several temperatures has been obtained using a temperature dependent binary interaction parameter.

Mutual diffusivity of the POE/n-hexane mixture has been determined experimentally at several temperatures and compositions and has been interpreted using a semi-empirical model, based on free volume concepts, in terms of n-hexane intra-diffusion coefficient and of a thermodynamic contribution accounting for the composition dependence of n-hexane chemical potential.

The theoretical interpretation of both sorption thermodynamics and mass transport properties of the POE/n-hexane system enables the estimation of these properties also for values of temperature and mixture composition that are outside the experimental range of this investigation..

Author Contributions: Conceptualization, writing— original draft preparation, review and editing G.M.; software, G.S.; validation, N.A.; formal analysis, D.T., G.S. and E.dM.; data curation, L.L.. All authors have read and agreed to the published version of the manuscript.

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