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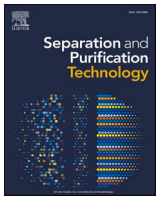

Modelling sorption thermodynamics of gases, vapors and gas mixtures in glassy polymers using a non-equilibrium version of PC-SAFT accounting for specific interactions and volume change

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ABSTRACT

Glassy polymers are among the materials of choice for membrane -based separations of gas and vapor mixtures. Sorption thermodynamics plays an important role in determining the separation performances of these materials. In this context, a general model which can deal with multicomponent sorption thermodynamics in glassy polymer/penetrants systems represents a theoretical challenge due to the possible complex interactional scenario characterized by the occurrence of cross and self- hydrogen bonds and/or by penetrant induced dilation of the glassy matrix. To this aim, the Dry Glassy Reference Perturbation Theory (DGRPT) framework has been implemented here, for the first time, in conjunction with the standard Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) model incorporating an association term that accounts for possible specific interactions. In particular, a modification of the standard DGRPT framework, based upon a self-consistent estimation of the free volume, is proposed to minimize the number of adjustable parameters of the DGRPT-PC-SAFT model.

In the present contribution we first validate the theoretical approach by addressing the modelling of sorption thermodynamics of Poly(1-trimethylsilyl-1-propyne) (PTMSP), a high glass transition temperature polymer, with the aim of elucidating the solubility data of CO_2/CH_4 binary gas mixtures at high pressure, available in literature. In addition, the capability of the model to predict penetrant induced dilation has been tested against literature volumetric data of PTMSP/ CH_3OH and PTMSP/DMC binary mixtures.

Then, the case of polyimides, a class of materials of interest for applications in the field of dehydration of alcohols and separation of polar/non-polar azeotropic mixtures, is considered. In this case, the theoretical approach has been used to interpret not only the overall sorption thermodynamics but also to provide quantitative predictions of different populations of interacting penetrant sorbed into the polymers. Experimental outcomes of in situ FT-IR, previously obtained by our research group for two binary polyimides/CH_3OH systems of technological interest, have been analyzed: polyetherimide (PEI)/CH_3OH and 6FDA-ODA/CH_3OH. The proposed case studies provide evidence for the efficacy of the DGRPT-PC-SAFT approach in describing the multicomponent sorption thermodynamics of gases mixtures at high pressures as well as of interacting vapor penetrants within amorphous glassy polymers.

1. Introduction

Polyimides and poly(1-trimethylsilyl-1-propyne) (PTMSP) represent materials of relevant interest for several applications ranging from membrane-based fluid separation processes to vapor barrier films for electronic devices. These materials exhibit high mechanical properties due to their high glass transition temperature and a remarkable chemical resistance up to elevated operative temperatures [1].

Glassy PTMSP shows one of the best performing capabilities in separation of CO_2/CH_4 and n-C_4/CH_4 mixtures [2]. In particular, since the

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diffusivity-selectivity for CO_2/CH_4 mixtures is close to unity, separation performances are essentially driven by the solubility of the penetrant in the glassy membrane [3]. On this respect, the modelling of the real solubility-selectivity behaviour within high free volume PTMSP represents a fundamental tool to properly design PTMSP membrane separation modules.

Also, the investigation of methanol sorption in polyimides [4–6] is of relevant interest since this class of materials finds application in natural gas separation [7–9], in the dehydration of alcohols and for removal of methanol from azeotropic mixtures containing organic compounds [10–13].

In view of self and cross hydrogen bonding, the detailed understanding of the interactional scenario occurring within a polymide/methanol mixture in a glassy state is fundamental to properly interpret the penetrant permeation properties [14,15] since interactions could modify the mechanical and mass transport properties as compared to the case of pure polymer [16–18]. To this regard, in our previous papers [19,20], we developed an experimental procedure based upon in-situ FTIR spectroscopy, which provides a clear quantitative picture of different kinds of interacting populations in the case of polyimides/water or polyimides/methanol systems.

Modelling sorption thermodynamics in glassy polymers is rather challenging since one should properly account for the non-equilibrium nature of the glassy state as well as for the possible occurrence of self- and cross-hydrogen bonding. An approach that successfully deals with the glassy nature of the polymer is the Non-Equilibrium Theory for Glassy Polymers (NETGP) proposed by Doghieri and Sarti [21,22] that it is rooted on the thermodynamics endowed with internal state variables [23,24]. It consists in the extension to the case of glassy systems of equilibrium models, based on Equations of State (EoS), originally developed to deal with sorption thermodynamics in rubbery polymers. To cope with systems displaying Hydrogen Bonding and other specific interactions, these equilibrium EoS models should also account for the association contributions. Statistical Associating Fluid Theory (SAFT) [25,26] is a class of EoS models characterized by a modular structure that can also include associative terms. In particular, the Perturbed-Chain SAFT (PC-SAFT) [27,28] model has been successfully employed to describe sorption thermodynamics in rubbery polymers in the presence of specific interactions [29–31].

The PC-SAFT model has been extended to interpret sorption thermodynamics in glassy polymers by using the NETGP procedure (NETGP-PC-SAFT theory) [32], that relies on the assumptions that the polymer mass density within the polymer/penetrant glassy mixture is kinetically locked at an out-of-equilibrium value and that the polymer is not soluble within the external penetrant phase. Under these assumptions, in the case of pure mean-field versions of EoS models, the pseudo – phase equilibrium established between the polymer/penetrant mixture and the penetrant(s) phase in contact with it is dictated by imposing, for each penetrant, the equality between the equilibrium chemical potential in the external penetrant phase and the non-equilibrium chemical potential within the glassy polymer phase provided in turn by the NETGP framework [21,22] (henceforth, this equality will be referred to as condition I). Notably, Sarti has further shown that the non-equilibrium expression for penetrant chemical potential is the same as the equilibrium one but calculated at the out-of-equilibrium value of the glassy polymer density within the mixture [21,22] (henceforth, this equality will be referred to as condition II). These results were proven, in the original NETGP formulation, in the case where only mean field interactions occur for which the sole internal state variable for the glassy mixture is the polymer mass density, that plays the role of an order parameter. If one considers the extension of equilibrium EoS models to account for specific interactions, beside the mean field ones, in general one must consider a higher number of internal state variables. This is the case of the NETGP extension of the equilibrium PC-SAFT model containing the associative term. Indeed, such an extension would require a re-examination of the NETGP procedure to demonstrate whether conditions I and II still hold.

The NETGP extension of the equilibrium PC-SAFT model containing the association term requires to consider additional internal state variables along with the corresponding expressions for their evolution kinetics. A way to cope with this complexity is by adopting an 'instantaneous equilibrium' (*IE*) hypothesis with reference to this additional set. In fact, this hypothesis remarkably simplifies the matter by considering that the associative interactions evolve with an instantaneous kinetics so that the associative contacts are assumed to be still provided by the related minimization conditions holding at equilibrium but evaluated in correspondence of the fixed non-equilibrium polymer density [33,34]. If this simplifying assumption is adopted, one has, however, to prove that in this case the two pseudo-equilibrium conditions (conditions I and II recalled above) still hold. In the SI file (see section S.1) we provide proof of that.

Indeed, Davis et al. [35] and Liu et al. [36] have already implemented the NETGP extension of the PC-SAFT containing the associative term to the aim of describing water sorption in a glassy PMMA matrix. The authors implicitly assumed the *IE* hypothesis for the association interactions variables but without demonstrating that conditions I and II were still applicable.

This *IE* hypothesis has been already successfully implemented by our group [15,34,37] in the NETGP extension of a lattice fluid EoS model accounting for Hydrogen Bonding, namely the Non-Random Hydrogen Bonding theory (NRHB) originally formulated by Panayiotou et al. [38,39].

More recently, Marshall et al. [40,41] used the NETGP protocol to extend to the non-equilibrium glassy state a simplified version of the PC-SAFT, again including specific interactions implicitly assuming the *IE* hypothesis. The relevant novelty consists in the fact that the method proposed by Marshall addresses also the swelling of polymeric matrix, occurring in the glassy state because of penetrant sorption, through a new thermodynamically self-consistent approach referred to as Dry Glass Reference Perturbation Theory (DGRPT). This approach, without introducing new parameters, realizes a significant improvement as compared to previous applications of the original NETGP theory in that the polymer density is neither assumed to be constant nor to be dictated by an empirical relationship [42–44] but is self-consistently provided by a series expansion around the polymer dry state of the polymer chemical potential calculated at actual penetrants concentration. The approach proposed by Marshall and its formal derivation is briefly described in section 2.

Penetrant induced swelling of the glassy polymer/penetrant mixture is generally observed in the case of sorption of light gases at high pressure, of vapors at high activities or of liquid compounds [1,45,46], so that the assumption that the polymer mass density within the mixture maintains the value that the pure polymer has right before the sorption test starts does not hold. Such volume dilation is commonly assumed to be an increasing function of penetrant composition at fixed pressure and temperature [1,42–46] and is considered to occur instantaneously as compared to the time scale of sorption kinetics in the glassy phase [47]. In this respect, Doghieri et al. [21] and Sarti et al. [22] inferred that the pseudo-equilibrium condition consisting in the equality of chemical potentials, rigorously obtained in the case of polymer matrix locked in a glassy state, is still valid but assuming now that at each sorption equilibrium condition the polymer density is fixed at the corresponding dilated value in the glassy mixture. Hence, any solubility calculation is formally brought back to the corresponding NETGP calculation performed in correspondence of such hypothetical fixed polymer mass density. Such operative assumption can be still implemented (under the *IE* hypothesis) also in the case of EoS models accounting for specific interactions. Indeed, this latter approach has been implicitly followed by Marshall in dealing with sorption of several vapor compounds in glassy polymers adopting the simplified version of PC-SAFT [40,41].

We remark that DGRPT model requires, for any penetrant, the estimation of the derivative of the polymer mass density with respect to the

corresponding penetrant mass concentration in the limit of dilute condition. In the case of polymers with high free volume such derivatives are reasonably taken equal to zero [40], alternatively, an empiric linear relationship is assumed in the case of "dense" (low free volume) polymers [41]. To deal with intermediate cases, Marshall proposed an approach specifically addressing the case of binary systems which introduces a further adjustable parameter ($0 \leq \lambda_{i,p} \leq 1$) to "weight" the empiric linear relationship; however, the author did not test such assumption and did not develop a possible extension of this approach to the multicomponent case [41].

In the present contribution we have implemented the DGRPT framework using the original version of PC-SAFT, containing the association term. To deal with the whole range of polymer/penetrant free volume, we have proposed here a self-consistent PC-SAFT procedure for multicomponent systems to estimate $\lambda_{i,p}$ as a function of the system concentrations, and, for the binary cases, we have compared the model performances in the case of $\lambda_{i,p}$ is calculated according to our procedure with the ones in the case of $\lambda_{i,p}$ is estimated as an adjustable parameter.

To validate the proposed DGRPT-PC-SAFT framework, in the case of high free volume polymers, we have investigated the prediction capabilities in terms of solubility-based separation of CO_2/CH_4 in PTMSP at typical operative conditions (35 °C and up to 35 bar) at several gas mixture concentrations. Moreover, we have also tested the prediction of penetrant induced dilation for PTMSP/CH_3OH and PTMSP/dimethylcarbonate (DMC) binary systems. Regarding "dense" polymers, we focused on methanol sorption in two amorphous glassy polymers namely, polyetherimide (PEI) and 6FDA-ODA, which are of interest in the dehydration of alcohols. These two binary systems have been previously investigated experimentally by our group [48] and are of relevant interest for the modelling assessment of the *IE* assumption referred to hydrogen-bonding interactions. In fact, these two systems display quite complex interactional scenario with two different methanol populations, including also a possible onset of methanol clustering at very high penetrant activity in the vapor phase. Previous investigations by in situ FT-IR have allowed us to determine quantitatively the self and cross specific interactions as a function of the penetrant concentration [48]. It is worth noting that, due to the affinity between methanol and the polymer matrix, one cannot exclude a priori possible swelling of the glassy polymeric matrix induced by the penetrant. Indeed, such an issue has been confirmed indirectly in the present contribution by comparing the implementation of the model without dilation effect, i.e., the original NETGP-PC-SAFT model, with the DGRPT-PC-SAFT model, both containing the association term. To this aim, we have first retrieved the binary model parameters by correlation of gravimetric solubility data and finally, the predictive capability of DGRPT-PC-SAFT model has been successfully validated in a full predictive fashion against the amount of cross and self-specific interactions established within the polymer glassy mixtures as measured by in situ FTIR spectroscopy.

2. Theoretical background

2.1. NETGP-PC-SAFT

PC-SAFT is an EoS model based on a perturbation of a model consisting of a chain of hard spherical segments taken as the reference fluid [27,28,49,50]. According to this model, the reduced Helmholtz energy of a single component fluid phase, $\tilde{a}$, can be expressed as the sum of different contributions:

$$\tilde{a} = \frac{A}{NkT} = \tilde{a}^{id} + \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc} + \tilde{a}^{dp} \quad (1)$$

where N is the total number of molecules, T the temperature and k the Boltzmann constant. $\tilde{a}^{id}$, $\tilde{a}^{hc}$, $\tilde{a}^{disp}$, $\tilde{a}^{assoc}$ and $\tilde{a}^{dp}$ represent the ideal gas, the hard sphere chain reference, the dispersion, the associative and the dipolar contribution, respectively. Beside the parameters present in the associating and dipolar terms, each component, being intrinsically described as a hard sphere chain, displays three pure mean-field parameters: the segment diameter at $T = 0$ K, σ_i, the number of segment diameters, m_i and the depth of the mean-field potential well, $\frac{\varepsilon_i}{k}$.

In a multicomponent phase the pairwise Berthelot–Lorentz combining rules are assumed:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij}) \quad (3)$$

Equation (3) introduces, for each couple of components *i*-*j*, the corresponding binary mean-field interaction parameter k_{ij}, usually assumed as adjustable parameters of the model.

The associative contribution, proposed by Chapman [25,26], introduces for any kind of specific interaction between an associative site of kind A on molecules i, A_i, and a dual associative site of kind B on molecules of species j, B_j, two corresponding additional parameters: $\varepsilon^{A_iB_j}$ and $k^{A_iB_j}$ which represent the corresponding specific association energy and the so-called association volume, respectively. We remark that the Chapman scheme intrinsically assumes that any associative site is univocally associated to a species of the system of interest; conversely, any species can in principle display several kinds of associative sites. Moreover, only dual associative sites (i.e. proton donor/proton acceptor or Lewis acid/base) can establish specific interactions. Such associative parameters can be, in principle, obtained by a non-linear regression of equilibrium data for mixtures involving the associated specific interactions. In particular, in the case of associative interactions exhibited by a pure component ($i = j$ in the adopted notation), the related associative parameters can be obtained, along with the three pure mean-field parameters described above, by a fitting procedure of liquid–vapor (LV) equilibrium data in the case of low molecular weight compounds or of equilibrium dilatometric data in the case of polymeric species. To minimize the number of adjustable parameters, the values of cross-interactions ($i \neq j$ in the adopted notation) parameters can be calculated using combining rules that have been proposed in literature [51]:

$$\varepsilon^{A_iB_j} = \frac{1}{2}\left(\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}\right) \quad (4)$$

$$k^{A_iB_j} = \sqrt{k^{A_iB_i} \bullet k^{A_jB_j}} \left(\frac{\sqrt{\sigma_i \sigma_j}}{1/2(\sigma_i + \sigma_j)}\right)^3 \quad (5)$$

Actually, equations (4) and (5) require that the *i*-th and *j*-th components are both self-associating (SA) substances, so that the two couple of corresponding parameters (namely, $\varepsilon^{A_iB_i}$, $k^{A_iB_i}$ and $\varepsilon^{A_jB_j}$, $k^{A_jB_j}$) are defined and they can be retrieved from the pure PC-SAFT parameters.

In presence of non-self-associating (NSA) species (e.g., carbonyl and ether groups), SA parameters are not defined, since these components can make only cross hydrogen bonds. Therefore, equations (4) and (5) can no longer be used directly. Several operative strategies have been proposed in literature to circumvent this problem, which still remains an open question. For instance, Kleiner et al. [50] proposed an operative extension of the use of equations (4) and (5) to the case that one SA and one NSA species are involved in the cross hydrogen-bonding. The authors propose to use Eq. (4) for the cross-association energy, setting the fictive self-interaction energy of the NSA site equal to zero. Moreover, the fictive self-interacting volume parameter of the NSA site is set equal to the corresponding one of the SA sites involved in the cross hydrogen-bonding. On this basis Eq. (5) can be finally applied to obtain the cross association $k^{A_iB_j}$. Of course, this approach cannot be applied to model cross-associations in presence of two NSA substances.

Very recently, Marshall et al. [51], in order to extend the use of equations (4) and (5) to the case of NSA species, proposed to estimate fictive $\varepsilon^{A_iB_i}$ and $k^{A_iB_i}$ of the NSA species (e.g., aldehydes, ketones and ethers) as adjusting parameters to accurately reproduce the phase behaviour with compounds which induce cross association, and to this

regard Eqs. (4) and (5) were consistently adopted to calculate the cross-association parameters. We remark that, in such scheme, the fictive self-association parameters of the NSA species are only used in Eqs. (4) and (5) for the prediction of the cross-association parameters. In other words, no self-interaction contributions are ascribed to such groups in the implementation of the model. In the present paper, the parameters obtained through the latter approach for ketones have been used to fully predict the cross hydrogen-bonding involving the carbonyl groups of the polyimides. Indeed, such assumption is reasonable in view of the local scale of the association interaction.

The dipolar contribution introduces a parameter (namely the dipolar moment) associated to any kind of dipole involved in the system. The dipolar moments can be retrieved by ab-initio calculations or are taken as additional adjustable parameters to be determined by non-linear regression of equilibrium data. In the present investigation, the FT-IR analysis [48] indicates the occurrence of strong specific interactions, thus making reasonable to disregard the dipolar contribution and allowing, at the same time, to minimize the number of adjustable parameters. Hence, in the following we only focus on the PC-SAFT model with associative contribution term.

As anticipated in the introduction section, in the case of NETGP-PC-SAFT model the pseudo- phase equilibrium condition, under the *IE* assumption for the associative internal state variables, is dictated by imposing, simultaneously for each penetrant, the equivalence of the equilibrium chemical potential in the external fluid phase and of the non-equilibrium chemical potential (calculated under *IE* hypothesis) within the polymer-penetrant phase. The polymer mass density, ρ_p, is imposed to be "kinetically" locked at an out-of-equilibrium value (See section S.1 of SI file).

As extensively discussed in the section S.1 of the SI file the calculation of the equilibrium chemical potential of the *i*-th penetrant in the external phase is performed by coupling the corresponding general non equilibrium expressions of the chemical potential with the EoS equation and the minimizations conditions with respect to the set of associative internal state variables. Conversely, the expression of the chemical potential of the *i*-th penetrant (under the *IE* assumption) within the glassy phase is obtained by coupling the corresponding non equilibrium chemical potential with the minimization conditions with respect only to the associative internal state variables set but in correspondence of a fixed out-of-equilibrium value of the volume of the mixture and so of the fixed associated polymer mass density for a given polymer mass in the polymer-penetrant mixture (in view of the assumption that the polymer is not soluble in the external phase). Therefore, to calculate the penetrant solubility in a glassy polymer-penetrant phase under *IE* condition, one needs the general expression of the non-equilibrium chemical potentials along with the minimization conditions with respect to the associative internal state variable and, for the external fluid phase, to the phase volume (i.e., the EoS equation). In particular, the minimization conditions with respect to the set of associative internal state variables are [25,26]:

$$x^{A_i} = \left(1 + \sum_j \frac{\rho_j}{Mw_j} \sum_{B_j} x^{B_j} \Delta^{A_i B_j}\right)^{-1} \tag{6}$$

Hereafter, $\Delta^{A_i B_j}$ represents the molecular association strength of the $A_i B_j$ interaction (in turn calculated by the two corresponding associative parameters), ρ_j represents the mass density of species *j* and x^{A_i} indicates the fraction (with respect to their total number) of the association sites of kind A (located on the species *i*) that are not involved in any possible association interaction. Finally, Mw_j represents the molecular mass of the *j*-th species.

Regarding the chemical potential, its general non-equilibrium expression can be obtained in our case as the sum of the ideal, hard-chain, dispersion and associative contributions. We refer to the original literature [27,28,49,50] for the expressions of the first three terms. As for the associative contribution, we have adopted the general expression introduced by Michelsen et al. [33], since, as detailed in section S.1 of the SI file, using Chapman's original expression would require solving an additional set of nonlinear equations, which increases the computational costs of the calculations. In particular, the general non-equilibrium expression adopted for the associative contribution, $\mu_i^{NE,assoc}$, to the chemical potential μ_i^{NE} is the following:

$$\frac{\mu_i^{NE,assoc}}{kT} = \sum_{A_i}(logX^{A_i} - X^{A_i} + 1) - \sum_j \frac{\rho_j}{Mw_j} \sum_{A_i}\sum_{B_j} X^{A_i} X^{B_j} \Delta^{A_i B_j} - \frac{1}{2}\sum_k \sum_j \frac{\rho_k}{Mw_k} \frac{\rho_j}{Mw_j} \sum_{A_k}\sum_{B_j} X^{A_k} X^{B_j} Mw_i \frac{\partial \Delta^{A_k B_j}}{\partial \rho_i} \tag{7}$$

2.2. Dry Glass Reference Perturbation Theory (DGRPT)

According to the described NETGP model framework, to account for polymer/matrix dilation induced by the penetrant when modelling sorption thermodynamics in glassy polymers, in principle one should know the out-of-equilibrium relationship between polymer mass density and the set of penetrant concentrations. To this aim, in the literature phenomenological expressions have been proposed, such as [1]:

$$\rho_p = \rho_p^0 \left(1 - \sum_i b_i \rho_i\right) \tag{8}$$

where ρ_p is the mass density of polymer in the polymer/penetrants mixture, ρ_p^0 is the pure polymer mass density right before the sorption test, ρ_i is the mass density of the *i*-th penetrant and b_i is the phenomenological swelling parameter associated to the polymer/*i*-th component pair. Such relationship, as well as any other similar empirical law [42–44], introduces in the NETGP framework an additional set of phenomenological adjustable parameters. To overcome this drawback, Marshall has proposed a procedure, referred to as Dry Glass Reference Perturbation Theory (DGRPT) [40,41], to self-consistently calculate ρ_p through the EoS model adopted within the NETGP framework. In the following, we briefly report the operative equation of the model referring the reader to the original literature for full details [40,41]. In line with the NETGP formalism, in the following we express the DGRPT equations in terms of the mass densities set, $\boldsymbol{\rho_s}$, whereas the original Marshall formalism adopts the number densities set, $\boldsymbol{\rho_s^{mol}}$, according to the PC-SAFT literature. The *i*-th component of $\boldsymbol{\rho_s}$ and $\boldsymbol{\rho_s^{mol}}$ represent, respectively, the mass density and the number density of *i*-th penetrant (subscript *s* stands for solute used here as synonymous of penetrant).

Moreover, when dealing with models including an additional set of state variables provided by the associative contacts, as is the case at hand, the *IE* assumption is implicitly adopted in the calculation of the expression of the whole set of chemical potentials. including the one of polymer. Thus, in the case of the PC-SAFT containing the associative term, it can be shown that the proper expression of the arbitrary μ_i (including also the polymeric component) can be written as (see section S.2 of the SI file for details):

$$\mu_i^{IE}(T,\rho_p,\boldsymbol{\rho_s}) \equiv \mu_i^{NE}(T,\rho_p,\boldsymbol{\rho_s},\boldsymbol{x}(T,\rho_p,\boldsymbol{\rho_s})) \tag{9}$$

where μ_i^{NE} represents the general non-equilibrium expression of the chemical potential of the i-th component and $\boldsymbol{x}^{IE}(T,\rho_p,\boldsymbol{\rho_s}) = \boldsymbol{x}^{EQ}(T,\rho_p,\boldsymbol{\rho_s})$ is the function that provides the minimization condition of the association internal variables set $\boldsymbol{x}$ of the PC-SAFT model, whose generic k-th component represents the number of unbonded associative site of kind k per number of molecules containing the site [25,26] (see also section S.1 of supporting information file for details on the *IE* assumption).

The starting point of the DGRPT is a Taylor expansion around the dry state, i.e., $\boldsymbol{\rho_s} = 0$, of the chemical potential of the polymer, μ_p, provided by the adopted EoS model under the underlining assumption that a function $\rho_p(T, \boldsymbol{\rho_s})$ does exist for any given ρ_p^0. Such a function is required to satisfy the limit "dry" condition, i.e., $\rho_p(T, \boldsymbol{\rho_s} = 0) = \rho_p^0$. ρ_p^0 represents, according to the NETGP framework, a parameter, dependent upon the viscoelastic sample history, that should be measured right before the sorption test at the given temperature. We recall that the *NE* as well as the *IE* expressions of the chemical potential are, in principle, not a function of the pressure P (see section S.1 of supporting information file) and, in this respect, the underlying functional dependence $\rho_p(T, \rho_s)$ at given ρ_p^0 is consistent with such formal dependence, since ρ_p^0 is reasonably assumed independent on the pressure in the case of sorption thermodynamics of gas as well as vapor mixtures in glassy polymer membranes.

Therefore, the DGRPT model accounts in principle only for sorption in glassy polymers with penetrant induced swelling in which the mechanical effect of pressure P is neglected.

More in detail, the composite function $\mu_p^{IE}(T,\boldsymbol{\rho_s}) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s})$ is expressed in terms of a Taylor series expansion around $\boldsymbol{\rho_s} = 0$, truncated at the first order term. In such calculation the $\rho_p(T,\boldsymbol{\rho_s})$ represents the unknown function, whose value at $\boldsymbol{\rho_s} = 0$, i.e., the dry polymer mass density, ρ_p^0, should be known experimentally or be considered as a parameter.

As it will be detailed in the following, in the expression of the Taylor expansion one only needs to know the values of the partial derivative of $\rho_p(T,\boldsymbol{\rho_s})$, with respect to the set of variables $\boldsymbol{\rho_s}$, evaluated at $\boldsymbol{\rho_s} = 0$. To this aim, it is useful to make some physical assumptions, in the DGRPT framework [40], on the components of $\nabla\rho_p(T,\boldsymbol{\rho_s})$ at given T and $\boldsymbol{\rho_s} = 0$. These assumptions make the first order term of the Taylor expansion to depend upon the unknown function $\rho_p(T,\boldsymbol{\rho_s})$ only through its assigned value in the "dry" limit ρ_p^0. Once the described first order Taylor expression is calculated, the determination of the unknown value of $\rho_p(T,\boldsymbol{\rho_s})$ (at specific values of the set $\boldsymbol{\rho_s}$ and for the assigned ρ_p^0) is obtained by equating the value of the approximate expression of the chemical potential calculated as a Taylor expansion truncated to the first order to the exact value of $\mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s})$.

In the DGRPT framework, Marshall proposed a more general (implicit) expression of the equation (8), which assures that the polymer mass density is positive for any physically admissible value of T, $\boldsymbol{\rho_s}$ and ρ_p^0, namely:

$$\rho_p = \rho_p^0 \exp\frac{f(T,\rho_p,\boldsymbol{\rho_s})}{RT} \tag{10}$$

where the function $f(T,\rho_p,\boldsymbol{\rho_s})$ plays therefore the role of the actual unknown function and it is defined by the equation (10). Such function must be equal to 0 at $\boldsymbol{\rho_s} = 0$(so that ρ_p consistently coincides with ρ_p^0 in such "dry" limit condition). The underlying additional assumption is that for any physically admissible ρ_p^0, Eq. (10) provides a unique solution $\rho_p(T,\boldsymbol{\rho_s})$.

In particular, based on the previous discussion, the DGRPT numerical procedure, to the first order, consists in calculating the value of f at given T, $\boldsymbol{\rho_s}$ and ρ_p^0, that is the solution of the following equation:

$$\mu_p^{IE}(T,\boldsymbol{\rho_s}) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s}) = \mu_p^{IE}\left(T,\rho_p^0,\boldsymbol{\rho_s} = 0\right) + \sum_j\left[\left(\frac{\partial\mu_p^{IE}}{\partial\rho_{s,j}} + \frac{\partial\mu_p^{IE}}{\partial\rho_p}\frac{\partial\rho_p}{\partial\rho_{s,j}}\right)\rho_{s,j}\right] \tag{11}$$

On the R.H.S of Eq. (11) chain rules of derivatives have been adopted on the basis of the $\mu_p^{IE}(T,\boldsymbol{\rho_s}) = \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s})$ relationship. Consequently, any $\frac{\partial\mu_p^{IE}}{\partial\rho_{s,j}}$ as well as any $\frac{\partial\mu_p^{IE}}{\partial\rho_p}$ is evaluated at $(T,\rho_p(T,\boldsymbol{\rho_s} = 0),\boldsymbol{\rho_s} = 0)$, i.e., at $(T,\rho_p^0,\boldsymbol{\rho_s} = 0)$ and any $\frac{\partial\rho_p}{\partial\rho_{s,j}}$ is evaluated at T and $\boldsymbol{\rho_s} = 0$. Hereafter the subscript j refers to the j-th component of the set $\boldsymbol{\rho_s}$.

Finally Eq. (10) is adopted at L.H.S of Eq. (11) to express at the given T and $\boldsymbol{\rho_s}$ the value of ρ_p in terms of the unknown f and of the assigned value of the parameter ρ_p^0. Incidentally, it is worth remarking that, on the basis of the imposed value of the first term on R.H.S of Eq. (11), the Eq. (11) at $\boldsymbol{\rho_s} = 0$ is expressed as $\mu_p^{IE}(T,\boldsymbol{\rho_s} = 0) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s} = 0),\boldsymbol{\rho_s} = 0) = \mu_p^{IE}\left(T,\rho_p^0,\boldsymbol{\rho_s} = 0\right)$ which trivially admits, as required, $\rho_p(T,\boldsymbol{\rho_s} = 0) = \rho_p^0$ as a solution of Eq. (11) so that $f = 0$ is equivalently obtained in such "dry" limit condition.

Once the solution value of f is obtained by solving Eq. (11) for a given T, $\boldsymbol{\rho_s}$, and ρ_p^0, the corresponding, ρ_p is provided by the equation (10). In this way, one can numerically obtain the expression of ρ_p as a function of T, $\boldsymbol{\rho_s}$ for the assigned ρ_p^0.

In the present discussion, following Marshall's approach [40], we deal with $\mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s})$ in which the minimization conditions with respect to $\boldsymbol{x}$ have been implicitly already substituted (see Eq. (9)).

So far, purposedly, we have presented a rather simplified discussion that is sufficiently detailed to introduce the fundamental aspects of the DGRPT procedure. However, it should be considered that, since $\boldsymbol{x}(T,\rho_p,\boldsymbol{\rho_s})$ is, in general, not available in closed form, the operative implementation of the DGRPT approach requires a more in-depth description which is the subject of section S.3 of the SI file.

In particular, referring to the L.H.S. of equation (11), one recognizes that, according to equation (9), the calculation of $\boldsymbol{x}(T,\rho_p,\boldsymbol{\rho_s})$ has to be performed at the current values of $\boldsymbol{\rho_s}$ and of ρ_p, the latter, in turn, being a function of the guessed value of f and of the given ρ_p^0 through the equation (10). As for the first term on R.H.S of Eq. (11), the calculation of $\boldsymbol{x}\left(T,\rho_p^0,\boldsymbol{\rho_s} = 0\right)$ is required. A less trivial calculation involves the determination of the derivative terms of the *IE* chemical potential appearing on the R.H.S. of the equation (11). To this regard, a numerical procedure is, in general, required, as described in section S.3 of the SI file. However, considering the case of the systems under analysis in the present investigation, the structure of the associative equations resulting from the chemical association scenario is such that these derivatives are available in closed form and such expressions can be found in section S.3 of the SI file.

In the case of a polymer displaying high free volume, the swelling response is small and very weakly dependent on sorption at low concentration of sorbate [40]. This assumption is formulated mathematically as:

$$\frac{\partial\rho_p}{\partial\rho_{s,j}}(T,\boldsymbol{\rho_s} = 0) = 0 \quad j = 1,2\cdots t \tag{12}$$

By coupling equations (11) and (12), we obtain the original DGRPT closure equation:

$$\mu_p^{IE}(T,\boldsymbol{\rho_s}) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s}) = \mu_p^{IE}\left(T,\rho_p^0,\boldsymbol{\rho_s}=0\right) + \sum_j \left(\frac{\partial \mu_p^{IE}}{\partial \rho_{s,j}}\rho_{s,j}\right) \tag{13}$$

where again any $\frac{\partial \mu_p^{IE}}{\partial \rho_{s,j}}$ is evaluated at $(T,\rho_p(T,\boldsymbol{\rho_s}=0),\boldsymbol{\rho_s}=0)$, i.e. at $(T,\rho_p^0,\boldsymbol{\rho_s}=0)$.

However, under the assumption of equation (12), DGRPT shows very poor capability of reproducing the behaviour of "dense" polymer/penetrant systems which exhibit continuous volume expansion even at low sorbate loading. To address this issue, very recently Marshall [41] proposed a modification of the original DGRPT approach to deal with "dense" polymer/penetrant binary systems. In particular, equation (12) in the binary case is substituted by the following relation:

$$\frac{\partial \rho_p}{\partial \rho_{s,1}}(T,\rho_1=0) = \frac{\rho_p - \rho_p^0}{\rho_1} \tag{14.a}$$

where subscript 1 indicates the unique penetrant and, on the R.H.S of Eq. (14), ρ_p is intended to be a function of T and ρ_1. In the present contribution, we propose a natural extension of Eq. (14) to the multicomponent case which reads:

$$\frac{\partial \rho_p}{\partial \rho_{s,j}}(T,\boldsymbol{\rho_s}=0) = \frac{\rho_p - \rho_p^0}{\sum_j \rho_{s,j}} \tag{14.b}$$

Consequently, after substitution in equation (11) one obtains:

$$\mu_p^{IE}(T,\boldsymbol{\rho_s}) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s}) = \mu_p^{IE}\left(T,\rho_p^0,\boldsymbol{\rho_s}=0\right) + \\ + \sum_j \left(\frac{\partial \mu_p^{IE}}{\partial \rho_{s,j}}\rho_{s,j}\right) + \sum_j \left[\frac{\partial \mu_p^{IE}}{\rho_p}\left(\rho_p - \rho_p^0\right)\right] \tag{15}$$

where any $\frac{\partial \mu_p^{IE}}{\partial \rho_{s,j}}$ and $\frac{\partial \mu_p^{IE}}{\partial \rho_p}$ are evaluated at $\left(T,\rho_p(T,\boldsymbol{\rho_s}=0),\boldsymbol{\rho_s}=0\right)$, i.e., at $\left(T,\rho_p^0,\boldsymbol{\rho_s}=0\right)$.

Marshall observed that equation (13) is able, as expected, to reproduce the behaviour of glassy mixtures with very high excess free volume with respect to the molecular size of the penetrant (e.g., PTMSTP/CH_3OH system), while equation (15) can satisfactorily describe the behaviour of very low excess free volume with respect to the molecular penetrant size (e.g., PMMA/CO_2). On this basis, starting with Eq. (15) for the binary case, Marshall introduced [41], without testing its performances, an adjustable binary parameter, $\lambda_{1,p}$, whose value ranges between 0 and 1 to account for intermediate cases. In particular, lower values of $\lambda_{1,p}$ indicate lower polymer swelling induced by the penetrant at low activity, which can be attributed to either a high available free volume within the polymer matrix or the small size of the penetrant. The proposed modification of Eq. (15) for the binary sub-case reads:

$$\mu_p^{IE}(T,\rho_1) \equiv \mu_p^{IE}(T,\rho_p(T,\rho_1),\rho_1) = \mu_p^{IE}\left(T,\rho_p^0,\rho_1=0\right) + \\ + \frac{\partial \mu_p^{IE}}{\partial \rho_1}\rho_1 + \lambda_{1,p}\frac{\partial \mu_p^{IE}}{\partial \rho_p}\left(\rho_p - \rho_p^0\right) \tag{16.a}$$

where $\frac{\partial \mu_p^{IE}}{\partial \rho_1}$ and $\frac{\partial \mu_p^{IE}}{\partial \rho_p}$ are evaluated at the given T, ρ_p^0 and at $\rho_1 = 0$. Consistently with Eq. (14.b), we also propose an implementation of $\lambda_{j,p}$ for each j-th penetrant in the general multicomponent extension of the equation (16.a) which reads:

$$\mu_p^{IE}(T,\boldsymbol{\rho_s}) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s}) = \mu_p^{IE}\left(T,\rho_p^0,\boldsymbol{\rho_s}=0\right) + \\ + \frac{\partial \mu_p^{IE}}{\partial \rho_p}\left(\rho_p - \rho_p^0\right)\sum_j \left(\lambda_{j,p}\frac{\omega_j}{1-\omega_p}\right) \tag{16.b}$$

where, ω_j is the mass fraction of the j-th penetrant.

2.3. Self-consistent PC-SAFT estimation of $\lambda_{j,p}$

As discussed, the parameter $\lambda_{j,p}$ is related to the induced dilation capability of the penetrant, which in turn decreases when the available free volume in the polymer/penetrants mixture is higher. According to this free-volume picture, we propose to estimate $\lambda_{j,p}$ in the framework of PC-SAFT model by the following equation:

$$\lambda_{j,p} = \frac{v_{cp}^{mol}}{v^{mol}} \tag{17}$$

where v_{cp}^{mol} and v^{mol} represent the close-packed molecular volume and the actual molecular volume of the mixture, respectively, and, according to Eq. (17), $1-\lambda_{j,p}$ represents the system fractional free-volume of the binary mixture. v_{cp}^{mol} is calculated self-consistently using the PC-SAFT model as:

$$v_{cp}^{mol} = \frac{\pi}{6\eta_{cp}}\left(m_p x_p d_p^3 + \sum_j m_j x_j d_j^3\right) \tag{18}$$

In Eq. (18) x_j, m_j and d_j are the molar fraction, the number of segments per chain and the actual diameter of the segment at given temperature [27] of the j-th penetrant, respectively. x_p, m_p and d_p are the molar fraction, the number of segments per chain and the actual diameter of the segment at given temperature [27] of the polymer species, respectively, finally, η_{cp} is the highest value of the packing fraction, η, calculated in correspondence of the closest packing of segments and it is equal to $\frac{\pi}{3\sqrt{2}}$ [27].

Notably, Eqs. (17)-(18) provide a unique multicomponent concentration-dependent function $\lambda_{j,p}$ (with $0 \le \lambda_{j,p} \le 1$) for the whole mixture, which accounts for the actual free volume available in the mixture as a function of the concentration, whereas the determination of it as a pairwise adjustable parameter could depend on the experimental range of data used in the regression. In particular, such issues can compromise the reliability of using the value of $\lambda_{j,p}$ obtained by a regression of binary data in the multicomponent mixture. Therefore, the proposed self-consistent approach not only allows to minimize the number of adjustable parameters, but it is also better suited to predict separation of multicomponent penetrant mixture, once the binary and pure component parameters of the DGRPT-PC-SAFT model are available.

By substituting Eqs. (17) and (18) in Eq. (16.b), we obtain:

$$\mu_p^{IE}(T,\boldsymbol{\rho_s}) \equiv \mu_p^{IE}(T,\rho_p(T,\boldsymbol{\rho_s}),\boldsymbol{\rho_s}) = \mu_p^{IE}\left(T,\rho_p^0,\boldsymbol{\rho_s}=0\right) + \\ + \sum_j \left(\frac{\partial \mu_p^{IE}}{\partial \rho_{s,j}}\rho_{s,j}\right) + \lambda\frac{\partial \mu_p^{IE}}{\partial \rho_p}\left(\rho_p - \rho_p^0\right) \tag{19}$$

In Eq. (19), λ is the multicomponent value of $\lambda_{j,p}$ calculated according to Eq. (18). In the present contribution, we investigate the reliability of Eqs. (16) and (19). In the following, we will refer to the DGRPT-PC-SAFT model with $\lambda_{j,p}$ estimated with a fitting procedure as 'model 'v1' and to the version with $\lambda_{j,p}$ (or equivalently λ) calculated by Eqs. (17) and (18) as 'model 'v2'.

3. Results and discussion

3.1. Pure component parameters

In the framework of NETGP procedure, including the DGRPT extension, the pure component parameters, the association parameters and the related mixing rules are coincident with the ones of the corresponding equilibrium thermodynamics model adopted, i.e., PC-SAFT

model in the case at the hand.

The pure component parameters of methanol have been obtained here by fitting simultaneously data for saturation pressures and for the corresponding densities of the liquid and vapor phases at LV equilibrium. We remark that the obtained values of the methanol parameters are slightly different from the ones calculated by Marshall [40], since he did not include saturation liquid densities in the fitting procedure. Since methanol is a self-associating species, five parameters have been adjusted to the experimental data. To this aim, the 2:1 association scheme has been used to represent its self-interaction scenario, i.e., two proton acceptor sites (on the oxygen atom) and one proton donor site (on the hydrogen atom on the OH group) have been assumed for each methanol molecule. The experimental data were taken from National Institute of Standards and Technology (NIST) Standard Reference Database 69 [53].

In Fig. 1, we report the comparison between the experimental data and the optimized model curves. For the sake of comparison, we also report the predicted curves calculated in correspondence of the parameters retrieved from [40], which, as expected, are close to our fitting results.

In the case of pure polyimides only the mean-field parameters were considered in the PC-SAFT model since no self-interactions occur (more on this later). The values of the parameters for each polyimide have been obtained by a non-linear regression of high pressure dilatometric data taken from the literature [34,54]. The comparison between the optimized model predictions and the experimental data of pure PEI and 6FDA-ODA are reported in Fig. 2.

Based on the molecular structure and on the outcomes of the FT-IR investigation [48], one can reasonably assume that for both the polyimides, each of the four C=O groups, located on a repeating unit, carry two proton acceptor sites, so that the total number of proton acceptor groups for repeating unit is 8. Consequently, no self-association is expected to occur, and no association parameters are then required in the non-linear regression of the polymer dilatometric data. However, in the polymer-penetrant binary systems of interest, cross-associations among the methanol proton donor site (hydrogen atom located on the OH groups) and the polymeric proton acceptor sites (two for each oxygen atom of the carbonyl groups) may occur. Since both the polymers considered here are NSA species, to adopt a predictive procedure for the association interactions, one can follow the procedure developed by Marshall et al. [52] described previously, by which one can calculate the cross-interaction parameters starting from the related self-association ones according to Eqs. (4–5). To this aim the use of "fictive" self-association parameters, $\epsilon^{A_iB_i}$ and $k^{A_iB_i}$, regarding the C=O groups is required. The so-called association scheme 2:0 has been selected for each carbonyl group consistently with the fact that no association contribution for the pure polyimide has to be introduced. In particular, Marshall et al. [52] have estimated such "fictive" self-association parameters for the C=O groups of ketones, as adjustable parameters in the simultaneous prediction of LV equilibrium data of several binary ketones-alcohols systems (adopting consistently Eqs. (4–5) for cross-association parameters). We took advantage from these previous evaluations using Eqs. (4–5) to predict the cross-association parameters for the two polyimide-methanol systems investigated, where we have assumed that the required "fictive" parameters of the C=O groups of the two polymers are equal to the ones determined in ref. [52] for the C=O groups of ketones.

Regarding the PTMSP, rubber density data are unavailable due to its very high glass transition temperature, which is a common feature of the high free volume polymers. In such a case, the values of PTMSP PC-SAFT parameters can be determined from the simultaneous fitting of sorption data in PTMSP of a series of pure penetrants whose PC-SAFT parameters are known. This procedure will be described in section 3.2.

The list of PC-SAFT parameters for pure components used in this investigation are reported in Table 1.

In Table 1, N^{A_i} and N^{B_i} represent the total number of proton acceptors (PA) and proton donors (PD) sites per molecule of type i, respectively.

3.2. Solubility separation of CO_2/CH_4 in PTMSP

Since PTMSP repeating units do not display any association sites, only the three pure mean-field parameters of the polymer need to be determined. Such parameters have been retrieved by the simultaneous regression of solubility data of five binary PTMSP/penetrants systems, namely: PTMSP/CH_3OH, PTMSP/DMC (experimental data taken from [46]) and PTMSP/CH_4, PTMSP/CO_2 and PTMSP/n-C_4H_{10} (experimental data taken from [3]). Notably, the specific interactions need to be considered only in the case PTMSP/CH_3OH (in particular, self-association of methanol).

As a consequence, in the case of DGRPT-PC-SAFT model v2, the whole set of adjustable parameters is given by the three pure mean-field parameters of PTMSP (σ_i, m_i and $\frac{\varepsilon_i}{k}$) along with a binary mean-field interaction parameter k_{ij} for each polymer/penetrant system. Regarding the DGRPT-PC-SAFT model v1, one needs to add $\lambda_{j,p}$ as adjustable parameter, one for each binary polymer/penetrant system, thus making the simultaneous fitting procedure not feasible in view of the limited number of data points in the available set of experimental data. Moreover, since PTMSP is a high free volume polymer, we also performed the same simultaneous fitting procedure with the "original" version of DGRPT-PC-SAFT (i.e., $\lambda_{j,p} = 0$ for each binary system) in order to compare the full predictive capabilities of the two approaches for the CO_2/CH_4 separation. Fig. 3 reports the comparison between the experimental data and the best fitting curves obtained with the two methods. In the case of vapors, the penetrant uptake is reported as a function of P/P_0, where P is the pressure of the vapor of phase in contact with the polymer and P_0 is the saturation pressure at the test temperature. The pure components parameters for the whole set of species considered are those reported in Table 1and the value of the density of pure PTMSP, ρ_p^0,

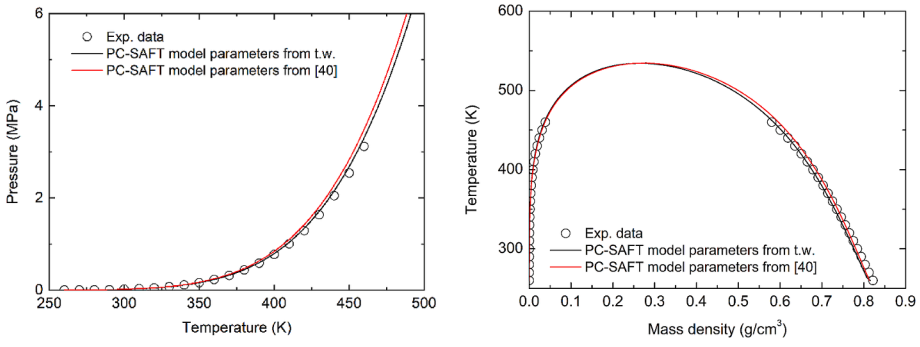

Fig. 1. Liquid-vapor equilibrium data for pure methanol [53] (empty circles) and results of best fitting by the PC-SAFT model calculated in this work (black solid lines) and predicted with the parameters retrieved from [40] (red solid lines). Left: saturation pressures. Right: saturation densities.

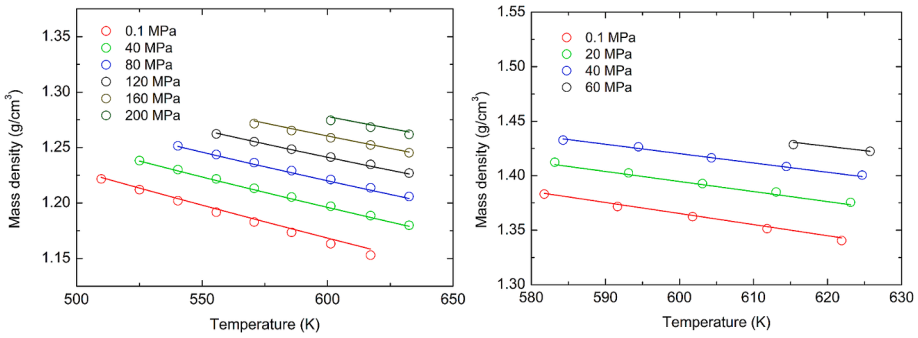

Fig. 2. Equilibrium dilatometric data [34,54] (empty circles) and results of best fitting by the PC-SAFT model (continuous lines). Left: PEI. Right: 6FDA-ODA.

Table 1
PC-SAFT parameters for pure components.

	σ_i(Å)	$\frac{\varepsilon_i}{k}$(K)	m_i	$\frac{\varepsilon^{A_iB_i}}{k}$(K)	$k^{A_iB_i}$	N^{A_i}	N^{B_i}	Ref.
CH_3OH	2.746	175.00	2.498	2258	0.055	2	1	This work
DMC	3.255	242.51	3.504	1000	0.1	2	0	[40]
CO_2	2.7852	169.21	2.0729	0	0	0	0	[27]
CH_4	3.7039	150.03	1.0000	0	0	0	0	[27]
n-C_4H_{10}	3.7086	222.88	2.3316	0	0	0	0	[27]
PTMSP ($DGRPT\ \lambda_{j,p} = 0$)	3.190	181.41	0.04465 × Mw[a]	0	0	0	0	This work
PTMSP (DGRPT v2)	3.215	190.55	0.04500 × Mw[a]	0	0	0	0	This work
PEI	3.385	365.73	0.02957 × Mw[a]	1000[b]	0.1[b]	$8\frac{Mw}{Mw_{ru}}$	0	This work
6FDA-ODA	3.057	269.05	0.03076 × Mw[a]	1000[b]	0.1[b]	$8\frac{Mw}{Mw_{ru}}$	0	This work

Mw_{ru} is the molecular mass of the repeating unit.
[a] Molecular weight of PTMSP, PEI and 6FDA-ODA have been assumed to be 100000 g/mol, 80000 g/mol and 100000 g/mol, respectively.
[b] Values taken from Marshall et al. [52] estimation for ketones systems.

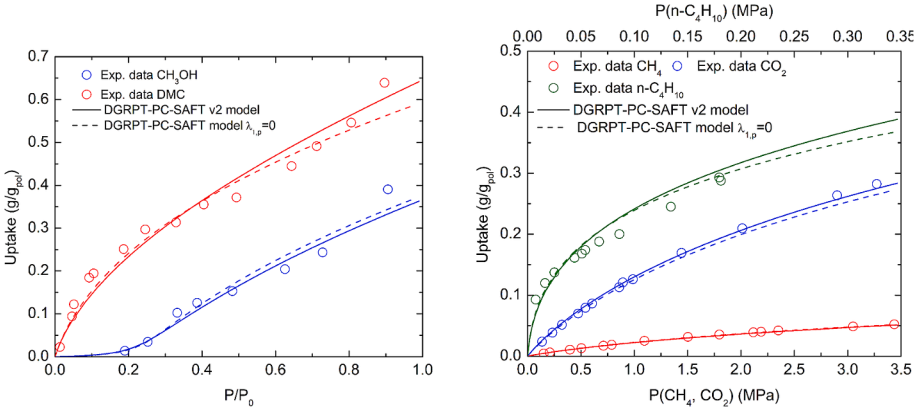

Fig. 3. Comparison of the experimental data and results of optimized fitting of two versions of DGRPT-PC-SAFT model for the sorption of: pure CH_3OH and DMC at 313.15 K (data taken from [46]) (left) and CH_4, CO_2 and n-C_4H_{10} at 308.15 K (data taken from [3]) (right) in PTMSP.

Table 2
Binary interaction parameters of PTMSP/penetrant systems.

	k_{ij} DGRPT v2 model	k_{ij} DGRPT model ($\lambda_{j,p} = 0$)
PTMSP/CH_3OH	−0.029	−0.034
PTMSP/DMC	0.040	0.032
PTMSP/CO_2	0.042	0.050
PTMSP/CH_4	−0.070	−0.062
PTMSP/n-C_4H_{10}	0.003	−0.004

is equal to 0.77 g/cm^3 [3,46]. Table 2 reports the optimized values of binary interaction parameters as determined from the two fitting procedures.

As expected for the case of PTMSP in the presence of low molecular weight penetrants, the two approaches exhibit similar satisfactory correlation capabilities, as also confirmed by the values reported in Tables 1 and 2. In particular, the DGRPT-PC-SAFT v2 model reproduces better the DMC solubility data at the highest activities. In fact, as highlighted by Marshall [41], the "original" DGRPT-PC-SAFT model (i.e., with $\lambda_{j,p} = 0$) can lose accuracy when the polymer/penetrant matrix acts as a "dense" system, which is reasonable the case for PTMSP/DMC system as compared to the PTMSP-methanol case, in view of the larger molecular

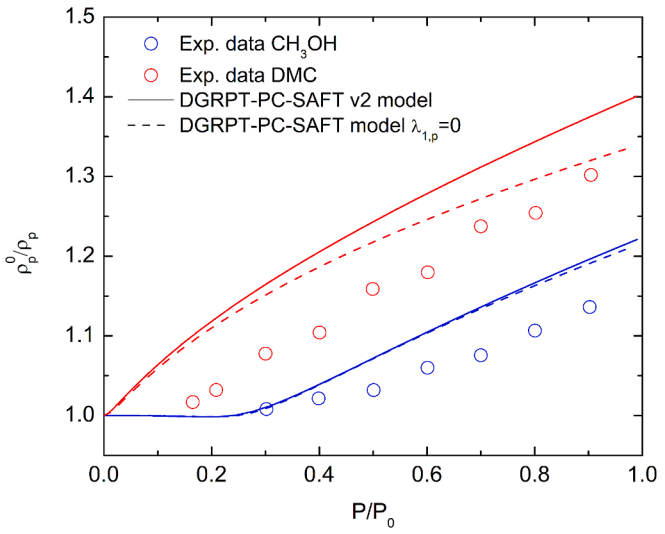

Fig. 4. Comparison of the experimental data [46] and the full model predictions of both approaches for dilation isotherms at 313.15 K of CH_3OH and DMC in PTMSP.

size of the DMC.

Once the model parameters have been retrieved, the model performances in terms of swelling have been tested against experimental data available in literature. To this aim, Fig. 4 reports the comparison between the predictions of the two implementations of DGRPT-PC-SAFT and the isothermal swelling data at 313.15 K [46]. The two approaches are able to reproduce the qualitative behaviour of dilation data, including the peculiar shape of the methanol at low activities, which is reasonably ascribed to the high free volume available in the polymer matrix. However, the two models display a quantitative mismatch with experimental volumetric data for both the penetrants. Indeed, similar quantitative overestimation in the case of the model with $\lambda_{j,p} = 0$ was found in the ref. [40] by Marshall et al. when implementing the same version of DGRPT but with the simplified PC-SAFT. The two DGRPT versions implemented in the present contribution predict quantitatively close values in the whole range of activities of methanol vapor investigated. Conversely, a quantitative discrepancy is observed for such two models in the case of DMC at increasing penetrant activities. We remark that the swelling measurement tests considered have been performed by optical equipment which requires the use of a gas carrier (hydrogen) to control the vapor activity, and the swelling determination assumes implicitly that the shape of the sample (membrane) is not affected by the penetrant (homothetic deformation). As a consequence, volumetric measurements are likely to be affected by greater uncertainty as compared to the well-established sorption tests [46].

A more robust validation of the performances of the theoretical approach is provided by comparing model prediction for the solubility related separation of binary penetrant mixtures in PTMSP when significant penetrant dilation occurs. To this aim, we focused here on system of technological interest, namely, PTMSP/CO_2/CH_4, at 308.15 K and at a total pressure up to 3.5 MPa. In Fig. 5, we report the predictions of the sorption of each component of the binary gas mixture provided by two versions of DGRPT model as a function of the total pressure and at different CO_2 molar concentrations in the external gas mixture.

Both models display excellent predictive capability overall the range of pressures and external concentrations considered. As already discussed, the high free volume of PTMSP, in combination with the small size of the two penetrants, results reasonably in similar predictive performance of the two approaches.

3.3. Polyimides/CH_3OH binary systems: hydrogen bonding estimation

Concerning polyimides/CH_3OH binary systems, once self-association parameters for pure components have been determined from fitting procedure on experimental data and the cross-association parameters have been obtained using Eqs. (4–5), only mean-field binary interaction

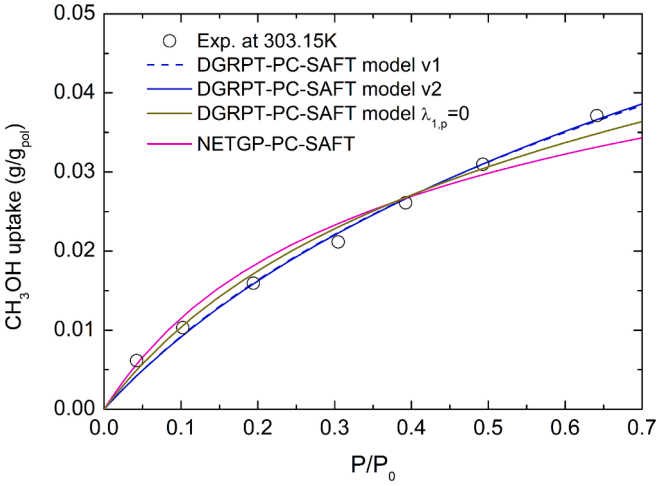

Fig. 6. Comparison of the experimental data [48] and results of optimized fitting of the three versions of DGRPT-PC-SAFT model and of NETGP-PC-SAFT model for the sorption of pure methanol in PEI at 303.15 K. The correlation parameters are $k_{1p} = 0.04899$ and $\lambda_{1,p} = 0.606$ for DGRPT-PC-SAFT model v1, $k_{1p} = 0.04962$ for DGRPT-PC-SAFT model v2, $k_{1p} = 0.04015$ for DGRPT-PC-SAFT with $\lambda_{1,p} = 0$ and $k_{1p} = 0.03166$ for NEGTP-PC-SAFT model.

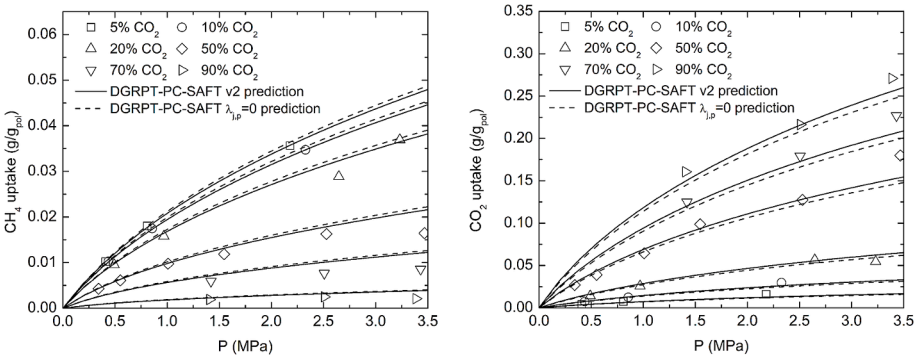

Fig. 5. Comparison of the experimental data [3] and the full predictions of both DGRPT-PC-SAFT approaches for sorption isotherms at 308.15 K of CO_2/CH_4 binary mixtures at different external molar fractions of CO_2 in PTMSP. The value of the pairwise interaction parameter of CO_2/CH_4, k_{ij}, is taken from [27] and it is equal to 0.065 (dimensionless).

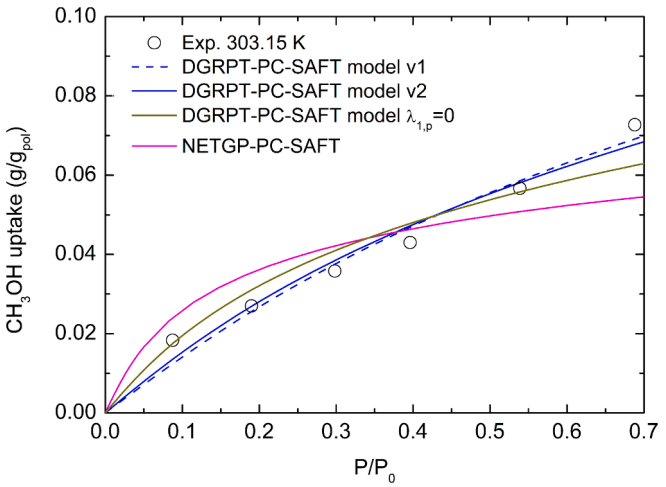

Fig. 7. Comparison of the experimental data [48] and results of optimized fitting of the three versions of DGRPT-PC-SAFT model and of NETGP-PC-SAFT model for the sorption of pure methanol in 6FDA-ODA at 303.15 K. The correlation parameters are $k_{1p} = 0.04731$ and $\lambda_{1,p} = 0.666$ for DGRPT-PC-SAFT model v1, $k_{1p} = 0.04050$ for DGRPT-PC-SAFT model v2, $k_{1p} = 0.01921$ for DGRPT-PC-SAFT with $\lambda_{1,p} = 0$ and $k_{1p} = -0.01561$ for NEGTP-PC-SAFT model.

parameters, k_{ij}, remain to be determined.

In interpreting experimental pseudo-equilibrium sorption isotherms of methanol in the two polyimides [48], we have adopted both DGRPT-PC-SAFT v1 and v2 models. The values of the dry polymer mass density, ρ_p^0, used in the model calculations are 1.260 g/cm^3 and 1.488 g/cm^3, respectively, for PEI and 6FDA-ODA, and have been taken from the literature [48].

Figs. 6 and 7 report the experimental solubility data taken from [48] along with the results of data fitting performed with the two versions (DRGPT-PC-SAFT model v1 and DRGPT-PC-SAFT model v2).

No swelling data are available for these two systems in literature, however, on the basis of FT-IR estimation, one cannot rule out that swelling induced by the penetrant occurs below a threshold around 5 %. For these reasons, in Figs. 6 and 7 we report the correlation capability of the original NETGP-PC-SAFT model in which the polymer mass density is fixed to its initial value ρ_p^0. Finally, for the sake of comparison, Figs. 6 and 7 also show the results of the optimized data fitting using the "original" DGRPT-PC-SAFT approach with $\lambda_{1,p} = 0$.

It is evident that neglecting the volume dilation induced by the penetrant (original NETGP-PC-SAFT model) does not allow a satisfactory correlation capability of the solubility data. Only a slight improvement is provided by the use of the "original" DGRPT-PC-SAFT model which indicates that both polymers behave as "dense" systems, and the penetrant induced swelling can occur even at low penetrant concentration. Conversely, the versions v1 and v2 of DGRPT-PC-SAFT models provide a satisfactory correlation capability for both binary polyimides/CH_3OH systems displaying similar values of k_{1p}. Such a result is consistent with the fact that Eq. (17) and (18) provide a range of values of $\lambda_{1,p}$ close to the optimized value of $\lambda_{1,p}$ obtained from the v1 model version. It is worth noting that the predicted swelling with the two versions of DGRPT model (v1 and v2 models) up to the maximum activity investigated is around 2 % and 4 % for PEI and 6FDA-ODA, respectively, which is as expected below the minimum value detectable by FT-IR spectroscopy.

Once the optimized set of parameters of the DGRPT models has been determined, one can predict the number of self and cross hydrogen bonds for each polymer/penetrant system investigated at a given temperature and penetrant concentration. In fact, from minimization conditions with respect to $\boldsymbol{x}$, i.e., Eq. (6), one can calculate the vector of contacts $\boldsymbol{x}$ under the *IE* assumption at the given T, penetrant concentration and polymer mass density obtained by DGRPT approach.

In turn, such values of $\boldsymbol{x}$ allow to calculate the corresponding moles of self and cross hydrogen bonds ($\frac{n_{11}}{m_p}$ and $\frac{n_{12}}{m_p}$, respectively) expressed per mass of polymer according to the following equation:

$$\frac{n_{11}}{m_p} = \frac{N^{A_1}(1 - x^{A_1})}{Mw_1 N_A} \frac{\rho_1}{\rho_p} \tag{20.a}$$

$$\frac{n_{12}}{m_p} = \frac{N^{A_p}(1 - x^{A_p})}{Mw_p N_A} \tag{20.b}$$

where N_A represents Avogadro's number. The oxygen atom of any methanol molecule exhibits two equivalent kinds of PA sites (which are here consistently described by assuming that both have the same couple of association parameters). Based on the "structure" of Eq. (6), once such equivalent sites are consistently described by a unique couple of associative parameters, as expected the two corresponding components of the set $\boldsymbol{x}$ present the same value, here indicated as x^{A_1}. Similarly, x^{A_p} takes the same value for all the corresponding components of $\boldsymbol{x}$ for all the equivalent PA sites of the oxygen atoms of carbonyl groups of the polymer backbone. Such equivalent PA sites are here consistently described by adopting for them a unique couple of association parameters.

In particular, in the PC-SAFT framework (and hence also in the DGRPT closure) any kind of association site is intrinsically located only onto one species of the system, hence the i-th component of $\boldsymbol{x}$ expresses equivalently both the number of association sites of kind i not involved in association with respect to its total number and the total number of the unique species displaying such kind of association site [25,26].

Therefore, here, the terms $N^{A_1}(1 - x^{A_1})$ and $N^{A_p}(1 - x^{A_p})$ express, respectively, the total number of methanol PA groups involved in specific interactions per total number of methanol molecules and the total number of PA groups of the polymer of interest which are involved in specific interactions per total number of polymeric molecules. Finally, since the two polyimides investigated do not display PD groups the Eq. (20) is trivially obtained.

Figs. 8 and 9 show the comparison of model prediction and experimental data taken from [48].

Consistently with the good correlation results obtained for the solubility data, both model v1 and model v2 exhibit a very satisfactory predictive capability of the associative contacts of the two investigated systems. In particular, for 6FDA-ODA/methanol, the model is able to reproduce quantitatively the trade-off between self and cross interactions that can be ascribed to the onset of methanol clustering within the system [48].

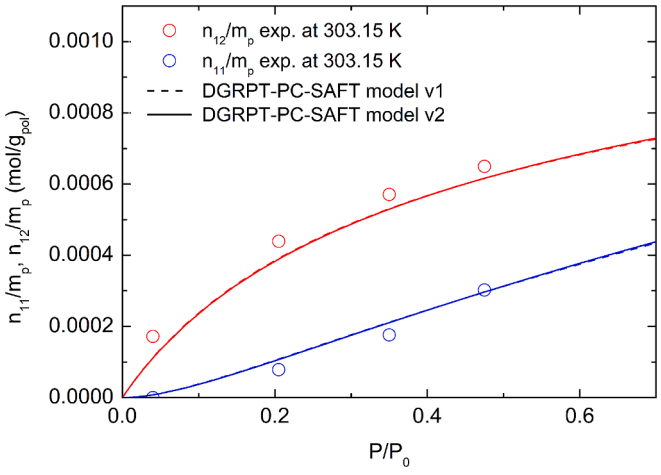

Fig. 8. Comparison of the experimental data [48] and the full predictions of both model versions for the self and cross hydrogen bonds of pure methanol in PEI.

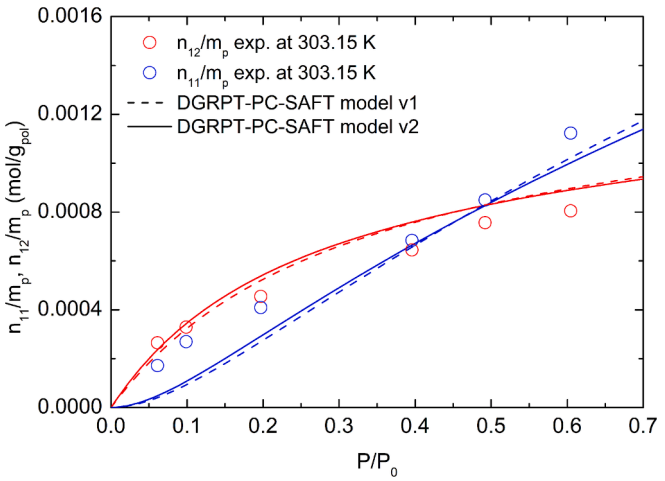

Fig. 9. Comparison of the experimental data [48] and the full predictions of both model versions for the self and cross hydrogen bonds of pure methanol in 6FDA-ODA.

4. Conclusions

The proposed version of DGRPT-PC-SAFT (v2) model, which is based on free volume inspired self-consistent estimation of the $\lambda_{j,p}$ parameters, has shown versatile model capability in dealing with multicomponent systems which span "continuously" from high free volume to "dense" polymer/penetrants phase. The v2 model allowed filling the gap between the two versions of the DGRPT proposed by Marshall in literature to address the low and high free volume limiting cases ($\lambda_{j,p} = 0$ and$\lambda_{j,p} = 1$ respectively) without introducing any additional pairwise adjustable parameter. Notably, v2 model exhibits in the case of high free volume or "dense" polymer/penetrant systems, similar model performances with respect to the corresponding DGRPT versions specifically developed in literature.

In particular, DGRPT-PC-SAFT v2 model shows full satisfactorily performances in terms of solubility correlation of several penetrants ranging from non-interacting gases to associating alcohols in three polymeric matrices exhibiting different level of free volume such as PTMSP and two polyimides (PEI and 6FDA-ODA). Remarkably, the model implementation proved to be successful in predicting solubility separation in a system of technological interest, i.e., CO_2/CH_4 in PTMSP at 308 K and total pressure up to 3.5 MPa in a wide range of concentration of the binary gas mixture. In addition, in the case of PTMSP matrix, the model has been also able to reproduce the qualitative behaviour of the penetrant induced swelling of PTMSP/CH_3OH and PTMSP/DMC binary systems.

To further test the model capability, we have also investigated two "dense" polymer/penetrant systems of technological interest exhibiting complex interactional scenario, i.e., PEI/CH_3OH and 6FDA-ODA/CH_3OH at 303 K and vapor activity up to 0.7.

The proposed DGRPT-PC-SAFT model provided, also in these cases, a satisfactory fitting of previously determined experimental sorption isotherms of methanol and a description of self- and cross-hydrogen bonding established within the polymer phases that is in very good qualitative and quantitative agreement with the outcomes of in-situ FTIR analysis performed previously, thus providing a detailed picture of the complex interactional scenario occurring in the glassy polymer/penetrant phase. Notably, model predictions were also able to reproduce quantitatively the occurrence of self/cross interactional crossover observed for the 6FDA-ODA/methanol system, as the activity of methanol vapor increases, marking the onset of methanol clustering. Overall, the polyimides-methanol results presented validate the proposed multidisciplinary procedure, (implemented for the first time in the general framework of PC-SAFT), supporting, in particular, the legitimacy of the *IE* hypothesis for the set of variables related to the association term, which has been, in general, implicitly assumed to be valid in the literature when applying the NETGP-PC-SAFT to interacting systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] T.-M. Durďáková, Z. Hrdlička, M. Dendisová, M. Švecová, O. Vopička, Swelling and plasticization of PDMS and PTMSP in methanol and dimethyl carbonate vapors and liquids: volume, mechanical properties, Raman spectra, Polymer 188 (2020) 122140, https://doi.org/10.1016/j.polymer.2019.122140.
[2] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390–400, https://doi.org/10.1016/j.memsci.2008.04.030.
[3] O. Vopička, M.G. De Angelis, G.C. Sarti, Mixed gas sorption in glassy polymeric membranes: I. CO_2/CH_4 and n-C_4/CH_4 mixtures sorption in poly(1-trimethylsilyl-1-propyne) (PTMSP), J. Membr. Sci. 449 (2014) 97–108, https://doi.org/10.1016/j.memsci.2013.06.065.
[4] K. Tanaka, H. Kita, M. Okano, K. Okamoto, Permeability and permselectivity of gases in fluorinated and non-fluorinated polyimides, Polymer 33 (1992) 585–592, https://doi.org/10.1016/0032-3861(92)90736-G.
[5] J.D. Wind, C. Staudt-Bickel, D.R. Paul, W.J. Koros, The effects of crosslinking chemistry on CO2 plasticization of polyimide gas separation membranes, Ind. Eng. Chem. Res. 41 (2002) 6139–6148, https://doi.org/10.1021/ie0204639.
[6] Y. Li, M. Yavari, A. Baldanza, E. Di Maio, Y. Okamoto, H. Lin, M. Galizia, Volumetric properties and sorption behaviour of perfluoropolymers with dioxolane pendant rings, Ind. Eng. Chem. Res. 59 (2020) 5276–5286, https://doi.org/10.1021/acs.iecr.9b03411.
[7] Z. Liu, W. Qiu, W. Quan, Y. Liu, W.J. Koros, Fine-tuned thermally cross-linkable 6FDA-based polyimide membranes for aggressive natural gas separation, J. Membr. Sci. 635 (2021) 119474, https://doi.org/10.1016/j.memsci.2021.119474.
[8] J. Deng, Z. Huang, B.J. Sundell, D.J. Harrigan, S.A. Sharber, K. Zhang, R. Guo, M. Galizia, State of the art and prospects of chemically and thermally aggressive membrane gas separations: Insights from polymer science, Polymer 229 (2021) 123988, https://doi.org/10.1016/j.polymer.2021.123988.
[9] M. Cai, J. Chen, H. Wang, J. Wu, S. Zhang, Y. Min, Polyimide-based thermal rearranged (TR) membrane for highly efficient natural gas separation: A review, Sep. Purif Technol. 355 (2025) 129624, https://doi.org/10.1016/j.seppur.2024.129624.
[10] D.L. Goff, E.L. Yuan, H. Long, H.J. Neuhaus, Polymer Materials for Electronics, Packaging and Interconnection ACS (1989) 93–100, https://doi.org/10.1021/bk-1989-0407.ch008.
[11] M.R. Coleman, W.J. Koros, Isomeric polyimides based on fluorinated dianhydrides and diamines for gas separation applications, J. Membr. Sci. 50 (1990) 285–297, https://doi.org/10.1016/S0376-7388(00)80626-2.
[12] I.A. Qazi, A.A. Abd, M.M. Hasan, M.R. Othman, Optimizing hydrogen purification performance by membrane from industrial waste of methanol production, Chem. Eng. J. Adv. 14 (2023) 100490, https://doi.org/10.1016/j.ceja.2023.100490.
[13] R. Esposito, M.A. Abdulhamid, L. Upadhyaya, A. Volkov, S.P. Nunes, Carboxyl-functionalized polyimide for polar/non-polar organic solvent separation by pervaporation, J. Membrane Sci. 713 (2025) 123277, https://doi.org/10.1016/j.memsci.2024.123277.
[14] G. Scherillo, G. Mensitieri, A. Baldanza, V. Loianno, P. Musto, M. Pannico, A. Correa, A. De Nicola, G. Milano, Weak interactions between poly(ether imide) and carbon dioxide: a multiscale investigation combining experiments, theory, and simulations, Macromolecules 55 (2022) 10773–10787, https://doi.org/10.1021/acs.macromol.2c01382.
[15] A. Baldanza, C. Brondi, V. Loianno, G. Mensitieri, G. Scherillo, Modelling relative humidity and temperature effects on CO_2 gas transport in polyetherimide, Polymer 291 (2024) 126595, https://doi.org/10.1016/j.polymer.2023.126595.
[16] T. Matsuura, Y. Hasuda, S. Nishi, Y. Noriyoshi, Polyimide derived from 2, 2'-bis (trifluoromethyl)-4, 4'-diaminobiphenyl. 1. Synthesis and characterization of polyimides prepared with 2, 2'-bis(3, 4-dicarboxyphenyl)hexafluoropropane dianhydride or pyromellitic dianhydride, Macromolecules 24 (1991) 5001–5005, https://doi.org/10.1021/ma00018a004.
[17] W.J. Chen, C.R. Martin, Highly methanol selective membranes for the pervaporation separation of methyl t-butyl ether/methanol mixtures, J. Membr. Sci. 104 (1995) 101–108, https://doi.org/10.1016/0376-7388(95)00017-7.
[18] W. Qiu, M. Kosuri, F. Zhou, W.J. Koros, Dehydration of ethanol–water mixtures using asymmetric hollow fiber membranes from commercial polyimides, J. Membr. Sci. 327 (2009) 96–103, https://doi.org/10.1016/j.memsci.2008.11.029.
[19] V. Loianno, A. Baldanza, G. Scherillo, R. Jamaledin, P. Musto, G. Mensitieri, A hyphenated approach combining pressure-decay and in situ FT-NIR spectroscopy to monitor penetrant sorption and concurrent swelling in polymers, Ind. Eng. Chem. Res. 60 (2021) 5494–5503, https://doi.org/10.1021/acs.iecr.1c00264.
[20] V. Loianno, G. Mensitieri, A. Baldanza, G. Scherillo, P. Musto, Combining FTIR spectroscopy and pressure-decay techniques to analyze sorption isotherms and

sorption kinetics of pure gases and their mixtures in polymers: The case of CO_2 and CH_4 sorption in polydimethylsiloxane, J. Membr. Sci. 652 (2022) 120445, https://doi.org/10.1016/j.memsci.2022.120445.
[21] F. Doghieri, G.C. Sarti, Nonequilibrium lattice fluid: a predictive model for the solubility in glassy polymers, Macromolecules 29 (1996) 7885–7896, https://doi.org/10.1021/ma951366c.
[22] G.C. Sarti, F. Doghieri, Predictions of the solubility of gases in glassy polymers based on the NELF model, Chem. Eng. Sci. 53 (1998) 3435–3447, https://doi.org/10.1016/S0009-2509(98)00143-2.
[23] G. Astarita, Thermodynamics: An Advanced Textbook for Chemical Engineers, Plenum Press, New York, 1989.
[24] Th. De Donder, P. Van Rysselberghe, Thermodynamic Theory of Affinity, Stanford University Press, 1936.
[25] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, SAFT: equation-of-state solution model for associating fluids, Fluid Phase Equilibr. 52 (1989) 31–38, https://doi.org/10.1016/0378-3812(89)80308-5.
[26] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, New reference equation of state for associating liquids, Ind. Eng. Chem. Res. 29 (1990) 1709–1721, https://doi.org/10.1021/ie00104a021.
[27] J. Gross, G. Sadowski, Perturbed-chain SAFT: an equation of state based on a perturbation theory for chain molecules, Ind. Eng. Chem. Res. 40 (2001) 1244–1260, https://doi.org/10.1021/ie0003887.
[28] J. Gross, G. Sadowski, Application of the perturbed-chain SAFT equation of state to associating systems, Ind. Eng. Chem. Res. 41 (2002) 5510–5515, https://doi.org/10.1021/ie010954d.
[29] M.C. Arndt, G. Sadowski, Modeling poly(N-isopropylacrylamide) hydrogels in water/alcohol mixtures with PC-SAFT, Macromolecules 45 (2012) 6686–6696, https://doi.org/10.1021/ma300683k.
[30] J. Liu, W.G. Chapman, Thermodynamic modeling of the equilibrium partitioning of hydrocarbons in nanoporous kerogen, Energy Fuels 33 (2019) 891–904, https://doi.org/10.1021/acs.energyfuels.8b03771.
[31] L. Liu, S.E. Kentish, Modelling of methane and n-butane sorption, diffusion and permeation in polydimethylsiloxane using PC-SAFT, J. Membr. Sci. 597 (2020) 117642, https://doi.org/10.1016/j.memsci.2019.117642.
[32] M.G. De Angelis, F. Doghieri, G.C. Sarti, B.D. Freeman, Modeling gas sorption in amorphous teflon through the non equilibrium thermodynamics for glassy polymers (NET-GP) approach, Desalination 193 (2006) 82–89, https://doi.org/10.1016/j.desal.2005.06.057.
[33] M.L. Michelsen, E.M. Hendriks, Physical properties from association models, Fluid Phase Equilibr. 180 (2001) 165–174, https://doi.org/10.1016/S0378-3812(01)00344-2.
[34] G. Mensitieri, G. Scherillo, C. Panayiotou, P. Musto, Towards a predictive thermodynamic description of sorption processes in polymers: The synergy between theoretical EoS models and vibrational spectroscopy, Mater. Sci. Rep. 140 (2020) 100525, https://doi.org/10.1016/j.mser.2019.100525.
[35] E.M. Davis, Y.A. Elabd, Prediction of water solubility in glassy polymers using nonequilibrium thermodynamics, Ind. Eng. Chem. Res. 52 (2013) 12865–12875, https://doi.org/10.1021/ie401713h.
[36] L. Liu, S.E. Kentish, Modeling of carbon dioxide and water sorption in glassy polymers through PC-SAFT and NET PEC-SAFT, Polymer 104 (2016) 149–155, https://doi.org/10.1016/j.polymer.2016.10.002.
[37] A. De Nicola, A. Correa, G. Milano, P. La Manna, P. Musto, G. Mensitieri, G. Scherillo, Local structure and dynamics of water absorbed in poly (ether imide): a hydrogen bonding anatomy, J. Phys. Chem. B 121 (2017) 3162–3176, https://doi.org/10.1021/acs.jpcb.7b00992.
[38] C. Panayiotou, M. Pantoula, E. Stefanis, I. Tsivintzelis, I.G. Economou, Nonrandom hydrogen-bonding model of fluids and their mixtures. 1. pure fluids, Ind. Eng. Chem. Res. 43 (2004) 6592–6606, https://doi.org/10.1021/ie040114+.
[39] C. Panayiotou, I. Tsivintzelis, I.G. Economou, Nonrandom hydrogen-bonding model of fluids and their mixtures. 2. Multicomponent mixtures, Ind. Eng. Chem. Res. 46 (2007) 2628–2636, https://doi.org/10.1021/ie0612919.
[40] B.D. Marshall, R. Mathias, R.P. Lively, B.A. McCool, Theoretically self-consistent nonequilibrium thermodynamics of glassy polymer theory for the solubility of vapors and liquids in glassy polymers, Ind. Eng. Chem. Res. 60 (2021) 13377–13387, https://doi.org/10.1021/acs.iecr.1c02194.
[41] B.D. Marshall, Modified dry glass reference perturbation theory for linear sorption in dense glassy polymers, Ind. Eng. Chem. Res. 62 (2023) 20029–20036, https://doi.org/10.1021/acs.iecr.3c03133.
[42] M. Minelli, S. Campagnoli, M.G. De Angelis, F. Doghieri, G.C. Sarti, Predictive model for the solubility of fluid mixtures in glassy polymers, Macromolecules 44 (2011) 4852–4862, https://doi.org/10.1021/ma200602d.
[43] M. Minelli, F. Doghieri, Predictive model for gas and vapor solubility and swelling in glassy polymers I: Application to different polymer/penetrant systems, Fluid Phase Equilib. 381 (2014) 1–11, https://doi.org/10.1016/j.fluid.2014.08.010.
[44] A. Baldanza, V. Loianno, G. Mensitieri, G. Scherillo, Predictive approach for the solubility and permeability of binary gas mixtures in glassy polymers based on an NETGP-NRHB model, Ind. Eng. Chem. Res. 61 (2022) 3439–3456, https://doi.org/10.1021/acs.iecr.1c04864.
[45] R.G. Wissinger, M.E. Paulaitis, Swelling and sorption in polymer-CO_2 mixtures at elevated pressures, J. Polym. Sci. Pol. Phys. 25 (1987) 2497–2510, https://doi.org/10.1002/polb.1987.090251206.
[46] O. Vopička, D. Radotínský, K. Friess, Sorption of vapor mixtures of methanol and dimethyl carbonate in PTMSP: Cooperative and competitive sorption in one system, Eur. Polym. J. 75 (2016) 243–250, https://doi.org/10.1016/j.eurpolymj.2015.12.015.
[47] V. Carlà, Y. Hussain, C. Grant, G.C. Sarti, R.G. Carbonell, F. Doghieri, Modeling sorption kinetics of carbon dioxide in glassy polymeric films using the nonequilibrium thermodynamics approach, Ind. Eng. Chem. Res. 48 (8) (2009) 3844–3854, https://doi.org/10.1021/ie800655w.
[48] M. Galizia, P. La Manna, M. Pannico, G. Mensitieri, P. Musto, Methanol diffusion in polyimides: A molecular description, Polymer 5 (2014) 1028–1039, https://doi.org/10.1016/j.polymer.2014.01.009.
[49] F. Tumakaka, J. Gross, G. Sadowski, Thermodynamic modeling of complex systems using PC-SAFT, Fluid Phase Equilibr. 228–229 (2005) 89–98, https://doi.org/10.1016/j.fluid.2004.09.037.
[50] M. Kleiner, G. Sadowski, Modeling of polar systems using PCP-SAFT: an approach to account for induced-association interactions, J. Phys. Chem. C 111 (2007) 15544–15553, https://doi.org/10.1021/jp072640v.
[51] J.P. Wolbach, S.I. Sandler, Using molecular orbital calculations to describe the phase behavior of cross-associating mixtures, Ind. Eng. Chem. Res. 37 (1998) 2917–2928, https://doi.org/10.1021/ie970781l.
[52] B.D. Marshall, C.P. Bokis, Revisiting the treatment of cross-association interactions in oxygenate mixtures with the polar PC-SAFT equation of state, Fluid Phase Equilibr. 529 (2021) 112867, https://doi.org/10.1016/j.fluid.2020.112867.
[53] National Institute of Standards and Technology (NIST) Standard Reference Database 69, 04/04/2024, https://webbook.nist.gov/chemistry/fluid/.
[54] G. Scherillo, L. Sanguigno, M. Galizia, M. Lavorgna, P. Musto, M. Mensitieri, Non-equilibrium compressible lattice theories accounting for hydrogen bonding interactions: Modelling water sorption thermodynamics in fluorinated polyimides, Fluid Phase Equilibr. 334 (2012) 166–188, https://doi.org/10.1016/j.fluid.2012.06.030.