Modeling mass transport in dense polymer membranes: cooperative synergy among multiple scale approaches

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The modeling description of basic transport phenomena of either liquid, gas or vapor molecules in dense polymeric membranes is of tremendous impact for the separation industry, which relies on solid models for the design of optimal process conditions, for the selection of the most suitable membrane materials as well as for the development of novel ones. Such models need to deal with several physical aspects and phenomena, spanning over broad time and length scales, thus requiring multiple approaches. The solid frameworks now available mainly rely on the solution–diffusion theory, in which equation of state models and free volume theories are applied for the description of thermodynamic and kinetic properties, to be coupled in appropriate transport schemes.

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Introduction

Membrane processes have become a real alternative to conventional separation methods in various sectors of industrial relevance, in view of their lightweight, compact and modular design, the ability to overcome some intrinsic thermodynamic limitations (e.g. azeotropes), moderate energy requirements and limited footprint. The available processes now are not only for water purification and desalination, but membrane separation is also suitable to gas separation (GS) [1] (e.g. hydrogen purifications, biogas or natural gas upgrading/sweetening, or carbon capture related applications), and to hydro-alcoholic or organic solvent mixtures separation, by pervaporation (PV) [2] and organic solvent nanofiltration (OSN) [3], respectively.

Polymeric membranes provide the best compromise between separation performances, resistance and ease of manufacturing, thus representing the state of the art system for these applications [4], using continuous and dense thin selective layers, in which the mechanism of dissolution and molecular transport provide the desired extent of separation, according to the well know solution–diffusion scheme [5].

Model description

The model description of membrane performance is important not only for appropriate separation engineering and the best design of operative conditions, but also to develop novel materials for targeted applications. Therefore, the attainment of the full physical picture of the transport process and the deep understanding of the mechanism requires a dedicated analysis, spanning from the polymer material properties, including the interactions with relevant penetrants, to the description of the transport rates across the membranes, with attention to the influence of the environment that can lead to possible detrimental effects over time (e.g. plasticization, aging, or fouling issues). Relevantly, these features are associated to different properties that may vary over a broad range of characteristic length and time scales, so that a sole approach can be hardly used for an accurate and appropriate model analysis, and there is a clear need of a multiscale method, for a proper and comprehensive understanding.

Purely molecular simulations may result inappropriate to describe the whole mechanism of penetrant transport in polymer membranes, particularly in the case of glassy polymers, being rather time consuming, with results that cannot be easily extended to different systems or conditions. For these reasons, only few examples are available in the literature [6–8]. The obtained accuracy may also be limited for practical uses, so that more accurate modeling is obtained by direct use of selected experimental data. Furthermore, some of the mechanisms, for example, those involving macromolecular rearrangements that take place over an extended period of time (e.g. aging or plasticization phenomena), are definitely out of reach.

In view of these limitations, relevant not only to membrane separation processes, integrated multiscale models [9] or coarse grained approaches [10] have been developed and proposed for the analysis and the prediction of polymer properties. The case of transport in dense polymeric membranes, in particular, may be conveniently

Macroscale models

described by macroscopic approaches, which rely on separate models for penetrant sorption and diffusion.

The description of fluid solubility, either of gases, vapors or liquids, in polymers is often obtained by activity coefficients methods, such as Flory Huggins [11], or by equation of state (EoS) models, as Lattice Fluid [12] or Statistical Associating Fluid Theory (SAFT) [13] approaches, suitable to describe equilibrium rubbery systems. An appropriate extension (Flory–Rehner) is also available to account for the presence of crosslinks [14,15]. Glassy systems require a different thermodynamic treatment due to their peculiar non-equilibrium nature, for which the Non Equilibrium Thermodynamics for Glassy Polymers (NET-GP) model is available [16,17••]. Other approaches involving partial or full adsorption contributions are limited to specific behaviors, with no predictive ability, and are characterized by serious phisical inconsistencies [11,18]. Therefore, they will not be considered here.

The main framework for the description of penetrant diffusion coefficient in polymeric materials is given by the free volume theory [19], endowed by different approximation levels, and applicable to all kinds of penetrant molecules. The concept relies on considering the presence of low-density regions at the nanoscale available for solute diffusion, which might dynamically evolve within the polymer matrix, and on the energy required by the penetrant to jump into that hole [20]. Simplified approaches provide penetrant diffusivities in the limit of infinite

dilution (e.g. light gases at moderate pressures) [21], in which the polymer structure is basically unaltered by the presence of the penetrant. Conversely, more elaborated formulations, accompanied to a larger number of parameters, are required to account for solute concentration dependence [22]. Relevantly, the free volume theory is readily available to evaluate the effect of a second component on the value of diffusion coefficient, that is, to predict the diffusivity of penetrant mixtures [23,24].

It is noteworthy that the actual driving force of the diffusion process, according to thermodynamic arguments, is given by the chemical potential gradient, which depends on solute concentration, pressure and temperature, and it is thus appropriate for the representation of transport phenomena.

Modeling multicomponent transport in polymer systems, however, is a delicate task, not all possible expressions are feasible for the diffusion coefficients, and a more thorough analysis of the mutual interaction of the diffusion coefficients of the different species is required. Thermodynamic limitations, indeed, have to be carefully considered in order to ensure the consistency and the robustness of the modeling approach, which has clearly to fulfill all thermodynamic constraints (in terms of Gibbs–Duhem relationship) and possibly symmetry requirements (Onsager criterion in linear relationships) [25,26]. For these reasons, dedicated transport procedures are available for modeling multicomponent transport, appropriately accounting for the effect of mutual interactions. The two (alternative) main approaches

Figure 1
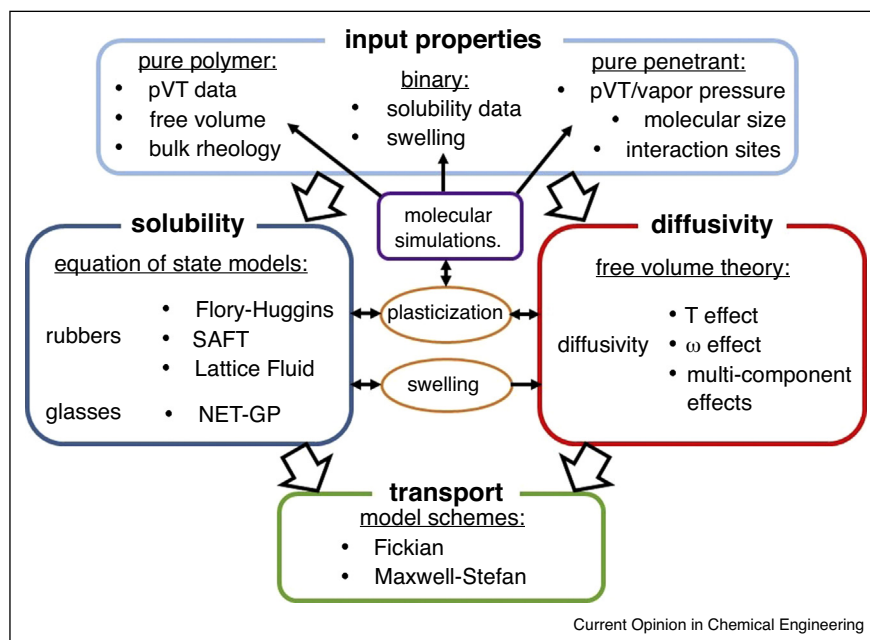
Working flow chart for modeling the multicomponent transport in a nonporous polymer membrane, according to the solution diffusion mechanism.

are derived according to generalized Fickian or Maxwell–Stephan schemes [27,28], which have to be complemented by an appropriate solubility and diffusivity model.

Figure 1 illustrates the working flow chart for modeling the multicomponent transport properties in a nonporous polymeric membrane.

The required input parameters for these macroscopic models are represented by bulk properties of pure fluids and polymers, typically obtained from experimental data. This is the case for both equations of state and free volume models for solubility and diffusivity, respectively, which make use of volumetric (for EoS and diffusion coefficient) and rheological properties (for diffusion only) of the polymers and a few characteristics for the penetrants. Such data are often already available in the literature for several (conventional) polymers or

experimentally accessible for most of polymers through independent measurements. However, this route may not be feasible, or simple, for some innovative or peculiar polymer species. Molecular models can be conveniently used to overcome such limitations, thus elaborating a multiscale strategy for penetrant transport. For instance, molecular dynamics has been used to retrieve of EoS parameters by direct determination [29] or from the *in-silico* simulation of the volumetric properties [30,31•]. The packing structure of the macromolecules can also be evaluated by molecular modeling, to identify the fractional free volume and time average of the cavity size distribution [32,33], useful for the diffusivity description of penetrants of different sizes and shapes.

Molecular models can be used not only for the determination of the properties of pure substances, but also for

Figure 2
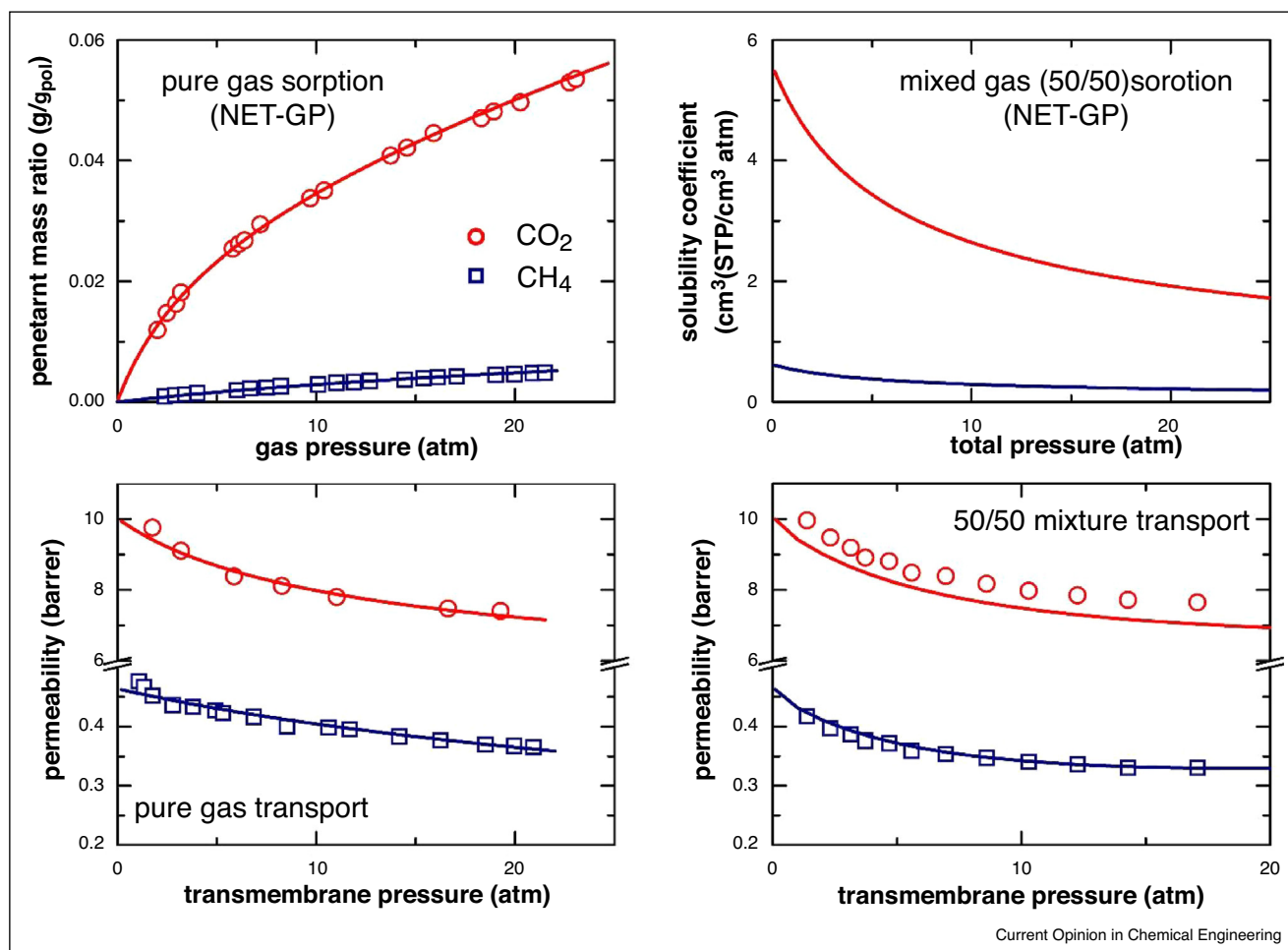
Multicomponent transport in polyarylate membrane for gas separation (CO_2/CH_4) at 35°C. **(a)** NET-GP thermodynamic model for the description pure gas sorption at different pressures [52•]; **(b)** mixed gas solubility for a 50/50 mixture calculated by NET-GP model [52•]; **(c)** gas permeability of the pure components by the STM-GP [52•]; **(d)** mixed gas permeability of the two components in a 50/50 mixture, at different transmembrane pressure [52•].

selected binary polymer/penetrant properties, which are required for the description of both solubility and transport. For instance, molecular dynamics have been employed for the direct simulation of diffusion coefficient of relevant penetrants [34•,35], for the evaluation of swelling and plasticization effects [36,37,38], or even to estimate multi-component transport properties [39].

Relevant modeling approaches have been also applied to predict membrane properties based on few characteristics of the polymer and penetrant species, mainly based on macroscopic approaches and relying on semiempirical correlations. Among the others, interesting analyses have been provided to interpret the upper-bound in the correlation between gas permeability and selectivity [40] for gas separation membranes [41,42].

Relevant modeling examples

The three membrane processes considered above, gas separation, pervaporation and organic solvent nanofiltration, have been analyzed thoroughly by different modeling approaches. Some relevant examples can be found in the literature in which all the different aspects described are carefully considered, for the case of gas separation [43,44•,45], pervaporation [46••,47,48•], and organic solvent nanofiltration [49,50,51••].

In particular, Figure 2 reports the case of the transport of a CO_2/CH_4 binary mixture (at fixed gas concentration) in glassy polyarylate membrane for gas separation [52•].

The NET-GP model, first applied to the analysis of pure gas sorption, describes well the experimental solubility data

Figure 3
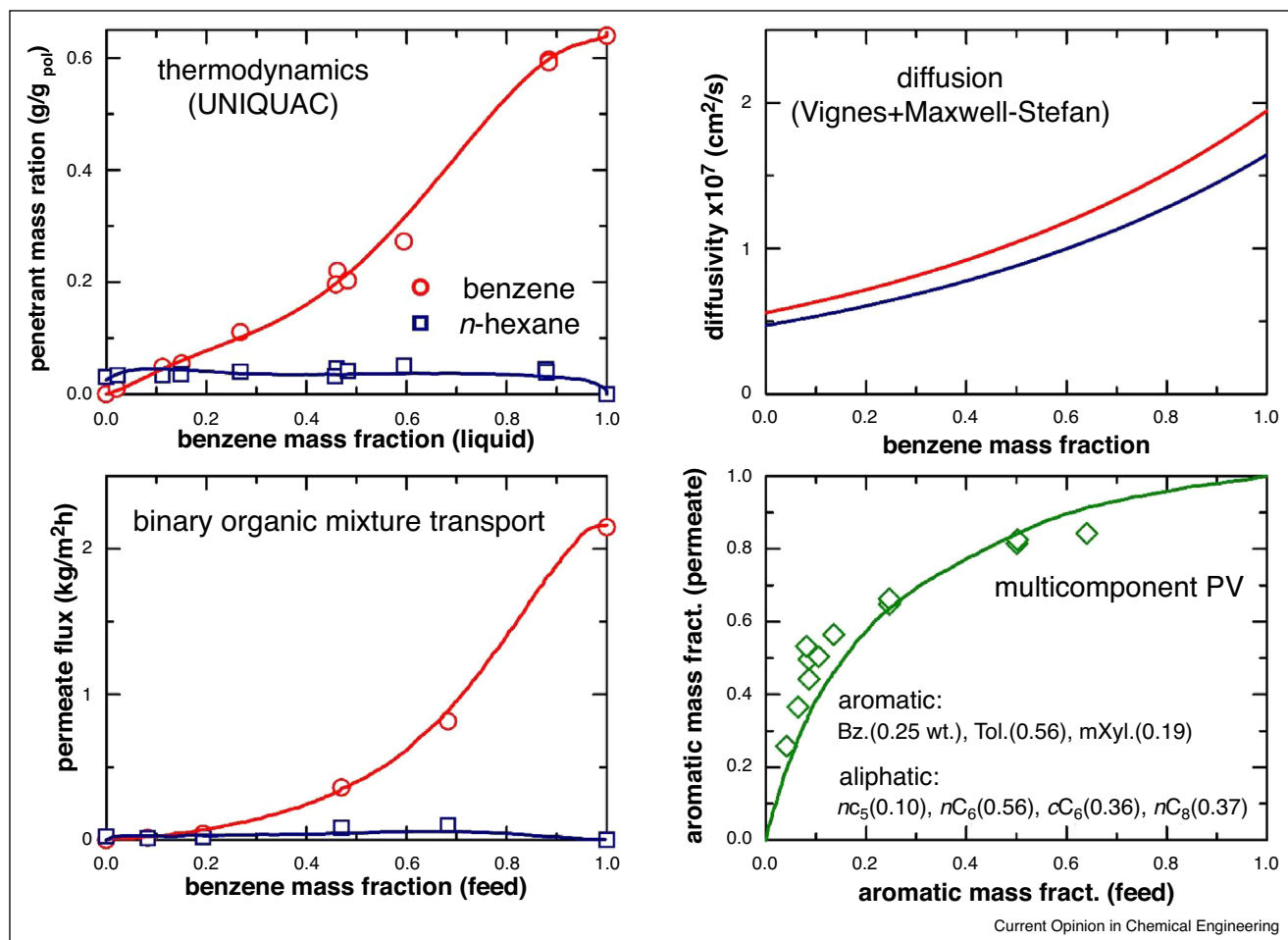
Multicomponent transport at 25°C in polyurethane membrane for pervaporation for the separation of aromatic/aliphatic organic compounds, and for benzene/n-hexane, in particular. **(a)** penetrant solubility for the binary mixture at different concentrations by UNIQUAC model [55]; **(b)** diffusion coefficient of the two penetrants as described by the Vignes approach in the Maxwell–Stefan framework [55]; **(c)** resulting fluxes of the two components in a pervaporation operation [55]; **(d)** resulting separation (permeate versus feed concentrations) for two reference aromatic and aliphatic multicomponent mixtures [55].

accounting for the associated penetrant-induced swelling; mixed gas solubility can then be obtained predictively, with the identification of competitive sorption effects. Gas transport is described by considering a simple dependence of gas diffusivity on its concentration in the polymer, and the negative chemical potential gradient as the driving force for the diffusion process: the transport parameters are retrieved from pure gas permeability. The approach for multicomponent transport is developed in a simple Fickian scheme able to account for the mutual interaction of the diffusion coefficients, and it allows then the prediction of mixed gas permeability at various pressures, based on the assumption of rather dilute polymer/penetrants mixtures due to the limited solubility of gaseous solutes. Alternative approaches (Flory–Huggins and PC-SAFT with a Maxwell–Stefan scheme) have been employed to

describe the behavior of crosslinked membranes for the separation of CO_2/hydrocarbons or CH_4/hydrocarbons mixtures [43,53], relevant for industrial processes for the purification of natural gas. More general mixtures would require to consider the presence of a number of different components, some of them present even in trace amounts. A very limited number of studies, however, has been devoted to this aim, mainly by means of phenomenological approaches [54].

Figure 3 reports the description of the separation of aromatic and aliphatic mixtures in a pervaporation operation using a dense polyurethane membrane [55].

The penetrant solubility is treated as liquid–liquid equilibrium (LLE) between the organic solvent mixture and

Figure 4
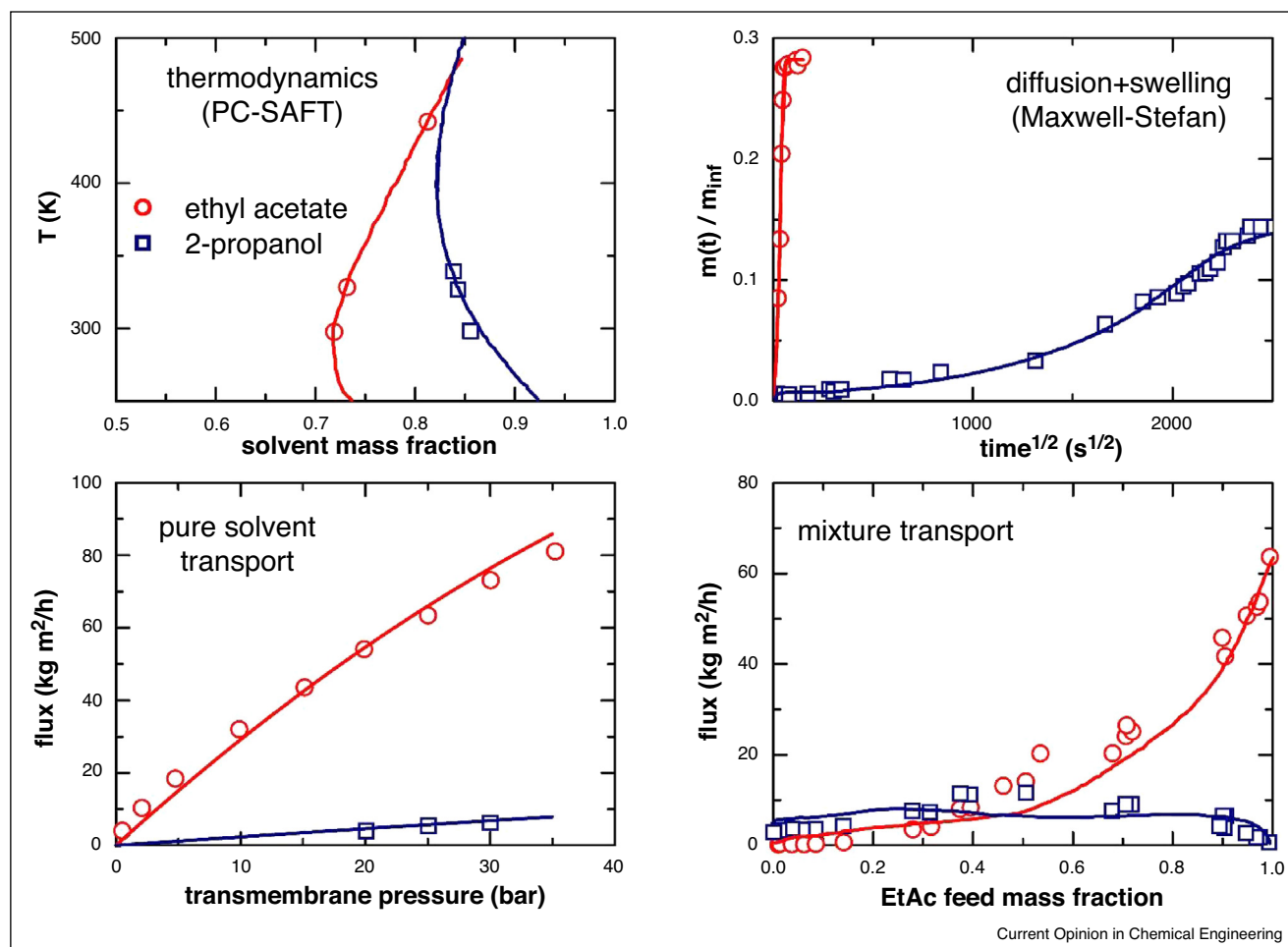
Multicomponent transport in polyimide-based membrane (STARMEM240^{TM}) for organic solvent nanofiltration and for the separation of ethylacetate and 2-propanol separation in particular. **(a)** PC-SAFT thermodynamic model for the description pure liquid solubility at different temperatures [57]; **(b)** penetrant diffusivities at 25°C described in the Maxwell–Stefan framework, also accounting for membrane swelling [58]; **(c)** transmembrane flux of the pure components at 25°C [56]; **(d)** transmembrane flux for the two components at 25°C, considering a liquid feed mixture of different concentrations at 25 bar of transmembrane pressure [55].

the polymer phase, and the UNIQUAC (or, alternatively, the Flory–Huggins) model is considered to describe phase equilibrium. The effect of plasticization on the penetrant diffusion coefficient is described by a simple correlation with the solutes concentration that accounts for penetrant size, modifying an early approach by Vignes. These properties are coupled in a Maxwell–Stefan framework, which allows the calculation of the transmembrane fluxes of the two components (benzene and hexane) of a binary mixture at different concentrations. The extension to a real mixture of several compounds (aromatic and aliphatic) is then straightforward.

Figure 4 shows the modeling description of transport properties in a polyimide-based membrane for organic solvent nanofiltration applied to the separation of ethyl acetate and propanol [56].

The model relies on a PC-SAFT thermodynamic approach, suitable to describe the solubility of the two pure liquids in the polymer membrane at different temperatures. The transport model considers pure substances diffusion, coupled with a mechanical equation (a simple Maxwell element) to account for swelling effects given by the viscoelastic response of the polymer below T_g. The transport model is developed in the Maxwell–Stefan framework, which provides the description of the transmembrane flux of the pure solvents as function of the applied pressure, and, ultimately, the prediction of the membrane performances with binary mixtures at different feed concentrations.

Conclusion and perspectives

The development and the use of macroscopic models for sorption and transport of low molecular weight species in nonporous polymers are of tremendous impact for membrane application, and it is thus a very popular topic in large expansion. In spite of the number of papers published, there is still the need to improve the model approaches developed so far, aiming to enhance the accuracy and the reliability of the phenomena description and of the predictive ability.

As a future outlook, a key aspect is related to the development of integrated and more general models able to describe, with the same approach, a broad spectrum of cases, ranging from glassy to rubbery polymers of different nature, with gas, vapors or liquid penetrants of various physicochemical properties.

The improved reliability of these models should allow their final implementation in the usual process simulation softwares, thus enabling the full design of a membrane process, in a similar fashion to conventional unit operations available in traditional chemical engineering. Moreover, the fundamental understanding of the material

properties and the physics of penetrant transport will be a precious knowledge for the design of novel separation membranes, looking for appropriate physically-sound correlations of membrane performances (including the upper-bound for gas separation) with relevant polymer material properties.

Finally, the assessment of the impact of polymer swelling or plasticization on membrane performances caused by separating gases or contaminants is of great relevance for the membrane community, together with the description of time deterioration of the membrane materials, as a consequence of physical aging effect. Both phenomena would require a comprehensive modeling approach, looking at multiple time and length scales, but their understanding and prediction represent a significant step forward for the operation of membrane systems for industrial separation and production.

Conflict of interest statement

Nothing declared.

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