



# Non-equilibrium compressible lattice theories accounting for hydrogen bonding interactions: Modelling water sorption thermodynamics in fluorinated polyimides

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## ABSTRACT

In this contribution the sorption thermodynamics of water in glassy fluorinated polyimides has been interpreted by using two non-equilibrium lattice models, accounting for hydrogen bond formation, which have been developed by extending, respectively, the Panayiotou–Sanchez (PS) and the Non-Random Hydrogen Bonding (NRHB) equilibrium models to the case of glassy polymers. The procedure used to extend the equilibrium models follows the same line of thought utilized by Doghieri and Sarti in deriving the Non-Equilibrium Thermodynamics for Glassy Polymers (NET-GP) model.

The approach has been found to be successful in interpreting experimental water sorption isotherms in two different perfluorinated polyimides, namely 6FDA-ODA and 6FDA-6FpDA. The models have been also found to be capable of supplying a good qualitative and quantitative estimate of the number of water–water and water/polymer hydrogen bonds, as emerged from the comparison of theoretical predictions with experimental data obtained by means of previous IR spectroscopic measurements.

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## 1. Introduction

Fluorinated polyimides have attracted in the last decades an increasing attention because of their exploitability in several fields, e.g. membrane based separation processes and protective coatings for electronic components. Such an interest is related to their peculiar properties, with particular reference to the good mechanical and chemical resistance and the high glass transition temperature, which make possible the use of these materials in operative environments characterized by high temperatures and contact with aggressive substances. In fact, the presence of fluorinated functional groups on the polymer backbone assures an elevated resistance to the most common solvents, due to the low values of cohesive energy density characterizing perfluorinated materials [1].

In this framework, sorption and transport properties of low molecular weight compounds in fluorinated polyimides is of relevant technological interest. This aspect is in fact of crucial relevance in membrane based applications, where materials with good chemical, mechanical and dimensional stability are required. In this field, fluorinated polyimides appear particularly promising because of their capability to keep such special properties also in the presence of solvents. Furthermore, fluorinated polyimides show good resistance to swelling and plasticization phenomena, which adversely affect membrane perm-selectivity [1,2].

In this context, it is of interest to investigate sorption of water in polyimides, since it may affect polyimides performances in both membrane applications and coating of electronic devices by modifying, respectively, gas separation properties and dielectric constant [3–5]. In fact, the reduced level of moisture absorption and of the value of dielectric constant typical of fluorinated polyimides is of particular relevance.

Gravimetric and spectroscopic analysis showed that both the amount of water absorbed and the diffusivity of water in polyimides depend strongly on the polymer chain structure, as well as on the presence of different functional groups on the polymer backbone [6–8]. This evidence confirms the importance of the interaction effects and puts in evidence that any modelling effort aimed at understanding

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## Nomenclature

### Symbols and definition

|                             |   |
|-----------------------------|---|
| $a_j^1$                     | number of proton acceptor groups of kind $j$ present on a molecule of type 1  |
| $A_{N_{ij}^{HB}}$           | affinity to the set of $N_{ij}^{HB}$ internal variables [J]   |
| $A_{N_{rs}^{NR}}$           | affinity to the set of $N_{rs}^{NR}$ internal variables [J]   |
| $A_{\rho_2}$                | affinity to the internal variable $\rho_2$ [ $\text{J g}^{-1} \text{cm}^3$ ]  |
| $A_{\rho_2}^E$              | affinity to $\rho_2$ in instantaneous equilibrium hypothesis at a given pressure, temperature, composition and polymer density [ $\text{J g}^{-1} \text{cm}^3$ ]  |
| $A_{12}^{OWP}$              | molar Helmholtz energy of formation of cross-hydrogen bonding between proton donors on water molecules and proton acceptors on the polymer backbone [ $\text{J mol}^{-1}$ ]   |
| $d_i^1$                     | number of proton donor groups of type $i$ on the molecule of type 1   |
| $E_{ij}^0$                  | molar internal energy of formation associated to hydrogen bonding between the proton donor group of type $i$ and the proton acceptor group of type $j$ [ $\text{J mol}^{-1}$ ]  |
| $E_{11}^{0W}$               | molar internal energy of formation of water self-HB between water molecules in pure water phase [ $\text{J mol}^{-1}$ ]   |
| $E_{11}^{0WP}$              | molar internal energy of formation of water self-HB between water molecules in the polymer–penetrant mixture [ $\text{J mol}^{-1}$ ]  |
| $G$                         | Gibbs energy of polymer penetrant mixture [J]   |
| $G_{ij}^0$                  | molar Gibbs energy of formation associated to hydrogen bonding between the proton donor group of type $i$ and the proton acceptor group of type $j$ [ $\text{J mol}^{-1}$ ]   |
| $G^E$                       | Gibbs energy of polymer–penetrant mixture in instantaneous equilibrium hypothesis at given pressure, temperature, polymer density, and composition [J]  |
| $k_{sw}$                    | penetrant swelling coefficient of the polymer–penetrant mixture as defined in Eq. (13) [MPa]  |
| $l_i$                       | lattice fluid parameter defined in Ref. [24]  |
| $m$                         | number of types of proton donors in the system  |
| $M_{W_i}$                   | molecular weight of component $i$ [ $\text{g mol}^{-1}$ ]   |
| $m_2$                       | mass of pure polymer [g]  |
| $n$                         | number of types of proton acceptors in the system   |
| $N$                         | number of moles of pure component   |
| $N_{ij}^{HB}$               | number of hydrogen bondings involving a proton donor of type $i$ and a proton acceptor of type $j$  |
| $n_1$                       | number of moles of component 1  |
| $n_2$                       | number of moles of component 2  |
| $n_1^{PE}$                  | number of moles of penetrant in the polymer–penetrant mixture at pseudo-equilibrium state in equilibrium with the penetrant external phase  |
| $\underline{N}_{ij}^{HB}$   | vector variable, whose generic component represents the total number of hydrogen bonding interactions between proton donor groups of type $i$ and proton acceptor groups of type $j$  |
| $\underline{N}_{rs}^{NR}$   | vector variable, whose generic component represents the effective number of non random contacts in the compressible lattice between mers of kind $r$ and the mers of kind $s$   |
| $\underline{N}_{ij}^{E,HB}$ | vector variable, whose generic component represents the total number of hydrogen bonding interactions between proton donor groups of type $i$ and proton acceptor groups of type $j$ in instantaneous equilibrium hypothesis at given pressure, temperature, polymer density, composition |
| $\underline{N}_{rs}^{E,NR}$ | vector variable, whose generic component represents the effective number of non random contacts in the compressible lattice between mers of kind $r$ and the mers of kind $s$ in instantaneous equilibrium hypothesis at given pressure, temperature, polymer density, and composition    |
| $N_{rs}^{NR}$               | symbol used for generic $rs$ component of the set of $\underline{N}_{rs}^{NR}$  |
| $N_{ij}^{HB}$               | symbol used for generic $ij$ component of the set of $\underline{N}_{ij}^{HB}$  |
| $n_{11}^{wp}$               | moles of self hydrogen bonding between the proton donor and the proton acceptor groups of water molecules within the polymer–water mixture [mol]  |
| $n_{12}^{wp}$               | moles of cross hydrogen bonding between the proton donor groups of the water molecules and the proton acceptor groups of the polymer within the polymer–water mixture [mol]   |
| $p$                         | pressure of the system [MPa]  |
| $P_i^*$                     | characteristic pressure of component $i$ [MPa]  |
| $p_0$                       | vapor tension of the penetrant [MPa]  |
| $\tilde{P}$                 | reduced pressure of the system  |
| $\tilde{P}_1$               | reduced pressure of the component 1   |
| $P^*$                       | characteristic pressure of the mixture [MPa]  |
| $q$                         | average number of lattice contacts per molecule in the polymer–penetrant mixture  |
| $q_1$                       | number of lattice contacts per molecule for component 1   |
| $r$                         | average number of cells occupied per molecule in the polymer–penetrant mixture  |
| $r_1^0$                     | number of lattice sites occupied per molecule of component 1 in the pure state (only defined in NELF and NET-GP SLHB model)   |
| $r_1$                       | number of lattice cells occupied by one molecule of component 1 in the polymer–penetrant mixture (in the case of NET-GP NRHB model it is used also for pure components)   |

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