SORPTION THERMODYNAMICS AND MASS TRANSPORT IN GLASSY AND RUBBERY POLYMERS IN PRESENCE OF HYDROGEN BONDING AND LEWIS ACID-BASE SPECIFIC INTERACTIONS

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The study of mass transport of low molecular weight molecules in polymers assumes a great interest both for theoretical, technology and engineering field. For example, the technologic importance of glassy organic polymers is well known, in fact application fields are extremely diverse, and they range from structural (hyperbaric widows) to environmental (membranes for industrial gas separation), or moreover to electronic field (ionic conductors, surface coatings for printed circuit boards). For this purpose, several attempts have been proposed in the literature, aimed at predicting mass transport of low molecular weight compounds (penetrants) within rubbery or glassy polymer-penetrant mixtures. Some approaches are rooted on rational non-equilibrium thermodynamics with internal state variables, which consist in order parameters quantifying the departure of glassy systems from the equilibrium conditions. In this framework, the constitutive class of non-equilibrium glassy polymer – penetrant mixture state is given by adding a set of order parameters to the external state variables which determine the equilibrium, such as pressure, temperature and composition. For example, Sanchez-Lacombe (S-L) model and its extension to the out of equilibrium state, Non-equilibrium Lattice Fluid (NELF) model, are widely used in literature to deal with sorption in glassy and rubbery polymeric membranes. However, they cannot take into account for specific interaction (i.e. hydrogen bonding and Lewis acid-base interactions). In addition, it has been demonstrated that S-L model is thermodynamically inconsistent, as ideal gas state approaches, and the correction, proposed in literature onto the original S-L model, only partially circumvent the inconsistency. On the other hand, Non-Randomness Hydrogen Bonding (NRHB) model and its extension to the Non-Equilibrium Thermodynamic Glassy Polymer (NETGP) state are lattice fluid models which are able to take into account for the aforementioned specific interactions.

The aim of this PhD thesis is to validate a model which allows to describe satisfactorily mass transport of mixtures of low molecular weight gases (or vapors) in glassy and rubbery polymers in presence of specific interactions (hydrogen bonding and Lewis acid-base interactions). The theoretical approach is supported by a new experimental setup specifically suited to measure sorption and diffusion of mixtures light gases (or vapors) in glassy and rubbery polymeric membranes. The experimental system is based on the combination of in situ FT-IR vibrational spectroscopy with the barometric pressure decay technique.

To this purpose, the first year of the PhD was primarily centered on studying literature about sorption thermodynamic and mass transport models for rubbery and glassy polymers; in particular, NRHB model and its extension to out of equilibrium (glassy state) NETGP-NRHB model have been selected, since their capability to take into account for hydrogen bonding and Lewis acid-base specific interactions. A first contribution consisted of demonstrating the thermodynamic consistency of the NRHB model and developing, for the first time, the explicit equations of NETGP-NRHB for multicomponent mixture. Finally, the model has been validated against experimental sorption data of binary mixtures of light gases in glassy polymers, available in literature.

Since a synergic development of experimental and theoretical approaches is needed, during the second year, a new hyphenated technique based on concurrent pressure-decay and in situ FT-IR vibrational spectroscopy measurements has been implemented to study sorption and diffusion of a low molecular weight compounds in polymeric membranes. In order to validate the hyphenated technique and verify its accuracy, PDMS-CO_2 system at 25°C with CO_2 pressure up to 9 bar has been selected due to the presence of many experimental data present in literature and the technological interest for this system. A further result, obtained by the combination of these two techniques, was the measurement of the PDMS swelling in presence of CO_2, on the basis of the FT-IR spectral analysis. Measured sorption, diffusion and swelling data are in good agreement with the data found in literature. From the theoretical point of view, to complete the description of the mass transport, i.e. the diffusion or the permeation phenomena, an approach based on Free Volume theories is applied to NETGP-NRHB, in which the driving force of the diffusive flux of the species *i* is proportional to the gradient of its chemical potential. The predicted permeability coefficients are in accordance with the experimental data found in literature and, in some case, they better agree the data than the predictions already present in literature.

Finally, in the third year of PhD research work, the hyphenated technique has been applied, for the first time, to study sorption of binary light gases mixtures in polymeric membranes; in particular, PDMS-CO_2-CH_4 system is selected to validate the new measurement system also for ternary mixtures. In parallel, permeation measurements involving a glassy polymer used in separation gas membrane applications have been performed, to this aim Polyetherimide (PEI) has been selected. Permeation measurements for the system PEI-CO_2-H_2O (at 1 atm and temperature up to 45°C) have been performed in order to model the permeability through a polymeric glassy membrane in presence of strong specific interactions (i.e. hydrogen bonding and Lewis acid-base interactions) and to validate the predictions with experimental data.
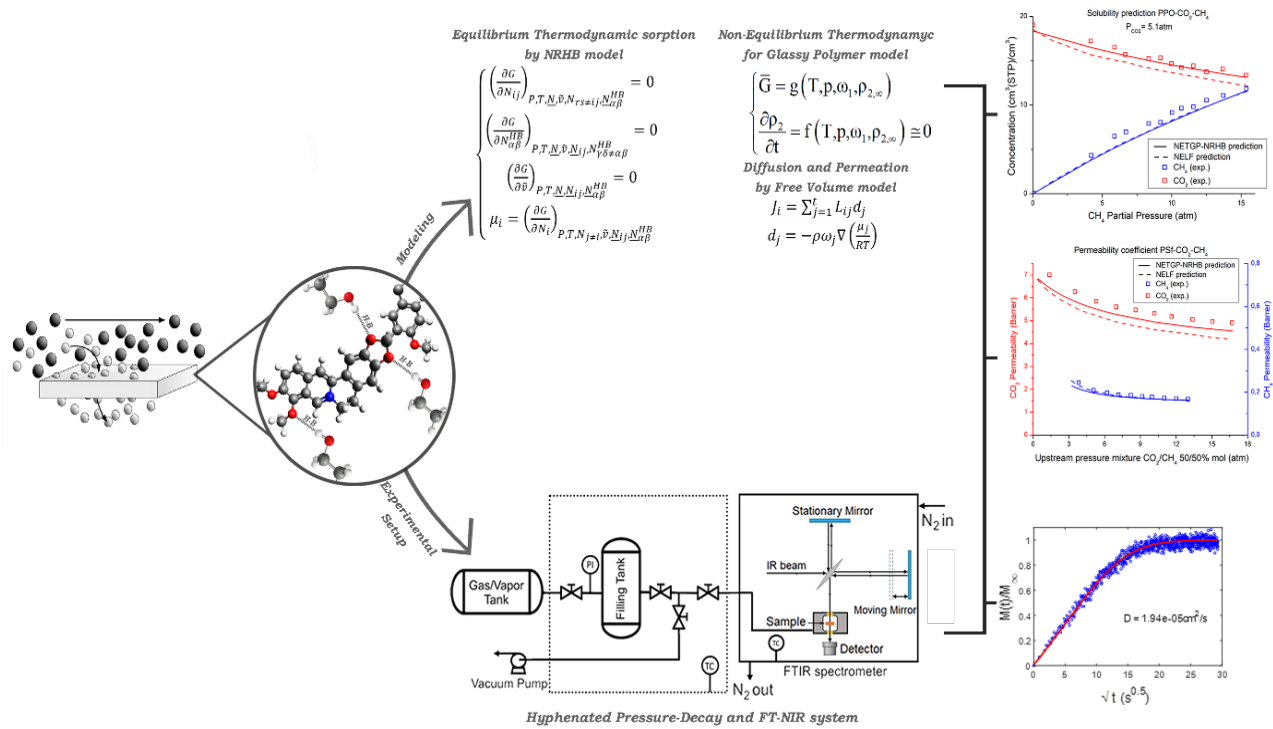
References:

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