**Non-ideal Multicomponent Adsorption in Thermally-rearranged Polybenzoxazole (TR-PBO) Membranes by Reactive Vacancy Solution Theory**

Alessio Caravella1\*, Adele Vaccaro1, Carmen Rizzuto2, Giuseppe De Marco3, Elena Tocci4

*1Department of Environmental and Chemical Engineering,
University of Calabria, Via P. Bucci, Cubo 44A, Rende (CS), 87036, Italy*

*2Department of Physics, University of Calabria, Via P. Bucci, Cubo 31C, Rende (CS), 87036, Italy*

*3Information Technology Center (ICT), University of Calabria, Via P. Bucci, Cubo 22B, Rende (CS), 87036, Italy*

*4National Research Council - Institute on Membrane Technology (ITM-CNR),
Via P. Bucci, Cubo 17C, Rende (CS), 87036, Italy*

*\*Corresponding author: alessio.caravella@unical.it*

**Highlights**

* Binary-mixture membrane adsorption isotherms are obtained by molecular dynamics
* The Reactive Vacancy Solution Theory is used to model the gas mixture adsorption
* Activity coefficients and selectivity are calculated up to 20 bar in non-ideal conditions
* Our approach allows a precise description of multi-adsorption at high pressure

**1. Introduction**

Polymeric membranes are nowadays the class of membranes mostly used in gas separation at moderate temperatures due to their relatively low cost compared to the ceramic ones. Thus, a considerable research work has been carried out to create polymeric films with high values of permeability and selectivity. In particular, the TR-PBO membranes have been extensively studied [‎1-4], reporting a detailed analysis on the free volume and its relation to solubility, diﬀusivity and permeability. These studies conclude that TR-PBO has high permeability mainly due to a high diﬀusivity owing to the higher amount of the free volume. However, the behaviour of these membranes in non-ideal conditions subject to multicomponent sorption at high pressure has not been considered yet in the literature, which is indeed the aim of our work.

**2. Mathematical approach to adsorption model**

The *Reactive Vacancy Solution Theory* (*RVST*) [5] is paired with the Wilson activity model for the adsorbate phase to predict the membrane behaviour at high pressure in non-ideal conditions. To do that, the single-gas isotherms of four light gases of interest (H2, N2, CH4, CO2) and their six binary-mixture isotherms were obtained by means of molecular dynamics at 35°C. Then, these data are used to calculate the parameters of the RVST by means of a robust in-house routine.

**3. Results and discussion**

Some results are shown in Figure 1 as adsorbate activity coefficients and adsorption selectivity. We can see that the activity coefficients are significantly different from the unity, this stating the strong system non-ideality, which thus cannot be modelled by an ideal adsorption model.

 

**Figure 1.** a) Adsorbate activity coefficients and b) Adsorption Selectivity as functions of the adsorbate
molar fraction for an equimolar four-species gas mixture at 35°C. The adsorbate composition refers to the
upper species in the selectivity definition and is let vary by changing the total pressure within [0.01, 20] bar.

Furthermore, interesting values of adsorption selectivity are found, with the CO2/H2 and CO2/N2 ones that are respectively estimated around 150 and 210 at a total pressure of 20 bar. These observations suggests possible applications of these materials to gas separation also as adsorbents rather than as membranes, since their perm-selectivity is expected to be lower than the adsorption selectivity due to their relatively high free volume.

**4. Conclusions**

In this work, the multicomponent adsorption of light gases – H2, N2, CH4, CO2 – in thermally-rearranged Polybenzoxazole (TR-PBO) membranes was described using the *Reactive Vacancy Solution Theory* (*RVST*) in order to deal with high-pressure and non-ideal conditions. For this purpose, both single-gas and binary-mixture isotherms were obtained by means of molecular dynamics techniques at 35°C. Afterwards, we interpreted these data by the reactive vacancy solution theory (RVST) paired with the Wilson activity model for the adsorbate phase, developing an in-house robust routine to calculated the model parameters.

Our approach, which can be generally applied to all membranes, allow us to predict the real adsorption behaviour of multicomponent mixtures at high pressure (at least up to 20 bar) and in non-ideal cases, where simple Langmuirian models used within the Ideal Adsorption Solution Theory (IAST) cannot satisfactorily describe the mutual adsorbate-adsorbate-adsorbent interactions present in conditions of interest for process industry.

**References**

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