**The Role of Competitive Sorption in CO2/CH4 Separation with Membranes**

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**Highlights**

* Sorption of CO2/CH4 mixtures in glassy polymers is characterized by strong competitive effects.
* Competition enhances the solubility‑selectivity, improving membrane separation.
* Sorption has a greater influence on the separation than diffusion in multicomponent conditions.

**1. Introduction**

Gas separation with membranes is described by the solution-diffusion model, according to which the process is governed by a combination of solubility and diffusivity factors. When a moderately condensable gas, like CO2, is involved in the separation, the solubility contribution plays a significant role in the process. Membrane materials characterization is often performed with pure gases. However, gas transport in mixed‑gas conditions generally deviates from the pure‑gas case. Competitive and synergistic effects are responsible for significant non-idealities, that cannot be properly evaluated with pure‑gas measurements. Therefore, to uncover the relevant physical effects and assess the membrane performance closer to actual operating conditions, multicomponent tests are necessary.

In this work the sorption of CO2/CH4 mixtures in several high-performance glassy polymers was characterized experimentally, by means of a modified pressure-decay apparatus [1], and modelled using thermodynamic-based and empirical models, with the aim of identifying a reliable predictive tool, to reduce or complement the experimental effort. Finally, mixed‑gas sorption measurements and literature multicomponent permeation data were coupled to evaluate gas diffusivity in multicomponent conditions and its effect on the separation.

**2. Methods**

Sorption of CO2/CH4 mixtures in several high free volume glassy polymers (PIM-1, TZ-PIM, PIM‑EA‑TB, PTMSP, Thermally Rearranged polymers) was evaluated at different compositions (10‑50 mol.% CO2) at 35 °C and up to 30 bar, using a dual‑chamber pressure‑decay apparatus coupled to a gas chromatograph [1]. Modelling of mixed‑gas sorption data was performed with the NELF model (non-equilibrium extension of the Sanchez-Lacombe equation of state) [2] and with the Dual Mode Sorption model [3]. Both models require only pure‑gas data in order to be parameterized and can be used to calculate multicomponent behavior predictively. Using the solution‑diffusion model, diffusivity coefficients were calculated in the mixed‑gas case, in order to evaluate the diffusivity contribution to the overall selectivity.

**3. Results and discussion**

The tests showed that the key feature of mixed‑gas sorption in glassy polymers is the reduction of the solubility of both species with respect to the pure‑gas case, due to competitive effects. However, the extent of this reduction is markedly different for the two gases, and is a function of mixture composition, temperature and pressure of the system, as it can be observed in **Figure 1** for the case of PIM‑1. In particular, in the presence of a second component, the less condensable gas (CH4) is excluded from the membrane to a much higher extent than CO2.   
This effect has a positive impact on the separation performance of the membrane materials, because it enhances the solubility-selectivity with respect to the ideal value, especially at high pressures, leading to increased ease of separation.   
Both models used to calculate mixed‑gas sorption were capable of capturing this reduction in solubility, however the NELF model showed a higher robustness and better quantitative agreement with the experimental data, also in the prediction of the solubility contribution to selectivity.   
CH4 diffusivity at multicomponent conditions was found to be systematically higher with respect to the pure‑gas case, due to the simultaneous presence of a swelling agent (CO2), which promotes a faster diffusion of CH4. As a result, the diffusivity differences contribute only slightly to the selectivity of the membrane materials in real multicomponent operating conditions.

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**Figure 1.** Sorption of CO2/CH4 mixtures in PIM-1 (symbols, [4]) at 35 °C and various mixture compositions, together with NELF model predictions (solid lines) and Dual Mode Sorption model predictions (dashed lines).

**4. Conclusions**

Sorption of CO2 and CH4 mixtures was measured in several glassy polymers suitable for CO2 separation. The main effect in these systems is competitive sorption, which leads to a strong exclusion of the less condensable gas (CH4) and results in an increased solubility-selectivity of the membrane. The NELF model successfully predicted this behavior, capturing also the effects of temperature and composition on the equilibrium, using only pure-gas parameters as input. Finally, a combined analysis of our measurements of mixed‑gas sorption and multicomponent permeability data from the literature, allowed to establish that sorption is the most significant factor for CO2/CH4 separation with these membrane materials.

**References**

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