298c Solvent-Membrane Interactions in Liquid Co2 and Organic Solvent Permeation through Mesoporous & Gamma - Alumina, Titania, and Zirconia Membranes

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Ceramic membranes are solvent resistant and thermally stable, providing a robust medium for separations in organic, compressed (liquid gas), and supercritical solvents. However, ceramic membranes are also hydrophilic and resist solvent permeation via solvent interactions with pore surfaces. The ultimate effect of these interactions is low solvent permeability and deviation from Darcy's law, which has been used extensively to predict convective water flux through mesoporous ($2 < d_p < 50$ nm) membranes. Due to the complex role of solvent-membrane interactions, there are currently no unifying models to predict solvent permeation through ceramic membranes. Liquid CO_2 and organic solvent permeation was examined through a series of mesoporous ceramic membranes with different selective layers; γ-alumina (5 nm), titania (1 and 5 KD), and zirconia (20 nm). In its liquid state, CO_2 acts as a non-polar organic solvent with comparable density and moderately lower viscosity, but with much lower surface tension (zero at critical point; 7.4 MPa and 304 K). Therefore, comparisons can be made between liquid CO_2 and organic solvents to examine the effect of surface tension on permeation. A custom high-pressure, cross-flow filtration system was used to investigate liquid CO_2 permeation in tubular membranes (Membralox™), while organic solvent permeation was examined using disk membranes (Sterlitech). Viscosity-corrected liquid flux values ($\eta J = k_m \Delta P$) were used to test the applicability of Darcy's law and to calculate/compare membrane permeability coefficients (k_m). Dry liquid CO_2 flux in 1 KD, 5 KD, and 5 nm membranes was a linear function of ΔP; however, k_m was 80-90% lower than that of water, indicating greater CO_2-membrane repulsion. Consecutive pressure cycles also revealed that irreversible CO_2 adsorption, via reaction with surface OH to yield carbonate-like species, may have reduced the effective pore size. When water was present (120 ppm), a significant reduction in CO_2 flux and non-linear permeation behavior was observed, which was attributed to (i) pore blockage by water followed by (ii) a reduction in the effective pore size due to physisorbed water. For the organic solvents, ethanol, butanol, and acetone exhibited transient permeation profiles, also consistent with a reduction in the effective pore size via adsorption. Pre- and post-water permeation indicated that adsorption was reversed with drying. Elucidating solvent-membrane interactions and their effect on non-aqueous solvent permeation (including hexane and toluene) will be a focal point of this presentation.