Reverse-Selective PTMSP Supported Ionic Liquid Membranes for Light Hydrocarbon Separations

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Rich in hydrocarbons other than methane, growing unconventional gas production motivates new separations challenges for the growing supply of natural gas liquids (NGLs). Membranes are advantageous for pre-fractionating NGLs from methane in small-scale, decentralized shale operations. In this work we report a reverse-selective supported ionic liquid membrane (SILM) platform based on varying compositions of the polyacetylene poly(1-trimethylsilyl-1-propyne), or PTMSP, and the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, or [hmim][Tf$_2$N]. In addition to their gas permeation properties, these membranes are characterized by their thermal stability, component miscibility, and mechanical properties. Gas permeability in SILMs is modest compared to those in the neat PTMSP. Ethane and propane permeability in SILMs increase nonlinearly with increasing transmembrane pressure, which translates to highly pressure dependent pure-gas C_2H_6/CH_4 and C_3H_8/CH_4 selectivities. Mixed-gas permeation experiments revealed that all gas permeabilities increase with increasing propane (or ethane) partial pressure while mixed-gas C_2H_6/CH_4 and C_3H_8/CH_4 selectivities increase only slightly. It is hypothesized that the ionic liquid first occupies the accessible free volume in the PTMSP support, thus exacerbating swelling due to highly condensable NGL sorption. Ionic liquid and NGL-induced swelling behavior of these membranes is quantified via density, sorption, and dilation measurements.