Solid-Liquid Equilibria of *p*-Xylene and *n*-Decane in Methane and Ethane Mixtures at LNG Conditions

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The formation and deposition of solids during the cryogenic processing of natural gas is a perennial risk for operators. If present in high enough quantities, heavy hydrocarbons including BTEX (benzene, cyclohexane, toluene, *p*-xylene and ethyl-benzene) aromatics and paraffins (*n*-hexane to *n*-decane) can lead to freeze-out problems in the cryogenic heat exchanger. A lack of experimental data for the solubility of such heavy hydrocarbons in LNG limits the accuracy of predictive engineering models used to avoid such problems. A specialized apparatus designed for visual measurements of solid-liquid equilibrium (SLE) and solid-liquid-vapor equilibrium (SLVE) at high-pressure cryogenic conditions was constructed and used to measure liquidus (melting) temperatures in binary mixtures of methane/ethane + *p*-xylene and methane + *n*-decane at varying compositions and pressures up to 30 MPa. A Peltier-cooled copper tip immersed in the liquid mixture was used to determine both freezing and melting points by varying the temperature of the copper tip relative to the stirred, bulk liquid. Solid-liquid equilibrium data for p-xylene + methane were measured for the first time at compositions ranging from $0 < x_{C1} < 0.52$ at pressures to 28 MPa. Melting conditions for *p*- xylene + ethane mixtures were measured at compositions from $0 < x_{C2} < 0.95$ at temperatures down to 200.8 K. Predictions made using the Peng-Robinson EOS as implemented in industry-standard software under-estimated the melting temperatures of methane + *p*-xylene by over 8 K while for ethane + *p*-xylene, the melting temperatures were over-predicted by over 30 K. Melting temperatures of methane + decane systems were also measured down to 233.7 K at $x_{C1} = 0.834$ and $p = 23$ MPa.