232f High-Pressure Phase Behaviour of the System Linear Low Density Polyethylene + N-Hexane + Ethylene: Experimental Results and Modelling

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Linear low density polyethylene (LLDPE) can be produced via the solution polymerization process. Ethylene polymerizes under high-pressure in a homogenous fluid phase to form polyethylene in an inert hydrocarbon solvent such as n-hexane. The fluid phase in the reactor should be at a pressure higher than the bubble point of the system. The reactor must be operated at a temperature lower than the lower solution temperature (cloud point) of the system and higher than the temperature at which the polyethylene crystallizes. The mixture leaving the polymerization reactor consists of polyethylene + n-hexane + ethylene and is throttled through a valve reducing the pressure producing a vapour to recover ethylene + n-hexane for reuse.

Experimental bubble point curves, cloud point curves and liquid-liquid-vapour boundary curves are presented for the LLDPE + n-hexane + ethylene system. The LLDPE sample was a hydrogenated polybutadiene (hPBD) with Mn=61.2 kg/mol and Mw=67.1 kg/mol. The experiments were carried out at process conditions in a temperature range of 360 to 510 K and pressures up to 15 MPa. The liquid-liquid-vapour boundary was measured up to a temperature where a three phase transition was no longer observed near a liquid – vapour critical point.

The experiments were modelled with the modified Sanchez-Lacombe (MSL) equation of state. Linearly temperature dependent binary interaction parameters were found for LLDPE + ethylene and LLDPE + n-hexane. The LLDPE + n-hexane binary interaction parameters were used to calculate the cloud points of two LLDPE + n-hexane systems reported by others. The LLDPE samples in these other systems had similar molecular structures but different molar mass distributions. The MSL equation provides a qualitative representation of the phase behaviour of all three systems.