

# Pressure versus Temperature Isochoric-Isoplethic Phase Equilibrium Trajectories for Binary and Ternary Systems related to the Supercritical Hydrogenation of Polybutadiene

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The traditional way of carrying out hydrogenation of unsaturated heavy compounds is in the presence of two fluid phases. This phase scenario forces the reaction to occur at low mass transfer rates and, therefore, at long reaction times. This drawback could be overcome by using a supercritical solvent or solvent mixture. In this case both, the hydrogen and the unsaturated heavy substrate, can be dissolved and form a single fluid phase. The analysis of phase transitions associated with the hydrogenation subsystems (i.e. ‘polymer + solvent’, ‘hydrogen + solvent’ and ‘hydrogen + polymer’ subsystems) is useful to select the operating conditions to achieve fluid homogeneity, at least, at the initial stage of the reaction. Changes in the slope of isochoric – isoplethic pressure vs temperature phase equilibrium trajectories indicate fluid-fluid phase boundaries of mixtures. In this work, phase transitions along with pressure vs temperature trajectories were measured for ‘pentane (C5) + dimethyl ether (DME)’ binary mixtures and ‘C5 + DME + polybutadiene’ ternary mixtures. A constant volume equilibrium cell was used to obtain the experimental data. Three different isopleths were measured for each system and, in turn, three different densities were tested for each isopleth. The temperature range covered was from 360 to 470 K and the pressure range was from 14 to 200 bar. The experimental data obtained were described using the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state (EoS). The results show that the model is capable of reproducing liquid-vapor transitions in the pressure vs temperature trajectories, together with the single-phase pressure vs. temperature behavior.

**Keywords:** Phase transitions; Hydrogenation; Isochoric-isoplethic trajectories; PC-SAFT EoS.