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Application of Lattice-Cluster Theory for Predicting High-Pressure Phase Equilibrium of Hyperbranched Polymer Mixtures

Leyuan Xu[1], Hao Zhang[2], Yue Wu[3,]*
[1]Department of Biomedical Engineering, [2]Department of Mechanical and Nuclear Engineering, [3]Department of Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, Virginia 23284 USA
*Corresponding author: wuy@vcu.edu

Hyperbranched (HB) polymers, one of those novel polymers with unique structures, have been receiving increased attention over the past two decades. Compared with linear polymers, HB polymer solutions exhibit a reduced viscosity and enhanced solubility, making them promising materials as fuel additives for lubrication in oil industry, as drug encapsulates for controlled release in biomedical engineering, and as selective solvents for extraction in extractive distillation and absorption processes in chemical engineering. Given their unique properties when compared with linear polymers, numerous groups have developed various models to predict the thermodynamic properties of partially or highly branched polymers. However, most of the models are based on the assumption of incompressible fluids and cannot take into account the pressure dependence of the thermodynamic properties along with the effect of branching. On the other hand, the branching effects are difficult to predict with those commonly used pressure-dependent equation of state (EoS) models such as cubic equations and statistical associating fluid theory (SAFT)-based EoS, since none of the parameters in the EoS was originally set to take account for the structural effect.

Recently, Langenbach *et al.* developed a high-pressure version of the lattice cluster theory (LCT) EoS specially designed for branched compounds. Unlike other commonly used EoS, LCT model performs the calculation of the statistical partition function that is directly related to the compound structures. In this high-pressure version of LCT EoS, the simplification of LCT model is proposed and the unoccupied lattice sites are introduced for the consideration of compressibility. Therefore a binary system A (solvent) + B (polymer) is treated as a ternary system A + B + C with C representing the voids. The simplified LCT EoS deals with the segment molar excess Helmholtz free energy, which is the summation of the entropic contribution and the first and second order energy contributions. Four parameters are needed for the calculation of thermodynamic properties, including the volume of a lattice site, V_0, and three interaction parameters, which are interaction parameters between solvent and solvent molecules, ε_{AA}, between solvent and polymer molecules, ε_{AB}, and between polymer and polymer molecules, ε_{BB}. These parameters are usually obtained by fitting to the experimental data.

The proposed LCT EoS is first used to predict the liquid-liquid phase behavior of hyperbranched polyester-carbon dioxide (CO_2) and the liquid-liquid and vapor-liquid phase behavior of hyperbranched polyester-propane mixtures with polymer. For each system, V_0 and ε_{AA} are obtained by fitting to the critical properties and vapor pressure data near the critical points for CO_2 or propane, while ε_{AB} and ε_{BB} are fitted to the experimental bubble points of the mixtures. The phase behavior predicted with the LCT model is in reasonable agreement with experimental data for mixtures containing higher than 70 wt% polymer at pressures to 20 MPa, but modelling results are not reported for mixtures with lower weight percent polymer.

There is still much work to be done to assess the predictive capabilities of this LCT EoS model, such as the prediction of phase behavior of branched polymer systems at extreme pressure and temperature conditions, the prediction of densities and other derivative properties at high pressures, and the prediction of thermodynamic properties for ternary systems. Another challenge for the future work is the modelling of hyperbranched copolymer or the hyperbranched polymer with different types of terminal groups.

Reference

Langenbach K, Enders S, Browarzik C, Browarzik D (2013). Calculation of the high pressure phase equilibrium in hyperbranched polymer systems with the lattice-cluster theory. J. Chem. Thermodyn. 59, 107-113.