Phase Diagrams Arising from the Interaction Between Depletion Flocculation and Molecular Phase Separation Mechanisms

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Fluids that comprise nano-colloids + non sorbing polymers + solvents arise in fields as diverse as nanomedicine, hydrocarbon production, and environmental science. Issues addressed include product formulation, process design, and mitigation strategies should undesirable behaviors occur. Success, however defined, relies on a detailed understanding of the related fluid physics and chemistry. Depletion flocculation, the interaction of a non sorbing polymer with nano-colloids in a good solvent leading to phase separation with polymer-rich and colloid-rich phases, is a well-established phase separation mechanism with diverse applications. In liquids comprising only molecules, liquid-liquid separation occurs due to repulsive interactions among different molecule types. In this work, phase compositions and phase diagrams for the ternary mixture polystyrene (mean molar mass ~ 237 kg/mol), cyclohexane, and silica nanoparticles (~7 nm average diameter) are presented. The phase diagrams are then discussed in relation to the upper critical end point (UCEP) temperature of the binary mixture polystyrene + cyclohexane (this work: 299 K). The interplay between molecular and colloidal effects leads to phase diagrams that were not previously anticipated. Some of these phase diagrams were observed directly. Other phase diagrams were inferred from phase diagram theory as transitional when colloid solid (C) and colloid gas (G) + liquid (L) phase behaviors overlap. Above the UCEP temperature, one new phase diagram including two colloid G=L critical points on a closed loop colloid G+L region was observed experimentally. A second new phase diagram with a L+G +C region and two colloid G=L critical points is inferred, but not observed experimentally, based on this work and prior work of others. Below the UCEP temperature, one new phase diagram was observed experimentally and a second new phase diagram was inferred based on measurements in this work and phase diagram theory. Implications of these findings and priorities for further study are introduced.