Diffusion and Thermodiffusion of the Ternary System Polystyrene+Toluene+Cyclohexane

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The inversion problem of the contrast factor matrix represents a notorious difficulty for two-color optical experiments on ternary liquid mixtures. We show how this problem can be circumvented for asymmetric systems, i.e., mixtures with very different molar masses of the constituents, by reasonable *a priori* assumptions about the directions of the diffusion eigenvectors. For this purpose, we have studied diffusion and thermodiffusion in the ternary system polystyrene+toluene+cyclohexane over the entire composition range of the binary solvent toluene+cyclohexane and for polymer concentrations up to 0.1 mass fractions by multi-color optical beam deflection (OBD). The polystyrene molar masses were 4.88 and 17.90 kg/mol. The OBD signals show a distinct bimodal dynamics. We attribute the fast mode to the interdiffusion of the two solvents at constant polymer concentration and the slow mode to the diffusion of the polymer with respect to the binary solvent. The amplitude of the fast mode vanishes in the pure toluene and the pure cyclohexane limits of the mixed solvent. The amplitude of the slow mode increases with polymer concentration. The composition and temperature dependence of the slow diffusion eigenvalue, the hydrodynamic correlation length, and the Soret coefficient of the polymer reflect the transition from a good to a theta solvent with increasing cyclohexane content and with decreasing temperature. Due to cross diffusion, cyclohexane reverses its migration direction between the fast and the slow mode, leading to a positive thermodiffusion but a negative Soret coefficient. The polymer thermodiffusion coefficients during the slow mode vary by approximately a factor of two, depending on the solvent composition. Rescaling with the solvent viscosity collapses all data onto a single master curve with an extrapolated value well known from various other binary polymer/solvent mixtures.