Phase separation induced by solvent addition is ubiquitous in many technologic and industrial processes, from preparation of pharmaceutical products, to formulation of cosmetics and insecticides, to liquid–liquid microextraction. The new microscopic phase formation induced by solvent addition takes place under the conditions far out-of-equilibrium. The growth dynamics of individual domains is determined not only by the concentration of compositions (thermodynamic aspects), but also by the temporal and spatial characteristics of the mixing process of the solvents (dynamic aspects). We have experimentally and theoretically investigated the effects from the mixing dynamics on the droplet formation under controlled flow conditions. A universal femtoliter droplet-based platform is developed for determination of partition coefficient in water and oil phases and for fast and sensitive nanoextraction of trace of hydrophobic compounds in aqueous solutions. We further revealed the droplet formation from liquid–liquid phase separation in a quasi-2D chamber. Remarkably, the droplets exhibit significantly enhanced mass transfer in confined spaces. This finding may of relevance to the interfacial process during oil extraction from underground by a...