TUNABLE FABRICATION OF MICROFLUIDIC EMULSIONS BY SPINODAL DECOMPOSITION
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ABSTRACT
We present a new method to produce microfluidic droplets, which does not require the use of specialized microchannel geometries. In our method, an initially homogeneous aqueous ionic liquid solution that exhibits lower critical solution temperature (LCST) is infused into a simple microchannel maintained above the LCST, thereby spontaneously forming a stable train of water-rich droplets dispersed in the continuous ionic liquid-rich phase. The use of chemically functional ionic liquid with tunable properties in such emulsion generation method promises novel flow-based chemical syntheses and separations not possible with conventional microfluidic systems.

KEYWORDS: Microfluidic droplets, Ionic liquid, Spinodal decomposition, Compartmentalization

INTRODUCTION
The widespread use of multiphase microfluidics in the chemical and biological sciences has enabled various applications such as the production monodispersed nanoparticles[1] and high throughput screening for drug discovery.[2] Current technologies for emulsion generation using microfluidics require the use of specialized microchannel geometries with or without the use of surfactants for the production of stable droplets.[3] We focus our attention on the spontaneous generation of chemically functional microfluidic emulsions via spinodal decomposition from binary water-ionic liquid mixtures that exhibit LCST. Crucially, we demonstrate the tunable fabrication of two-phase fluid structures including spherical droplets, lamellar flows and segmented droplet trains without the use of specialized microchannel geometries. The high surface-to-volume ratios in microfluidics enable rapid temperature changes to regulate phase behavior, besides allowing the possibility of steady-state operation at any point in the mixture phase diagram. We also present a simple application in rapid compartmentalization of a pair of organic dyes within from an initially homogeneous mixture.

THEORY
Spinodal decomposition refers to a process whereby a homogeneous mixture spontaneously and uniformly separates into distinct phases.[4] Spinodal decomposition occurs when a binary mixture of water-ionic liquid solution with LCST-type behavior is dispensed into heated microchannels (Fig. 1a). Phase separation under an applied shear leads to a competition between the growth and deformation of fluid domains, resulting in different flow morphologies.[5] For example, under low shear conditions, flow-induced coalescence results in the formation of stable segmented droplet trains. The rapid temperature-induced phase separation provides enormous biphasic contact area during the early development of the two-phase system, thus paving a way for the rapid compartmentalization of organic solutes.

EXPERIMENTAL
Fig. 1a is a schematic of the simple microchannel layout used in our experiments, consisting of merely an inlet and an outlet. The microchannels are molded in polydimethylsiloxane (PDMS) using soft lithography[6] from master patterns fabricated on silicon wafers using photolithography on a negative photoresist SU-8(2050). Molded channel patterns are bonded to glass slides pre-coated with a thin layer of PDMS following activation of both surfaces in an oxygen plasma for 35 s. The relevant microchannel dimensions are width \( w = 300 \mu m \), height \( h \sim 130 \mu m \), and channel length \( L \sim 0.44 m \). A binary mixture of 40 w/w% tetrabutylphosphonium trifluoroacetate (P4444 +CF3COO−) and water, recently developed by Kohno and Ohno,[7] is delivered into the uniformly heated microfluidic channel by means of a syringe pump (Harvard, PHD 2000). Still images and videos of the flow are captured using a camera (Basler) through a stereomicroscope (Leica) to observe the dynamic phase behavior in response to rapid temperature changes and varying flow speeds. For experiments involving the dynamic spinodal decomposition, the microchannels are heated from ~24°C to ~40°C at the rate of 0.1°C/s by means of a heated stage. Microchannels are maintained at a uniform temperature of 32°C for experiments involving the rapid compartmentalization of organic solutes.
RESULTS AND DISCUSSION

Liquid-liquid extraction involving the selective partitioning of molecules between two immiscible phases is one of the most popular methods for isolation and purification of organic compounds.\cite{8} Mass transfer across phase boundaries is often limited by the interfacial area between the two phases in contact. To demonstrate the concept of rapid compartmentalization, the understanding of dynamic spinodal decomposition is crucial. Fig. 1b illustrates the dynamic spinodal decomposition in laminar flow – the development of two-phase structures, from sub-micron aqueous-rich domains at the critical point to clearly demarcated segmented two-phase flows. As the system traverses the spinodal line through a uniform ramp increase in temperature at the rate of 0.1°C/s, the tremendous interfacial area generated at the critical point, where the incipient second phase appears, eventually coarsens to reduce interfacial free energy. The simple crossing of the spinodal line of an LCST system on-chip allows for the rapid compartmentalization to take place via the provision of an enormous surface area.

We demonstrate a simple application of rapid compartmentalization of organic moieties from an initially homogeneous mixture. Fig. 1c depicts compartmentalization of two dyes, reactive red 120 (polyethylene glycol 8000 conjugate) and methyl blue, under isothermal operation at 32°C. The kinetics of microextraction has been previously studied either as a means for separation and purification,\cite{10} or as a way to produce droplets with a specified solute concentration.\cite{11} Here, nearly instant compartmentalization of organic solutes can be achieved when the system operates above the LCST, thereby eliminating the waiting time required for the equilibrium concentration to be reached. In addition, the concentration of solutes within the water-rich droplets or the ionic liquid-rich continuous phase can too be regulated via temperature manipulation. The properties of the two phases become more dissimilar with an increase in temperature, thereby altering the relative affinity and hence the equilibrium partition coefficient of solutes within the two-phase system. The concentration of solutes in each phase can thus be tailored for specialized applications.

Finally, we report an interesting phenomenon where an increase in flow speed from 0.4 mm/s to 2 mm/s results in a remarkably different flow morphology during dynamic phase separation as observed in Fig. 1d. In contrast to the nearly isotropic behaviour obtained under low shear, the high shear rate for the 2 mm/s flow yields elongated thread-like struc-
tures instead. This observation is consistent with previous experimental and simulation results for Couette flows, where the spinodal decomposition of a binary mixture under a uniform and steady shear field leads to the competition between the growth and the deformation domains induced by the shear field.[5, 9] The development of a more anisotropic structure is thus not unexpected for a laminar flow under a stronger shear field, as the phase bands stretch along the flow direction.

CONCLUSION

We have demonstrated the spontaneous production of chemically functional microfluidic droplets via spinodal decomposition from an initially homogeneous binary mixture that exhibits LCST behavior. The crux of this paper lies in the ability to form liquid segments from an originally homogeneous mixture for rapid chemical compartmentalization without the use of surfactants or specialized microfluidic geometries. Coupled with the use of varying flow speeds, the high surface-to-volume ratios in microfluidics can be exploited for the use of rapid temperatures changes in phase behavior modulation for dynamic operation at any point in the mixture phase diagram. Spinodal decomposition of flowing aqueous-ionic liquid mixtures promise broadly tunable and rapidly switchable microfluidic two-phase flows, which lead to tantalizing, hitherto unforeseen opportunities in on-chip chemical and biochemical experiments.

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