Supporting Information

Droplet Microfluidics with a Nanoemulsion Continuous Phase

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Mechanism for Heat-Assisted Chemical Interaction

Here we explore the interesting issue of (mono)directionality of material transfer in the heat-assisted chemical interactions between the continuous and dispersed phases described in the main text, where we observed that irrespective of droplet size, KSCN was always released from its 'home droplets' to the surrounding continuous phase and finally transported into the droplets containing FeCl₃. Using Ostwald ripening as a surrogate indicator (see below), we demonstrate that this is due to the dramatically different material release rates between KSCN and FeCl₃.

Ostwald ripening is a direct consequence of a fast material release from one droplet to the continuous phase; therefore, comparing the difference in rates of Ostwald ripening, one can infer *relative* material release rates.¹ Thus, we compared the destabilization of two nanoemulsions - 20%wt KSCN-in-dodecane (10%wt Span 20) and 20%wt FeCl₃-in-dodecane (10%wt Span 20) - at 50°C, by measuring the turbidity change as a function of time. As mentioned by Mason et al,² with such a small droplet size and a narrow size distribution, the main emulsion destabilization mechanism is Ostwald ripening; this was unequivocally substantiated by our observation that both emulsions showed a uniform decrease in transmittance across different heights of the vial with time. Next, as shown in Figure S1, we observed that the transmittance of KSCN-loaded nanoemulsion decreased much faster than that of the FeCl₃-loaded nanoemulsion, thus proving that KSCN has a higher rate of release than FeCl₃, and providing a facile explanation for the observed monodirectional mass transfer.



Figure S1. Turbidity characterization of the destabilization of a 20%wt FeCl₃-dodecane emulsion and a 20%wt KSCN-dodecane emulsion.

To further elaborate the underlying mechanism, we postulate that the heat-driven interphase transport of chemical species between the nanodroplets and microdroplets is driven by *differences in solubility* of the various species in the continuous phase. Theoretically, we reason that FeCl₃ is less soluble in dodecane than KSCN. Ions typically remain unsolvated in hydrocarbons, with a high energy penalty for dissolution. The penalty is higher for high valence-to-radius ratio ions, such as Fe³⁺. Literature data³ shows that Fe³⁺ has a bare ionic radius of 69 pm, while K⁺, has a radius of 138 pm; similarly, amongst the anions, Cl⁻ has a radius of 181 pm. We estimated that the SCN moeity has an atom end-to-end radius of 228 pm (calculated by DFT method using Q-Chem); the actual ionic radius is even larger because of the additional negative charge. Experimentally, since Ostwald ripening rate is also proportional to the dispersed phase solubility in the continuous phase, the faster destabilization of KSCN-loaded nanoemulsion provides an indirect proof of its higher solubility. However, we note that direct measurements of the solubility of these ions to validate our theoretical and (indirect) experimental arguments would require further work that is beyond the scope of the current study. We therefore leave it to a further detailed mechanistic study.

References

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