Electronic Supplementary Information for:

Optical Calorimetry in Microfluidic Droplets

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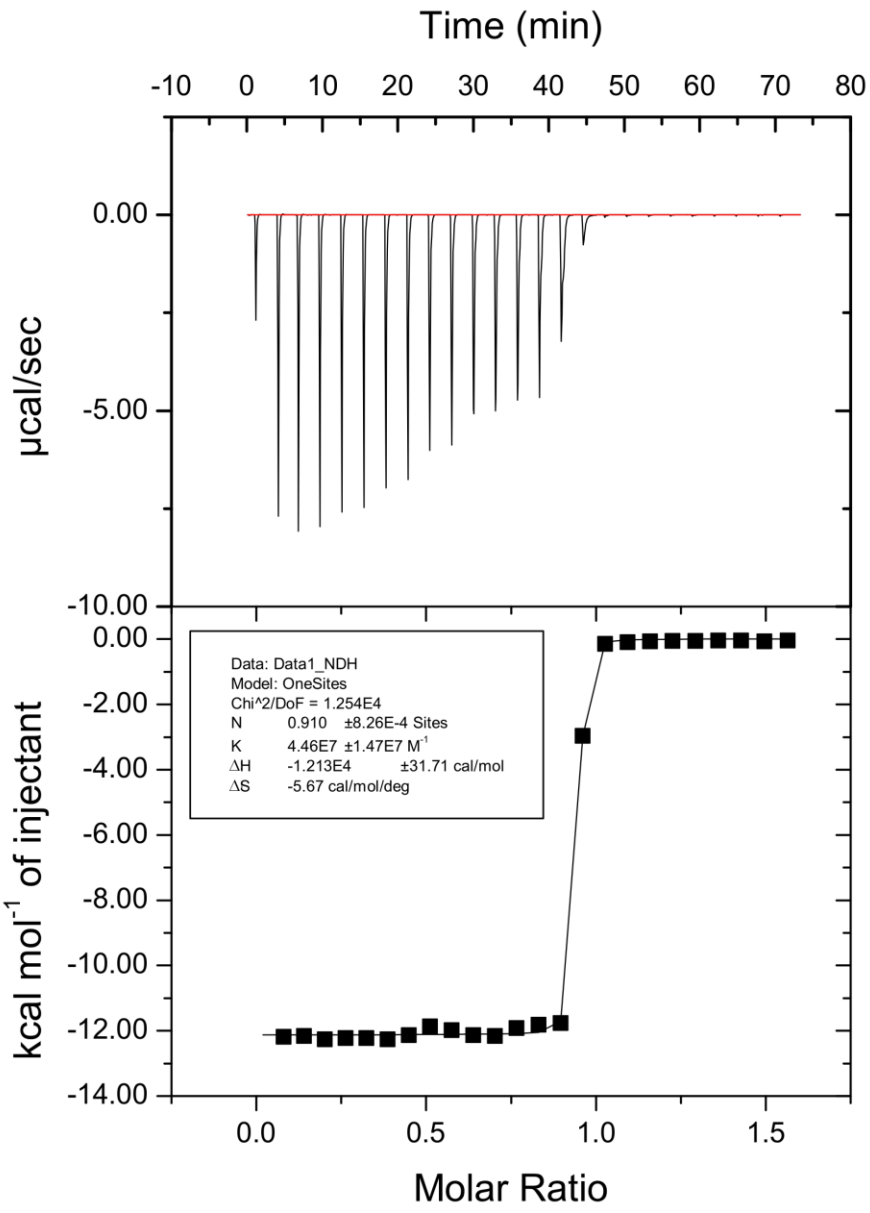
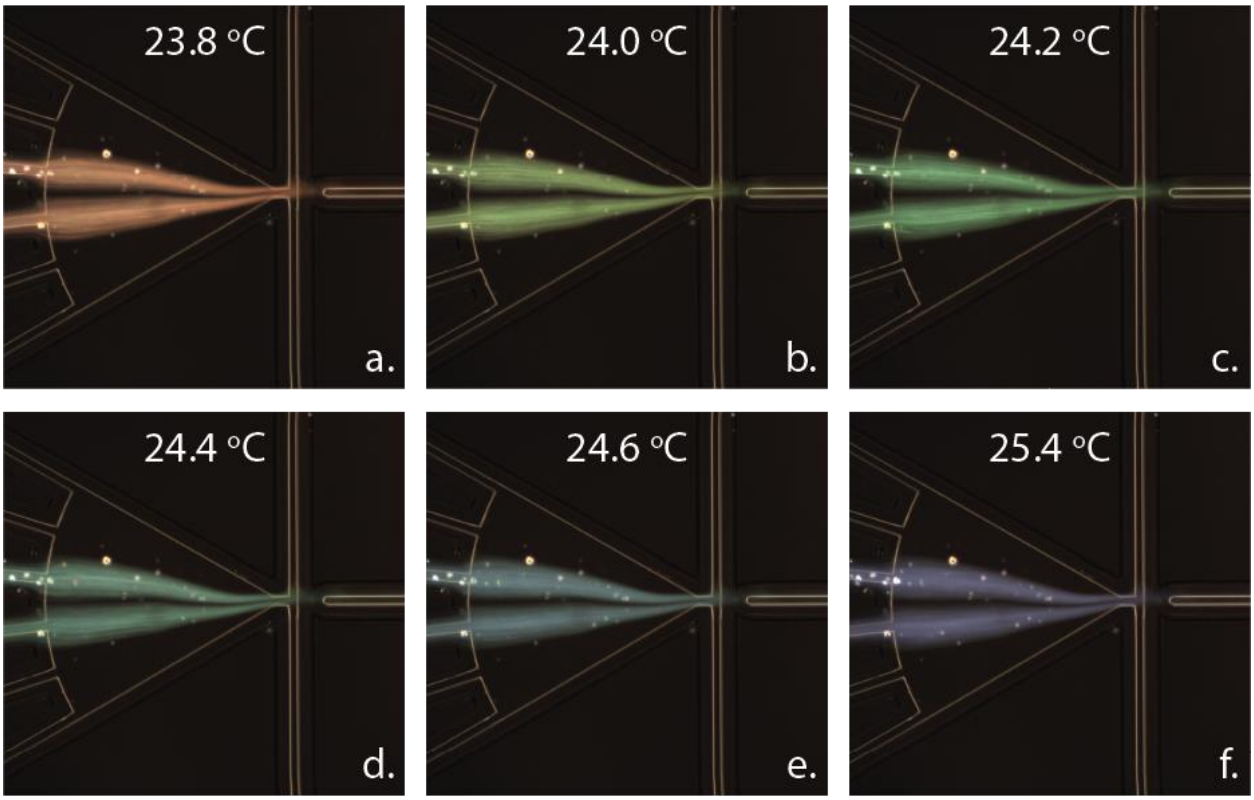
ITC data



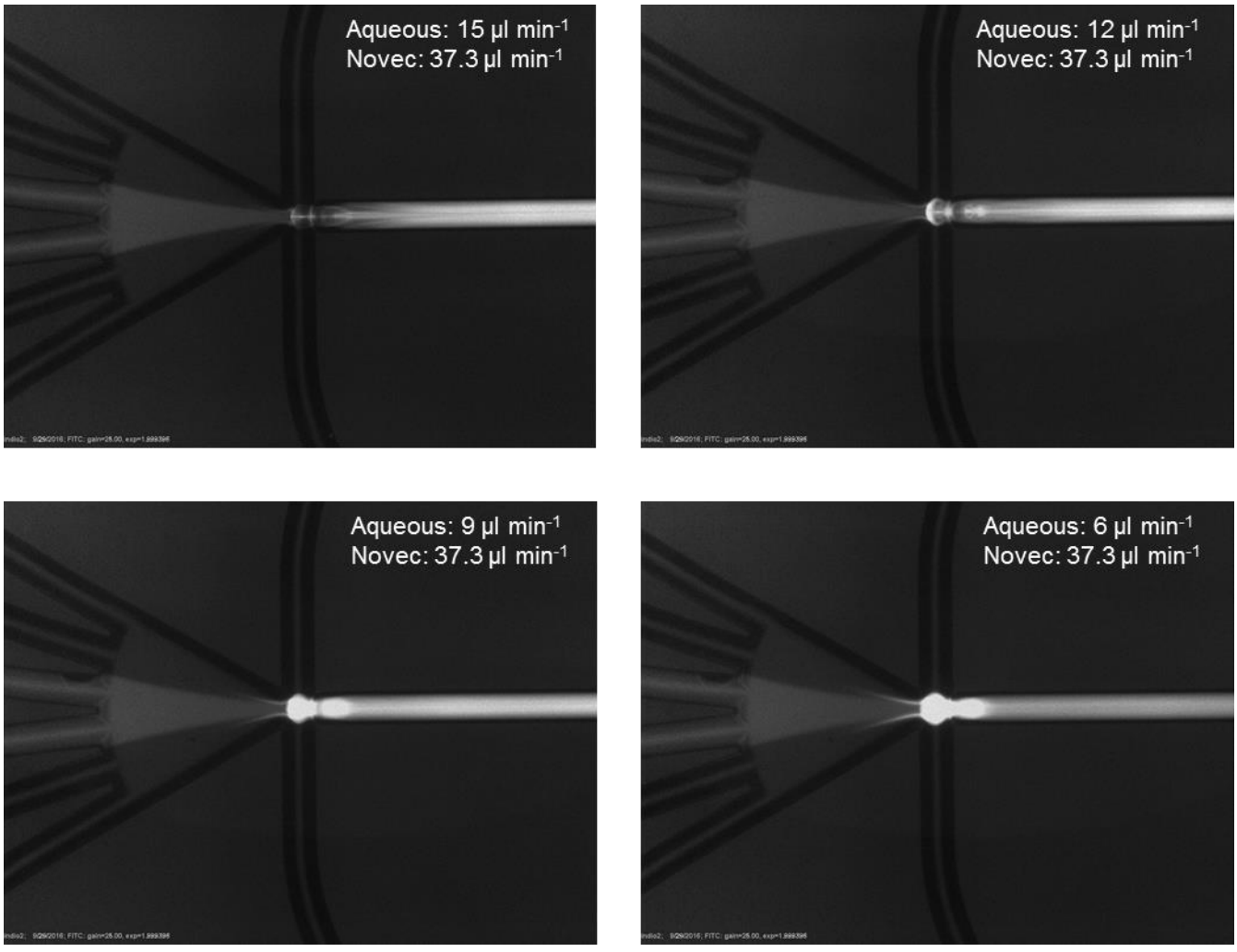
Supplementary Figure 1: Titration of EDTA with $CaCl_2$. Binding of CaCl2 to EDTA was measured at 25 °C in 100 mM Tris-HCl (pH 7.5), 0.015% (w/v) Triton X-100. The sample cell (200 µL) contained EDTA (500 µM), and the injection syringe contained 5 mM $CaCl_2$.



Supplementary Figure 2: Microphotograph of the color change of TLC microparticles in response to temperature. 5x objective, ≈2 sec exposure. Water/0.015% Triton X-100.

Supplementary Table 1: Mixing rates at various flow conditions. ** Some binding of fluo-4 to Ca^{2+} occurs prior to droplet generation

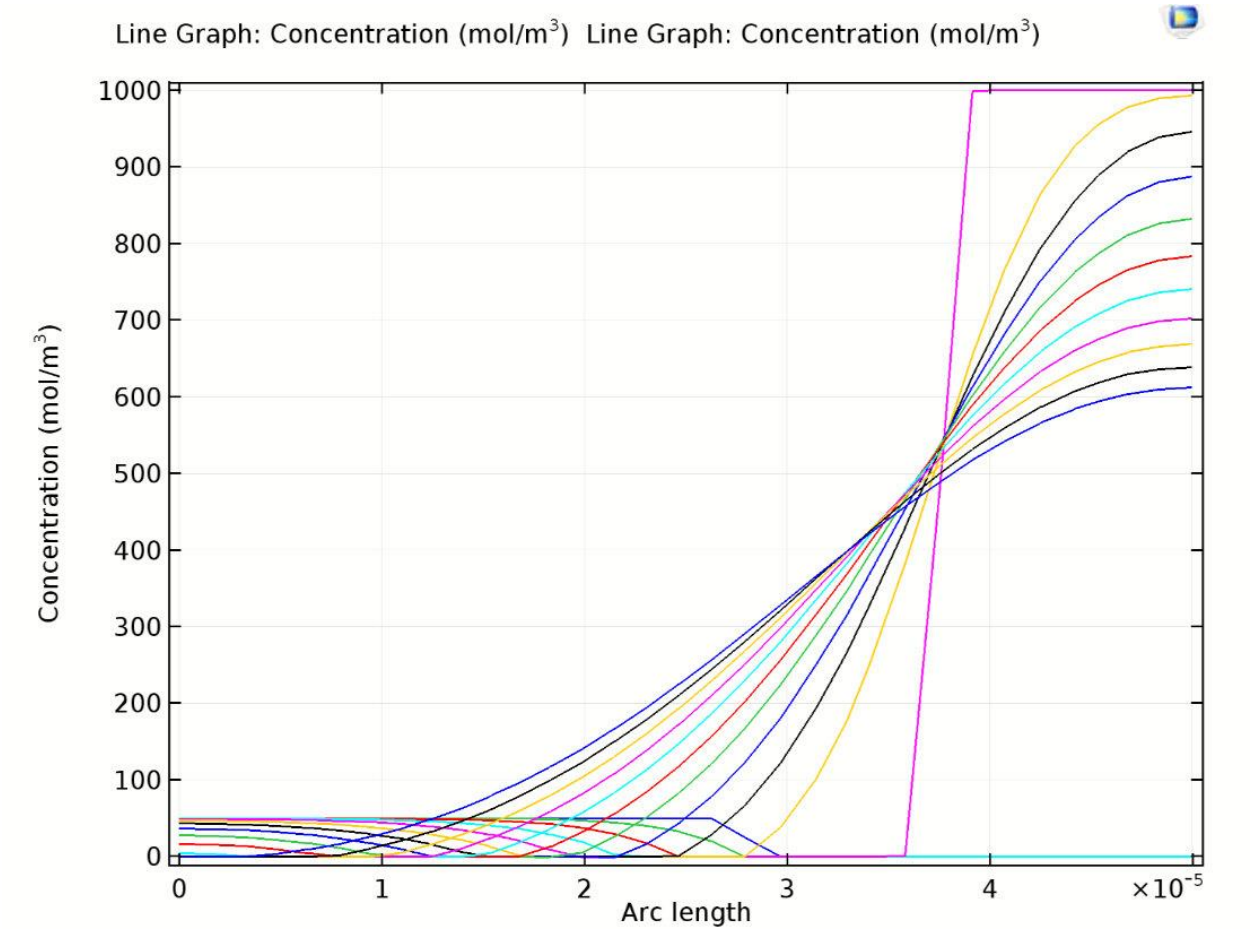
Combined aqueous flow rate (µl/min)	Novec 7500 flow rate (µl/min)	Total fluid flux (µl/sec)	Droplet generation rate (Hz)	Linear flow rate (mm/s)	Distance for 90% mixing (mm)	Time for 90% mixing (ms)
22.5	37.3	0.997	716	83.9	0.75	9
15	37.3	0.872	477	73.4	0.70	10
12	37.3	0.822	382	69.2	**	NA
9	37.3	0.772	286	64.9	**	NA
6	37.3	0.722	191	60.7	**	NA



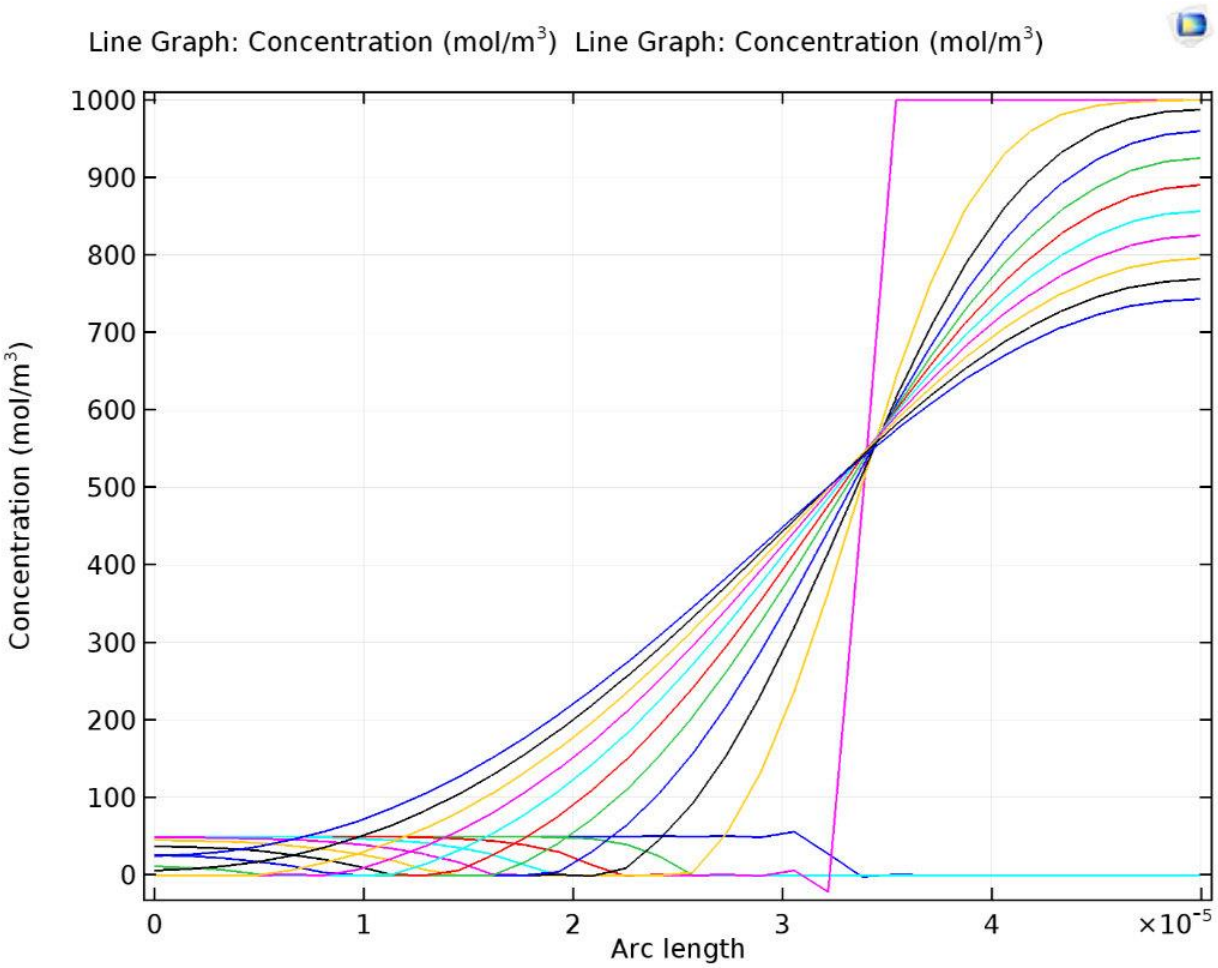
Supplementary Figure 3: Microphotograph (2 s exposure, individual droplets are invisible) showing time-averaged fluorescence arising from mixing inside droplets formed by combining equal volumes of CaCl2 (5 mM), EDTA (1 mM), and Fluo-4 (54 µM), in MOPS (20 mm, pH 7.2). Aqueous streams were in the same configuration as described in Figure 6 of the article.

Supplementary Table 2: Parameters used in the COMSOl model. Value of ΔH was obtained from ITC measurements. Values for Novec 7500 from product data sheet (http://multimedia.3m.com/mws/media/65496O/3mtm-novectm-7500-engineered-fluid.pdf).

Name	Value	Units	Description
T_{ref}	298.15	[K]	Reference temperature
$[EDTA]_0$	0.05	[mol/liter]	Initial concentration of EDTA
$[CaCl_2]_0$	1	[mol/liter]	Initial concentration of $CaCl_2$
D_{EDTA}	1.09E-09	[m^2/s]	Diffusivity of EDTA in water
D_{CaCl2}	1.09E-09	[m^2/s]	Diffusivity of $CaCl_2$ in water
k	1.00E+07	[1/((mol/liter)*s)]	reaction kinetic rate constant
ΔH	-50578	[J/mol]	Heat of reaction, measured using ITC
K_{Novec}	0.06477	[W/m*K]	Thermal conductivity of Novec 7500 at T_{ref}
K_w	0.607	[W/m*K]	Thermal conductivity of water at T_{ref}
C_{pNovec}	1128.455	[J/kg*K]	Specific heat capacity of Novec 7500 at T_{ref}
C_{pw}	4138	[J/kg*K]	Specific heat capacity of water at T_{ref}
ρ_{Novec}	1613.6875	[kg/m^3]	Density of Novec 7500 at T_{ref}
ρ_w	997	[kg/m^3]	Density of water at T_{ref}



Supplementary Figure 4: Concentration profiles of EDTA (initial 50 mM) and $CaCl_2$ (initial 1 M) over time for the 'with spacer' condition (for t = 0 through t = 100 ms at 10 ms time steps).



Supplementary Figure 5: Concentration profiles of EDTA (initial 50 mM) and CaCl2 (initial 1 M) over time for the 'no spacer' condition (for t = 0 through t = 100 ms at 10 ms time steps).