Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Microfluidics with *In Situ* Raman Spectroscopy for the Characterization of Immiscible Non-Polar/Aqueous Interfaces

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Supporting Information

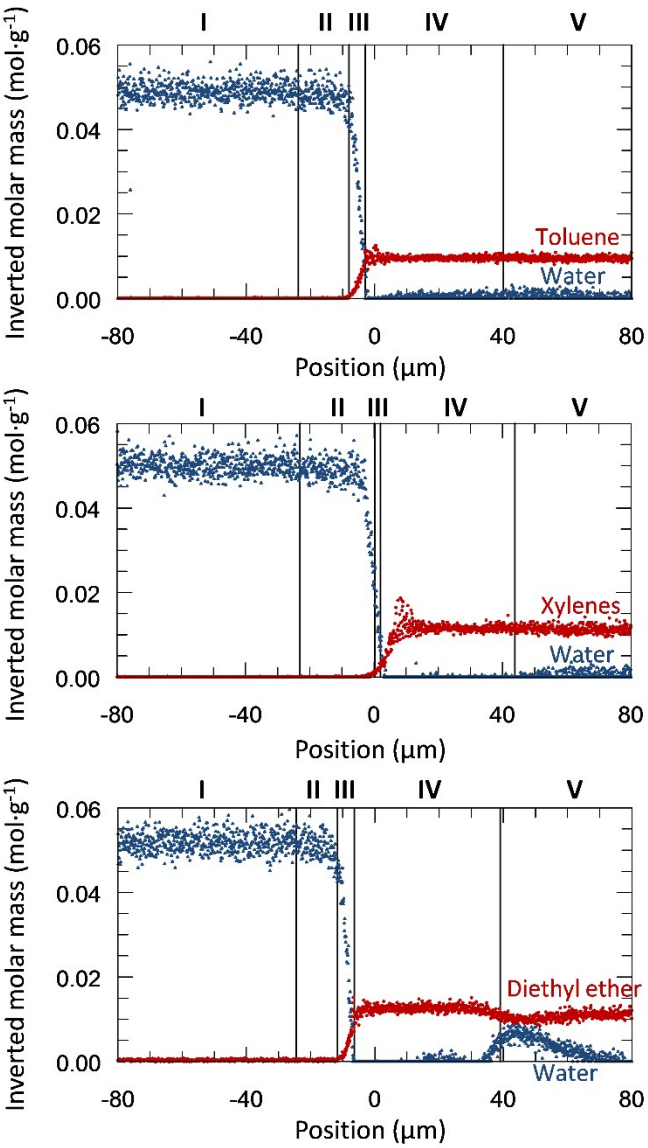

Fig. 1S Mass balance of the species based on the inverted molar mass of each species for fluid-aqueous media [${M_i}^{-1} = C_i/\rho^*$, where ρ^* is the fluid apparent density (kg·m^{-3}) and C_i is the concentration of the specie i (mol·m^{-3})]. In the zones I and II, the inverted molar mass is constant, which means that the mass balance is closed and that the density profile is accurate. Therefore, the internal standard (acetonitrile) can be used to acquire the density profile. Similar behaviour is observed for zone IV and V.

Zones: **I**: Aqueous bulk; **II**: Aqueous rarefaction; **III**: Mixture; **IV**: Hydrophobic shockwave; **IV**: Hydrophobic bulk.

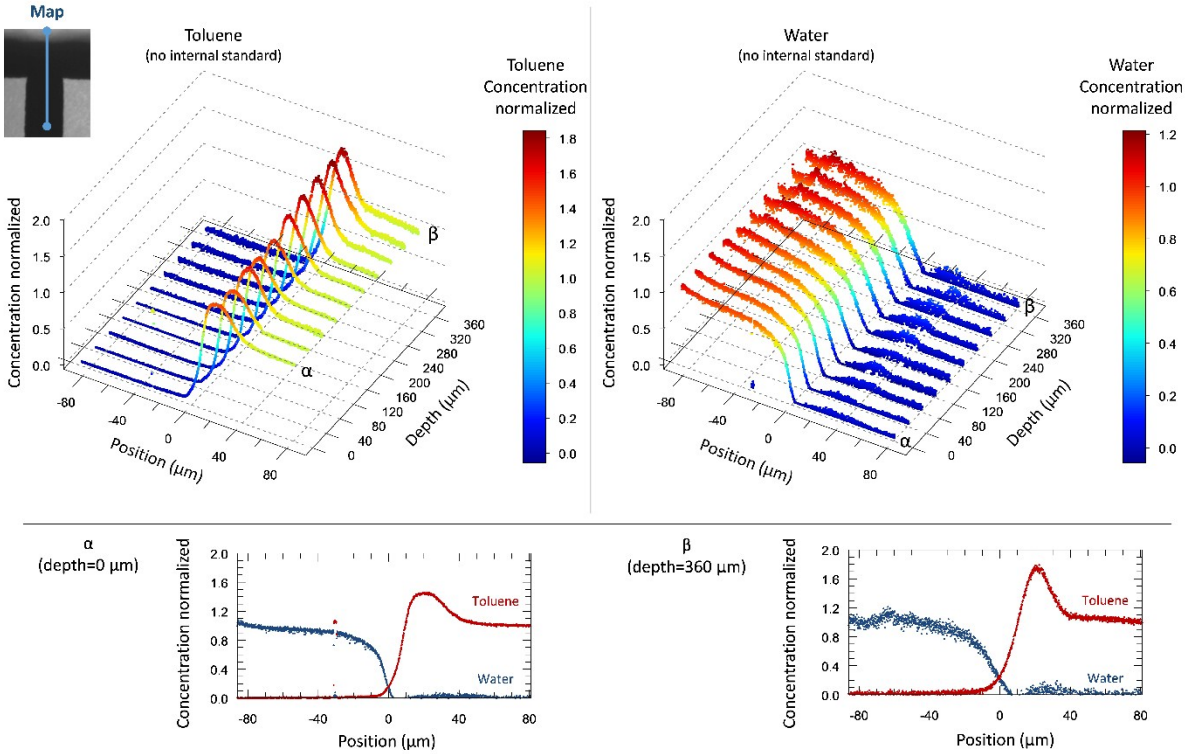

Fig. 2S Map of the bulk-to-bulk region for a toluene-water system without acetonitrile (313.15K and water flow-rate of 20 μL·min^{-1}). In the graphics is presented the concentration normalized by the bulk of each species (water and toluene) in function of the position and the depth. Looking at the 3D figures, the water and toluene profiles have similar behaviour (zones) and the variations (zones upper and lower location) start at the same location. The upper (near 0 μm) and lower profiles (near 360 μm) have slightly different on the maximum value for toluene (β figure). For water, there are not differences between upper and lower profiles (α figure). Since, the depth resolution used is about ~12 μm and no significant variations of the profiles behaviour was detected with the depth, we can assume that the results will not be subject to depth interferences.

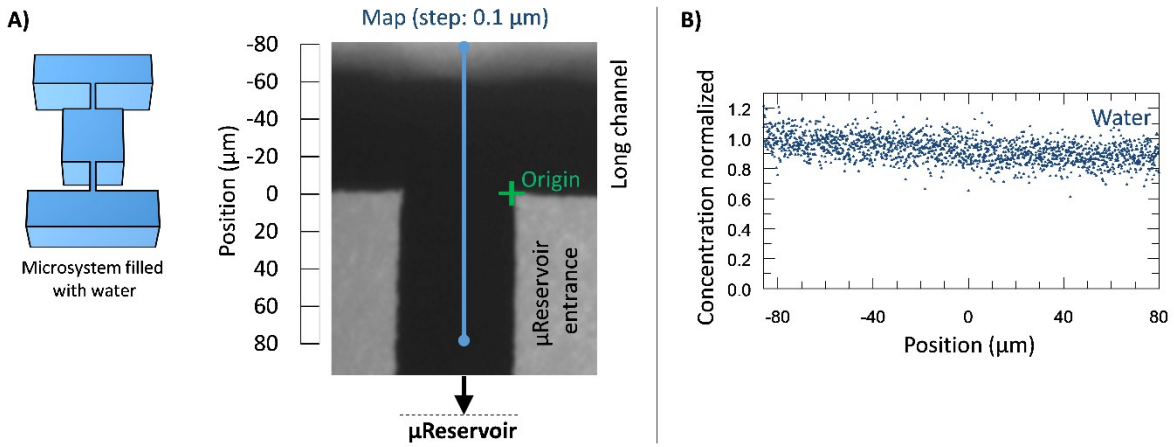

Fig. 3S A) Map of the bulk-to-bulk region for a pure water system (313.15K and water flow-rate of 20 µL·min^{-1}). **B)** Water concentration normalized by water bulk as a function of its position (blue line on Fig. 3S A). Regarding B, the results show that there are no effects of refraction or reflection created when the laser goes from the long channel to the µReservoir entrance.