Supplementary Section

Derivation of Capillary Filling of Biphasic Plug

We mathematically derive the condition for capillary filling of the biphasic plug. Capillary filling of the first phase is described by the pressure differences that occurs across the interface using the Young-Laplace equation,

$$\Delta P_1 = \frac{\gamma_1 \cos\theta_1}{R}$$

where, ΔP_1 is the pressure difference between first phase (aqueous) and the atmosphere, γ_1 is the surface tension, θ_1 is the contact angle between the first phase and glass capillary and R is the radius of the glass capillary.

Using Young-Laplace for phase 2 (oil) capillary filling, we assume that a thin film develops from the first phase but is negligible in height; therefore the radius of curvature of the second phase can be assumed to be a perfect sphere equal to that of the glass capillary ($\theta = 0$).

$$\Delta P_2 = \frac{\gamma_{12}}{R}$$

where ΔP_2 is the pressure difference between first and second phase, γ_{12} is the interfacial surface tension, and R is the radius of the glass capillary.

For the 2nd phase to fill the capillary, the following condition will need to occur where

$$\Delta P_1 > \Delta P_2$$

Substituting Young's equation into left side of the above equation, we derive the following expression,

$$\gamma_{SV} - \gamma_{SL} > \gamma_{12}$$

γ_{SV} is the surface tension between first phase and atmosphere and γ_{SL} is the surface tension between first phase and glass capillary. Therefore, capillary filling of the biphasic plug only occurs when the above condition is met.

First Phase	Second Phase	γ_{12} (mN/m)	$\gamma_{SV} - \gamma_{SL}$ (mN/m)	Experimental Observation (Fill vs. No Fill
0 % Triton X-100 in DI Water	FC 40	35.58	28.31	No Fill
0.01 % Triton X-100 in DI Water	FC 40	10.55	13.35	Fills Slowly
0.1 % Triton X-100 in DI Water	FC 40	2.78	12.23	Fill
1 % Triton X-100 in DI Water	FC 40	2.88	11.86	Fill
0 % Triton X-100 in DI Water	FC 40 1 % PFO	7.33	28.31	Fill
0.01 % Triton X-100 in DI Water	FC 40 1 % PFO	3.09	13.35	Fill
0.1 % Triton X-100 in DI Water	FC 40 1 % PFO	0.38	12.23	Fill
1 % Triton X-100 in DI Water	FC 40 1 % PFO	0.40	11.86	Fill

Table S1: With the capillary tube set horizontally, 10 µL of a first phase was pulled into the capillary, followed by 10 µL of a second immiscible phase, as indicated in the table above. The capillary tube was visualized to determine if the immiscible phases were displaced (indicated as pulled vs. no pull). Of the cases tested it was determined that if $\gamma_{SV} - \gamma_{SL}$was lower than γ_{12}, no pulling was seen, consistent with the model shown in Figure 2.