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Supplementary Material for the manuscript

Ultrafiltration of saline oil-in-water emulsions stabilized by an anionic surfactant: Effect of surfactant concentration and divalent counterions

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S1. Calculation of the Kolmogorov length scale

The Kolmogorov length scale, η , is the size of the smallest eddy in a turbulent flow field and is given by:

$$\eta = \left(\frac{v^3}{\varepsilon}\right)^{1/4} \tag{S-1}$$

where ν (m²/s) is the kinematic viscosity of the fluid and ε (J/s/kg) is the average rate of dissipation of turbulence kinetic energy per unit mass of fluid.

The following values were used as inputs:

- Impeller diameter, D = 0.05 m
- Density of the emulsion, $\rho = 997 \text{ kg/m}^3$ (approximated by that of water)
- Viscosity of the emulsion, $\mu = 8.94 \cdot 10^{-4}$ kg/m/s (approximated by that of water)
- Emulsion volume, V = 1 L
- Impeller constant, $K_T = 1.26$ (value for a pitched-blade turbine (45°) with 4 blades)
- Rotational speed, n = 1000 rpm
- Mixing time, t = 1200 s

The calculated values are:

- Reynolds number for the impeller: $N_{Re} = D^2 n \rho / \mu = 46467$
- Mixing power: $P = K_T n^3 D^5 \rho = 1.82 \text{ W}$
- Mean velocity gradient: $\bar{G} = \sqrt{P/(\mu \cdot V)} = 1425.8 \text{ s}^{-1}$
- Energy dissipation rate: $\varepsilon = P/(\rho \cdot V) = 1.82 \text{ W/kg}$
- Kolmogorov length scale: $\eta = (\mu^3/(\rho^3 \cdot \varepsilon))^{1/4} = 25078 \text{ nm}$

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S2. Calculation of the mean velocity gradient

The mean velocity gradient in the membrane channel can be approximated using the Hagen–Poiseuille equation, which gives the following expression for \bar{G} (i.e., shear rate) at a distance d_p from the wall:

$$\bar{G} = \left[\frac{dv}{dz}\right]_{z=\frac{d_p}{2}} = 6\frac{v}{H}\left(1 - \frac{d_{drop}}{H}\right) \tag{S-2}$$

where v is the average crossflow velocity in the membrane channel and H is the height of the membrane channel (in our experiments v = 0.1 m/s and H = 2 mm). Near the membrane surface, \bar{G} is ~ 300 s⁻¹.

S3. Critical pressure and oil droplet rejection by a porous membrane

The critical pressure for an oil droplet of diameter $d_{\rm drop}$ suspended in an emulsion of interfacial tension σ (N/m) to enter a cylindrical membrane pore of diameter d_{pore} is given by [1, 2]:

$$\Delta P_{crit} = \frac{4}{d_{pore}} \sigma \cos \varphi \left[1 - \left(\frac{2 + 3\cos\varphi - \cos^3\varphi}{4\left(\frac{d_{drop}}{d_{pore}}\right)^3 \cos^3\varphi - (2 - 3\sin\varphi + \sin^3\varphi)} \right)^{1/3} \right]$$
 (S-3)

where $\varphi=180^{\circ}-\theta$. The prefactor $4d_{pore}^{-1}$ in eq. (S-3) is the ratio of the cross-sectional circumference to the cross-section area of the cylindrical pore. The approximation of cylindrical geometry is accurate for Anopore membranes; for membrane pores of other geometries, however, the pre-factor will be different.

The most conservative estimate for the 0.02 μ m membrane and the smallest droplet (0.678 μ m as detected by light diffraction) of HWSS-0.1 emulsion gives the lower bound of ΔP_{crit} = 19.3 bar. This is ~ 25 times higher than the initial transmembrane pressure (~ 0.7 bar; calculated based on Hagen-Poiseuille equation) in a DOTM test with a clean Anopore membrane and almost 4 times higher than the maximum operating pressure for the membrane (~ 5.2 bar). Although the complete rejection was not confirmed experimentally, in our previous work [3] we did measure 100% rejection for an emulsion/membrane system, which can serve to provide an appropriate conservative estimate of rejection in the present study. In the earlier study we used the same emulsion and the same type of membrane but with a pore size 10 times larger. The oil content was determined by IR and UV-vis spectroscopies after solvent extraction from the aqueous emulsion. Thus complete oil rejection can be assumed.

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