

SUPPORTING INFORMATION

pH-Tunable Electrokinetic Movement of Droplets

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1 Analytical Prediction vs. Experimental Data at 1 mM surfactant Concentration and Different pH

Comparison of the analytical predictions and experimental data for the EK velocity of oil droplets with different diameters stabilized by 1 mM LDAO surfactant at different pH values are shown in figure 1. The graphs are fitted using the surface charge, wall potential and effective slip length based on eq. 2 in the main manuscript. A least squares regression strategy was used to minimize the differences between the measurements and the fitted data.

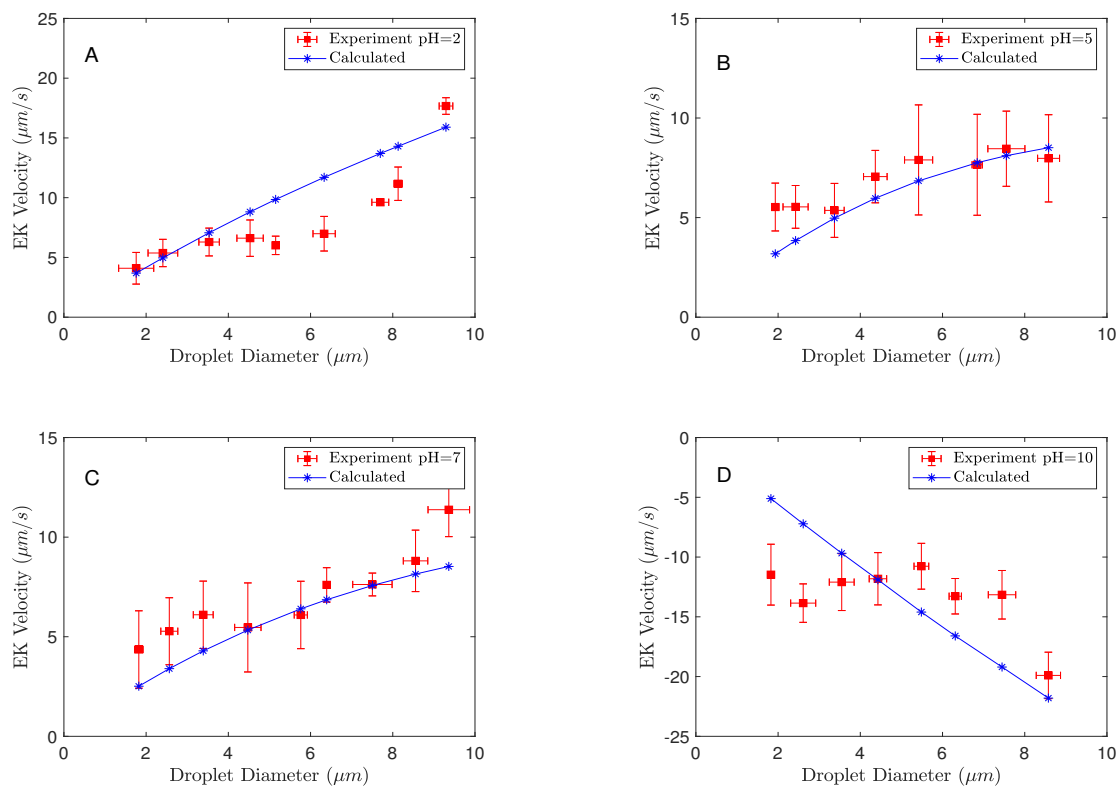


Figure 1: Comparison of analytical predictions presented by P.Gopmandal et al.¹ for the EK velocity of the hydrophobic fluid droplets with current experimental data at different $p\text{H}$.

2 The Effect of Surfactant Concentration on the EK Velocity of Droplets at *pH* 2 and 10

A reduction of the EK velocity by increasing the surfactant concentration at *pH* 2 is exhibited in figure 2A. Based on our DLS results, droplets are positively charged at this *pH* and all surfactant concentrations, meaning that EP is towards the negative electrode. As discussed previously, PDMS is positively charged at this *pH*, and EOF is towards the positive electrode. This is because this *pH* is below the isoelectric *pH* of the PDMS,² and the fully protonated and positively charged monomers or dimers adsorbed to it. Therefore, the EP and EOF are opposite to each other (see figure 5C in the main manuscript). Since these three surfactant concentrations are below the CMC of the LDAO surfactant in the cationic state, the absolute magnitude of the PDMS ζ -potential is expected to increase by increasing the surfactant concentration. So, the EOF is expected change in this order: $EOF_{1\text{ mM}} > EOF_{0.7\text{ mM}} > EOF_{0.4\text{ mM}}$. EP of the droplets also increases by increasing the surfactant concentration because of the increase in magnitude of the droplets ζ -potential ($\zeta_{\text{droplet-1 mM}} > \zeta_{\text{droplet-0.7 mM}} > \zeta_{\text{droplet-0.4 mM}}$). However, by increasing the surfactant concentration and consequently, the interaction of more ions in the electrolyte (Cl^- and OH^-) with the adsorbed monomers on the oil droplets, the effect of SC on reduction of the EP could become more important as described previously. As a result, the absolute EK velocity decreases by increasing the surfactant concentration.

Surfactant monomers exist in the zwitterionic form at alkali *pH*, and they are not expected to change the ζ -potential of the PDMS and oil droplets at this range. However, our results showed that by increasing the surfactant concentration, the absolute magnitude of the EK velocity of the droplets increases as shown in figure 2B. At this *pH*, the PDMS and the oil droplets are both negatively charged and therefore EOF and EP are in opposite directions (see figure 5D in the manuscript). By increasing the surfactant concentration from 0.4 mM to 1 mM, more monomers are adsorbed on the PDMS and the droplets. Micelles are also expected to get adsorbed on the PDMS and droplets at 1 mM surfactant concentration because this concentration is close to the

CMC of the surfactant in non-ionic state.³⁻⁵ This leads to interaction of more ions in the electrolyte (Cl^- , OH^- and Na^+) with the monomers adsorbed on the PDMS and the droplets, changing their ζ -potential in this order: ($\zeta_{1\text{ mM}} > \zeta_{0.7\text{ mM}} > \zeta_{0.4\text{ mM}}$). Since the initial absolute magnitude of the droplets' ζ -potential⁶ is greater than the PDMS at this pH ,² we hypothesize that the interaction of these ions in the electrolyte with the droplets, make their ζ -potential more negative compared to the PDMS. Consequently, the EP is stronger than the EOF, and the magnitude of the EK velocity increases by increasing the surfactant concentration.

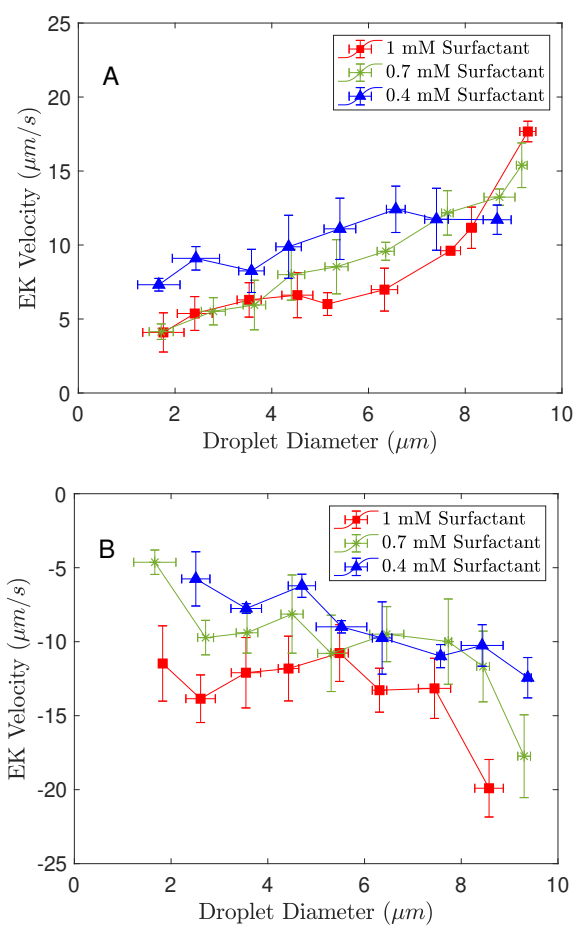


Figure 2: The effect of surfactant concentration on the EK velocity of the oil droplets with different size at A) $\text{pH}=2$, B) $\text{pH}=10$.

3 Analytical Prediction vs. Experimental Data at $pH=7$

Figure 3 shows the comparison of the analytical predictions and experimental data for the EK velocity of oil droplets with different size at $pH=7$ and different surfactant concentration. The graphs are fitted using the surface charge, wall potential and effective slip length based on eq. 2. A least squares regression strategy was used to minimize the differences between the measurements and the fitted data.

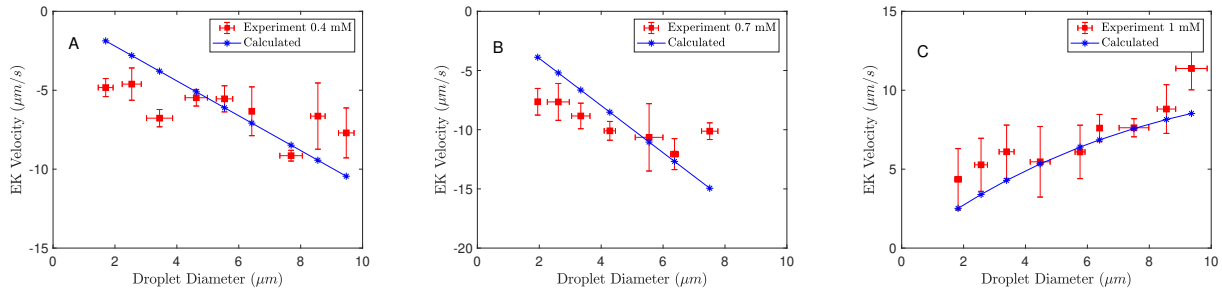


Figure 3: Comparison of analytical predictions presented by P.Gopmandal et al.¹ for the EK velocity of the hydrophobic fluid droplets with current experimental data at $pH=7$ for different surfactant concentration.

References

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