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Phase Transfer Catalyst-Assisted Pickering Emulsification
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The goal of this project is to investigate the effect of phase-transfer catalyst (PTC) functionalization on particle interfacial assembly for use as emulsifiers in systems containing common surfactant additives. The PI proposed multi-scale approaches, namely bulk emulsion characterization, mesoscale drop behavior, and particle adsorption to establish connection between particle properties, emulsion stabilities, and emulsion process design. Our research objectives are (1) Investigate the role of PTCs in spontaneous particle adsorption and Pickering emulsion formation. (2) Determine emulsion phase behavior in a mixed particle-surfactant system.

Results:

1. One-step surface modification via PTC ion exchange

We have synthesized zirconium phosphate (ZrP) nanosheets as model 2D particles for emulsion stabilization. The surface chemistry of the nanosheets was modified with different tetraalkylammonium cations to render the particles surface active. This was achieved simply by exfoliating α-ZrP with different tetraalkylammonium hydroxides. We have measured the surface tension of the suspensions to characterize the surface activity and adsorption behavior of these particles. We observed that short chain PTC have little effect on nanosheet wettability whereas longer chain PTC significantly reduced the suspension surface tension. Interfacial tension data demonstrated similar behavior. Interestingly, while reduction in surface tension are often associated with particle adsorption, suspensions of ZrP-TBA were not able to stabilize emulsions. Work is still in progress to increase the surface hydrophobicity further with tetrapentylammonium functionality.

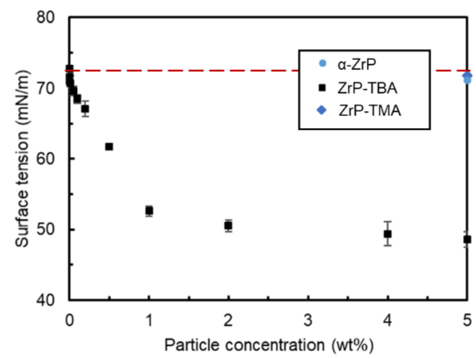

Figure 1: Surface tension of suspensions containing pristine α-ZrP crystals (●), ZrP-TBA nanosheets (■), and ZrP-TMA nanosheets (♦).

2. Comprehensive emulsion state diagram – role of particle loading and phase ratios

We prepared a series of emulsions containing varying amounts of common surfactant additives of the nonionic type and ZrP nanosheets at the full range of water-to-oil ratios. Figure 2 shows that emulsions undergo the classic catastrophic phase inversion from the water-in-oil (w/o) type to the o/w type emulsion at increasing water fraction. The addition of ZrP-TBA nanosheets to the water phase significantly improved the long-term stability of o/w emulsions from the perspective of emulsion separation. In contrast, rapid emulsion separation was observed without particle additives (< 30 min, Figure 3 insert). Increasing ZrP-TBA particle loading had a positive effect on emulsion stability. On the other hand, the improvement in emulsion stability was absent with ZrP-TMA

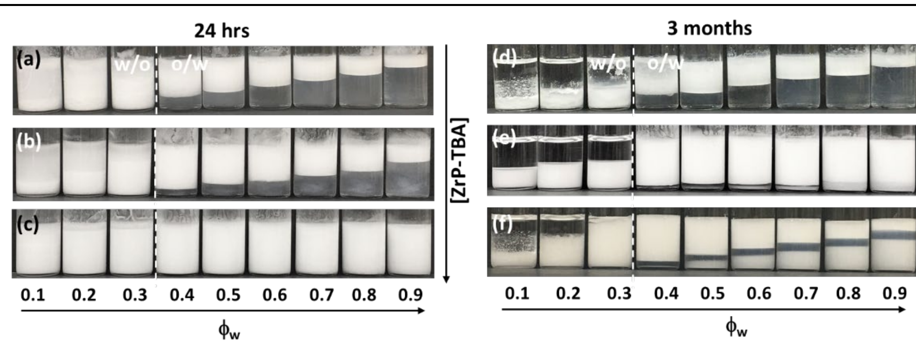

Figure 2: Photographs of water – mineral oil emulsions stabilized by Span 80 and varying concentrations (0~5 wt%) of ZrP nanosheets at different water fractions ϕ_w. Concentrations of Span 80 in mineral oil phase is fixed at 1 wt%, and the water phase contain (a) no particles, (b) 1 wt% ZrP-TBA, (c) 5 wt% ZrP-TBA, (d) no particles, (e) 5 wt% ZrP-TBA, and (f) 5 wt% ZrP-TMA. Photos were taken 24 h (left panel) and 3 months (right panel) after emulsions preparation. Dashed line notes the onset of catastrophic phase inversion from w/o emulsion to o/w emulsion.

nanosheets (see the distinct phase separation in Figure 2(e)), suggesting the lack of particle adsorption to interfaces and the formation of Pickering emulsions.

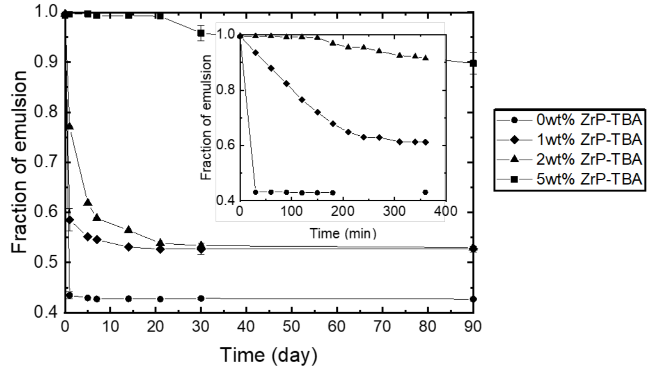

Figure 3: Kinetics of emulsion phase separation for oil-in-water emulsions (ϕ_w = 0.7) containing 1 wt% Span 80 and varying amounts of ZrP-TBA nanosheets.

The presence of nanosheets at oil-water interface was be indirectly verified with drop morphologies: we observed highly non-spherical drops for emulsions containing ZrP-TBA nanosheets in both the continuous and dispersed aqueous phase (Figure 4). This can be contributed to particle jamming at interfaces and the formation of a solid film at the oil-water interface.

3. Stability of emulsions through microfluidics

Having determined that TBA-functionalized nanosheets can enhance bulk emulsion stability, we have started investigating the coalescence behavior using microfluidics. We have contructed PDMS coalescence microchips where drops are collected at a widening collector. Arrested (partial) coalescence has been observed for drops with TBA-functionalized nanosheets and coalescence statistics are currently under way.

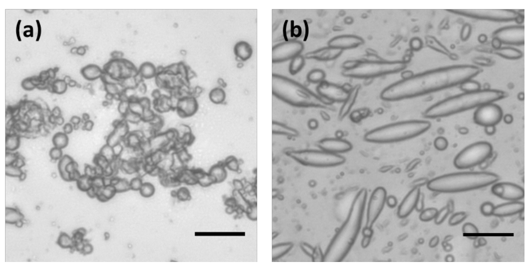

Figure 4: Optical micrographs of (a) w/o (ϕ_w = 0.1) and (b) o/w (ϕ_w = 0.9) emulsion stabilized by 1 wt% Span80 and 5 wt% ZrP-TBA. Scale bars: 25 μm.

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Impact on PI Career and Students:

The grant provided support for one third-year PhD student. Through this project, the student has developed expertise in particle synthesis, surface characterization, microfluidics, and a range of imaging capabilities. Two undergraduates has also been involved in different aspects of this project where they learned about image analysis. The research has resulted in two conference presentation (one presented by the student at the ACS Colloids & Surface Science Symposium), and two manuscripts are being prepared. This grant allowed the PI's research group to explore the area of 2D particle adsorption and emulsions. This project has also led to new collaborations for the PI, a vital advance for their career development.