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# Stimuli-Responsive, Hydrolyzable Poly(Vinyl Laurate-co-vinyl Acetate) Nanoparticle Platform for In Situ Release of Surfactants

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demonstrate both the efficacy of the NP system for surfactant delivery and the ability of the released surfactant to alter wettability and stabilize an oil-water emulsion.

KEYWORDS: polymers, nanomaterials, controlled release, surfactants, stimuli-responsive polymers, hydrolysis, emulsions, wettability

# 1. INTRODUCTION

Surfactants have been extensively studied and are indispensable in a wide spectrum of industries including pharmaceuticals,<sup>1–4</sup> manufacturing,<sup>5–9</sup> oil spill remediation,<sup>10,11</sup> oil recovery,<sup>12–14</sup> detergency,<sup>15,16</sup> and food industry.<sup>17–19</sup> Their amphiphilic structure consists of a hydrophilic polar group attached to a hydrophobic tail with varying lengths and branching. The opposing polarity of their structure and preferential segregation at the interface allows for lowering of the interfacial tension (IFT) between two or more immiscible phases and altering the wetting state of a substrate.<sup>20–22</sup> A subset of applications comprises enhanced oil recovery and environmental remediation including oil spill cleanup and removal of soil contaminants.<sup>23</sup> A practical challenge with surfactant deployment in these applications is that they are susceptible to fast adsorption at various surfaces and interfaces, which limits their availability and effectiveness.<sup>24</sup>

laurate, a commercially available surfactant. All these measurements

In oil reservoirs, deposition of heavy organic matter and polar components alters the wettability of the oil-bearing formation from an originally water-wet to a heterogeneous strongly oil-wet or mixed-wet state.<sup>25</sup> Surfactant-assisted flooding is widely used as a chemical stimulant to alter wettability, lower the oil-water IFT, and create emulsions/ foams to boost oil production.<sup>12</sup> However, designing an optimized and cost-effective surfactant flood remains a challenge due to premature adsorption at the rock surface, pore blockage, and scaling/corrosion.<sup>12</sup> To alleviate surfactant loss due to adsorption inside the porous media, the use of sacrificial chemicals (e.g., polymers) has been explored, which leads to high implementation costs and associated formation damage.<sup>26,27</sup> Nanoencapsulated systems have also been investigated as an alternative method for efficient surfactant delivery. Zhao et al.<sup>28</sup> evaluated a nanofluid system by immobilizing an anionic surfactant (Soloterra 964) to aminoterminated silica nanoparticles (SiNPs-NH<sub>2</sub>) via electrostatic interactions. Mesoporous silica nanocarriers have also been considered; immobilization of surfactants relies on the presence of silanol groups on the surface that can bind to various organic compounds.<sup>29,30</sup> For example, de Freitas et al.<sup>31</sup> studied the encapsulation of diethanolamides (DEA) in SBA-15 silica NPs and observed full release at oil-water interfaces. Nourafkan et al.<sup>32</sup> proposed porous TiO<sub>2</sub> as nanocarriers to deliver a blend of surfactant mixtures consisting

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#### Scheme 1. Synthesis of the PPEG Precursor



#### Scheme 2. Synthesis of p-(VL-co-VA) NPs<sup>a</sup>

NP Synthesis



"Injection and subsequent hydrolysis of the NPs produce surfactant molecules that can assist in displacing residual oil from a limestone reservoir matrix. (a) hydrolysis generates carboxylic acid and (b) carboxylic acid reacts with the mineral to produce CO<sub>2</sub> and an anionic surfactant.

of anionic alkyl aryl sulfonic acid (AAS) and nonionic alcohol ethoxylated (EA) surfactants. They reported a reduced surface interaction of the surfactant molecules with the rock surfaces. De Avila et al.<sup>33</sup> proposed polystyrene NPs (PSNPs) to encapsulate ionic (sodium dodecyl sulfate, SDS) and nonionic (nonyl-phenol ethoxylate-10, NF-10EO) surfactants, which can be released by an oil uptake-triggered swelling. However, the easy dissociation of the surfactant molecules from the host, due to the relatively weak, noncovalent interactions (Hbonding, van der Waals, electrostatic, and hydrophobic effects), limits travel and availability deep into the reservoir similar to the deployment of neat surfactants.<sup>34</sup> To that end, the design of stimuli-responsive NPs for delivery of surfactants deep into the reservoir is a worthwhile endeavor for a number of applications.<sup>35,36</sup>

In this paper, we demonstrate such a platform based on hydrolyzable NPs. The NPs consist of a poly(vinyl laurate-*co*vinyl acetate) core with a poly(ethylene glycol) (PEG) protective shell (Scheme 1). The release mechanism, as illustrated in Scheme 2, involves slow hydrolysis of the ester group to generate carboxylic acid, which subsequently reacts with the carbonate surface to produce carboxylate salts. In addition to the surfactant generation, during hydrolysis, the generated carboxylic acid assists using the stimulation of carbonate formations and the generated carbon dioxide (CO<sub>2</sub>) gas promotes conformance control.<sup>37,38</sup> The ratio of constituent monomers and the PEG length, which acts as a protective shell, were optimized to achieve colloidal stability, while ensuring a proper hydrolysis rate of the ester side chain. In addition, the hydrolysis kinetics and the surfactant release profile were systematically studied under various salinity and temperature conditions. The study represents a step forward in our ability to manipulate and control oil—water interfaces and might pave the way for practical solutions in a number of important applications.

#### 2. MATERIALS AND METHODS

**2.1. Materials.** Vinyl laurate (>99.0%), vinyl acetate (>99.0%), sodium persulfate (>98.0%), 3-allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt solution (40 wt % in water), hexadecane (99%), 4,4'-

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bis(2-benzoxazolyl) stilbene dye, and sodium laurate (SL, 99–100%) were purchased from Sigma-Aldrich. *N*-dodecyl-*N*,*N*-dimethyl-3ammonio-1-propanesulfonate (>98.0%) was obtained from Chem-Impex Inc. 2-Propanol (>99.0%) was purchased from Fisher Chemicals. Maleic anhydride (>99.0%) and polyoxyethylene(-23)lauryl-ether were obtained from Sigma-Aldrich. Sodium chloride (NaCl), calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O), magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), and sodium bicarbonate (NaHCO<sub>3</sub>) were purchased from Sigma-Aldrich. A regenerated cellulose dialysis tubing with 10K molecular weight cutoff (MWCO) was purchased from ThermoFisher Scientific. All chemicals were used as received without further purification.

**2.2. Preparation of the Polymerizable PEG-Based Shell.** The synthesis of the polymerizable PEG (PPEG) shell precursor is illustrated in Scheme 1. Maleic anhydride and polyoxyethylene-(23)-lauryl ether were mixed in a 1:1 molar ratio and heated at 150 °C for 2 h, after which they were kept at 130 °C for 8 h under continuous nitrogen gas purge and stirring.

**2.3. Emulsion Polymerization of p-(VL-co-VA) NPs.** Poly(vinyl laurate-*co*-vinyl acetate) [p-(VL-*co*-VA)] NPs were synthesized by free-radical emulsion copolymerization of vinyl laurate and vinyl acetate (3:1 molar ratio). 0.08 g of the *N*-dodecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate zwitterionic surfactant, 0.4 g of the allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt solution comonomer, 0.6 mL of 2-propanol, 0.04 g of sodium bicarbonate (NaHCO<sub>3</sub>), and 0.2 g of PPEG were mixed thoroughly in 11 mL of deionized (DI) water. To the abovementioned solution, 0.57 g of vinyl laurate and 0.072 g of vinyl acetate were added under vigorous stirring to form an emulsion. 0.02 g of sodium persulfate was then added, and the emulsion was heated at 60 °C overnight. The product was purified by dialysis using dialysis tubing (10K MWCO) and suspended in DI water for 7 days with frequent water replacement.

**2.4. Characterization of the PEG-Coated p-(VL-co-VA) NPs.** NP size and zeta potential in DI water at 25 °C were determined using a Zeta Nanosizer (Malven Instruments, UK). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a Tescan Mira3 FESEM and an FEI Tecani 12 BioTwin TEM, respectively.

**2.5. Alkaline Hydrolysis Accelerated Test.** Accelerated alkaline hydrolysis tests were conducted using 0.1 M sodium hydroxide (NaOH) in either DI water or seawater (see chemical composition in Table S1).<sup>39</sup> The NaOH solution was mixed with the suspension of the NPs in a 1:1 weight ratio and stirred at 320 rpm at 25 or 80 °C. Aliquots were collected periodically and titrated with 0.01 M hydrochloric acid (HCl). The hydrolysis kinetics were estimated using eq 1

hydrolyzed fraction = 
$$\frac{\text{mol}_{\text{NaOHi}} - \text{mol}_{\text{HCl added}} - \text{mol}_{-\text{COOH(surf)}}}{\text{mol}_{\text{NaOHi}}}$$
(1)

where  $mol_{NaOHi}$  is the initial number of moles of sodium hydroxide in the medium,  $mol_{HCladded}$  is the number of moles of hydrochloric acid added during the titration to neutralize the solution, and  $mol_{-COOH(surf)}$  is the number of moles of the carboxylic acid contribution from the PEG shell.

**2.6. Conductivity Measurements.** Conductivity measurements were conducted using an EXTECH meter. The conductivity of various samples was benchmarked to that of commercially available sodium laurate. Because the concentration of laurate is three times that of acetate, the former represents the majority of the product derived upon hydrolysis of the NPs. Conductivity measurements were performed in either DI water or 0.2% sodium chloride (NaCl) to simulate the conditions present during hydrolysis.

**2.7. Contact Angle Measurements.** The surfactant ability to alter the wettability of a substrate was investigated using static contact angle measurements.<sup>40,41</sup> 0.5 g of calcite powder was pressed into 13 mm diameter pellets and submerged in *model* oil under vacuum to generate an oil-wet surface. The model oil was prepared by mixing 0.01 M stearic acid with 50 mL of hexadecane and stirring at 50 °C

overnight.<sup>40</sup> A drop of the unhydrolyzed or hydrolyzed NP mixture was placed on the substrate, and contact angle measurements were collected over time and compared to the neat SL surfactant in DI water or seawater solution.

**2.8. Laser Confocal Scanning Microscopy.** Confocal microscopy images were obtained using a Zeiss LSM 710 confocal laser scanning microscope with a Plan-Apochromat  $\times 25$ , 1.40 water-immersion objective. Emulsions were prepared by vortexing equivolumetric amounts of a suspension of the NPs with model or crude oil. To assist with imaging in the case of model oil, 4 mg of 4,4'-*bis*(2-benzoxazolyl) stilbene fluorescent dye (hydrophobic dye that segregates to the oil phase) was added. Addition of a fluorescent dye to crude oil was *not* necessary because of its autofluorescent properties. For the confocal experiments, a few milliliter aliquots of the emulsion were placed on the microscope prior to imaging.

# 3. RESULTS AND DISCUSSION

**3.1. NP Synthesis and Characterization.** The first step involves the synthesis of the PPEG by reacting maleic anhydride and polyoxyethylene-(23)-lauryl ether in a 1:1 molar ratio. The successful formation of the PPEG was confirmed using FTIR (Figure 1). The spectrum in Figure 1a



**Figure 1.** Transmission FTIR spectra for the PEG-based shell. (a) Synthesized polymerizable maleic anhydride/polyoxyethylene-(23)-lauryl ether, (b) unreacted mixture of maleic anhydride and polyoxyethylene-(23)-lauryl ether (1:1 molar ratio), (c) maleic anhydride, and (d) polyoxyethylene-(23)-lauryl ether.

shows peaks at 1102 cm  $^{-1}$  assigned to the ether (C–O–C) stretching vibration, while the peak at 1780 cm<sup>-1</sup>, due to the asymmetric stretching of C=O from the maleic anhydride, disappears after the reaction, confirming good conversion of the maleic anhydride.<sup>42</sup> The thus synthesized PPEG was then copolymerized with the two vinyl monomers (vinyl laurate/ vinyl acetate in a 3:1 molar ratio). Note that PPEG is used to stabilize the hydrophobic latex core and that PEGylation is widely used to stabilize colloidal systems in brine for a range of industrial and biological applications.<sup>43-46</sup> For example, ultrahigh colloidal stability was achieved under high ionic strengths and extreme pH conditions for thiolated DNA on gold NPs (AuNPs) in PEG mixtures.47 The incorporation of the hydrophilic comonomer, allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt solution, can further enhance the stability and the size distribution of the polymeric latex.<sup>48,49</sup> The NPs were characterized by DLS, TEM, and SEM (Figure 2). All measurements confirm the formation of spherical p-(VL-co-VA) NPs with a size of 55.0  $\pm$  8 nm and a zeta potential of -54 mV.



**Figure 2.** (a) Size distribution of unhydrolyzed NPs obtained from DLS measurements and TEM images (b,c) of unhydrolyzed p-(VL-*co*-VA) NPs. The scale bar is 50 nm for (b) and 200 nm for (c). The corresponding SEM images (d,e) of unhydrolyzed p-(VL-*co*-VA) NPs. The scale bar is 1  $\mu$ m for (d) and 500 nm for (e).



Figure 3. (a) Schematic showing the production of surfactant molecules after hydrolysis of the polymeric core and (b) conductivity measurements of SL in DI water and 0.2% sodium chloride (NaCl), respectively.

**3.2. Critical Micelle Concentration Determination.** The critical micelle concentration (CMC) is an inherent characteristic property of surfactants and can be determined using conductivity measurements.<sup>50</sup> The measured CMC values for neat SL in DI and 0.2% NaCl were 0.026 and 0.017 M, respectively (Figure 3), consistent with values reported in the literature.<sup>51</sup> Based on these results, we have opted to use in all follow-up experiments 1000 ppm or less of NPs to ensure that the concentration of the released surfactant remains below the CMC value.

3.3. Hydrolysis Kinetics. Owing to our interest in the slow release and delivery of surfactants for both environmental remediation and enhanced oil recovery applications, we then studied the hydrolysis kinetics at different temperatures and salinities. To that end, a solution of sodium hydroxide was used in an accelerated hydrolysis test to evaluate the release of the surfactant. The bare p-(VL-co-VA) NP core exhibits a fast hydrolysis profile in 0.1 M NaOH at 80 °C (Figure S1c), yielding ~66% hydrolysis after 1 day. This prompted the need to incorporate a PEG shell to inhibit the accessibility of hydroxyl groups for a more controlled, slow-release profile. The following sections describe the hydrolysis behavior of PEGylated NPs under various temperature and salinity conditions. In addition, the amount of surfactant release from the NPs was compared and contrasted to that of neat SL. Although our primary objective is to design NPs with a slowrelease profile under neutral reservoir conditions (pH  $\sim 7.5$ 

with a continuous release lasting over several months), an accelerated hydrolysis test allows the study of the interplay of various stimuli conditions in relatively short periods of time.

3.3.1. Effect of Temperature. Alkaline-assisted hydrolysis of the ester side chain of vinyl laurate using sodium hydroxide produces lauric acid, which reacts with sodium ions from NaOH to yield the sodium salt (R-COO<sup>-</sup>Na<sup>+</sup>). Figure 4



Figure 4. Calculated % of hydrolysis using titration with 0.01 M HCl for p-(VL-co-VA) NPs with 0.1 M NaOH solution in DI water at 80 and 25 °C. The lines have been added as a guide to the eye.

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Figure 5. TEM images of hydrolyzed p-(VL-co-VA) in DI water showing gray patches around the NPs.

shows the release profile in 0.1 M sodium hydroxide either at 25 or 80 °C. The release profile under alkaline conditions shows two distinct regimes: an initial increase followed by a plateau. The conversion after 23 days is about 11 and 30% at 25 and 80 °C, respectively. The release is consistent with an initial consumption of the produced carboxylic acid via the hydrolysis of the NPs by the basic ions  $[OH^-]$  in solutions after which the produced acid becomes less soluble bringing the reaction to an equilibrium. From the extent of hydrolysis, we estimate the concentration of released SL to be 1795 and 4980 ppm for the low and high temperature conditions, respectively. Although an initial quick increase in the release is observed at both low and high temperatures, the release reaches a plateau at the low temperature, while it keeps increasing at the higher temperature.

In base-catalyzed hydrolysis, the structural characteristics and the chain length of the aliphatic ester groups have a pronounced effect on the rate of the reaction.<sup>52</sup> As the chain length increases, such as in vinyl laurate, the reaction rate decreases, which is a feature desirable for our targeted applications, where slow release is required. TEM images of the hydrolyzed p-(VL-co-VA) NPs (Figure 5) show lowcontrast bright patches, in addition to the NPs, that are attributed to the released surfactant molecules from the NPs. The TEM images further reveal the presence of NP clusters that retain their spherical morphology because the hydrolysis reaction did not proceed to completion, where the NPs will no longer be present. DLS measurements (Figure S2b) show an increase of NP size after the hydrolysis to  $77 \pm 23$  nm with a reduction in zeta potential to around -9 mV. We attribute the increase of NP size to slight aggregation caused by the reduction in zeta potential.

3.3.2. Effect of Water Salinity. To evaluate the effect of salinity on the rate of release, p-(VL-co-VA) NPs were suspended in a brine solution intended to mimic seawater.<sup>39</sup> Figure 6a shows the release profile in seawater using 0.1 M NaOH. The addition of sodium hydroxide to seawater caused slight precipitation of calcium and magnesium ions to produce the corresponding hydroxides. Solutions of high ionic strength trigger a faster surfactant release compared to DI water. The degree of hydrolysis and conversion is 22 and 76% at 25 and



**Figure 6.** (a) Surfactant release profile of p-(VL-co-VA) NPs with 0.1 M NaOH in seawater at 80 and 25 °C. The lines have been added as a guide to the eye. (b) Schematic of the effect of salt-catalyzed hydrolysis and disruption of H-bonding.

80 °C, respectively. Recall that the corresponding values in DI water were 11 and 30%.

Furthermore, hydrolysis in the presence of salts, particularly alkali chlorides (e.g., NaCl), has been reported extensively to enhance the generation of acids, most notably in the depolymerization of cellulose to generate various acids (e.g., levulinic acid) for the production of biofuels.<sup>53</sup> The formation of water–anion networks via hydrogen bonding in highly concentrated chloride solutions plays a significant role in disrupting the ester–water-coordinated clusters and facilitates the accessibility of the hydroxyl ions  $(-OH^-)$  to the carbonyl



Figure 7. Contact angle profiles and corresponding optical images taken on a calcite pellet saturated with model oil (0.01 M stearic acid in hexadecane). Measurements were conducted: in DI water (a,b) and in seawater (c,d). The profiles are for droplets consisting of water, 1000 ppm SL surfactant, 1000 ppm unhydrolyzed p-(VL-co-VA) NPs, and the hydrolyzed p-(VL-co-VA) in NaOH at 80 °C.

groups, as depicted in Figure 6b. 54,55 Furthermore, in low salt concentration, the hydrophilic components in PEG form strong hydrogen bonds with the surrounding water molecules, which allows for a uniformly dispersed protective shell.<sup>56</sup> In solutions containing salt, cations form complexes with the PEG disrupting the structured shell,<sup>57</sup> which allows the nucleophilic hydroxyl  $(-OH^{-})$  ions to react with the ester group leading to faster hydrolysis. In addition, salts dissociate into their constituent cations and anions and may alter the acidity/ basicity of the solution depending on the nature of their conjugate acid or base.<sup>58</sup> Lastly, molecular interactions of cations with carboxylic acids have been studied extensively in wastewater treatment.<sup>59</sup> Most notably, carboxylates (R-COO<sup>-</sup>) tend to exhibit high affinity in forming ion pairs with monovalent cations in solution.<sup>60,61</sup> Under the hydrolyzing pH conditions ( $\sim$ 13), the (-COOH) groups of lauric acid are deprotonated and the reaction with the cations present drives the hydrolysis reaction forward consistent with our results. The increase in NP size after the hydrolysis is more prominent in seawater (Figure S2c) to  $142 \pm 31$  nm and a reduction of zeta potential charge to  $\sim -4$  mV. Again, the increase of NP size is attributed to slight aggregation caused by the reduction in zeta potential, which is more pronounced in seawater compared to DI water.

**3.4. Static Contact Angle Measurements.** Sessile drop contact angle measurements were conducted under ambient

conditions on an oil-wet calcite substrate to investigate the ability of the hydrolyzed NP suspension to alter wetting. To confirm the presence of stearate ions on the oil-wet calcite pellet, FTIR measurements were carried out (Figure S3). The spectrum of oil-wet calcite contains peak characteristics of both stearate and calcite (i.e., 1710 and 2850-2930 cm<sup>-1</sup> are due to the C=O and C-H stretching vibrations, respectively, and 1410 cm<sup>-1</sup> is attributed to the carbonate ions present in calcite).<sup>62</sup> The contact angle profile of a droplet of DI water (Figure 7a,b) starts at 118° followed by a slow gradual decrease due to the spontaneous imbibition within the calcite pores. We next used for the measurements water droplet suspensions that have been "spiked" with the hydrolyzable NPs. To achieve maximum surfactant release from the NPs and, thus, maximum surfactancy, a highly concentrated 1 M NaOH solution was used for the hydrolysis. The results of the hydrolyzable NPs were also compared to a water solution of neat SL. A droplet containing neat SL starts at a lower initial contact angle, 100°. When a suspension of unhydrolyzed p-(VL-co-VA) NPs is used, the initial contact angle is 113°, which undergoes an accelerated decrease and crosses that of commercial SL after 25 min. We attribute the behavior of the suspension containing unhydrolyzed p-(VL-co-VA) NPs to the intrinsic function of NPs as surfactants (e.g., formation of Pickering emulsion). In contrast, the *hydrolyzed* p-(VL-co-VA) NPs collected at different time intervals exhibit better

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**Figure 8.** Confocal micrographs of (a) model oil (mixture of 0.01 M stearic acid in hexadecane) in DI water, (b) unhydrolyzed p-(VL-*co*-VA) NPs in model oil–DI water, and (c) hydrolyzed p-(VL-*co*-VA) NPs in model oil–DI water. The volume ratio of oil to the water phase is 1:1.



Figure 9. Confocal micrographs of (a) crude oil in DI water, (b) unhydrolyzed p-(VL-co-VA) NPs in crude oil–DI water, and (c) hydrolyzed p-(VL-co-VA) NPs in crude oil–DI water. The volume ratio of oil to water is 1:1.

surfactancy compared to other solutions. We attribute this behavior to a combination of the intrinsic surfactancy of the NPs combined with the effect of the released surfactant. As expected, the longer the hydrolysis rate and the more surfactant released into the solution, the lower will be the contact angle. The relatively faster hydrolysis profile in brine discussed earlier is further confirmed with the contact angle measurements (Figure 7c,d). The *hydrolyzed* p-(VL-co-VA)

NPs in seawater showed the best efficacy by altering wettability from a contact angle of  $75^{\circ}$  to complete spreading after 15 min. As with the measurements in DI water, the longer the hydrolysis time, the lower will be the contact angle, which is consistent with the higher amount of the released surfactant in the solution with time.

**3.5. Laser Confocal Scanning Microscopy.** Emulsions are of great practical interest in many industrial and scientific

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applications.<sup>63,64</sup> To evaluate the potential of p-(VL-co-VA) NPs in emulsifying oil-water mixtures, a suspension of the hydrolyzed NPs was mixed with either model or crude oil. For comparison, similar experiments were carried out with unhydrolyzed NPs. Confocal microscopy images of model oil in DI water (Figure 8a,b) show thermodynamically unstable blobs that undergo fast Oswald ripening resulting in larger droplet sizes. In contrast, when the oil is mixed with a suspension of NPs that have been hydrolyzed in 1 M NaOH (Figure 8c), an emulsion with much smaller droplet size is seen consistent with the production and release of the surfactant from the NPs that leads to emulsification. Similar results were obtained for crude oil-water mixtures (Figure 9). Figure 9b,c emphasizes the difference in behavior between the unhydrolyzed and hydrolyzed p-(VL-co-VA) NPs. As before, the presence of the surfactant from the addition of the already hydrolyzed NPs to the oil-water mixture stabilizes the emulsion and produces smaller droplets.

# 4. CONCLUSIONS

In summary, hydrolyzable p-(VL-co-VA, 3:1 molar ratio) NPs were synthesized, and their efficacy for slow and controlled release of the surfactant generated via hydrolysis of the ester side chain was demonstrated. The hydrolyzable NPs with a size of ~55 nm and a zeta potential of -54 mV consist of a poly(VL-co-VA) core stabilized by a PEG shell. Hydrolysis kinetics in an accelerated, base-catalyzed reaction show release of about 11 and 30% of the available surfactant at 25 and 80 °C, respectively. The corresponding values in seawater are 22 and 76%, respectively. In addition, the effectiveness of the NPs in altering the wettability of a hydrophobic, oil-wet substrate was evaluated and compared to that of neat, commercially available SL. Finally, confocal microscopy demonstrated the ability of the NPs to produce surfactant molecules in situ and to stabilize oil-water emulsions supporting their potential applications in diverse fields including hydrocarbon recovery and oil spill remediation.

#### ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c04977.

Size distribution of p-(VL-co-VA) NP cores from DLS and TEM analyses, release profile of p-(VL-co-VA) NP cores at 80 °C in DI water, size distribution of PEGylated p-(VL-co-VA) NP from TEM analysis, size distribution of hydrolyzed PEGylated p-(VL-co-VA) NPs after treatment in 1 M NaOH and 0.1 M NaOH in DI water and seawater, respectively, FTIR spectra of the powdered calcite pellet saturated with model oil, stearic acid, and calcite powder, and salt composition for the seawater solution used in the accelerated hydrolysis (PDF)

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#### **Author Contributions**

B.S.A conducted the experiments and wrote the manuscript draft. M.A.H conducted TEM and confocal microscopy imaging, suggested experiments, and revised the manuscript. G.Q advised on the NP synthesis and experimental plan to capture the release, M.Y·K offered advice on system requirements for field applications, advised on experimental setup for contact angle measurements, and reviewed and made suggestions to the manuscript. E.P.G guided the work, recommended experiments, and reviewed and edited the manuscript.

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## Notes

The authors declare no competing financial interest.

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#### ABBREVIATIONS

CMC, critical micelle concentration PPEG, polymerizable polyethylene glycol shell p-(VL-co-VA), poly(vinyl-laurate-co-vinyl-acetate) NPs SL, sodium laurate IFT, interfacial tension

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