Thermal stability of oil-in-water Pickering emulsion in the presence of nanoparticle, surfactant, and polymer

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Introduction

Oil-in-water (o/w) emulsions stabilized by conventional surfactants and colloidal particles have been studied extensively for various practical applications. Such emulsions are also used in the upstream oil and gas industry but with limited success due to their poor thermal stability and relatively larger droplets size providing difficulty to penetrate well into the oil reservoirs. Pickering emulsions have attracted considerable practical interest in several other fields including oil and gas industry due to their enhanced stability. Oil-in-water (o/w) emulsions are usually stabilized by surfactant or nanoparticle or by both but show poor thermal stability which limits their use for high-temperature applications. In this work, a novel formulation of o/w emulsion stabilized using nanoparticle-surfactant-polymer system is investigated for the formulation of thermally stable Pickering emulsion. The conventional oilfield polymer polyacrylamide (PAM), surfactant, sodium dodecylsulfate (SDS), and nanoparticles such as, SiO₂, clay, and CuO in varying concentration are used. It is observed that the nanoparticle in the presence of surfactant and polymer synergistically interacted at the oil–water interface. The effect of temperature, pH, and salinity on the interfacial tension is investigated to understand the thermal stability. The emulsion system with partially hydrophobic clay nanoparticles in the presence of PAM and SDS shows higher thermal stability as compared to fully hydrophilic SiO₂ nanoparticles. In the presence of salt, NaCl (1.0 wt%), the thermal stability of clay and SiO₂ stabilized emulsions is observed to be further promoted at higher temperatures. Scanning electron microscopy (SEM) images confirm the existence of a structured and rigid layer of nanoparticle at the oil–water interface.

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ABSTRACT

Pickering emulsion offers potential applications in several fields including oil and gas industry due to their enhanced stability. Oil-in-water (o/w) emulsions are usually stabilized by surfactant or nanoparticle or by both but show poor thermal stability which limits their use for high-temperature applications. In this work, a novel formulation of o/w emulsion stabilized using nanoparticle-surfactant-polymer system is investigated for the formulation of thermally stable Pickering emulsion. The conventional oilfield polymer polyacrylamide (PAM), surfactant, sodium dodecylsulfate (SDS), and nanoparticles such as, SiO₂, clay, and CuO in varying concentration are used. It is observed that the nanoparticle in the presence of surfactant and polymer synergistically interacted at the oil–water interface. The effect of temperature, pH, and salinity on the interfacial tension is investigated to understand the thermal stability. The emulsion system with partially hydrophobic clay nanoparticles in the presence of PAM and SDS shows higher thermal stability as compared to fully hydrophilic SiO₂ nanoparticles. In the presence of salt, NaCl (1.0 wt%), the thermal stability of clay and SiO₂ stabilized emulsions is observed to be further promoted at higher temperatures. Scanning electron microscopy (SEM) images confirm the existence of a structured and rigid layer of nanoparticle at the oil–water interface.

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factors such as, nanoparticle concentration, pH, and ionic strength \[15,21\]. Recently, it was observed that long-term stability can be achieved by using appropriate NaCl concentration, where flocculated microsized SiO\(_2\) nanoparticle aggregates are generated and enhanced the droplet stability against coalescence \[22,23\]. A few researchers have observed that o/w emulsion stabilized by surfactant and nanoparticle with controlled pH and NaCl concentration can produce significant improvements in emulsion stability by controlling the particle wettability and degree of flocculation \[24,25\]. It is also observed that silica and laponite nanoparticles do help to reduce the size of emulsion droplets. This indicates their potential application in enhanced oil recovery (EOR) where stability and droplet size have been a constraint for successful application \[26,27\].

At ambient conditions, emulsion can show stability for hours to months depending on the formulation conditions. Increase in temperature leads to the destabilization of emulsion by progressive increase in sedimentation and coalescence of droplets \[28\]. Even though the nanoparticle-stabilized emulsion shows enhanced stability with reduction in Ostwald ripening and droplet size, the trenchant factor associated with thermal stability of these emulsions is the sustainment of interfacial tension (IFT) with increase in temperature \[26,29,30\]. In spite of having many appealing properties, nanoparticle-stabilized emulsion still needs further development for their applications at high temperature conditions.

A water-soluble polymer, such as, polyacrylamide (PAM) has been widely used in upstream oil industry for EOR operations \[31\]. Our recent studies show that water-soluble polymers such as xanthan gum can be used effectively to formulate nanofluids for drilling fluid design application \[32,33\]. It is well understood that polymer acts as a stabilizer and increases the viscosity of water thus improving the oil recovery \[8\]. The use of water-soluble polymer PAM along with nanoparticle and surfactant shows the possibility for the formation of thermally stable o/w emulsion which is not been reported in the literature. In this work, a novel formulation of o/w emulsion stabilized using nanoparticle–surfactant–polymer system using PAM, sodium dodecylsulfate (SDS), and nanoparticle is investigated for the formulation of thermally stable Pickering emulsion. Various nanoparticles, such as, hydrophilic SiO\(_2\) (\(\approx\)15 nm diameter), partially hydrophobic clay (<80 nm diameter), and CuO (<40 nm diameter) are used. The effect of various parameters such as, temperature, pH, and salinity are studied on the stability and IFT of the developed o/w emulsion system.

**Materials and methods**

**Materials**

The details on the chemicals used in this study are listed in Table 1. Aqueous solutions are prepared by using an accurate analytical weighing balance (Reptech\(^{\text{TM}}\) RA-1012 with a repeatability of ±0.0001 mass fraction) and a homogenizer (Remi\(^{\text{TM}}\) RQT-127/D with mixing speed ranges from 300 to 6000 rpm). Water used in all experiments is purified by deionization and filtration with a Millipore\(^{\text{TM}}\) Elix-10 purification apparatus. The oil is purchased from a commercial retail outlet of Hindustan Petroleum Corporation Ltd, India. The supplied oil is lubricating oil with a flash point of around 488 K and density 0.97 gm/cc.

**Preparation of aqueous polymer solutions**

A typical range of PAM concentration (800, 1000, 1200, 1500, 2000, and 2500 ppm) is found to be useful for the purpose \[31\]. First, a mother solution of polymer with concentration 2500 ppm is prepared using gravimetric method. Aqueous solutions of PAM of different concentrations of 800, 1000, 1200, 1500, and 2000 ppm are prepared from the precise amounts of 2500 ppm solution using dilution. A best suited polymer concentration of 1000 ppm is selected from preliminary investigations on the thermal stability of emulsion prepared for the formation of o/w-emulsion for the study.

**Preparation of emulsion using surfactant, nanoparticle and polymer solution**

Two types of emulsion systems are investigated for the thermal stability. The one stabilized by surfactant–polymer and the other stabilized by nanoparticle-surfactant-polymer system. Typically, anionic surfactants such as SDS has HLB value much higher. In order to synchronize the HLB value of SDS (HLB = 40) with that of oil (HLB = 10), a conventional detergent (ingredients such as, 5–15% anionic surfactants; oxygen-based bleaching agents, viz., <5% non-ionic surfactants, phosphonates, polycarboxylates, and zeolites) along with SDS is used in the ratio of 57:43, respectively, to get HLB of 9.98 close to that of oil. Surfactant mixture of SDS and detergent (henceforth referred as ‘surfactant’) is then chosen for the preparation of emulsion. CMC value of surfactant blend is determined by surface tension measurements using spinning drop video tensiometer (SVT 20 N, Data Physics\(^{\text{®}}\), Germany). CMC is defined as the minimum concentration at which the surface tension values are ceased to be almost constant. The CMC of surfactant for various polymer solutions are listed in Table 2. A 1000 ppm polymer concentration is used as the base concentration for the preparation of all o/w emulsion systems containing 0.25 volume fraction of oil to formulate all emulsion systems for further studies. Surfactant concentration slightly higher than CMC (CMC + 10% of CMC) corresponding to 1000 ppm polymer solution is used (Table 2). O/w emulsion stabilized by surfactant–polymer (henceforth referred as surfactant stabilized emulsion unless specified) is prepared with a surfactant concentration of 0.22 wt% mixed in 1000 ppm polymer aqueous solution. To prepare nanoparticle-surfactant-polymer stabilized emulsions (henceforth

<table>
<thead>
<tr>
<th>Chemical/nanoparticles</th>
<th>Purity, mass fraction</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic SiO(_2) with APS: 15 nm</td>
<td>0.995</td>
<td>Sisco Research Laboratories</td>
</tr>
<tr>
<td>Partially hydrophobic clay with APS: &lt;80 nm</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Partially hydrophobic CuO with APS: 40 nm</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Polycrylamide</td>
<td>&gt;0.90</td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylsulfate</td>
<td>0.90</td>
<td>SNF Floerger Ranbaxy Fine Chemicals Limited Merek</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>0.99</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1**

Details on the chemicals and nanoparticles used in the study.

<table>
<thead>
<tr>
<th>Polymer concentration, ppm</th>
<th>Experimental critical micelle concentration (CMC) wt%</th>
<th>Surfactant concentration CMC + 10% of CMC (wt %)</th>
<th>Thermal stability range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.22</td>
<td>CMC(0.22) + 10% = 0.242</td>
<td>316–332</td>
</tr>
<tr>
<td>1000</td>
<td>0.20</td>
<td>CMC(0.20) + 10% = 0.220</td>
<td>318–334</td>
</tr>
<tr>
<td>1200</td>
<td>0.08</td>
<td>CMC(0.08) + 10% = 0.088</td>
<td>315–332</td>
</tr>
<tr>
<td>1500</td>
<td>0.10</td>
<td>CMC(0.10) + 10% = 0.110</td>
<td>313–335</td>
</tr>
<tr>
<td>2000</td>
<td>0.08</td>
<td>CMC(0.08) + 10% = 0.088</td>
<td>316–334</td>
</tr>
<tr>
<td>2500</td>
<td>0.08</td>
<td>CMC(0.10) + 10% = 0.110</td>
<td>314–331</td>
</tr>
</tbody>
</table>

**Table 2**

Critical micelle concentration and thermal stability range for surfactant–polymer stabilized o/w emulsion.
referred as nanoparticle stabilized emulsion unless specified), nanoparticles, viz., SiO$_2$, clay, and CuO for varying concentration from 0.1 to 10 wt% are used and added accordingly to the surfactant–polymer based o/w emulsion. Homogenizer is set at constant speed of 3000 rpm for 1 h for the preparation of emulsion samples. To investigate the long-term creaming stability, all emulsion systems are kept at room temperature for more than 3 weeks.

Stability and characterization of nanoparticle-surfactant-polymer stabilized emulsion

The thermal stability against coalescence of nanoparticle-surfactant-polymer stabilized emulsion is investigated using a microscope (Motic microscope, Hong Kong) with an in-built imaging software Motic Images Plus 2.0 and attached thermal stage (Thermocon Instruments Pvt. Ltd., Bangalore, India). The effect of temperature on the physical structure of dispersed droplets is monitored and captured using a digital camera (Moticam-10) attached with the optical microscope. The dispersed droplet size distribution is determined by dynamic light scattering (DLS) technique using a particle size analyzer (Zetasizer Nano-ZS, Malvern Instruments, UK). The interfacial emulsion structure and deposition of nanoparticles are examined by scanning electron microscopy (SEM) using a scanning electron microscope (ZEISS-Ultra-55, Germany). The frozen o/w emulsion samples stabilized by nanoparticle-surfactant-polymer system are placed to cover glasses carefully. The cover glasses with individual samples are attached to aluminum stubs with adhesive taps and examined using a scanning electron microscope [34]. The pH of the emulsion is determined by using a pH meter (Horiba Ltd., Japan). Few samples stabilized by higher clay nanoparticle concentration are diluted before the size measurement to avoid diverse scattering effects.

Interfacial tension measurements

The IFT measurements are performed by using spinning drop video tensiometer (SVT 20 N, Dataphysics®, Germany). The experimental IFT results are obtained using a fast image processing system and extremely dynamic electronically operated instrument designed software SVTS 20 IFT. The instrument could automatically measure and record the IFT. The tensiometer is tested and calibrated before each measurement. In this study, interfacial tensions are measured for oil-in-surfactant + polymer solution, oil-in-nanoparticle dispersions in surfactant + polymer solution and oil-in-nanoparticle dispersions in surfactant + polymer solution with NaCl.

Results and discussion

The characterization and thermal stability of nanoparticle-surfactant-polymer stabilized o/w emulsion systems are discussed and compared with the surfactant–polymer stabilized emulsion systems. The effect of various parameters such as temperature, pH, and NaCl concentration on the thermal stability and dispersed droplet size are presented. IFT measurements are also discussed in detail to elaborate the interfacial deposition of nanoparticle and surfactant to reduce the surface tension and their effect on the thermal stability. The studies on DLS and SEM are provided to give further insights into the investigation.

Characterization and stability of surfactant–polymer stabilized emulsion

The scheme of formulation and microscopic image of surfactant–polymer stabilized emulsion at ambient condition (at 298 K) are shown in Fig. 1a and b. The o/w emulsion which is prepared in the presence of surfactant alone is observed to be unstable against
creaming and creamed after 2–3 h of emulsification as shown in Fig. 1a. The nanoparticle-surfactant–polymer stabilized emulsion is found to be more stable against creaming even after 23 days of emulsification. The rate of creaming primarily depends on the droplet diameter and the viscosity of the continuous phase [26]. The prepared emulsions are left to stand in transparent cups to visualize the creaming stability by monitoring the position of the interface between water and emulsion phase with time. When the separation of water from the emulsion phase is faster, more is the upward movement of the interface with time, which corresponds to the higher rate of creaming. It is observed that the rate of creaming for the surfactant–polymer emulsion is higher as compared to the nanoparticle-surfactant–polymer stabilized emulsion due to the presence of larger size of the droplets in the former (see Fig. 1b). It is well-known that the droplet size and the density of the dispersed phase (oil in this case) influence the viscosity of the emulsion system. In case of surfactant–polymer o/w emulsion system, larger oil droplets move towards the surface relatively faster than the nanoparticle-surfactant–polymer stabilized system due to lower density and larger droplet size. In case of the nanoparticle-surfactant–polymer stabilized emulsion, the formation of small size oil droplets due to the enhanced deposition of nanoparticles results in higher density in the o/w emulsion system consequentially retarding the movement of oil droplets. It is also observed in our subsequent studies that the near-zero shear viscosity (measured using Anton-Paar rheometer; model no. MCR52) of 1.0 wt% clay stabilized emulsion system is 0.76 Pa s (at 298 K, shear rate 1.0 s⁻¹) higher than the surfactant–polymer stabilized o/w emulsion, which is 0.19 Pa s (at 298 K, shear rate 1.0 s⁻¹), thus, affecting the creaming behavior. The thermal stability range for emulsions is evaluated by monitoring the position of the interface with time at (a) 319 K; (b) 324 K; (c) 329 K; (d) 334 K; (ii) Effect of temperature on the average droplet size with corresponding droplet packing (insets) for surfactant–polymer stabilized emulsion.

Stability of nanoparticle-surfactant–polymer stabilized emulsion

A series of experiments were conducted to investigate the temperature stability of nanoparticle-surfactant–polymer stabilized emulsions for coalescence. Table 3 shows the thermal stability range for various nanoparticle-surfactant–polymer stabilized emulsion systems prepared with varying nanoparticle concentrations. For nanoparticle-surfactant–polymer stabilized emulsion, the temperature (at which droplet destabilizes) had significantly shifted to higher ranges of 346 K for SiO₂ and 348 K for clay nanoparticle (see Table 3), respectively, as against surfactant–polymer stabilized emulsion which is at maximum of 318 K (see Table 2). It is observed that the nanoparticle such as, SiO₂ and clay, in the presence of surfactant and polymer, show favorable effect on the thermal stability than surfactant alone. CuO nanoparticle shows relatively lower range of thermal stability than the other nanoparticles.

Table 2. Thermal stability of nanoparticle-surfactant–polymer stabilized emulsions (m).
two nanoparticles (Table 3). The thermal stability of Pickering emulsions is the result of the steric barrier provided by the strong adsorption of the nanoparticles at the oil–water interface. Lesser the size of the nanoparticle or nanoparticle aggregates, higher is the interfacial adsorption. The reason for the higher thermal stability of emulsion prepared using, for example clay nanoparticle than CuO nanoparticle may be attributed to the extent of surfactant adsorption affecting the flocculation behavior of nanoparticle and the adsorption at the oil–water interface [7]. In this study, it is observed that the emulsions prepared with clay nanoparticle showed higher thermal stability than CuO nanoparticle. It is expected that the presence of surfactant improves the surface properties of the clay nanoparticles to make them less flocculated [22] indicating strong interfacial adsorption at the oil–water interface. In case of emulsion prepared with CuO nanoparticle, the lower thermal stability may be attributed to the formation of CuO aggregates thereby decreasing their surface energy and enhancing the flocculation of CuO nanoparticle to form larger crystals. This results in the reduced adsorption at the oil–water interface. These findings are consistent with the previous studies on the effect of surfactant on CuO nanoparticle aggregation [35–37]. However, the study indicates that the use of an oilfield polymer PAM helps to stabilize the o/w emulsion under synergistic effect with surfactant and nanoparticle by increasing the thermal stability range as reported in Table 2 for surfactant–polymer stabilized (see Fig. 4). The droplet diameter increases to 9.27 μm after 2 h of destabilization with increase in temperature becomes much more difficult due to the deposition of compact nanoparticle layer at the oil droplet surface. This may not be possible for the emulsion stabilized solely by surfactant. Fig. 3 shows the effect of temperature on the thermal stability of nanoparticle-surfactant-polymer stabilized emulsion. It is observed that 1.0 wt% clay stabilized o/w emulsion are relatively finely packed than 1.0 wt% SiO2 stabilized o/w emulsion. In case of emulsion stabilized by 1.0 wt% SiO2, the emulsion is observed to be stable up to 346 K. In case of 1.0 wt% clay stabilized emulsion, the droplet destabilization occurs at 348 K with less clustered emulsion structure as compared to 1.0 wt% SiO2 emulsion system. It is to be noted here that the clay nanoparticle helps to stabilize the emulsion better than SiO2 stabilized emulsion system which may be due to the partial hydrophobic nature of the former than fully hydrophilic nature of SiO2 nanoparticle. These research findings are in line with the results of Vignati et al. [19] who concluded that nanoparticles with intermediate wettability yielded higher stability due to very large free energy of adsorption. At low nanoparticle concentrations (i.e., at 0.1 wt%), it is also observed that the nanoparticle-surfactant polymer stabilized emulsions have relatively much lower resistance for coalescence with increases in temperature as compared with higher concentrations of nanoparticle (Table 3). The coalescence stability of Pickering emulsions primarily depends on the particle concentration, wettability, and the particle flocculation controlled by the particle–particle interaction [20,40]. For Pickering emulsions, the concentration of the nanoparticle must be optimum (1.0–6.0 wt%) to entirely secure the droplet surface from kinetic ripening as low concentration of nanoparticle (<1.0 wt%) can leave large areas of the oil–water interface uncovered, indicating enhanced droplet ripening and flocculation [38,41]. This accounts for the lowest thermal stability at a very low nanoparticle concentrations (see Table 3). As the concentration of nanoparticle increases, the surface of the droplets gets optimally coated by the nanoparticle and forms a compact network at the oil–water interface hindering coalescence [38] and increasing thermal stability. However, subsequent increases in the nanoparticle concentration does not help to improve the thermal stability range, rather reduces the stability of o/w emulsion system, probably due to the competition of nanoparticle to get adsorbed at the oil–water interface resulting in the saturation and affecting the stability of micelles [38,40]. The droplet size distribution for surfactant–polymer stabilized and nanoparticle-surfactant-polymer stabilized emulsion system is determined using DLS technique and shown in Fig. 4 for a sample case. It is observed that with increase in the nanoparticle concentration, the number of droplets and their clustering increases with decrease in the droplet size. The droplet size for surfactant–polymer stabilized emulsion ranges from 6 to 7 μm (see Fig. 4). The droplet diameter increases to 9.27 μm after 2 h of emulsification due to droplets coalescence. However, the average

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Polymer concentration, ppm</th>
<th>Surfactant concentration CMC + 10% of CMC (wt %)</th>
<th>Nanoparticle concentration (wt %)</th>
<th>Thermal stability range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>1000</td>
<td>CMC(0.20) + 0.02 = 0.22</td>
<td>0.1%</td>
<td>330–342</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0%</td>
<td>346–371</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.0%</td>
<td>344–372</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%</td>
<td>342–366</td>
</tr>
<tr>
<td>CuO</td>
<td>1000</td>
<td>CMC(0.20) + 0.02 = 0.22</td>
<td>0.1%</td>
<td>326–348</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0%</td>
<td>331–360</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.0%</td>
<td>329–364</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%</td>
<td>328–361</td>
</tr>
<tr>
<td>Clay</td>
<td>1000</td>
<td>CMC(0.20) + 0.02 = 0.22</td>
<td>0.1%</td>
<td>335–362</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.0%</td>
<td>348–372</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.0%</td>
<td>348–371</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10%</td>
<td>347–369</td>
</tr>
</tbody>
</table>

Characterization of nanoparticle-surfactant-polymer stabilized emulsion

Nanoparticle-surfactant-polymer stabilized emulsions are observed to show significant droplet coalescence/destabilization at elevated temperatures as compared to the surfactant–polymer stabilized emulsion. The trait which made emulsion a suitable candidate for high-temperature environment is the sustainment of droplet packing with restricted coalescence against temperature. The obtained observations are in agreement with results of Yu et al. [38] and Juárez and Whitby [39] who reported that the droplet destabilization with increase in temperature becomes much more difficult due to the deposition of compact nanoparticle layer at the oil droplet surface.
The droplet diameter for 1.0 wt% SiO2 stabilized emulsion is observed to be in the range of 2–2.5 μm after 23 days of emulsification which is significantly less than the size of surfactant–polymer emulsified droplets (Fig. 4). In addition, the average droplet diameter does not increase significantly with time for 1.0 wt% SiO2 stabilized emulsion and observed to be as 5.95 μm after 2 months (Fig. 4). The DLS analysis indicates that the average droplet size measured after 23 days of emulsification for clay and SiO2 nanoparticle stabilized emulsion system is observed to be 3.65, 1.90, and 2.89 μm corresponding to the 1.0 wt% clay, 5.0 wt% SiO2, and 5.0 wt% clay, respectively. It is observed that the oil droplet size decreases with increase in the nanoparticle concentration and the rate of droplet coalescence is much less as compared to the surfactant–polymer stabilized emulsion. The addition of nanoparticle in the surfactant–polymer emulsion system significantly improves the stability by providing a steric resistance against droplet coalescence that forms by the synergistic interaction of polymer PAM with nanoparticle in the presence of surfactant [42,43].

In order to confirm the interfacial deposition of nanoparticle at the oil–water interface, the emulsion stabilized by SiO2 and clay of
1.0 wt% concentration are investigated by SEM study. A few SEM images of the emulsion stabilized by nanoparticle (SiO$_2$ and clay) are shown in Fig. 5. Dark patches represent the oil and white patches represent the flocculated nanoparticles multilayer adsorption around the oil droplets. From the SEM images, it is observed that the nanoparticles form a close packed layer around the oil droplets. Our results show that emulsion with high nanoparticle concentrations (5 and 10 wt%) is found to have more clustered emulsion structure as compared to low nanoparticle concentration (1.0 wt%). For example, the emulsion stabilized with high nanoparticle concentration such as 10 wt% clay displays more clustered structure of oil droplets (Fig. 6) as compared to low concentration of nanoparticle (1.0 wt%) (Fig. 3). From the results, it is concluded that the nanoparticle in the presence of surfactant and polymer enhances the thermal stability of o/w emulsion which finds potential use for high-temperature applications such as in enhanced oil recovery and drilling fluid design.

Effect of salinity on the thermal stability of nanoparticle stabilized emulsion

The effect of salt, NaCl, is investigated for varying concentrations of 1, 5, and 10 wt% on both the thermal stability and emulsion structure of nanoparticle-surfactant-polymer stabilized o/w emulsion system. It is observed that the thermal stability range for nanoparticle-surfactant-polymer stabilized emulsions for 5.0 and 10.0 wt% NaCl could not be determined due to their unstable nature resulting in quick destabilization of the emulsion [44]; however, lower concentration of 1.0 wt% NaCl shows improved results on the thermal stability of the emulsion system and was hence reported. Table 4 shows thermal stability range for the effect of 1.0 wt% NaCl concentration on various nanoparticle-surfactant-polymer stabilized emulsion system. It is expected that an appropriate concentration (1.0 wt%) of NaCl promotes interfacial adsorption of nanoparticle by marginal flocculation of the nanoparticle [22] and helps in reducing the repulsive interactions between nanoparticles. The salt (1.0 wt%) also helps to partially improve the wettability of nanoparticle, thus, improves the adsorption of nanoparticle at the oil–water interfaces enhancing the emulsion stability. With further increase in the concentration of salt (above 1.0 wt%), nanoparticle gets more flocculated due to the further reduction in electrostatic repulsions between nanoparticles, thus, reducing their adsorption at the oil–water interface. These findings are consistent with the reported studies [24,25,28]. The higher range of thermal stability is observed for emulsion system stabilized by 1.0 wt% SiO$_2$ + 1.0 wt% NaCl, 1.0 wt% clay + 1.0 wt% NaCl, and 5.0 wt% clay + 1.0 wt% NaCl, which are thermally stable up to 350, 356, and 358 K, respectively, without showing any significant destabilization among droplets. As shown in Fig. 7, for 1.0 wt% clay + 1.0 wt% NaCl emulsion, destabilization of the oil droplets starts only after 356 K and flocculation free structure of coalesced droplets is achieved at about 384 K. This shows a marked increment in the temperature stability of nanoparticle-surfactant-polymer stabilized emulsion system in the presence of appropriate concentration of NaCl (1.0 wt%) which is from 346 (1.0 wt% SiO$_2$) to 350 K (1.0 wt% SiO$_2$ + 1.0 wt% NaCl) and 348 (1.0 wt% clay) to 356 K (1.0 wt% clay + 1.0 wt% NaCl) as observed from droplet microscopic images shown in Fig. 7.
Emulsion stabilized by 10 wt% clay + 1.0 wt% NaCl shows droplet destabilization almost similar to that of emulsion stabilized solely with 10 wt% clay (refer Fig. 6 and Fig. 8).

Effect of pH on the stability of nanoparticle-surfactant–polymer stabilized emulsion

Effect of pH on the stability of nanoparticle-surfactant-polymer stabilized emulsion is investigated. It is observed that the emulsion formulated at original pH (8.5 for 1.0 wt% SiO2 and 9.0 for 1.0 wt% clay) are stable with negligible change in the average droplet size. It is also observed that the average droplet size at original pH and pH slightly higher than original such as 10.20 and 11.60 are least (see Fig. 9a). In addition, 1.0 wt% SiO2 stabilized emulsion shows moderate droplet packing (though in clustered form) as shown by the microscopic insets at pH values of 10.20 and 11.60 (Fig. 9a) than pH values of 5 and 3. Fig. 9b shows the effect of pH on the coalescence stability and emulsion structure in terms of IFT for nanoparticle-surfactant-polymer stabilized emulsions prepared at ambient temperature of 298 K. IFT for nanoparticle-surfactant–polymer stabilized emulsions is minimum at original pH condition indicating the formation of a stable nanoparticle-surfactant–polymer stabilized emulsion with no droplet coalescence. IFT for nanoparticle-surfactant-polymer stabilized emulsion increases with decrease in pH (5 and 3) reducing the emulsion stability. It is observed that the pH of an emulsion system can significantly affect the emulsion stability by changing the wettability of the nanoparticle [38]. The decrease in pH may lead to the deposition of hydroxide ions at the oil–water interface, thus, making the nanoparticle ionized, hydrophilic, and swollen [38]. The hydrophilic nanoparticle can no longer remain at the oil–water interface due to the improved affinity towards water. This results in the increase in IFT [45] and subsequently leading to the Ostwald ripening resulting in a significant increase in droplet size due to coalescence. For 5.0 and 10 wt% clay stabilized emulsions, average droplet size and IFT determination is very difficult to determine and could not be performed due to the dense population of clay particles limiting instrument capability.

IFT measurement for emulsion system

IFT measurements are performed at original pH after emulsification. It is observed during the addition of nanoparticle to the surfactant–polymer stabilized emulsion that IFT reduces due to the

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Nanoparticle concentration (wt%)</th>
<th>Surfactant concentration (wt%)</th>
<th>Salt concentration (wt%)</th>
<th>Thermal stability range (K)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>1.0</td>
<td>0.22</td>
<td>1.0</td>
<td>350–379</td>
<td>Improved thermal stability without droplet agglomeration</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.22</td>
<td>1.0</td>
<td>348–373</td>
<td>Improved thermal stability with droplet agglomeration</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.22</td>
<td>1.0</td>
<td>356–384</td>
<td>No significant improvement in thermal stability and packing</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>0.22</td>
<td>1.0</td>
<td>358–382</td>
<td>Improved thermal stability without droplet agglomeration</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.22</td>
<td>1.0</td>
<td>346–370</td>
<td>Slightly improved droplet packing not thermal stability</td>
</tr>
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Fig. 6. Microscopic images for nanoparticle-surfactant-polymer stabilized o/w emulsion (10 wt% clay) at various temperatures: (a) 348 K; (b) 355 K; (c) 362 K; (d) 369 K.
Fig. 7. Microscopic images for nanoparticle-surfactant-polymer stabilized o/w emulsion (1.0 wt% clay + 1.0 wt% NaCl) at various temperatures (Table 4): (a) 357 K; (b) 367 K; (c) 378 K; (d) 384 K.

Fig. 8. Microscopic images for nanoparticle-surfactant-polymer stabilized o/w emulsion (10 wt% clay + 1.0 wt% NaCl) at various temperatures: (a) 347 K; (b) 356 K; (c) 364 K; (d) 370 K.
enhanced adsorption of nanoparticles in the presence of surfactant at the oil–water interface to facilitate the formulation of nanoparticle stabilized emulsion. This may be credited to the change in wettability of nanoparticle due to the presence of a surfactant, making nanoparticle aggregates of tuned wettability to promote their interfacial adsorption at oil droplets [46]. For each emulsion system, the IFT is measured at 298 K for 2 h to decide the final equilibrium value of IFT between oil drop and solution [47]. The equilibrium value of IFT for all cases is observed to decrease for few minutes and then stabilizes. The error associated with IFT measurement for the surfactant–polymer and nanoparticle-surfactant-polymer stabilized emulsions lies in the range of 0.6–1.5%. Addition of nanoparticle SiO$_2$ (concentration ≥ 0.1 wt%) to surfactant–polymer stabilized emulsion reduces IFT from 1.10 to minimum value of 0.12 mN/m for 10 wt% SiO$_2$. The effect of NaCl (1.0 wt%) facilitates further reduction in the IFT to 0.09 mN/m. The minimum values of IFT achieved during the course of experiment are 0.08 and 0.06 mN/m which are associated with 1.0 wt% SiO$_2$ + 1.0 wt% NaCl and 5.0 wt% SiO$_2$ + 1.0 wt% NaCl emulsion system, respectively, which are consistent with the previous results on IFT studies [46,47]. The minimum IFT value for nanoparticle clay stabilized emulsion system for 1.0 wt% clay + 1.0 wt% NaCl is found to be 0.09 mN/m.

**Effect of elevated temperature on the IFT**

Fig. 10 shows the effect of temperature (298–371 K) on coalescence stability in terms of IFT for surfactant–polymer and nanoparticle-surfactant-polymer stabilized emulsion prepared at original pH condition. It is observed that IFT for emulsions prepared by surfactant–polymer system decreases rapidly from 1.10 (at 298 K) to 0.01 mN/m (at 371.8 K) due to the weakening of
improves from 346 to 350 K (1 wt% SiO₂) and from 348 to 356 K (0.06 and 0.01 mN/m) of the IFT measurement with increase in temperature (see Fig. 10). This is due to the adsorption of nanoparticle at the oil–water interface providing a steric resistance against temperature.

The phenomenon of IFT reduction with temperature for nanoparticle-surfactant-polymer stabilized emulsion is further observed to be improved in the presence of 1.0 wt% NaCl. As shown in Fig. 10, for 1.0 wt% clay + 1.0 wt% NaCl stabilized emulsion, IFT reduces gradually from 0.09 (at 298 K) to 0.05 mN/m (at 371.80 K). The results show that an appropriate NaCl inclusion promotes interfacial adsorption of nanoparticles by offering promising IFT sustainment with increase in temperature [46]. This beautiful peculiarity offers promising application of nanoparticle-surfactant-polymer stabilized emulsion over conventional emulsion stabilized solely by surfactant. The investigation regarding the change in average droplet size under the influence of pH, NaCl, and temperature for the system of nanoparticle-surfactant-polymer emulsion is in conformity with the previous investigated results for surfactant–polymer and nanoparticle-surfactant-polymer emulsion system [7,10,16,23]. The effect of NaCl on IFT, droplet size, and thermal stability is favorable and exceptional. For 1.0 wt% SiO₂ nanoparticle stabilized emulsion in the presence of 1.0 wt% NaCl, average droplet size reduces to 2.07 μm. However, appropriate NaCl addition promotes enhanced interfacial adsorption of nanoparticle with limited polydispersion and droplet clustering. These findings indicate promising use of nanoparticle-surfactant-polymer stabilized Pickering emulsion for complex environment.

Conclusion

The synthesis, characterization and thermal stability of surfactant–polymer and nanoparticle-surfactant–polymer stabilized oil-in-water (o/w) emulsions in the presence of surfactant; sodium dodecyl sulfate (SDS), and aqueous PAM polymer solution are investigated. It is observed that the thermal stability of emulsion stabilized solely by surfactant is very poor. It is demonstrated for the first time the use of triple emulsifier reduces gradually from 0.09 (at 298 K) to 0.05 mN/m (at 371.80 K). The results show that an appropriate NaCl inclusion promotes enhanced interfacial adsorption of nanoparticles by offering promising IFT sustainment with increase in temperature [46]. This beautiful peculiarity offers promising application of nanoparticle-surfactant-polymer stabilized emulsion over conventional emulsion stabilized solely by surfactant. The investigation regarding the change in average droplet size under the influence of pH, NaCl, and temperature for the system of nanoparticle-surfactant-polymer emulsion is in conformity with the previous investigated results for surfactant–polymer and nanoparticle-surfactant-polymer emulsion system [7,10,16,23]. The effect of NaCl on IFT, droplet size, and thermal stability is favorable and exceptional. For 1.0 wt% SiO₂ nanoparticle stabilized emulsion in the presence of 1.0 wt% NaCl, average droplet size reduces to 2.07 μm. However, appropriate NaCl addition promotes enhanced interfacial adsorption of nanoparticle with limited polydispersion and droplet clustering. These findings indicate promising use of nanoparticle-surfactant-polymer stabilized Pickering emulsion for complex environment.

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