Journal of Industrial and Engineering Chemistry 22 (2015) 324–334

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

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

Tushar Sharma [a,b], G. Suresh Kumar [a], Bo Hyun Chon [c], Jitendra S. Sangwai [a,*]

[a] Petroleum Engineering Program, Department of Ocean Engineering, Indian Institute of Technology Madras, Chennai 600 036, India
[b] School of Petroleum Technology, Pandit Deendayal Petroleum University, Gandhinagar 382007, India
[c] Department of Energy Resources Engineering, Inha University, Incheon 402-751, South Korea

ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form 10 July 2014
Accepted 15 July 2014
Available online 23 July 2014

Keywords:
Oilfield
Polymer
Pickering emulsion
Nanoparticle
Surfactant
Thermal stability

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, SiO_2, 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.

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 potential applications and long-term stability [1–3]. It is known that the interaction between the nanoparticle and surfactant can stabilize or destabilize oil-in-water emulsion [4–6]. Emulsion preparation and long-term stability is typically observed to be a function of surfactant type, composition, and optimum emulsifier concentration [7]. In addition, critical micelle concentration (CMC) and hydrophilic–lipophilic balance (HLB) values are vital for the formation and stabilization of any surfactant-based emulsion [8,9]. However, it is observed that the conventional emulsions stabilized solely with surfactants are not thermally stable [10,11] and hence the use of nanoparticle along with co-surfactant seems to be a promising approach to create thermally stable emulsion [1,5].

Previous studies revealed that the wettability of nanoparticle plays a crucial role in stabilizing nanoparticle-based emulsions [4,12–14]. Tuned wettability leads to the formulation of very stable nanosized emulsion droplets where droplet surface is covered by silica nanoparticle (~50 nm diameter) [15]. Few researchers have investigated the effect of wettability of silica nanoparticle along with the surfactant on the stability of Pickering emulsion [16–18]. It is observed that the silica nanoparticle synergistically interacted with surfactant generating stable o/w emulsion. This is due to the fact that the nanoparticles get adsorbed at the oil–water interface with high-adsorption energy which is attributed to the tuned wettability offered by the surfactant deposition on the nanoparticle surface [17–20]. Emulsion stability also depends on various

* Corresponding author. Tel.: +91 44 2257 4825; fax: +91 44 2257 4802.
E-mail addresses: jitendrasangwai@iitm.ac.in, jitendrasangwai@yahoo.com (J.S. Sangwai).

http://dx.doi.org/10.1016/j.jiec.2014.07.026
1226-086X/

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 (~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® RA-1012 with a repeatability of ± 0.0001 mass fraction) and a homogenizer (Remi® 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® 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.

Table 1
Details on the chemicals and nanoparticles used in the study.

Chemical/nanoparticles	Purity, mass fraction	Supplier
Hydrophillic SiO_2 with APS: 15 nm	0.995	Sisco Research Laboratories
Partially hydrophobic clay with APS: <80 nm	0.99	
Partially hydrophobic CuO with APS: 40 nm	0.99	
Polyacrylamide	>0.90	SNF Floerger
Sodium dodecylsulfate	0.90	Ranbaxy Fine Chemicals Limited
Sodium chloride (NaCl)	0.99	Merck

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®, 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 2
Critical micelle concentration and thermal stability range for surfactant–polymer stabilized o/w emulsion.

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