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Oil-in-water Pickering emulsions stabilized with functionalized multi-walled carbon nanotube/silica nanohybrids in the presence of high concentrations of cations in water

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ABSTRACT

Functionalized multi-walled carbon nanotube (MWCNT)/silica nanohybrid was synthesized and proposed as a stabilizer for oil-in-water Pickering emulsion. Carbon nanotube-to-silica weight ratio was a decisive factor influencing the performance of the synthesized nanohybrid. The results showed an appropriate value of such a ratio for a sol–gel synthesized nanohybrid structure was 28–33%. The emulsion formation time was dictated by the adopted mixing strategy such that without any mixing or ultrasonication it took 12 days for stabilization to be established. Conversely, the use of ultrasonication accompanied by mechanical mixing reduced this time to less than 4 h. Another key factor pertained to the type of the cation contained in water. Bivalent cations, such as magnesium and calcium, changed the hydrophilic–lipophilic balance more intensely than the sodium univalent cation. The nanohybrid holds a great promise to be adopted in enhanced oil recovery (EOR) processes as it does not require any emulsifier and mechanical treatment.

1. Introduction

Gradual reductions in oil extraction from old reservoirs on the one hand and the increasing demand for oil on the other hand have encouraged scientists to apply emerging novel technologies for enhanced oil recovery (EOR) [1–4]. In this respect, nanotechnology, as a leading edge and promising technology, has recently attracted the attention of many scientists. Various strategies have so far been proposed for implementation of this technology in EOR processes, among which are the use of polymeric nanocomposites [5,6], synthesis and application of emulsions and micro-emulsions in EOR process [7–9], the use of nanocatalysts in water and oil interface within oil reservoirs [10–12], employing nano-surfactants [13,14], and the injection of metallic nanomaterials into the oil reservoirs [15]. The diversity in these listed efforts to integrate nanotechnology in EOR processes can be attributed to the following factors: (A) intense diversity in the type of oil and its reservoirs, (B) diversity in EOR mechanisms and methods, (C) the area in nanotechnology application is still in its infancy and the effectiveness of each proposed method has to be proved in practical terms. Difficult conditions such as high temperature (over 80 °C) and pressure of the reservoir, porosity of the media, variety of reservoir rocks, the presence of electric charges within the rocks, availability of different ions at high concentrations in the formation water, and diversity in the type of crude oil are among the decisive parameters that affect the choice of an EOR method [3]. Synthesis of nanomaterials as the stabilizing agents for Pickering emulsions of oil-in-water (O/W) or water-in-oil (W/O) has been recently addressed [16]. Due to the unique properties of carbon nanotubes (CNTs) and silica nanoparticles, their nanohybrid structures may be used as the stabilizer for O/W emulsions, specifically. CNTs are inherently hydrophobic, however, their structures can be modified by functionalization with carboxylic functional groups through partial oxidation mechanism.

The use of silica as the stabilizer of Pickering emulsions is a common practice in research [16]. The reasons for the use of CNTs and silica nanohybrids are as follows: (A) Hydrophilic and hydrophobic characteristics can be imparted to these two compounds of different structures and properties. (B) CNTs

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structure and metal oxides have favorable catalytic properties, and their nanohybrids would inevitably inherit the catalytic properties [12].

Generally, the multi-walled carbon nanotube (MWCNT)/silica nanohybrids can be synthesized through the following two methods: the implementation of silica structures in MWCNT formation reaction [17], and incorporating MWCNT in the reaction to form silica structure. The most important parameters that affect the synthesis of nanohybrid through inclusion of MWCNT into silica structure formation reactions are as follows: nanohybrid synthesis method, type of silica structure that is formed in the nanohybrid production process, and the ratio of silica to MWCNT.

Silica has different structures, namely MCM41, SBA15, spherical nanoparticles and aerogel. The structure and synthesis method have considerable effects on the properties of silica including hydrophilicity or hydrophobicity. Several important techniques to synthesize silica structures are sol–gel, hydrothermal, and co-precipitation [18–23].

The type of silica structure is dependent on its formation method; so when a nanohybrid is formed by inclusion of MWCNT in the reaction to form silica structure, the selected method affects the type of nanohybrid structure. In addition, low thermal resistance of functionalized carbon nanotubes at high temperatures (above 100 °C) is a limitation for choosing the nanohybrid formation method.

In this research, functionalized MWCNT/silica nanohybrid was synthesized through a modified sol–gel method in which oil-in-water Pickering emulsions were used as stabilizers at high concentrations of Na^+, Ca^{2+}, and Mg^{2+} cations. Taking into consideration the fact that the formation water in real systems may contain other ions at lower concentrations than the above ions, the behavior of the nanohybrid that stabilizes Pickering emulsion was studied in the water samples taken from two oil reservoirs from the southwest of Iran. Emulsion stabilization rate was also studied at various conditions. To this end, the rates of spontaneous emulsification were evaluated first without using a mixer, then by using a mixer, and finally by using an ultrasonic homogenizer. Finally, a set of analyses including SEM, TEM, XRD were conducted to give insights to characterization and morphology of the nanohybrid structure. In addition, FTIR spectroscopy and zeta potential measurements were carried out in order to study the interactions between cations and the nanohybrid.

2. Experimental

2.1. Materials

MWCNT was supplied by Nanotechnology Research Center of Research Institute of Petroleum Industry (RIPI) [24]. Functionalized nanotubes were prepared through refluxing by a 12 molar nitric acid solution (70 mL acid/g MWCNT). Sodium silicate (SiO_2/Na_2O = 2.1) was used as the precursor to form the silica structure. $CaCl_2·2H_2O$, $MgCl_2·6H_2O$, and NaCl (Merck) were the ionic salts used in this study. The oily phase used in this research was kerosene supplied by Tehran Oil Refinery. Formation water samples and their analyses were taken from Water and Environment Research Centre of Research Institute of Petroleum Industry (RIPI).

2.2. Production of nanostructured nanohybrid

Functionalized MWCNTs were added to silica formation reaction in order to produce these types of nanohybrids by sol–gel method. The functionalized MWCNT was kept in 50 mL of 2.5% hydrochloric acid at 80 °C with a stirring rate of 300 rpm until the functionalized MWCNT was fully distributed. Afterwards, the sodium silicate was transformed by dripping into mixture with the rate of 10 drops per minute until a viscous and cloudy gel was formed. The final product was dried at 80 °C for 24 h.

Weight ratio of MWCNT to silica played a key role in the properties of the product. The weight ratio of MWCNT was adjusted to achieve the hydrophilicity and hydrophobicity structural balance. A ratio of 28–33% (weight of MWCNT to the overall weight of the nanohybrid structure) was determined in experiments as an appropriate ratio to create the desirable HLB.

2.3. Two-phase systems

Three types of two-phase systems were prepared and analyzed in this research: de-ionized water/oil system, salts-containing water/oil, and formation water/oil. The behavior of the nanohybrid was studied individually and all together in the presence of the three ions Na^+, Ca^{2+}, Mg^{2+} in salts-containing water/oil system. The ratio of ions in the sample was determined according to the ratio of ions in formation water samples of reservoir located in the southwest of Iran. Table 1 lists the samples concentration while Table 2 summarizes the ion content of the water samples taken from the two oil fields in the southwest of Iran.

In addition to the ions mentioned in Table 2, there were other ions in water, including sulfate, sulfite, ferrite, lithium, and nitrate. Relatively, the amounts of these ions were negligible. Due to the simultaneous presence of calcium and magnesium ions in the formation water samples, these ions were considered in one group while sodium ion was considered in another group. The ratios of calcium, magnesium, and sodium were determined according to the ratios of the samples denoted by *f* and *g* in Table 2. The amount of nanohybrid in all samples was constant and it was equal to 0.1 wt%. Water oil volume ratio was equal to 10 in all the samples (water/oil = 10).

2.4. Method of nanohybrid distribution in water and oil two-phase system

Nanohybrids distribution was compared through three following methods: without using a stirrer, by using a mechanical stirrer, and by using an ultrasonic bath and stirrer. When a mechanical stirrer (400 rpm) was used, the mixture was mixed for 24 h at room temperature. In the third method, the mixture was put in the bath for 15 min and then they were stirred for 30 min with a mechanical stirrer. Stable emulsion formation time was different in each of the methods.

2.5. Analysis methods

Images of nanohybrid structures were obtained by a Hitachi SEM (F4160) and a Philips TEM (EM208). The structure was analyzed prior and subsequent to the formation of emulsion by XRD using a Philips X'Pert MPD with a copper anodic tube. FT-IR (Perkin Elmer Frontier^{TM}) analysis was also carried out in order to study the probable effects of ions dissolved in water on the functional groups of nanohybrid structure. Accelerated surface area and prosimetry system (ASAP) (Micromeritics ASAP 2010)

Table 1
Concentration of ions in water in various synthesized samples.

Sample	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)
a	0	0	0
b	0	0	40 000
c	3000	750	0
d	6000	1500	0
e	6000	1500	10 000