JCRS

Journal of Chemical Reactivity and Synthesis 2023: 13(1) 51-65

Research Article

Synergistic effect of disordered mesoporous silica and nonionic surfactant on demulsification efficiency of water-in-crude oil emulsions

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ARTICLE INFO:

Received:
10 December 2023

Accepted:
28 January 2023

Available online:
15 February 2023

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ABSTRACT

This study focused on their usefulness as a nano demulsifier. KIT-1 was characterized via FT-IR, XRD, SEM and Nonyl phenol ethoxylates (n = 6, 12 and 20 denoted as NPE-6, NPE-12 and NPE-20 respectively) surfactants were used with commercial demulsifier. The result showed that composition of KIT-1 and nonyl phenol ethoxylates (NPEs) in crude oil emulsion greatly improve the demulsification efficiency of the original demulsifier. It was found that the best demulsifier composition for breakdown of crude oil emulsion was the one based (NPE-12) and KIT-1. The results clearly showed that the sample with the best water separation performance would raise demulsification efficiency to a value of 95%.

Keywords: Water in crude oil emulsions; Demulsifiers; Demulsification efficiency; Nonyl phenol ethoxylates; Disordered mesoporous silica KIT-1

1. Introduction

Most of crude oils are exploited in an emulsion form, therefore water in the crude oil emulsion needs to separate [1]. These emulsions are very harmful in the petroleum industry due to their corrosion damage, catalyst poisoning in downstream refinery operations, then it is necessary to separate the water completely from the crude oils before transporting or refining them [2]. Today, chemical demulsification is the most widely applied method of eliminating such undesirable emulsions [3]. Nanotechnology has already made important contributions to improve many industries and many technologies, such as environmental science, energy, electronics, food, cosmetics, medicine, and aerospace. The oil and gas industry have become increasingly interested in using nanotechnology in recent years [4].

In the refining processing, incoming crude oil mix with a fresh "wash water" to extract the water-soluble salts and hydrophilic solids. The water in crude oil emulsion (W/O emulsion) is usually stabilized by hydrocarbons in the form of asphaltenes, resins and waxes [5]. These natural emulsifiers coagulate on the water-oil interface causing it to form a stable film around the droplets which prevent coalescence of the dispersed water droplets [6]. In a refinery desalting process, wash water was mixed with crude oil to eliminate dissolved salts. The demulsifier is injected into the emulsion and thoroughly mixed. Subsequently emulsion may be broken, followed by the crude oil dehydration [7].

One of the problems of using demulsifier is the formulation of commercial demulsifier contains organic solvent which causes some disadvantages including, flammability, toxicity. Another problem of applying conventional demulsifiers is that these are expensive which increased refinery processing cost [8]. We have recently shown the application of functionalized MSN in crude oil demulsification [9]. The present study aims at reducing using dosage of commercial demulsifier by applying effective composition of KIT-1, as disorder mesoporous silica, with NPEs to improve demulsification of W/O emulsions. No work in the literature describes the separation of water from W/O emulsion by KIT-1, as far as we know.

2. Experimental

2.1. Materials and method

All chemicals were obtained from Aldrich or Merck and were used without further purifications unless otherwise stated. The size and morphology of nanoparticles were characterized by a field-emission scanning electron microscope (FESEM, TESCAN MIRA3-XMU) with an acceleration voltage of 0.2-30 kV. X-RAY diffraction (XRD) pattern was recorded with a Rigaku Ultima IV diffractometer (Rigaku, Japan) using CuKα radiation ($\lambda = 0.15406$ nm). To study the surface of nanoparticles, Fourier transform infrared (FT-IR) spectra was obtained with a Perkin-Elmer BX-II IR spectrometer using KBr Pellet.

A commercial demulsifier and crude oil sample were obtained from reservoirs in southern Iran. The crude oil sample's characteristics and chemical composition are listed in Table 1. Throughout the experiments, deionized water was used all the chemicals were used without further purification.

Table 1. The characterization of the crude oil

Physical characterization/mass percentage	**Value**
API gravity at 15 °C	30
Viscosity at 20 °C (mm^2 / s)	36
Salt content (P.T.B)	5
Asphaltene (%w/w)	4.5
Resin (%w/w)	8
Saturated hydrocarbon (%w/w)	46
Aromatic hydrocarbon (%w/w)	32
Water and residue	5

NPE-6, NPE-12 and NPE-20 used in this work are supplied from Isfahan copolymer company. Some physical and surface properties of particles are listed in Table 2.

Table 2. Some physical and surface properties of NPEs

NPE[a]	Moles EO [b]	HLB[c]	Cloud Point[d]	pH[e]
NPE-6	6	11	Insoluble	5-7
NPE-12	12	14	78-81	5-7
NPE-20	20	16	73-76	5-7

[a] Nonyl phenol ethoxylates (n = 6, 12 and 20 denoted as NPE-6, NPE-12 and NPE-20 respectively)

[b] Ethylen oxide (EO)

[c] HLB range: <10 w/o emulsifier,>10 o/w emulsifier,10-15 good wetting agent,16-18 solubilizing agent
[d] Cloud point: °C, 1 wt% aqueous solution
[e] pH: 5% in water

2.2. Preparation of water in crude oil emulsion

Water/oil emulsions were prepared by adding 5 vol.% water to the crude oil at 60 °C and completely mixed using a mixer. The emulsion was stable for weeks without phase separation.

2.3. Procedure for the synthesis of KIT-1

KIT-1 was synthesized according to our previous paper [10].

2.4. Demulsifier evaluation

The impact of KIT-1 and NPEs on the performance of the commercial chemical demulsifier was investigated. To this end, firstly a sample free of nanoparticle that contains industrial amount of chemical demulsifier, namely reference 100, was prepared. Similarly, reference 30 with only 30% amount of the industrial demulsifier was also produced. Both samples were chosen as reference states and the results of the demulsification performance testing were compared with them. Afterwards, KIT-1 and NPEs were separately added to the samples of reference 30 and thoroughly mixed by sonication and mixer respectively, to produce the required samples for further performance testing. After this step, the amount of water separation was measured by bottle test method. The most effective composition was specified by the results of bottle tests.

2.5. The bottle test

The industrial demulsifier for the understudied crude oil was added to 100 mL crude oil emulsion and KIT-1 with NPEs were injected via a micro-syringe in the emulsion. After mixing the prepared sample, it was poured in a graduated cylinder then settled on the hand magnet in a water bath with different temperatures, the demulsification performance was measured in different times by the measurement of separated water from the emulsion sample. Finally, the demulsification efficiency (DE) was calculated with the aid of the following formula. [11,12] Where V is the volume of the separated water and V_0 is the volume of the initial water. Relative errors in estimating the volume of the separated water from the bottle test are around 3% percent.

$$DE\ (\%) = V/\, V_0 \times 100 \qquad \text{Eq. (1)}$$

2.6. Measurement of the salt content

W/O emulsions contain salt dissolved in the aqueous phase [13]. The residual salt content of W/O emulsion was evaluated to investigate the accuracy of the bottle test results and to determine the demulsification performance, after the bottle settling on a hand magnet. For the purification of the crude oil, it is necessary that the salt content be less than 5 P.T.B (pounds of salt per thousand barrels of crude oil) in heavy crude oil. Because salt is dissolved in water, a decrease in salt indicates a reduction in water in the treated oil. In this case, it is possible to use the terms desalting and demulsification instead of each other. The amount of salt was measured before and after the bottle test by standard IP 77 test method [14].

Potanciumeter (Zag chemi co, Iran, Model PTR-79) and glass electrode Ag/Agcl (azar electrode, Iran) were used for potential different and respectively. pH measurements were made with a digital pH meter (Horbia, Japon, Model pH F-11). Hot plate magnetic stirrer (Pars faraso, Iran, Model F-60) and dijital scale (Sartorius, Swiss, Model PB210D) was used.

2.2. PVC membrane-coated electrode

The electrodes were prepared from a graphite bars (3mm diameter and 50mm long). The graphite bars were polished and put in a concentrated HNO_3 solution overnight to clean the surface of the graphite bars. Then, the bars were rinsed with THF and once again polished and washed with distilled water and allowed to dry. A mixture of ionophore (benzo-18-

crown-6) and PVC, plasticizer (DOP) and carbon powder (for increasing the electrical conduction and mechanical stability of coated membrane) to give a total mass 300 mg was dissolved in about 5 mL of THF and the solution was mixed well. The graphite bar was coated by dipping it into the membrane solution for a few seconds and allowed to dry overnight. The electrode was conditioned in 0.001 M Calcium nitrate for 24 h, and stored in mild concentration solutions of Calcium nitrate, when not in use. The coating solution was stable for several days and could be used for construction of new membranes.

2.3. Apparatus and potential measurements

All potential measurements were made with a potentiometer having ±0.01 mv accuracy with an Ag/AgCl reference electrode. All measurements were carried out at 25 °C with a cell type:

Ag/AgCl;KCl(satd.)‖Ca^{2+} sample solution | Ion selective membrane | graphite bar

The potential readings were made after the potential reached to a constant value. The performance of the electrode was investigated by measuring the potential of Ca^{2+} solutions over the range of 1.0×10^{-8} to 1.0×10^{-1} M. The data were plotted as observed potential vs the logarithm of Ca^{2+} cation concentration.

3. Results and discussion

3.1. Sample characterization

SEM was used to characterize the morphology of the KIT-1 sample. Fig.1 depicts the SEM of the KIT-1 sample. KIT-1 exhibits a coral-like structure, as is easily seen.

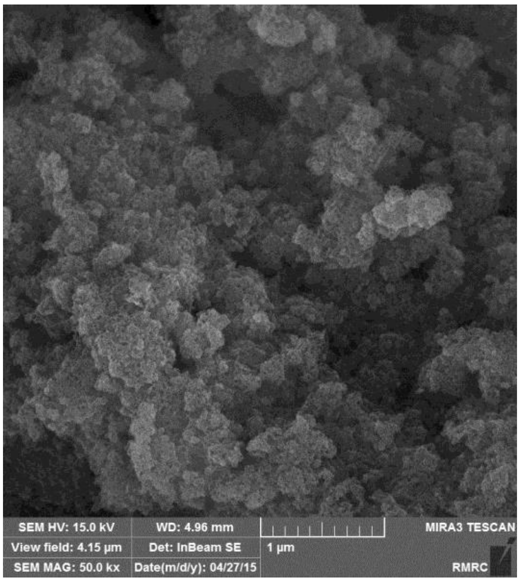

Fig .1. FESEM of KIT-1

The quality and structural ordering of synthesized materials were identified by powder X-ray diffraction (Fig. 2). Broad peaks which correspond to (100), (200). diffraction with lattice space d100 ~ 4.01 nm. the diffractions are weakened and broadened, showing that KIT-1 has a more disordered structure. The crystal size of nanoparticles is calculated with the Scherrer equation (Eq.2)

$$D = K\lambda / (\beta \cos \theta) \qquad \text{Eq. (2)}$$

Where D (nm) is the crystal size of the nanoparticle, K is the so-called shape factor, that is a typical value of about 0.9, λ = 1.15406 nm in our experiment is the X-ray wavelength, β is the full width at half the maximum intensity (FWHM) in radians. θ is the Bragg angle which is related to the position of the peak in degree [15-17].

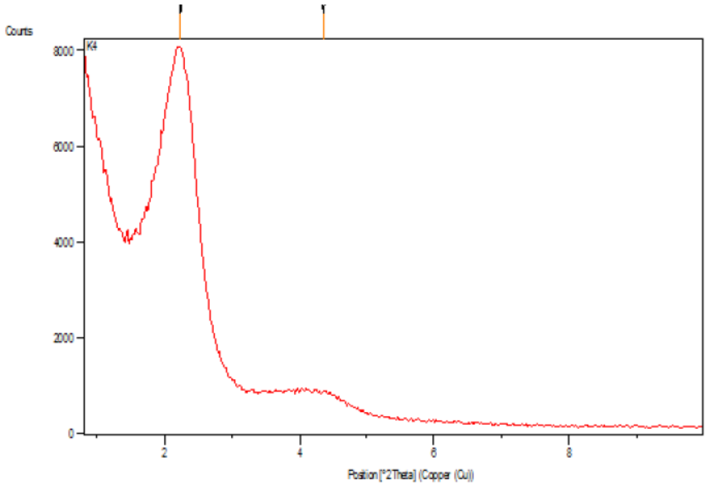

Fig. 2. XRD pattern of KIT-1

FTIR spectra for the KIT-1 is shown in Fig. 3. The spectra display the bands typical of materials of the KIT-1 type. The stretching and bending modes of adsorbed water molecules are attributed to the bands at 3429 and 1632 cm^{-1}, respectively. Si-O-Si asymmetric vibrations are represented by the bands at 1084 cm^{-1}; its symmetric vibration of Si-OH is represented by the band at 960 cm^{-1}; stretching vibration of Si-O-Si is represented by the band at 800 cm^{-1}; and bending vibration of Si-O-Si, is represented by the band at 462 cm^{-1}

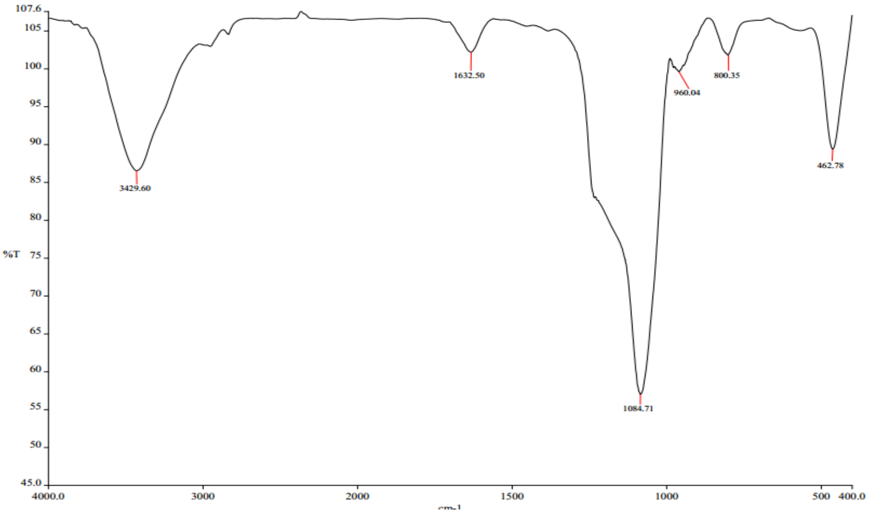

Fig 3. FT-IR spectra of KIT-1.

3.2. Effect of KIT-1 on dewatering efficiency

The effect of KIT-1 dosages is shown in Fig. 4. This figure shows that there is an optimum value when adding KIT-1 at 3 ppm. At higher KIT-1 concentration, KIT-1 interactions are increased which reduce their interfacial activity, leading to lower demulsification efficiencies. Fig.4. shows demulsification efficiency at the best conditions by the bottle test method. According to this figure, addition of particles results in a 35% enhancement of the reference 30.

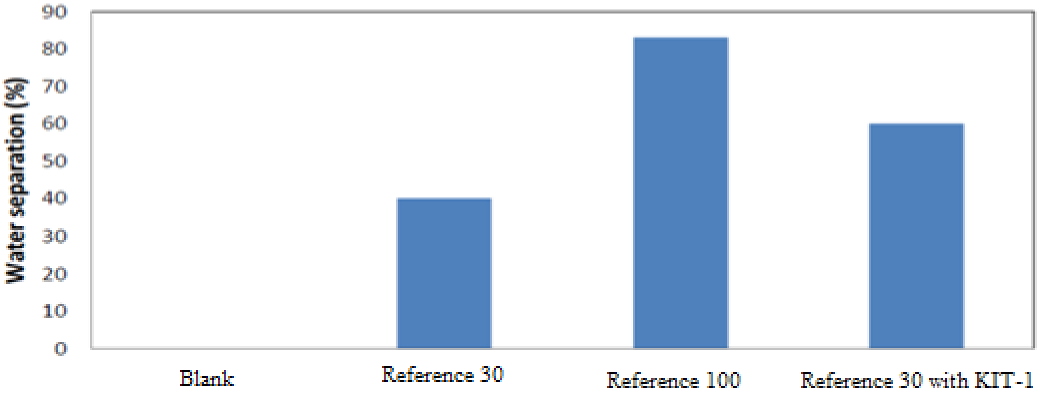

Fig. 4. Bottle test results of KIT-1 at 3 ppm concentration on dewatering efficiency of reference 30, Other conditions: settling time: 2h, heat temperature: 70 °C

In the present work, nonyl phenol ethoxylates (n = 6, 12, 20) are separately mixed with other ingredients to break crude oil emulsions. The effects of three kinds of NPEs along with KIT-1 were examined. 1, 3, 6, 9, 12 and 15 ppm of all of the nonyl phenol ethoxylates and 3 ppm of KIT-1 were added into the reference 30. The results present in Fig.5. showed that the systems based on NPE-12 are more effective than other. It can be concluded that NPE-12 was the best among the tested surfactants in the applied blends. This may be explained on the basis of their hydrophile-lipophile balance (HLB). Owing to low HLB, NPE-6 has a less affinity to migrating to the water/crude oil interface. Moreover, NPE-20 has high HLB, However, hydrogen bonding between OH group and asphaltene causes instability of water droplets but it makes more hydrophilic, which this consequently causes entrapping a more fraction of NPE-20 in the aqueous phase, instead of adsorption in the water/crude oil interface.

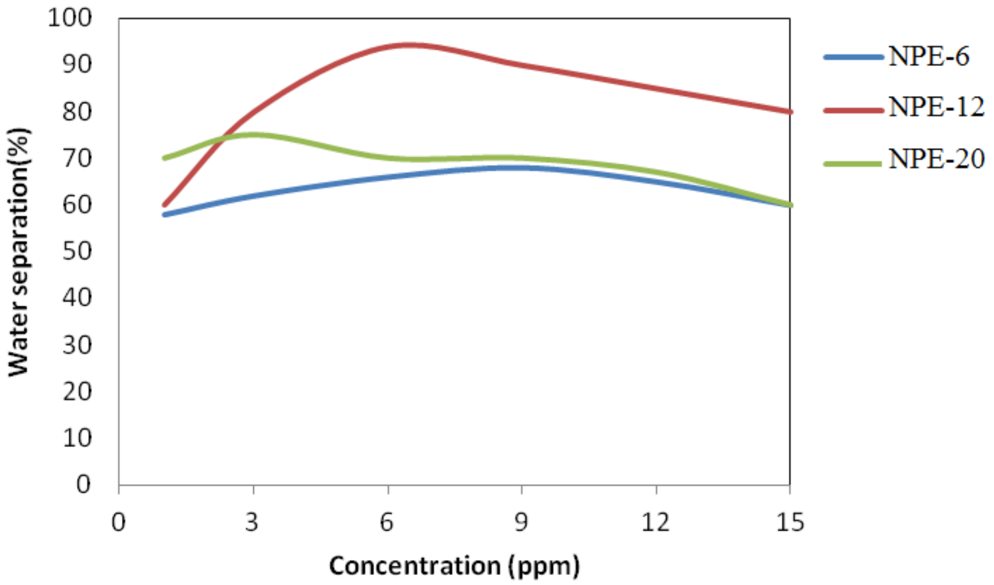

Fig 5. Effect of different NPEsconcentration (ppm) along with 3 ppm KIT-1 on demulsification efficiency of reference 30 (the bottle test)

3.3. Temperature effect

To investigate the effect of temperature on demulsification, a set of reference 30 bottle tests were done in 25°C, 50 °C and 70 °C with optimal concentration of the NPEs (other conditions were the same). The performance of different concentrations of nonyl phenol ethoxylates for the three different temperatures is shown in Table 3. Demulsification time decreases by temperature increasing from 25°C to 70°C. To explain this observation, it can be concluded that, temperature increasing leads to the crude oil viscosity decreasing and also destabilization effects cause by extent of water droplets movement [7]. Both factors make the momentum between two water droplets increases and coalescence occurs. Thus, the demulsification temperature has an important role on the rate of water separation from W/O emulsions.

Table 3. Effect of different NPEsconcentration (ppm) along with 3 ppm KIT-1 on demulsification efficiency of reference 30 at various temperatures

		25°C		50°C		70°C	
Type of demulsifier	Ratio	DE%	Time(min)	DE%	Time(min)	DE%	Time(min)
NPE-6: KIT-1	9:3	55	200	60	120	66	70
NPE-12: KIT-1	6:3	75	165	85	60	94	30
NPE-20: KIT-1	3:3	60	180	65	95	70	50

3.4. Effect of NPE-12 and KIT-1 on demulsification efficiency

As mentioned earlier, the bottle test was conducted once again to investigate the effect of settling time and NPEs dosage on the DE (%) in the presence of KIT-1. The settling time required for the optimum dosage of NPEs to achieve the DE (%) of 94 (highest possible value) was investigated. The settling time was observed to be 2 h in the case of reference 30 sample while the sample with NPE-12 and KIT-1 (added to reference 30) had a settling time of about 30 min at 70°C. According to the experiment conducted by, the presence of nano demulsifiers decreases the viscosity of oil more rapidly than conventional demulsifiers.

3.5. Measurement of the salt content

According to the applied IP-77 standard test, this method is intended for the determination of total halide concentration in crude petroleum, topped crude, residual cracking stock, and fuel oil. The salt content of the demulsified crude oil is lower than the 5 P.T.B which is maximum allowable value of the salt content. At the optimum dosage of KIT-1 and NPE-12 which is estimated in the previous section, the result is 3.2 P.T.B. it lay in the allowable range of oil salinity and the treated oil can completely meet the requirements of industrial usage.

4. Conclusions

The experiment showed that the demulsification performance of commercial demulsifier greatly enhance by using theKIT-1 and NPE-12. Due to higher activity and hydrophilicity of nanoparticles than macromolecule demulsifier, KIT-1 pass through water/oil interfacial films then arrive water phase and increase the density of water phase, so the interfacial film is destroyed, and water is separated of W/O emulsion. Performance of KIT-1 and NPE-12 on efficiency improvement of dewatering is more effective at high temperature. According to the results, NPE-12 shows a better demulsification effect than other ethoxylated nonylphenols because of its appropriate HLB. NPE-12 improves DE in low dosage (6 ppm). One of the most important chemical characterizations of nonionic surfactant is neutrality, they have not counter ion; therefore, they don’t cause corrosion. Simultaneous applying of KIT-1 and NPE-12 reduce the demand to the amount of conventional demulsifier which is decreased crude oil processing cost and adverse effect of conventional demulsifier on environment.

Acknowledgments

This work was supported by the research facilities of Ahvaz Branch, Islamic Azad University, Ahvaz, Iran.

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