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# Investigation of the Simultaneous Chemicals Influences to Promote Oil-in-Water Emulsions Stability during Enhanced Oil Recovery Applications

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## Acronym

1-Emulsion Stability → ES

2-Zeta potential → ZP

3-Nano Particles → NPs

4- Cationic surfactant → CS

5-Ultra-Pure water → UPW

6-Ion Strength → IS

7-Stability Index → SIn

8-Inter Facial Tension → IFT

9-Weight Percent → wt%

10-Cationic Surfactant → CS

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**Abstract**

Emulsion application in Enhanced Oil Recovery (EOR) processes is a common and practical subject in petroleum industry. Considering the chemical usage limitations, quantitative understanding of the ability of chemicals to improve other chemical performance is very important. In the present article, the coincident impacts of nanoparticles, salts and surfactants on interfacial tension reduction as well as zeta potential for determining the best emulsion stability have been examined. Resultant findings have shown that cobalt oxide nanoparticle and aluminum ions lead to an improvement in emulsion stability than each individually. Resulted emulsion stability indexes for cobalt oxide nanoparticles and aluminum ions are 0.48 and 0.49 at 25°C and 0.54 and 0.66 at 50°C, respectively. Nonetheless, their simultaneous presence, i.e., dispersion of cobalt oxide optimum weight percent in crude oil and dissolving of optimum aluminum ions concentration in water, change the stability indexes to 0.64 and 0.75 at temperatures of 25°C and 50°C, respectively. Presence of dispersed silica nanoparticles with low weight percent resulted in stability indexes of 0.49 and 0.43 at temperatures of 25°C and 50°C, respectively, but at high concentration because of repulsive forces against the asphaltene molecules, emulsion stability drops eventually with indexes of 0.35 and 0.26 at temperatures of 25°C and 50°C, respectively. While presence of cationic surfactant in the phase that silica nanoparticle is dispersed in, rises emulsion stability and viscosity. In all cases, along with emulsion stability increasing, quantities of zeta potential became more negative. But results of silica nanoparticle show that descending negative zeta potential trend of media does not lead to stability necessarily. This paper, quantitatively demonstrated that the effect of chemical co-existence by stimulating the polar molecules of crude oil caused a significant difference in emulsion stability than using the chemicals individually.

**Keywords:** Emulsion stability, Oil-in-Water emulsion, Zeta potential, Nanoparticles, Surfactant, Ions hydration

## Introduction

Chemical flooding as one of the most promising EOR method displaces the trapped oil in the reservoir by reducing the interfacial tension at the oil-emulsion interface due to capillary effect. Formation and stabilization of emulsion phase are most vital stages during a chemical flooding. Accordingly the size distributions of emulsions give crucial information about understanding the underlying mechanism of stability and penetration into the porous media. Tertiary oil recovery methods directly depend on oil-water-rock interfaces properties such as contact angle, capillary forces, wettability, viscos forces and IFT. All these parameters related to a dimensionless quantity called Capillary Number,  $N_c$ . This number represents blocked oil mobilization to enhance oil recovery.

Emulsions are defined as a media that droplets suspensions of an immiscible fluid with diameter greater than  $0.1 \mu\text{m}$  dispersed in another fluid. Small droplet size and existence of an interfacial film around oil droplets lead to kinetic stability of O/W emulsion. Hence emulsifying agents such as clay particles, added chemicals, or crude oil components like asphaltenes, waxes, resins, and naphthenic acids are used to form stable O/W emulsions. Surface-active agents or emulsifiers try to stabilize the interface against coalescence by decreasing the interfacial tension between blocked oil and displacing fluid. Therefore, permeable paths are blocked by emulsions with dispersed phase drops and fluid is forced to pass through upswept sections. In result higher overall sweep and displacement efficiency would achieve [1]–[3].

An ordered interfacial film with a certain strength is formed by absorbed asphaltene molecules which contain aromatic and polycyclic aromatic hydrocarbons, at the oil-water interface. Thus the emulsion with absorbed asphaltene on W/O interface has the strongest stability. This high stability of W/O emulsion by asphaltene is mainly because of interfacial active asphaltene (IAA) subfraction which is included less than 2 wt % of whole asphaltenes. High content of sulfoxide groups of this subfraction induces the hydrogen-bonding interaction between neighboring water and IAA molecules. This causes high interfacial activity of IAA molecules and to produce a rigid film with aging consequently. Oil and interface viscosity are found to increase with asphaltene concentration. The droplet coalescence is controlled by strong elastic interface film formed by asphaltene molecules which results emulsion stability. This phenomena is indicated as the crucial stabilization mechanism what is more asphaltene and its concentration play the dominating role in O/W emulsion stability [4]–[7].

Additionally, using nanoparticles shows several evidence that causes synergic effects on water injection performance and helps to prevent any asphaltene precipitation [8]–[10].

Metal or oxide base nanoparticles have noticeable uses in oil recovery enhancement investigations. These nanoparticles have several positive properties such as very high area/volume ratio, very high suspension ratio, excellent surface adsorption and also catalyst ability. Currently, nanoparticles are multitask application materials in petroleum and gas industry[11]–[13]. Using nanoparticles in order to increase oil recovery is classified as one of the new and novel Enhanced Oil Recovery (EOR) methods. Therefore, Nanoparticles could be considered as an appropriate option to recover residual oil because of their various capacity and potential. For instance, most of EOR methods are seeking to improve the oil recovery factor by

wettability alteration but formation damage caused by heavy hydrocarbon particles could plug pore throats and leads the operation to failure[6]–[17]. Small particle size of nanoparticles gives them the ability to enter into the pores and elicit the oil without trapping [18]–[20]. Alteration of main fluid properties and changing mobility ratio to a appropriate value, emulsion stabilizing ability, better and faster heat transferring in thermal methods and more compatibility with environment compared with other materials are the main reasons to persuade industry to use nanoparticles in EOR processes[14]–[16], [21]–[23].

Based on acidic and amphoteric properties of these nanoparticles, they have different effects on oil-water emulsion stability[22], [23]. While water-in-oil emulsion is been creating, a stable film is formed around the water droplets that avoids the water droplets coalescence to each other and keeps emulsion stable[24], [25]. Dispersed nanoparticles in water, interact with asphaltene molecules due to the negative charged and polar asphaltene particles. Water-wet nanoparticles have more tendency to stay in water phase therefor they are much less soluble in oil phase. On the other hand, oil-wet nanoparticles dispersed easily in oil than water phase and increases the nanoparticles concentration in oil phase which accordingly rises the interaction with asphaltene molecules. The formed film around the water droplets in oil phase during emulsion formation, improves the emulsion stability and resists the droplets coalescence when derived ions from nanoparticles have acceptable effects in media[26], [27].

In emulsion, each nanoparticle is under influence of repulsive electrostatic, attractive Van der Waals and capillary forces[28]. Furthermore, emulsion stability directly depends on droplets interaction. Electric double layer justifies the resistance between thin films around droplets and emulsion stability. Each nanoparticle has two electrical layers around itself, first one Stern layer which its charge isn't changeable and diffuse layer which its charge may change[29], [30]. Due to these properties of oxide nanoparticles, they are able to attract asphaltene particles but the attraction force is not equal in oil and water system, because nanoparticles behavior is not the same in oil and water phase. If asphaltene places in interface of oil and water, it will cause emulsion stability. Therefore, amount of oil-in-water emulsion droplet creation has close relationship with presence of nanoparticles in that phase and accordingly asphaltene adsorption[30], [31].

In recent years, researchers are succeeded to create a stable oil-water emulsion and improve the crude oil properties, by means of nanoparticles and their oxide. This emulsion is consisted of nanoparticles with catalyst and adsorb properties. These nanoparticles by spreading through the porous media or/and production pipes can have different positive effects on fluid properties like asphaltene elimination due to interface adsorption process [28], [29]. Polarity of asphaltene molecules and surface charge of nanoparticles cause serious interaction between asphaltene and nanoparticles [32]. Gavreilatatos et al. in 2017 [33] showed that the presence of nanoparticles even at low concentrations, postpones the oil-water emulsion separation significantly. Also, they stated that increasing the silica oxide nanoparticle concentration, improve the emulsion stability but causes nanoparticles aggregation inappropriately. In 2005, Saleh et al. [34] studied the effect of highly charged polyelectrolyte-grafted silica nanoparticles on oil-in-water emulsion. They showed that small amount of this nanoparticle 0.44 wt% is able to stabilize emulsion phase for

very long time like 6 months. After that Kubowicz et al. in 2010 [35] used nanometer-sized gold nanoparticle as stabilizer in emulsion phase. They studied the oil droplets interfacial structure by X-ray scattering. They reported  $30 \text{ nm}^2$  for obtained area per nanoparticle at the interface of oil droplet. Moreover, Binks et al. in 2010 [36] used dynamic headspace analysis to study the emulsion evaporation rate which was stabilized by wither surfactant and nanoparticles. They stated that adsorbed film of nanoparticle is more effective than surfactant film. Additionally, Mohammadi et al. in 2011 [37] investigated the effect of titanium, zirconium oxide and other different oxides on asphaltene stability. They observed that asphaltene particles in nanofluids at acidic condition are not able to precipitate because the nanofluids acts like a dispersant. Greff et al. in 2011 [38] expressed that metal nanoparticles participate in breaking bond between carbon and sulfur as catalyst which lowers asphaltene amount and increases the aromatic and saturated materials and consequently decreases oil viscosity meaningfully. Then Worthen et al. in 2014 [39] investigated the effect of zwitterionic surfactant and silica nanoparticles on formation and stabilization of oil-in-water emulsions. They reported surfactant and nanoparticles performed synergistically to create a finer emulsion with higher stability. This synergic improvement of two amphiphiles was even higher than high salinity synthetic seawater aqueous case. Furthermore Pilapil et al. in 2016 [40] widely studied Pickering and non-Pickering emulsions to clarify the mechanisms of emulsions stabilization. They explained that stabilizing particles like nanoparticles (which are wet by both liquid phases exist in liquid-liquid interface) are the key factor in Pickering emulsion stabilization. They provide a mechanical barrier in droplet coalescence process. Also, they suggested that silica nanoparticle accumulated in the coherence phase and entropic forces which are caused by them are the main reasons of why non-adsorbed particles impart stability to the emulsion. Saïen and Fadaei 2018 [41] investigated the effect of silica nanoparticle and CTAB surfactant on emulsion interfacial tension and proved surfactant presence of NPs is improved with surfactant adsorption and leads to significant interfacial tension decrease consequently. Also Zhao et al. 2018 [42] proved this fact during spontaneous imbibition in other work and showed silica NP is an appropriate selection for EOR. After that Kumar and Mandal 2018 [43] study the nano-emulsion formation, characterization and evaluate its thermodynamic and physicochemical properties. They reported silica NP was successful to improve kinetic stability, viscosity and interfacial tension of emulsion.

Although the effects of many chemicals on emulsion stability are checked in previous studies, their simultaneous effects have been rarely studied. In the present study, the coincident effects of nanoparticles, salts and surfactants have been examined. The used chemicals upon to their specifications were dispersed or dissolved in continuous (water) or discontinuous (oil) phases. Considering the changes established in the water or oil phases, chemicals were selected and based on previous results; four successive novel procedures were designed to form the emulsions and check their stability. Furthermore, time and temperature influences on the emulsion stability and also rheological behavior of the formed emulsions have been investigated.

## 2-Materials and Methodology

### 2-1-Materials

A light crude oil (34 °API) which has a noticeable amount of asphaltene content e.g. 3.46wt% has been used to form oil-in-water emulsions. Ultra-pure water with Total Dissolved Solid (TDS=0) and zeta potential value of zero has been used to prepare the synthetic brine and dispersing the crude oil for emulsions formation as well.  $\text{AlCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaCl}$  salts of Merck company were used to investigate the ions effects on emulsions stability. Cobalt oxide ( $\text{Co}_3\text{O}_4$ ) and silica ( $\text{SiO}_2$ ) nanoparticles of US Research Nanomaterials Inc. were selected for examination of nanoparticles effects on the stability behavior of emulsions (TEM and constituents' quantity of used nanoparticles are provided in appendix section, Figure 13 , Table 2, Table 3).

### 2-2-Methodology

Figure 1 indicates all implemented procedures to investigate the effects of different chemicals on stability of emulsions. Experiments were performed successively, e.g. each step was designed and performed according to the results of previous step. The objectives of procedures are classified as follow:

Procedure#1: Determining the effects of dispersed  $\text{Co}_3\text{O}_4$  NPs in crude oil on ES and ZP.

Procedure#2: Examining the role of  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  in ES and ZP.

Procedure#3: Investigating the effects of dispersed  $\text{SiO}_2$  NPs in water phase on ES and ZP.

Procedure#4: Testing the effect of CS on ES and ZP

After determining target ion optimum concentration (which has the highest ES among all ions) and also the optimum wt% of  $\text{Co}_3\text{O}_4$  NPs, both were added to the continuous (water) and discontinuous (crude oil) phases, respectively, to check their simultaneous effects. In the next step, by taking the advantage of negative silica NPs surface charge for increasing the stability of O-in-W emulsion, different wt% of silica NPs were added to the continuous phase. Thereafter, upon to the obtained results, a cationic surfactant was added to the continuous phase in presence of silica and  $\text{Co}_3\text{O}_4$  NPs to examine its effect on ES.

#### 2-2-1-Procedure#1

- i. Cobalt oxide NPs with 0.01, 0.05, 0.075, 0.10, and 0.15 wt% were mixed with crude oil, individually.
- ii. The Cobalt oxide NPs were dispersed using Ultrasonic apparatus with power of 120w and 30min time.
- iii. 5cc of prepared crude oil (step i) was took using sampler.

- iv. A 50cc beaker containing 25 cc of UPW was placed on a magnetic stirrer with 10000 rpm and the crude oil (step iii) was slowly added into it (two prepared samples at two temperatures of 25°C and 50°C individually for each NPs concentration).
- v. The measurement procedure proceeded.

### 2-2-2-Procedure#2

- I. 0.01, 0.05, 0.075, 0.10, and 0.15 mol/L of each ion ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ ) were added to UPW, individually (calculated amount of  $\text{AlCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaCl}$  salts were added to the water so that the specified mole per liter (i.e., IS) of each target ion be present in the solution).
- II. The prepared brine was placed on a magnetic stirrer for 30 minutes to dissolve the added salt in the UPW.
- III. 25 cc of the synthetic brine was poured in a 50cc beaker. (at first, more volume of brine was made (step I) to decrease the calculation errors).
- IV. The 50cc beaker containing 25cc brine was put on a magnetic stirrer with 10000rpm and 5cc of the crude oil was slowly added to it using a sampler. (two prepared samples at two temperatures of 25°C and 50°C individually for each ion concentration).
- V. The measurement procedure was implemented.

### 2-2-3-Procedure#3

This procedure is implemented in two same time procedures to prepare A) brine as continuous phase, and B) dispersed cobalt oxide NPs into crude oil as discontinuous phase. The preparation steps were as follow:

- A. The same steps of procedure #2(section 2-2-2 from I to IV) was performed for determined optimum ion concentrations at two temperatures of 25°C and 50°C, individually.
- B. Lower than and equal weight percent of determined optimum cobalt oxide NPs concentrations at two temperatures of 25°C and 50°C from section 2-2-1 were prepared according to procedure#1 (from i to iv).
- C. 25 cc of prepared brine (from step A) and 5 cc of crude oil samples (from step B) were mixed with a magnetic stirrer to form emulsions (like the forth step of procedures 1 and 2).
- D. The measurement procedure proceeded for each sample.

### 2-2-4-Procedure#4

This procedure is designed to examine the effects of silica NPs on ES when obtained optimum weight percent of cobalt oxide NPs (from procedure#1) is dispersed in crude oil.

- A. Procedure#1(from step i to vi) was repeated for two resulted optimum cobalt oxide concentrations at two temperatures of 25°C and 50°C, individually.



B. Silica NPs with various concentration of 0.01, 0.05, 0.075, 0.10, and 0.15 was individually dispersed in to UPW using ultrasonic using Ultrasonic apparatus with power of 120w and 30min time, and then 25cc of it was poured in a beaker.

C. 25 cc of prepared silica nanofluid (from step B) and 5 cc of crude oil containing dispersed cobalt oxide NPs (from step A) were mixed with a magnetic stirrer for emulsions formation like the forth step of procedures 1, 2, and 3.

D. Measurement procedure proceeded for each sample.

F. All above steps were repeated for the case which in its B step a fixed concentration of cationic surfactant of 100 ppm was dissolved in the prepared silica nanofluids.

### **2-2-5- Measurement Procedure**

The prepared emulsion was poured into a test tube and allowed to reach steady condition for 90 mins. This procedure is illustrated at the bottom of Figure 1.

#### **2-2-5-1- Emulsion Stability Test**

i) A sampler was used to take a sample from the middle of test tube and putting it on a lamella glass.

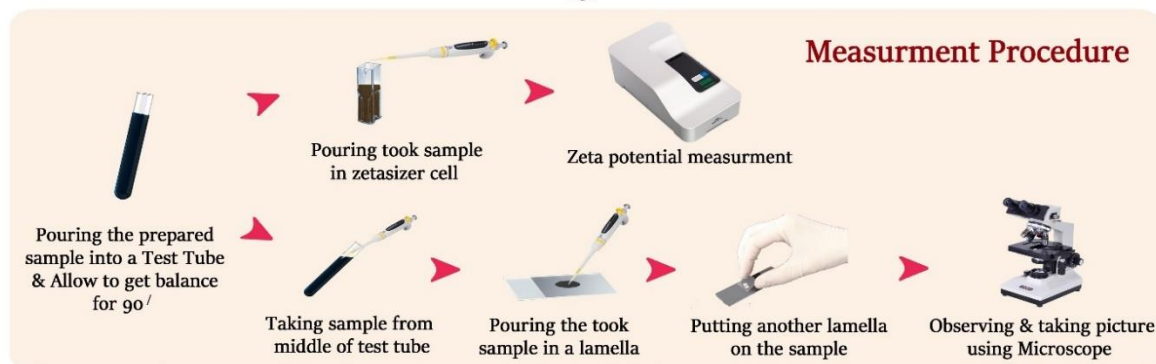
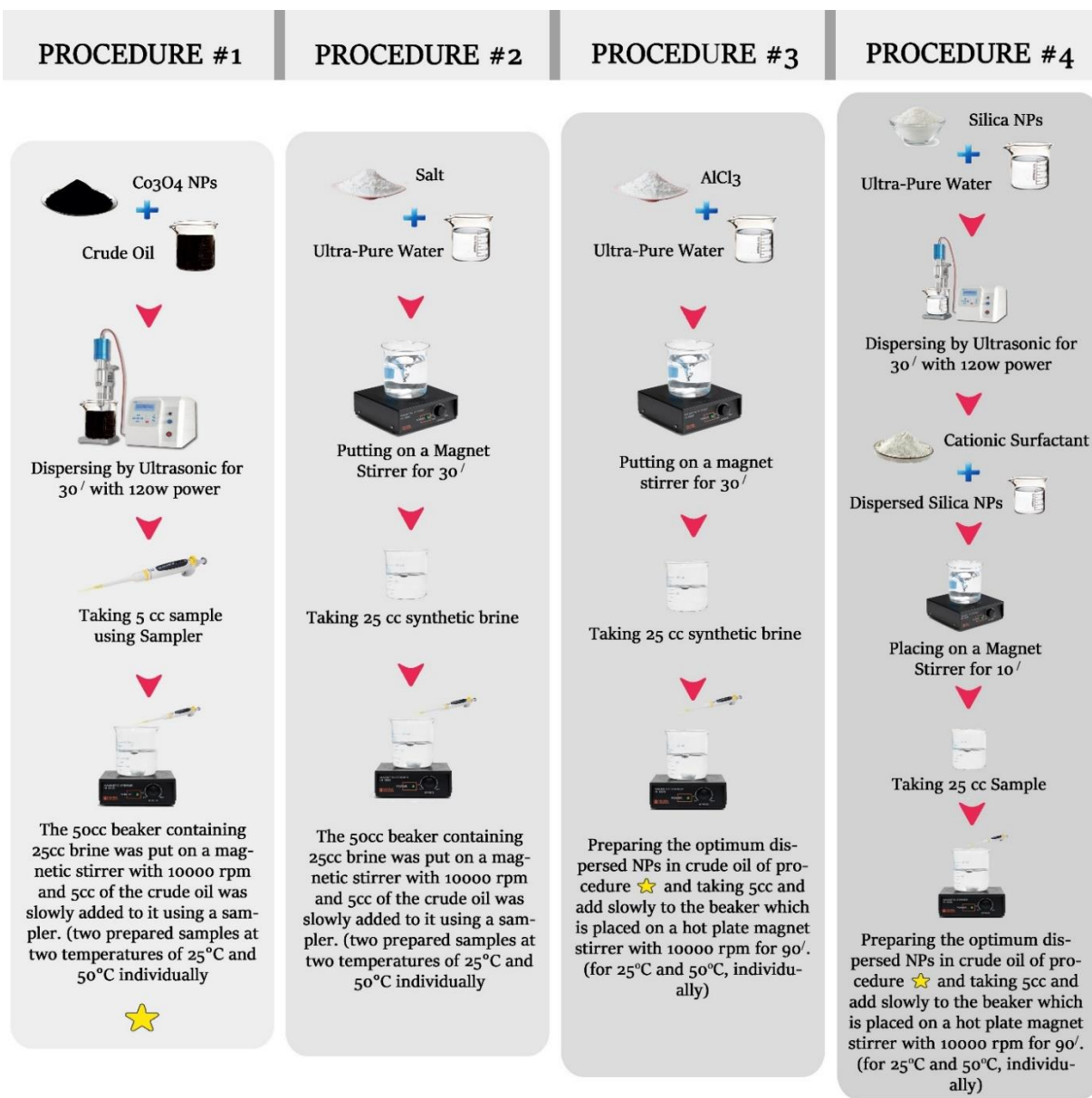
ii) Another lamella glass was insert on the emulsion sample to spread it on the lamella glass (of prior step).

iii) The picture of formed emulsions was taken by a Microscope.

iv) The ratio of oil-in-water emulsion number with size of less than  $1000 \mu\text{m}^2$  to the number of all emulsions were considered as stability index (SIn). Using ImageJ software, the number of O-in-W emulsion ratio with size of less than  $1000 \mu\text{m}^2$  was calculated[11].

#### **2-2-5-2- Zeta potential test**

i) Using a sampler to take a sample from the middle of test tube and pouring it into a Cuvette to measure the zeta potential.



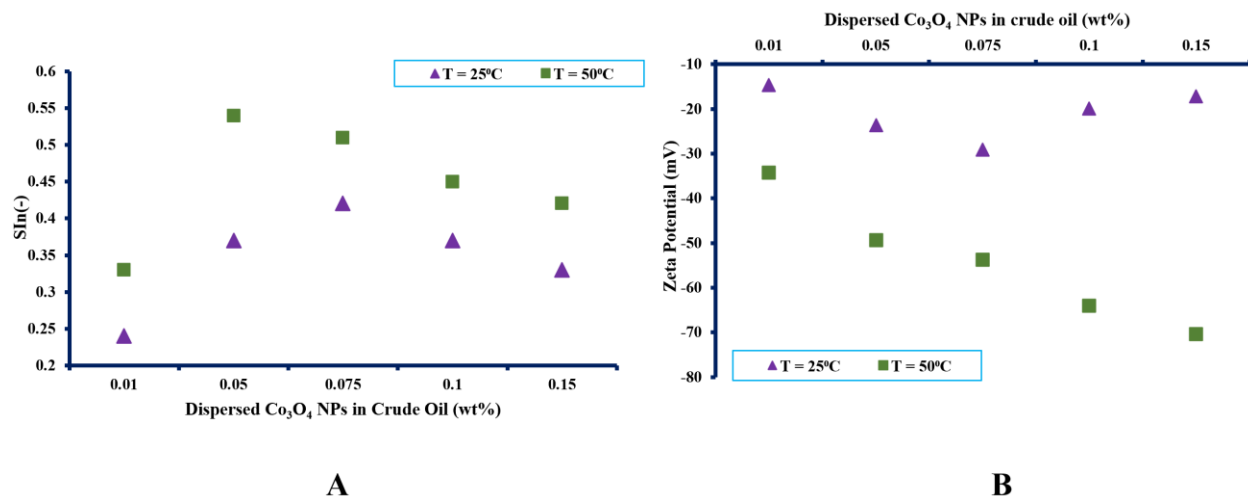
**Figure 1:** Designed procedures for formation and stability examination of oil-in-water emulsions

### 3-Results & Discussion

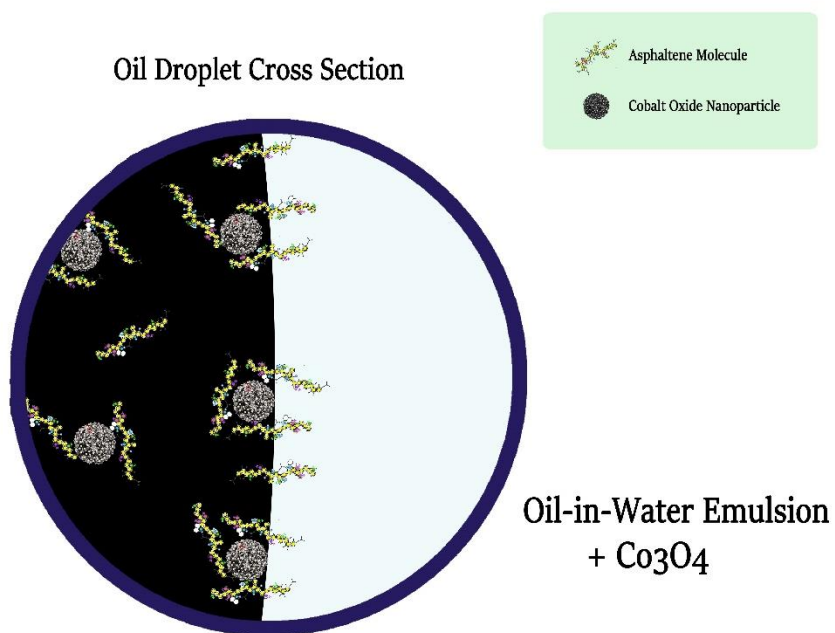
#### 3-1-Effects of $\text{Co}_3\text{O}_4$ NPs on ES

NPs due to their structure, have no interfacial activities. When cobalt oxide NPs are dispersed in crude oil, their specific properties show a gradual decline in crude oil viscosity as a result of increasing weight percent of dispersed  $\text{Co}_3\text{O}_4$  NPs. Thus, a nearly unstable solubility will occur for the heavy components of crude oil specially asphaltene molecules. Asphaltene molecules upon to their molecular structures, in addition to solubility in oil, have a weak tendency to accumulate in water/ oil interface as well. The created near stability condition of asphaltene solubility by cobalt oxide NPs, causes an opportunity for the asphaltene to stick to the  $\text{Co}_3\text{O}_4$  NPs surface and change their surface charge towards boosting hydrophilic tendency. With asphaltene concentration increasing on the water/oil interface, they can act as emulsifier and cause IFT reduction and consequently the larger emulsions would be able to withstand the breaking[11].

As it is evident from Figure 2, increasing the weight percent of cobalt oxide NPs, result in more negative zeta potential. This means that, by increasing the NPs concentration, there has been an increase in the potential of asphaltene presence on the oil/water interface (Figure 3). Comparison of Figure 2-A and 1-B indicate that, as zeta potential be more negative, the ES increases due to repulsion forces between emulsions. At the temperature of  $25^\circ\text{C}$  the maximum SIn is happened in the wt% of 0.075 with value of 0.48 whereas the value of 0.54 for SIn at 0.05wt% is the maximum for  $50^\circ\text{C}$ . Generally speaking, in all NPs wt%, the  $50^\circ\text{C}$  cause more ES than  $25^\circ\text{C}$ . Figure 2-A displays that increasing the NPs wt% after the optimal concentrations at two temperatures of  $25^\circ\text{C}$  and  $50^\circ\text{C}$ , causes a gentle decrease and leveling off in higher concentrations. Reduction of stability in higher cobalt oxide NPs concentration is because of asphaltene solubility reduction and their aggregation due to more crude oil viscosity decreasing. This phenomenon will intensify at higher temperature ( $50^\circ\text{C}$ ) upon to simultaneous effects of temperature on crude oil viscosity and its effect on asphaltene instability. Moreover, the NPs concentration increasing, cause a limitation for interface accessibility of asphaltene molecules and NPs.



**Figure 2:** A) Stability Index of O-in-W emulsions with presence of Cobalt oxide NPs in oil, B) Zeta potential values of O-in-W emulsions with presence of Cobalt oxide NPs in oil.



**Figure 3:** Reduction IFT due to gathering cobalt oxide NPs and asphaltene on the interface of emulsions

### 3-2- Effects of Various Ions on ES

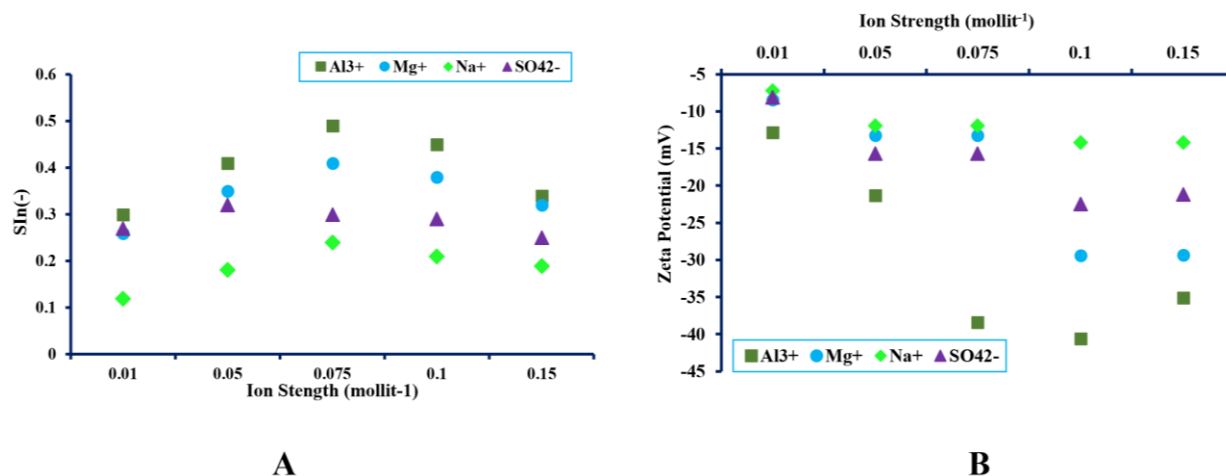
Being effective or not in absorption process of asphaltene which are exist in the crude oil to the oil/water interface, depends of type of ion, the value and symbol of its valence, and also the hydration ability. Aluminum ( $\text{Al}^{3+}$ ), magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^+$ ), and sulfate ( $\text{SO}_4^{2-}$ ) are the target ions that the effects of their different concentration on ES have been examined. Hydration process strongly depends on crystal network energy as an endothermic reaction and forming ion-dipole bond between water molecules and ions as an exothermic reaction. In fact, the emitted energy of forming ion-dipole bond, provide the required energy of crystal network energy of salts. Therefore, the better hydration of ions causes the better ions solubility. A good hydration happens when the target ion has more valences than the others and in case of valence equivalency, the ion which has the more ratio of electrical charge to area (i.e., the ion with smaller radius) will hydrate well. A good hydration causes more solubility and the ions would be able to reach the interface of the oil/ water and consequently, stimulate the asphaltene molecules in the crude oil so that their tendency to get closer to the interface intensify.

The most striking feature in the obtained SIn for different ions at ambient temperature (Figure 4-A) is the hitting a pick at ion strength of 0.075 mol/lit. This trend indicates the salting-in and salting-out effects very clearly. As stated earlier, the hydration severity for ions with different valences will be determined with their charge density (proportional to atomic radius and valences). Therefore, according to radius size of all investigated ions (Table 1) the better hydration capability can be ranked as follow[44]:  $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+ > \text{SO}_4^{2-}$ . As expected, the sequence superiority of ES is like the same trend of hydration capability. The same consistency of zeta potential and ES in presence of cobalt oxide NPs (in the previous section (3-1)) is observed for investigation of different ions as well. With increasing ions concentration, ion strength increases and salting out effects cause the asphaltene concentration reduction on the interface and result in a decreasing in ES. Figure 4-B demonstrates the zeta potential of the oil/water emulsion. In oil-in-water emulsions, the oil drops act as a colloidal particle. Therefore, the polar molecules gathering on its interface cause the measured zeta potential to be more negative. As the ion concentration increases, salting-out effects will affect the emulsion interfaces, and in addition to increasing IFT, zeta potential curve experience a smooth decline. The hydration of  $\text{Al}^{3+}$  and its effects on the asphaltene molecules is illustrated in Figure 6.

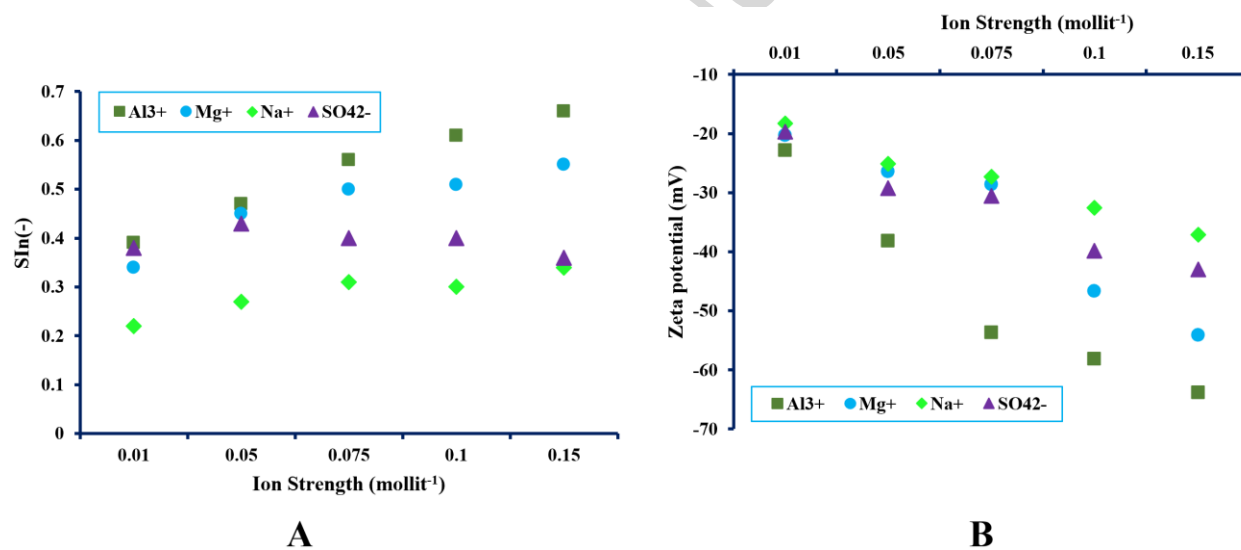
Rising the temperature shows its effect with continuous increasing of SIn (Figure 5-A) as a results of zeta potential decreasing (to be more negative) and boosting repulsion forces between emulsions (Figure 5-B).

**Table 1:** Atomic radius of target ions[44]

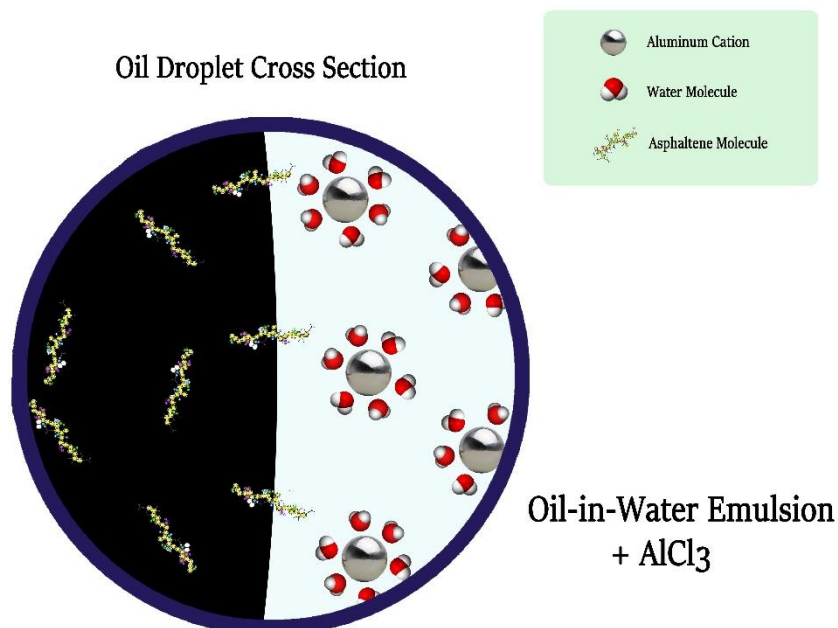
Ion	$\text{Al}^{3+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{SO}_4^{2-}$
Radius (Å)	0.53	0.72	1.02	2.42



**Figure 4:** Effects of different ions on emulsion stability at 25°C, A) stability index vs different ion strength of Al<sup>3+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup> B) zeta potential vs different ion strength of Al<sup>3+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>.



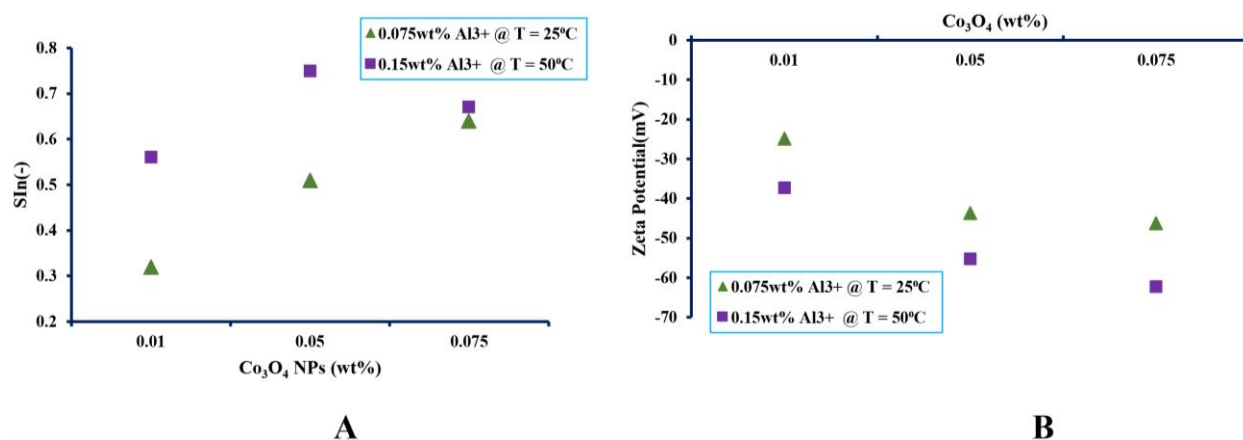
**Figure 5:** Effects of different ions on emulsion stability at 50°C, A) stability index vs different ion strength of Al<sup>3+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup> B) zeta potential vs different ion strength of Al<sup>3+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>.



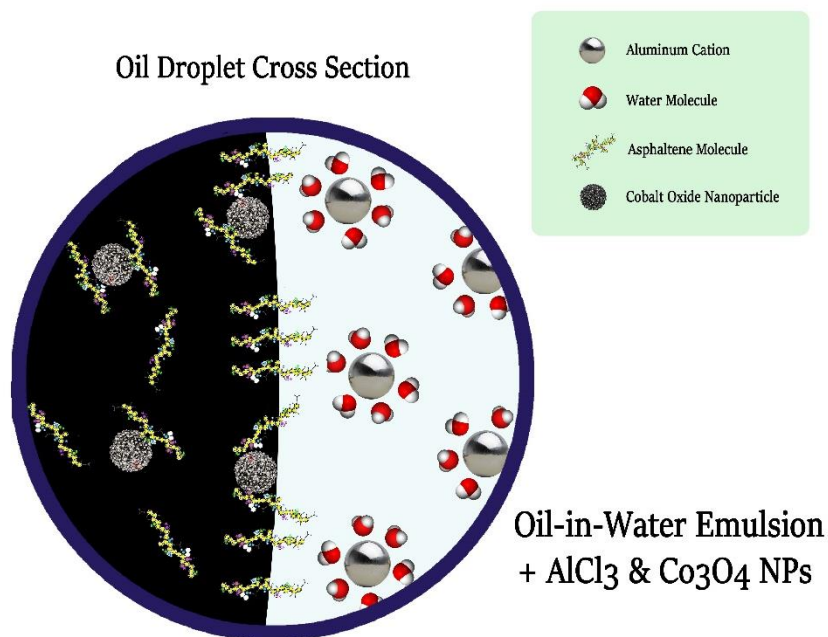
**Figure 6:** Reduction IFT due to gathering Stimulated asphaltene molecules by Al<sup>3+</sup> on the interface

### 3-3-Simultaneous Effects of NPs and Ions

To check the impacts of dispersed cobalt oxide in crude oil when the obtained optimum concentration of aluminum is dissolved in the continuous phase (water), the NPs concentrations equal and less than optimum wt% (i.e., 0.01, 0.05, and 0.075 wt%) are considered to be dispersed in crude oil for fixed optimum Al<sup>3+</sup> ion strengths of 0.075 and 0.15 at two temperatures of 25°C and 50°C, respectively. As it is obvious from Figure 7, at 25°C, the asphaltene gathering on the interface will increase due to increasing of NPs so that the condition will prepare for asphaltene to act as an in-situ surfactant along with NPs (Figure 8). By comparison of Figure 2 and Figure 7 at 25°C, the existence of the optimal aluminum ion concentration in water phase, cause the superiority of 0.08, 0.1, and 0.15 in SIn for NPs presence of 0.01, 0.05, and 0.075 wt%, respectively. At 50°C, adding the optimum Al<sup>3+</sup> concentration, lead to increasing of ES more than 25°C, nonetheless, at 50°C the NPs with concentration of 0.075 has a remarkable ES fall value of 0.15. This means that the presence of cation in water could not compensate for the lack of NPs performance at high temperature and the solution ES have the same behavior as Figure 2-A.



**Figure 7:** Affecting ES by different cobalt oxide wt% in a fixed optimum Al<sup>3+</sup> concentration, A) emulsion stability index at two temperatures of 25°C and 50°C, B) zeta potential at two temperatures of 25°C and 50°C



**Figure 8:** Simultaneous effects of cobalt oxide NPs and Aluminum ions on IFT reduction

### 3-4-Effects of Silica NPs and CS on ES in Presence of Co<sub>3</sub>O<sub>4</sub> NPs

#### 3-4-1-Effect of Different Concentration of Silica NPs on ES

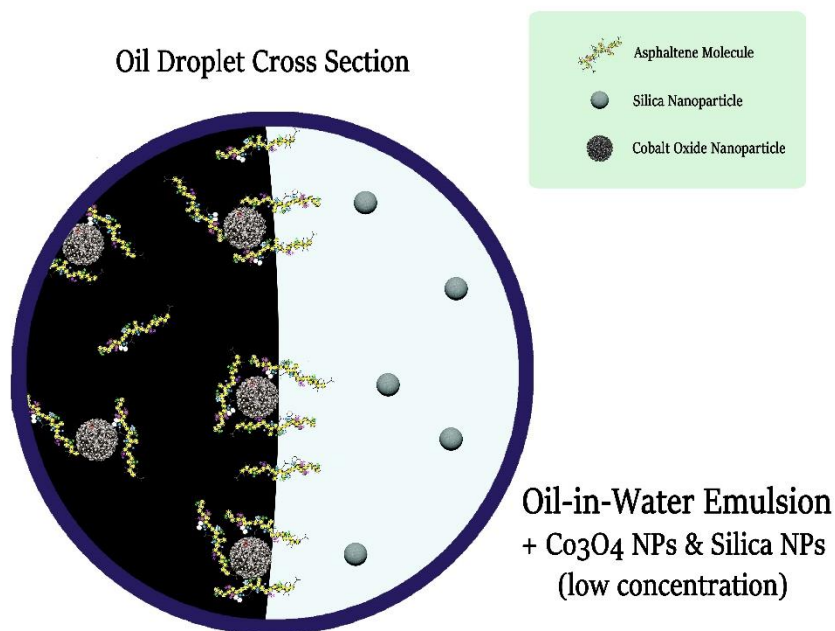
Silica NPs have a negative surface charge so that in the case of dispersing in the water phase the zeta potential decreases (more negative). (silica NPs have a negative zeta potential in a wide range of pH). Since the ES was increasing when the zeta potential was more negative (previous



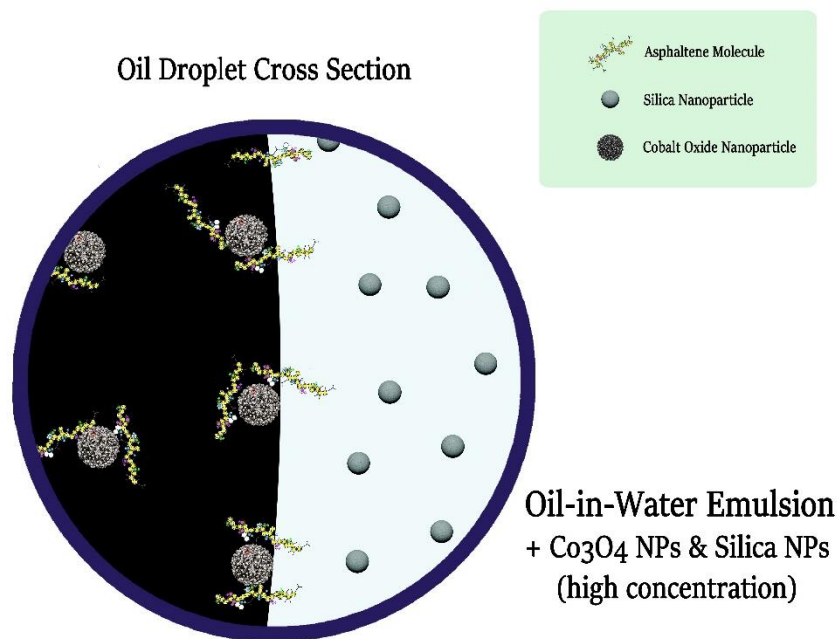
results), and with the knowledge of that silica NPs have no activity in the oil and water interface, it was decided to check the ES when silica NPs are dispersed in water phase.

Figure 11-A demonstrates that, for two optimum concentrations of cobalt oxide NPs (0.075 wt% and 0.15 wt% at 25°C and 50°C, respectively) increasing silica NPs in weight percent below 0.05 and 0.01 (at 25°C and 50°C, respectively), have been caused the ES increment. With increasing silica NPs concentration, in fact the number of particles with negative surface charge will increase and as a result of that, in low concentration (Figure 9), existence of the silica NPs causes a repulsion force and prevent from oil drops coagulation, therefore, the number of formed small emulsions at the earlier time, due to the negative silica NPs charge has been last approximately fixed.

In NPs wt% more than the concentration in which the ES has been hit the peaks ( Figure 11-A), the negative charge of NPs will affects the gathered asphaltene on the emulsion interface, repel them towards crude oil bulk (inside the oil drop - Figure 10) and consequently, IFT increases and ES decreases.



**Figure 9:** Effect of low silica NPs wt% on IFT reduction



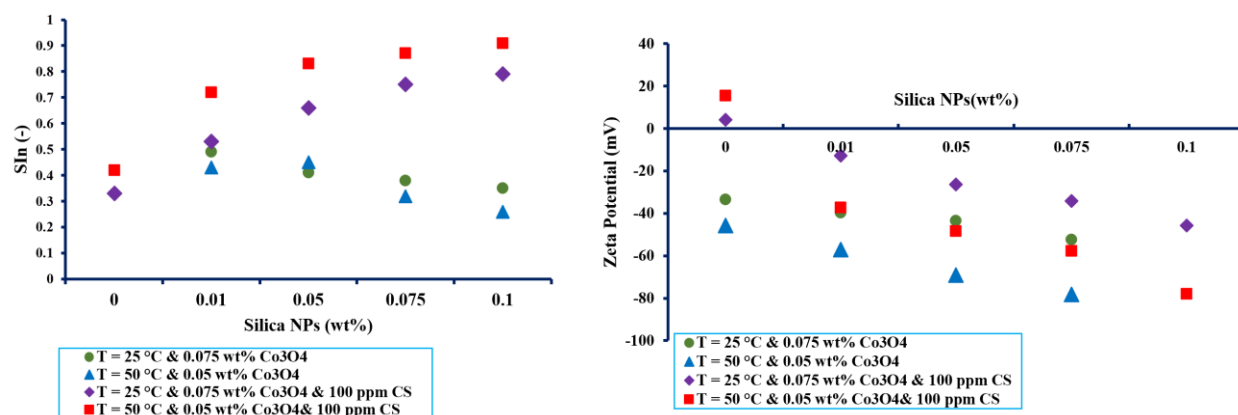
**Figure 10:** Effect of low silica NPs wt% on IFT reduction

### 3-4-2- Effects of Silica NPs on CS Performance in ES

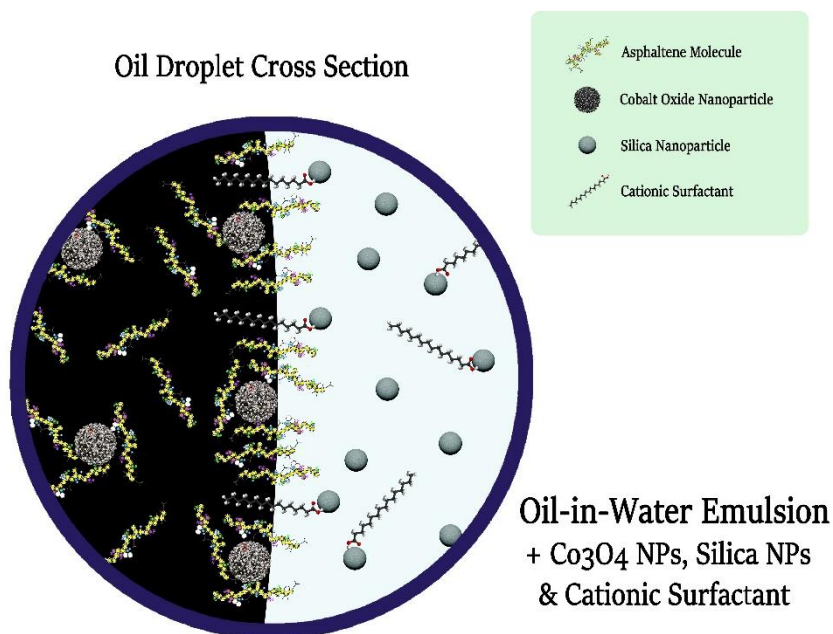
Although use of surfactants as an emulsifier are very usual, but miscibility of oil and water phases due to high surfactant concentration is the most important issue that should be avoided for forming emulsions. In fact, a high concentration of surfactant can change the emulsion type by continuous and discontinuous phases substitution. In the present work, a cationic surfactant is used with an experimentally calculated critical micelle concentration (CMC) of 450 ppm. A fixed concentration of 100ppm from CS was considered to check the effects of various silica NPs concentration when optimal cobalt NPs of 0.075 and 0.15wt% are dispersed in the crude oil at 25°C and 50°C, respectively. As it can be observed from Figure 11-A, with increasing the silica NPs, CS tends to them and change their polarity and surface charge to have more tendency for having interfacial activities, and as a result of that, along with CS will place on the interface and IFT and ES, decreases and increases, respectively (Figure 11-A) (the calculated IFT using pendant drop method [45][46] for optimum concentrations has been reported in appendix ,Table 4, Table 5, Figure 20, and Figure 21). In low concentrations of silica NPs, ES is increased with a steeper slope than high concentration, that could be because of CS concentration reduction in the continuous phase (water) and placing on the oil/water interface, thus, in high silica NPs concentration, there is not more accessible CS for silica NPs in the water to place on the interface.

Zeta potential results indicate that the CS without silica NPs weighs the emulsion charge to be positive and with increasing silica NPs, the zeta potential trend has been changed to negative values whereas the continuous phase with same silica NPs when there is no CS, reports more

negative zeta potential. This may be another proof for reaction between silica NPs and CS (Figure 11-B). Figure 12 indicate the cross section of an emulsion in presence of silica and cobalt NPs and CS.



**Figure 11:** Effects of silica NPs and its contribution with CS in presence of cobalt oxide NPs, A) emulsion stability index at two temperatures of 25°C and 50°C, B) zeta potential at two temperatures of 25°C and 50°C.



**Figure 12:** IFT reduction due to presence of cobalt NPs, silica NPs, and CS

### 3-5- Classification of emulsion size

As it can be observed from Figures 13 and 14, at 25°C and 50°C, the combination of cobalt oxide NPs and silica NPs together with CS has the maximum stability index among the other optimum chemical's concentration. At two temperatures of 25°C and 50°C The superiority of the used chemicals in formation of emulsion in the ranges of  $[10^{-8} - 10^{-6}] \mu\text{m}^2$  can be ranked as follow:

optimum Cobalt oxide (Nps & Silica Nps & CS )> optimum ( $\text{Al}^{3+}$  & Cobalt oxide NPs)> optimum ( $\text{Al}^{3+}$ )

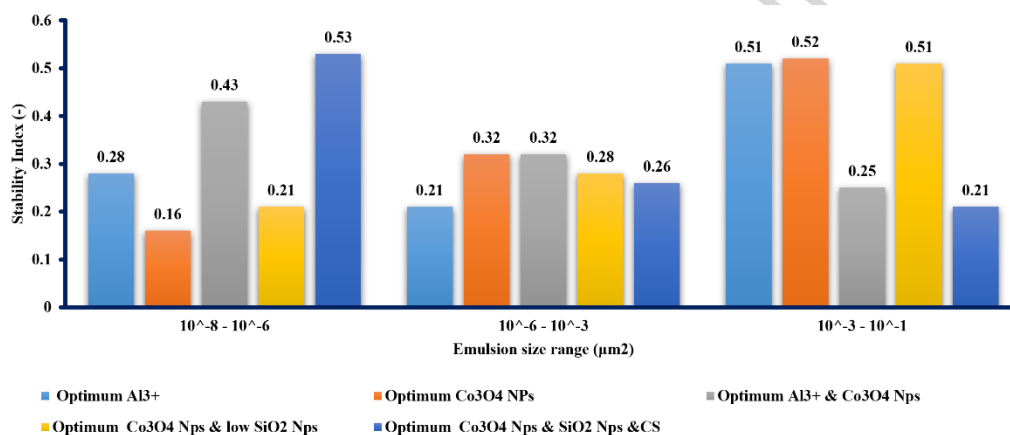


Figure 13: size classification of formed emulsion at 25°C

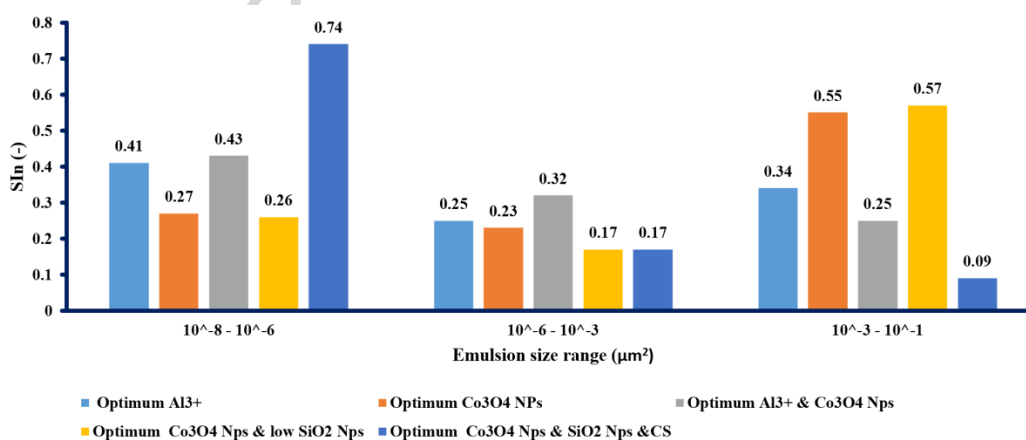


Figure 14: size classification of formed emulsion at 50°C

### 3-6- Effect of Time on ES

According to procedure#3 the ES test has been performed for two obtained optimum concentration of i)  $\text{Al}^{3+}$  & Cobalt oxide NPs, ii) Cobalt oxide NPs & Silica NPs & CS, at time intervals of 1, 6, 12, 48, and 72 hrs (Figure 15-A and Figure 15-B). Resultant findings reveal that the formed emulsion in the range of  $[10^{-8} - 10^{-6}] \mu\text{m}^2$  has been reduced after about 12 hrs, and then there was a leveling off trend. In one hand, the coalescence of the emulsions in that range, cause an increase in the number of emulsions which are in the range of  $[10^{-6} - 10^{-3}] \mu\text{m}^2$ , and on the other hand, the coalescence of the emulsion in the range of  $[10^{-6} - 10^{-3}] \mu\text{m}^2$  leading increase of emulsion number in the range of  $[10^{-3} - 10^{-1}] \mu\text{m}^2$ . Generally speaking, as time elapses, the emulsion numbers in the ranges of  $[10^{-6} - 10^{-3}] \mu\text{m}^2$  and  $[10^{-3}-10^{-1}] \mu\text{m}^2$  will be decreased and increased, respectively.

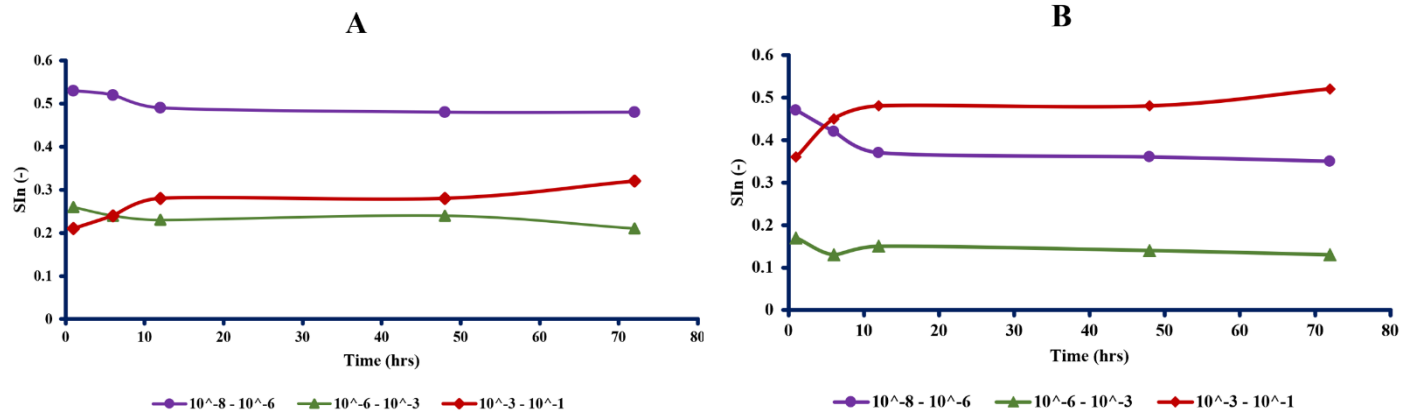
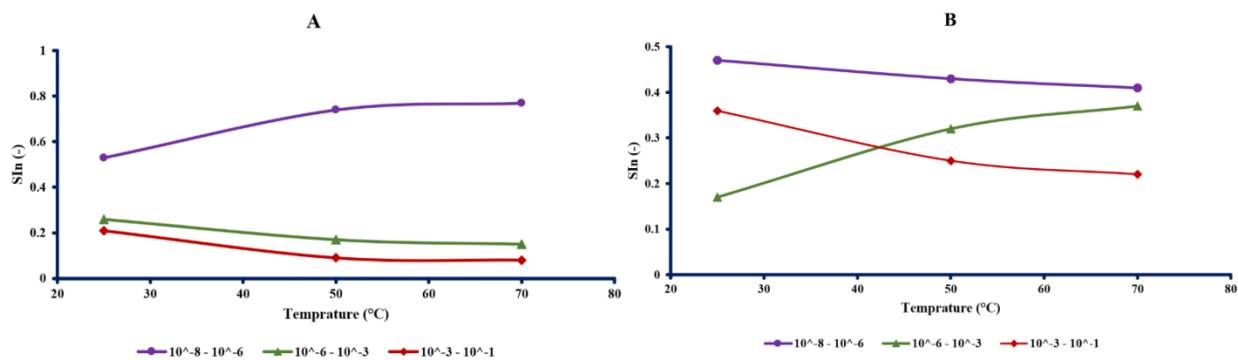


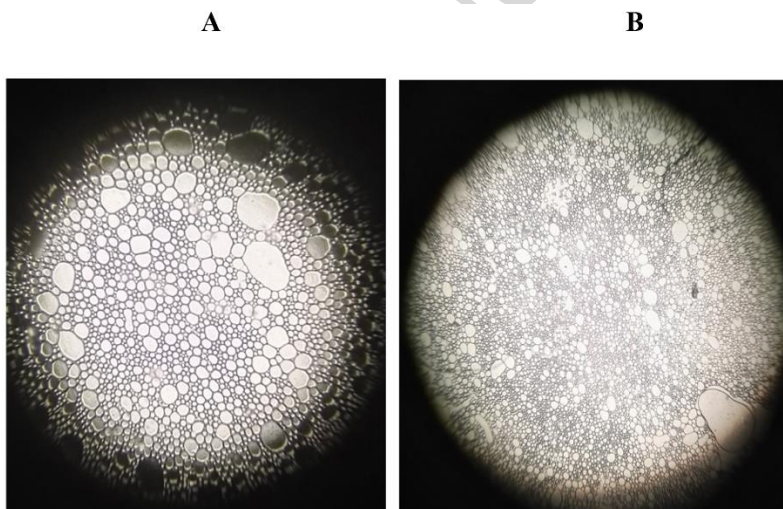
Figure 15: Emulsion size variation vs time A) Cobalt oxide NPs & Silica NPs & CS, B)  $\text{Al}^{3+}$  & Cobalt oxide NPs

### 3-7-Effect of Temperature on ES

As it can be seen from Figure 16, ES test has been done for two obtained optimum concentration of i)  $\text{Al}^{3+}$  & cobalt oxide NPs, ii) cobalt oxide NPs & silica NPs & CS, at three temperatures of  $25^\circ\text{C}$ ,  $50^\circ\text{C}$ , and  $70^\circ\text{C}$ . The obtained results indicate a significant effect on the emulsion numbers in the range of  $[10^{-8} - 10^{-6}] \mu\text{m}^2$  in case of Cobalt oxide NPs & Silica NPs & CS presence in the system and its SIn has been increased by 0.77. Figure 16-B demonstrates that, increasing temperature leading an increase in the emulsion numbers in the range of  $[10^{-6} - 10^{-3}] \mu\text{m}^2$ . The different trends of same emulsion size range of  $[10^{-8} - 10^{-6}] \mu\text{m}^2$  could be due to the difference of their IFT reduction ability. Figure 17 indicates the obtained images of formed Emulsions by optimum cobalt oxide NPs & silica NPs & CS and also optimum  $\text{Al}^{3+}$  & cobalt oxide at  $70^\circ\text{C}$ .



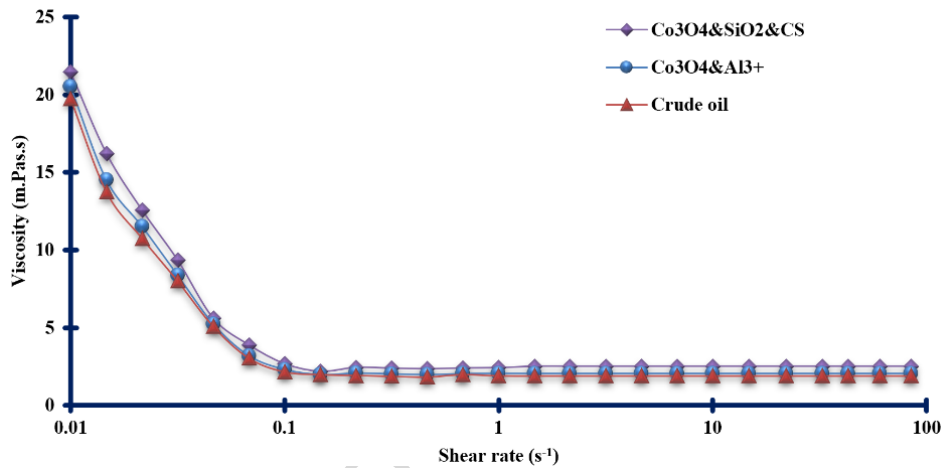
**Figure 16:** Emulsion size variation vs temperature A) Cobalt oxide NPs & Silica NPs & CS, B)  $\text{Al}^{3+}$  & Cobalt oxide NPs



**Figure 17:** Formed Emulsions at 70°C by A)  $\text{Al}^{3+}$  & Cobalt oxide NPs B) cobalt oxide NPs & silica NPs & CS

### 3-8- Emulsions Rheology

Viscosity of emulsions versus shear rate for optimum concentration of i) crude oil and distilled water, ii) Cobalt oxide NPs & Al<sup>3+</sup>, and iii) Cobalt oxide NPs & Silica NPs & CS, have been measured using Anton Paar MCR-302 rheometer. Figure 18 indicates that the measured viscosity for optimum concentration of Cobalt oxide NPs & Silica NPs & CS has a positive shift towards greater viscosity, which is probability due to the oil / water interfaces increasing. This is while crude oil and distilled water and also Cobalt oxide NPs & Al<sup>3+</sup>, have viscosities closer to each other than cobalt oxide NPs & silica NPs & CS.



**Figure 18:** Measured rheology of emulsions for i) crude oil and distilled water, ii) cobalt oxide NPs & Al<sup>3+</sup>, and iii) cobalt oxide NPs & silica NPs & CS

## Conclusion

Using different chemicals to stabilize the emulsions has a concentration limit. Therefore, after an optimum point, due to the chemical nature or the phase which has been dissolved or dispersed in it, the performance of chemical will be weakened by more increasing its concentration. However, in this study with the cooperation between optimum chemicals concentration, the stability index has been improved compared to the index of each chemical individually. Investigation of ions effect on ES indicates the superiority of aluminum for more charge density as well as its better hydration. The obtained emulsion stability index for the simultaneous presence of optimal Cobalt oxide NPs and aluminum ions represent an increase of about 0.2 and 0.15 (at 25 °C and 50 °C, respectively) compared to individually obtained values for cobalt oxide NPs and aluminum. The dispersed silica NPs in the water phase has no significant impact on the value of SIn. In low concentration, silica NPs negative charge causes repulsion forces and prevents emulsion coalescence, whereas in high concentration repel the asphaltene from the interface to the oil emulsion inside. On the plus side, existence of cationic surfactant along with silica NPs, outline a high recorded ES with indexes of 0.79 and 0.91 at 25 °C and 50 °C, respectively. To recapitulate, an appropriate ES increment as well as viscosity increment have been resulted due to cooperation of the cobalt oxide and silica NPs together with asphaltene and the cationic surfactant, respectively.

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## Appendix








Table 2: Cobalt Oxide Powder SiO<sub>2</sub> Certificate of Analysis

Co/(Cobalt)	Ni	Fe	Pb	Mn	Cu	Ca	Mg	Na	Si	Al	S
>74	0.02	0.01	0.01	0.01	0.003	0.01	0.01	0.01	0.02	0.01	0.01








Table 3: Silicon Oxide Powder SiO<sub>2</sub> Certificate of Analysis

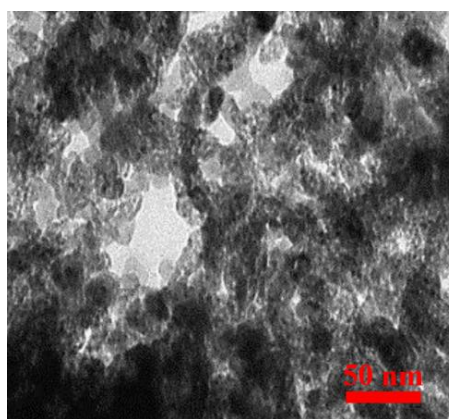
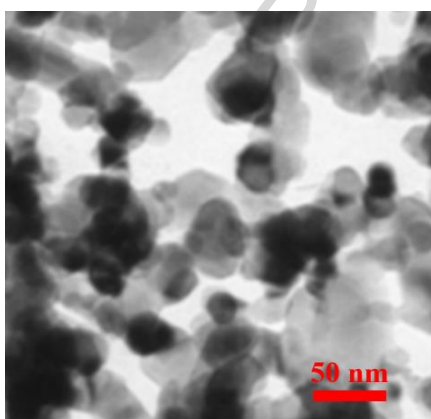
SiO <sub>2</sub>	Ti	Ca	Na	Fe
>99%	<120ppm	<70ppm	<50ppm	<20ppm

Table 4: Shaped oil drop for IFT measurement @ 25°C

Used optimum chemicals	Shaped oil drop
Distilled water	
0.075 (mol/lit) Al <sup>3+</sup>	
0.075 wt% Cobalt oxide	
0.1 wt% Silica NPs + 0.05 wt% Cobalt oxide	
0.01 wt% Silica NPs + 0.05 wt% Cobalt oxide	
0.075 (mol/lit) Al <sup>3+</sup> + 0.05 wt% Cobalt oxide	
0.05 wt% Cobalt oxide + 0.1 wt% Silica NPs + 100 ppm CS	

**Table 5:** Shaped oil drop for IFT measurement @ 50°C

Used optimum chemicals	Shaped oil drop
Distilled water	
0.075 (mol/lit) Al <sup>3+</sup>	
0.075 wt% Cobalt oxide	
0.1 wt% Silica NPs + 0.075 wt% Cobalt oxide	
0.01 wt% Silica NPs + 0.075 wt% Cobalt oxide	
0.15 (mol/lit) Al <sup>3+</sup> + 0.075 wt% Cobalt oxide	
0.075 wt% Cobalt oxide + 0.1 wt% Silica NPs + 100 ppm CS	

**Figure 19:** TEM Images, left → cobalt oxide NPs, right → silica NPs

**Table 6:** Emulsion photo using microscope


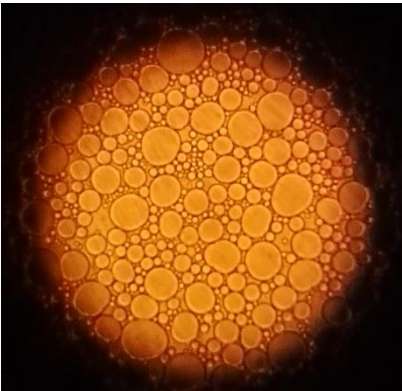
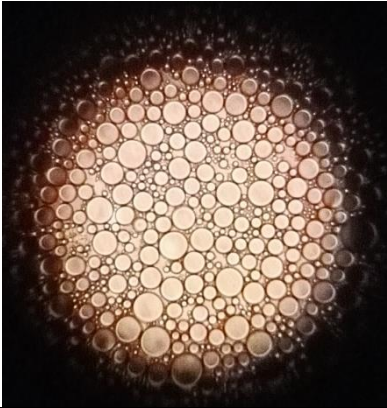
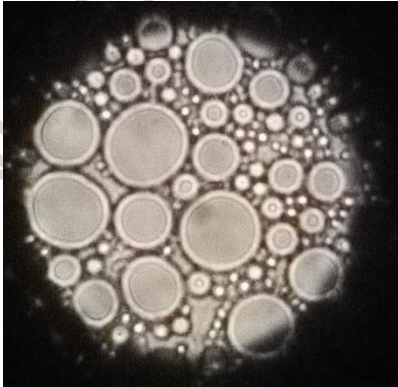
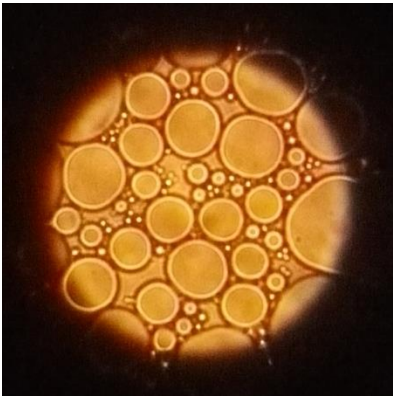
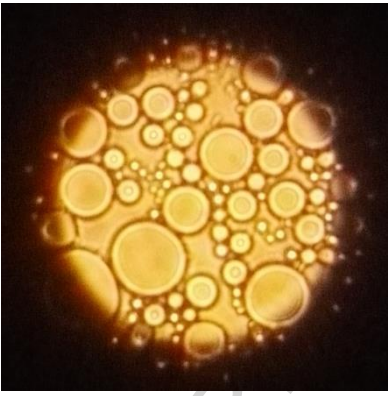
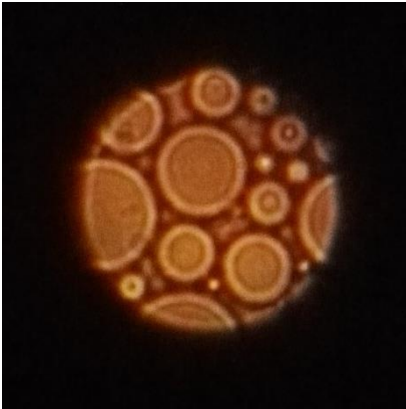
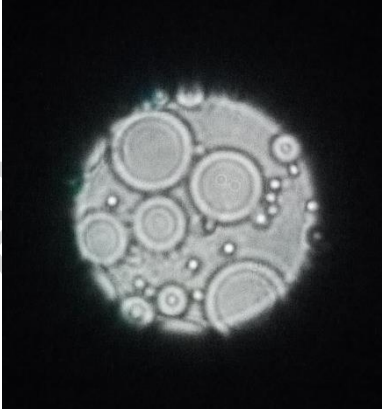
	
<b>0.075 wt% Cobalt oxide + 0.1 wt% Silica NPs + 100 ppm CS @ 50°C</b>	<b>0.05 wt% Cobalt oxide + 0.1 wt% Silica NPs + 100 ppm CS @ 25°C</b>
	
<b>0.15 (mol/lit) Al<sup>3+</sup> + 0.075 wt% Cobalt oxide @ 50°C</b>	<b>0.075 (mol/lit) Al<sup>3+</sup> + 0.05 wt% Cobalt oxide @ 25°C</b>

Table 7: Emulsion photo using microscope

	
<b>0.01 wt% Silica NPs + 0.075 wt% Cobalt oxide @ 50°C</b>	<b>0.1 wt% Silica NPs + 0.05 wt% Cobalt oxide @ 50°C</b>
	
<b>Distilled water @ 50°C</b>	<b>Distilled water @ 25°C</b>



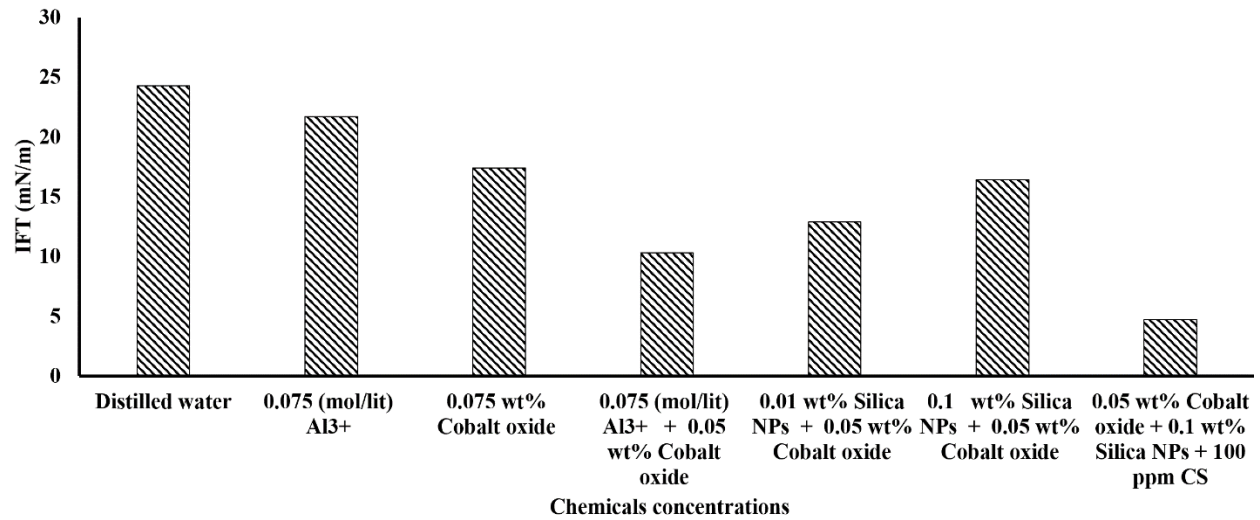


Figure 20: Measured IFT of optimum concentrations of used chemicals at 25°C

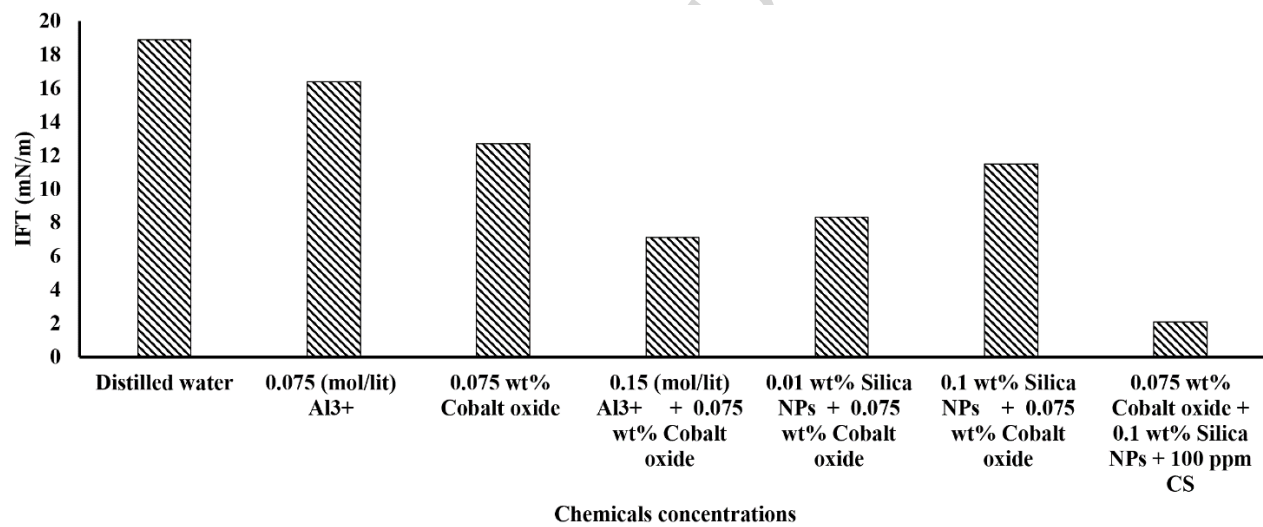
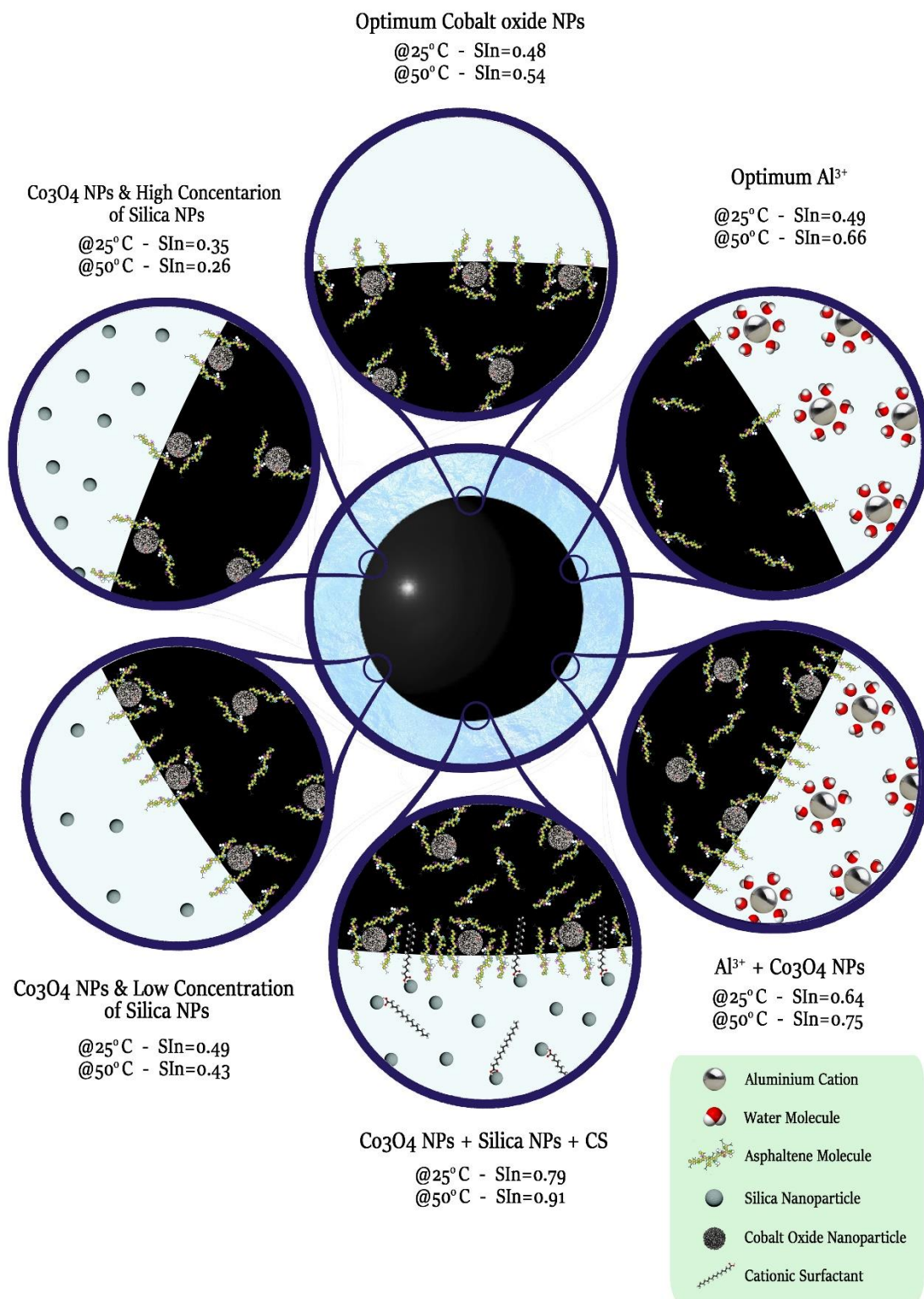


Figure 21: Measured IFT of optimum concentrations of used chemicals at 50°C

## Graphical Abstract



## Highlights

- ❖ **The Emulsion Stability (ES) profoundly affected by presence of other chemicals along with Co<sub>3</sub>O<sub>4</sub> Nano Particles (NPs).**
- ❖ **Zeta potential varies to boost ES due to cooperation of hydrated Al<sup>3+</sup>, Cobalt oxide and silica NPs, and surfactants.**
- ❖ **low and high concentration of silica NPs behaves differently in the presence or absence of cationic surfactant (CS).**
- ❖ **Interface activity intensification of cobalt oxide and silica Nanoparticles by surfactants causes a significant ES.**