CATALYTIC EFFECT OF ZINC OXIDE NANOPARTICLES ON OIL-WATER INTERFACIAL TENSION

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New synthesized nano materials have immensely attracted the researchers for further development of nano enhanced oil recovery method particularly in nano flooding. Interfacial tension measurement tests are the effective ways to identify proper nanomaterials for enhanced oil recovery by nano/surfactant flooding. In this work zinc oxide nano-crystallites were synthesized using self-combustion technique for application in enhanced oil recovery (EOR). The synthesized sample were used to the measure interfacial tension between their aqueous phase and crude oil phase to investigate the efficiency of the nanoparticles in reduction of interfacial tension. Therefore this research is intended to investigate the effect of Zinc Oxide (ZnO) nanoparticles towards surface/interfacial tension. Practically ZnO nanoparticles were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron microscope (FESEM) in order to understand its structure, size, shape and morphology. The characterization results reveal the hexagonal structure of ZnO. Pendant drop experiment was carried out to further understand the effect of nanoparticles on Interfacial Tension (IFT). Since the Zinc Oxide solution was very “cloudy” the drop phase could not be identified and the interfacial tension was not calculated by the software. Due to this reason, the Surface Tension (ST) was calculated with different concentration. The results show high value of ST 35.57 mN/m at 0.3 wt % of ZnO nanoparticles.

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1. Introduction

The reduction in oil trapping is the primary objective of any enhance oil recovery technique. The main reason of oil trapping within the pores is capillary forces. Recently nano enhanced oil recovery is gaining interest for newly developed nano materials, surfactants and their significant interfacial properties to operate the capillary forces in favor of easily access oil [1]. One of the novel methods in subject of Enhanced Oil Recovery (EOR) is nanoflooding which can improves the water flooding sweep efficiency by reducing the interfacial tension of water–oil system [2]. The adhesion of nanoparticles at the surface is suitable for wettability alteration from oil wet to water wet [3]. Practically, zinc oxide (ZnO) used widely for its catalytic properties. Apart from that, it also used for its remarkable properties in electrical & electronic and photochemical as well. It is utilized as catalytic agent due to its larger surface area [4]. This particular phenomenon would lead towards high catalytic activity. Zinc Oxide composed of

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80.34% of zinc and the remaining is oxygen. Its structure and synthesizing method would manipulate the physical and chemical properties. This compound widely used as additive for rubbers, plastics, paints, lubricants, and batteries. For this project, Zinc Oxide capability of reducing interfacial tension would be studied in detail. Zinc oxide nanoparticles having high surface charge act as surface active agents and replaced the surfactants. The small size of nanoparticles can penetrate through small pores and mobilize the capillary trapped oil [5]. The adsorption of nanoparticles at rock surface in the reservoir can alter the wettability from oil wet to water wet [6; 7]. The high surface charge interaction with oil water interface changes the interfacial properties. The relation between capillary pressure (P_c), wettability (cosθ) and interfacial (γ) tension is given by Equation (1)

$$P_c = \gamma . C = \frac{2\gamma \cos\theta}{R} \tag{1}$$

Where C is the curvature of the interface and R is the pore radius. If we reduce the interfacial tension the capillary pressure reduces and recovery increases [5; 8]. The addition of nanoparticles increases the viscosity of displacing fluid due to which mobility ratio decreases [9]. The increase in the viscosity of displacing fluid and reduction in interfacial tension ultimately increases the capillary number. The capillary number (N_c) is the ratio of viscous to capillary forces. There is inverse relation between interfacial tension and capillary number (N_c).

2. Experimental Methodology

2.1. Synthesis of ZnO nanoparticles

The Zinc oxide nanoparticles were synthesized using sol-gel auto combustion method and then calcined to obtain nanopowder [10]. The aqueous solution of Zinc nitrate ($Zn(NO_3)_2.6H_2O$) and citric acid ($C_6H_8O_7$) were prepared in de-ionized water [11]. The mixture of zinc nitrate and citric acid heated at 90°C on hotplate and magnetically stirred until the gel form. After the gel formation the stirrer removed and the gel heated at 300°C. The self-combustion occurred which directly convert the gel in to nano powder. The powder is then crushed and sintered for phase enhancement. The ZnO nanoparticles were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) to investigate the crystal structure, shape and size. Besides that, EDX also used to determine the chemical composition of sample as well.

2.2. Nanofluid Preparation

A pendant drop test was carried to study the effect of Zinc Oxide (ZnO) based nanofluid on Interfacial tension (IFT) reduction. Firstly, the solution was prepared as stated in Table1. Surfactants or surface active agents are chemical substances that are adsorbed on interface between two fluids. The surface properties are changed with reduction in interfacial tension (IFT) by surfactants [12]. In this study, Sodium dodecyl sulfate (SDS) used as surfactant for nanoparticles. The SDS is an organic anionic surfactant with the formula $CH_3(CH_2)_{11}SO_4Na$.

Table1: Weight % age of ZnO Nanoparticles

Weight Percentage, %	ZnO, g	Sodium dodecyl sulfate (SDS), g	Water, ml
0.05	0.05	0.10	99.85
0.10	0.10	0.20	99.70
0.20	0.20	0.40	99.40
0.30	0.30	0.60	99.10
0.40	0.40	1.00	98.60
0.50	0.50	1.25	98.25

The pendant drop test had been carried out for Zinc Oxide to study the effects on interfacial tension reduction.

3. Results and Discussion

3.1. XRD Results

The phase identification of the nano powders was recorded by X-ray diffraction with Cu-Kα radiation. Three reflections (010), (002) and (011) have been observed, which are similar to the observed reflections in ZnO bulk [13]. The diffraction peaks obtained are very sharp and narrow indicating that the nanocrystalline ZnO possess high crystallinity as shown in Figure 1. The results show hexagonal structure of ZnO and matched with JCPDS No. 96-4182. The crystallite size was also measured by X-ray line broadening technique using the Scherrer formula indicated in Equation.(2):

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

Where, k is polarization factor, λ is wavelength of Cu-Kα line (1.5406°A) and β is the full width half maximum (FWHM) of (011) reflection peak and is the Bragg's angle about (011) peak. The value of crystallite size thus calculated shown in Table 2. Zinc oxide nanostructures are in crystalline form with the hexagonal wurtzite phase and high purity [14]. Zn atom is arranged in hexagonal close packing and each Zn ion is surrounded by four oxygen atoms to form tetrahedron. Every tetrahedron is connected through the corners to form the 3-D structure[15; 16]. The average crystallite size of ZnO NPs was calculated by the Debye–Scherrer formula was found to be 37nm

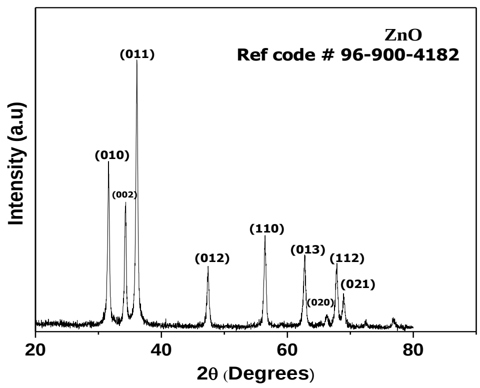

Fig. 1: Powder XRD Pattern of ZnO [17]

Table.2: Crystallite size of ZnO Nanoparticles

No.	Pos. [°2Th.]	d-spacing [Å]	FWHM [°2Th.]	(hkl)	Crystallite Size only [nm]
1	31.5981	2.83157	0.1574	(010)	64.62422
2	34.3212	2.61289	0.2362	(002)	41.20389
3	36.1031	2.48791	0.0984	(011)	125.3033
4	47.4529	1.91599	0.2362	(012)	43.01852
5	56.4273	1.63071	0.3542	(110)	29.17918

3.2. Characterization of Zinc Oxide using Field Emission Scanning Electron Microscope (FESEM)

The shape, size, surface morphology and composition of the synthesized sample has been obtained from Zeiss Supra 55 VP Field emission scanning electron microscope (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX) respectively. FE-SEM and EDX was used to determine the Zinc Oxide texture, size, shape and composition. Figure 2 shows FESEM images of Zinc Oxide (ZnO) nanostructures under several magnifications and EDX spectra. It can be seen that ZnO particles are in the nanometer range. The agglomeration shows high surface charges [18].

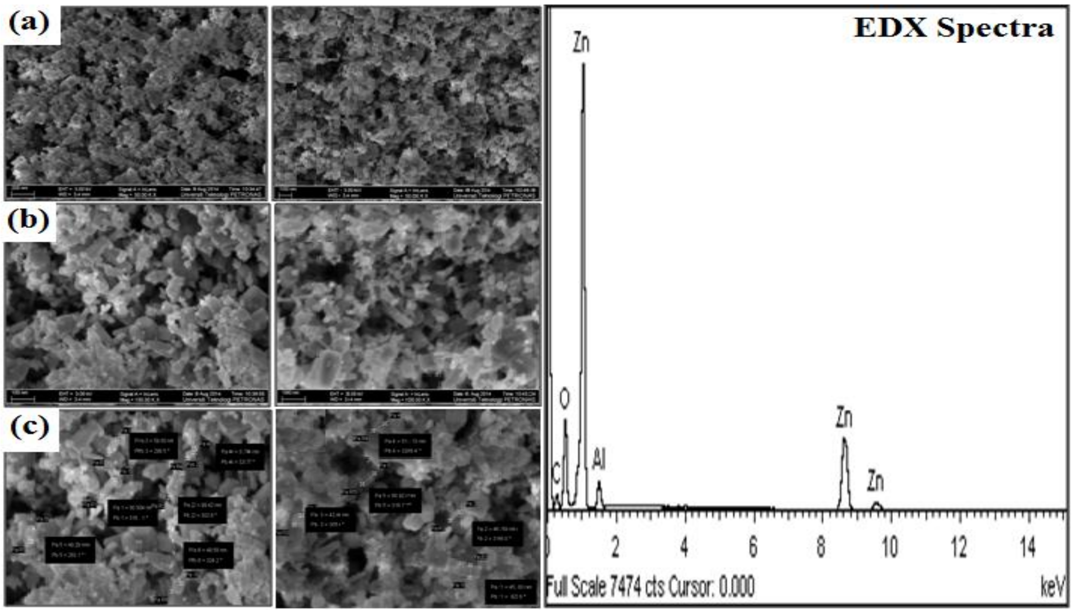

Fig. 2: FESEM images of ZnO nanoparticles with magnification (a) 100 K (b) 50 K (c) size distribution and EDX spectra

Figure 2 shows the Zinc Oxide spherical shape clusters and agglomeration. This particular shape can be seen clearly in Figure 2(c).
Figure 2(c) provides a clear overview on size distribution that exist in Zinc Oxide (ZnO) sample. The size of ZnO nanoparticles varies from 42.44nm up to 60.92nm. But in general the average size of ZnO sample is around 50nm [19]. The particles are spherical in shape and uniform distribution [20].

3.3. Pendant drop test

A pendant drop test was carried out to find the Interfacial Tension (IFT) of the liquids. Firstly, a Dubai crude oil was tested for IFT with air. The Figure 3 below shows the pendant drop test result. The Surface Tension for this case is 27.43 mN/m.

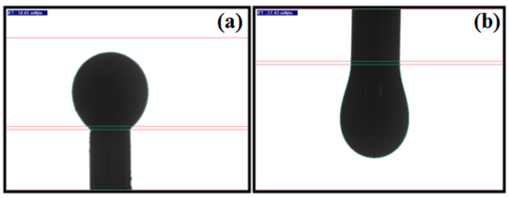

Fig. 3: Pendant Drop Test between (a) Dubai Crude Oil and Air (b) Dubai crude oil and water

Next the IFT between Crude Oil and Water were studied as shown in Figure 3(b). The figure below shows the results obtained from pendant drop test. The Interfacial Tension for this case is 18.65mN/m [21].

Soon after that, the Interfacial Tension between crude oil and Zinc Oxide (ZnO) were studied. Unfortunately, due to Zinc Oxide's "cloudy" fluid nature the pendant drop test could not be proceed any further. For the pendant drop experiment a clear solution is preferred to ease the interfacial tension calculation. Due to this major setback in calculation of interfacial tension (IFT) for Zinc Oxide (ZnO), the previously mentioned methodology was altered. The surface tension (ST) for varying concentration zinc oxide was calculated instead of interfacial tension (IFT).

3.4. Pendant Drop Test for Zinc Oxide

Pendant drop test for zinc oxide was carried out by using air as the second phase. This particular method was conducted since the drop phase could not be identified when the crude oil is used. The primary objective of this test was to study the effect of varying concentration of ZnO NPs on Surface Tension (ST). The Figure 4 shows the pendant drop image for Zinc Oxide at various concentrations. Surfactant and ZnO nanoparticles concentration has significant effect on surface tension as shown in Figure 5. Six different concentrations were used to measure the surface tension. The surface tension was measured time interval one second. Initially from 0.05 wt% to 0.3 wt % ST increases and then a rapid decrease at 0.4 wt % and 0.5 wt % has been observed. The decrease in ST due to the higher concentration (1 wt % and 1.25 wt %) of SDS for sample 5 and 6. The variation in ST was observed due to accumulation and adsorption of surfactant molecules [22].

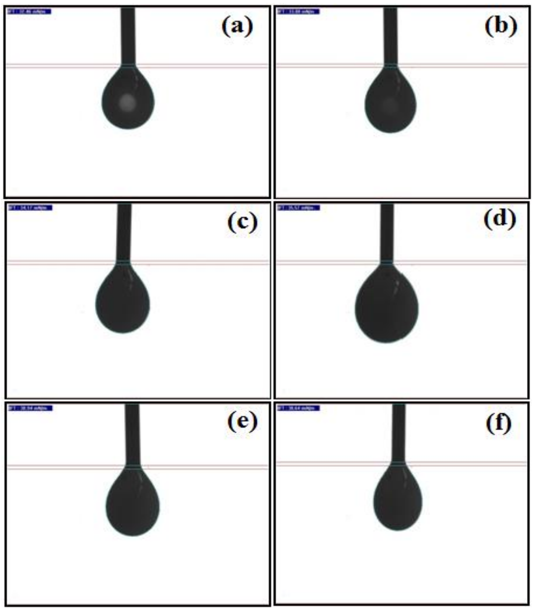

Fig. 4: ST Test for ZnO at (a) 0.05 (b) 0.1 (c) 0.20 (d) 0.30 (e) 0.40 (f) 0.50 wt%

The value of the IFT for each concentration is presented in Table 5.

Table 3: Surface Tension (ST) of Zinc Oxide (ZnO)

Zinc Oxide (ZnO) Concentration (wt %)	ST (mN/m)		
	1st Trial	2nd Trial	Average
0.05	32.46	32.87	32.67
0.10	33.08	33.07	33.08
0.20	34.17	34.86	34.52
0.30	35.57	35.82	35.70
0.40	30.94	30.78	30.86
0.50	30.64	30.84	30.74

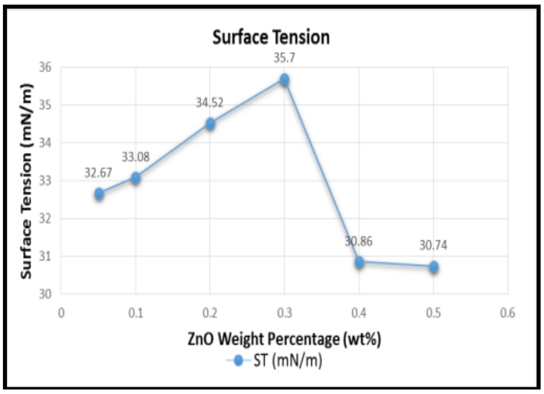

Fig. 5 : Surface Tension (ST) graph of Zinc Oxide (ZnO)

The value of Surface Tension increases gradually up to 0.3 weight percentage of Zinc Oxide and falls at 0.4 and 0.5. The Sodium Dodecyl Sulphate (SDS) proportion is higher for 0.4 wt % and 0.5 wt % of Zinc Oxide [23]. Therefore it could be the reason for the drop in the ST.

4. Conclusion

Interfacial tension (IFT) is an important quantity in Enhanced Oil Recovery. IFT play a vital role on oil recovery mechanism specially for changing capillary forces. By lowering the IFT, the production can be improved consequently. The pendant drop test is proven to be essential in determining which concentration is suitable to enhance the production. The results show that the surface tension decreases by increasing ZnO concentration. Therefore, nanoparticles with high surface tension capable of reducing oil-water Interfacial tension.

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