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Effects of Mixing Conditions, Oil Type and Aqueous Phase Composition on Some Crude Oil Emulsions

O. Omole and O.A. Falode

Department of Petroleum Engineering, University of Ibadan, Ibadan, Nigeria

Abstract: The ease of formation of emulsions is described for some crude oil systems in which the mixing conditions, oil type, aqueous phase composition and concentration are varied. The most stable emulsions have quality that ranged between 10 and 20% while the least stable have quality that ranged between 50 and 60%. Droplet coalescence was highest at 2 min agitation and below 5000 rpm. Addition of 70% FY crude to BL crude caused 24% emulsion stability increase while a decrease of 50% in emulsion stability was observed upon dilution with hexane relative to toluene. The stability of emulsions is not affected by variation in brine concentration within 100-200,000 ppm range. In general, optimum pH for resolution of alkaline-based emulsions was between 10 and 11 and between 6 and 7 for brine. Finally, the effect of increasing the pH of the aqueous phase is explored. It is shown that, at sufficiently high pH, unstable emulsions were produced while at low pH, stable emulsions were formed.

Key words: Crude oil, emulsion, oil type, aqueous phase type, stability

INTRODUCTION

Crude oil is seldom produced alone. Often, it is commingled with water that creates many problems during oil production. Formation water may be produced as free water (i.e., water that settles out fairly rapidly) or in the form of emulsions^[1]. Every day the complex petroleum industry faces the challenge of resolving several types of emulsions. Production techniques result in stable crude oil/water emulsions that require aggressive treatment methods. The formation and stability of the emulsion depends on a variety of factors including production history such as thermal and pressure cycles and energy input. Oil gravity, contaminants, water content, water salinity and pH also determine its nature^[2]. The process of recovering crude oil from beneath the earth begins by forcing a blend of oil and water through a vertical casing to the surface. The resulting shear energy and pressure decline produces a "tight" oil/water emulsion once at the surface. Enroute to the production equipment, where primary separation and dehydration takes place, many emulsions are heated, pressurized, pumped and pushed through pipelines. Once at the production facility, the emulsion is generally a homogenized blend of oil, water, gas and contaminants. Lift techniques which include primary production, gas-lift, beam pumps, steam flooding, CO₂ flooding, polymer flooding and submersible pumps produce a different oil/water emulsion for the production equipment to process^[3]. Perhaps the most damaging

variable is the energy input into the emulsion to move it to the production equipment. Most of the energy moves the oil/water/gas mixture through the pipeline overcoming elevation changes and frictional losses. However, some fraction of the energy produces shear between the oil and water phases. As the shear energy (i.e. pressure drop across orifices and valves) increases so does the interfacial area^[3]. Whole crude oils, in addition to a mixture of hydrocarbon fractions, contain a non-homogeneous blend of a variety of compounds, such as surfactants, anions, cations, clay, sand, silt and bacteria^[4]. These compounds, ranging in concentrations from trace to percentage levels, contribute in varying degrees to the emulsion stability, coalescence and separation rates. Additionally, several water properties may also be important and contribute to the emulsion stability. These properties are water density, pH, salinity and suspended solids^[5]. An understanding of this production history can provide the separator, dehydrator and desalter designer with some valuable insight into the nature of the crude oil and water emulsion.

This study therefore investigates the influence of some variables on the nature and stability of emulsions.

MATERIALS AND METHODS

Materials: Reagent-grade n-hexane 99.9% purity Toluene were purchased from Merck. Chemical Co. (Brazil). De-ionized water used in this study was

supplied by IITA water plant. Brine used in this study composed of simple salt (NaCl). The two Nigerian crude oil types (Bonny Light and Forcados Yorkri) used for the emulsion studies were obtained from N.N.P.C Warri, Nigeria.

Methods

Preparation of emulsions: Crude oil emulsions were prepared by dispersing a known volume of water in oil using a Halmilton Beach mixer and food blender operating at speed range of 1000-18000 rpm for 2 min. The emulsions were then transferred into 100 mL stoppered, graduated measuring cylinders and thermostated at 25°C, unless otherwise stated. Immediately after homogenization, the type of emulsions was determined by measuring the conductivity of the emulsions using a digital conductivity meter with Pt/Pt black electrodes and by observing what happened when a drop of each emulsion was added to a volume of either pure oil or pure water^[6].

Storage of emulsion samples: The emulsion samples were stored in separate 100 mL measuring cylinders at an approximately constant temperature of 25±2°C in the laboratory. As the storage containers are not insulated or heated, the emulsions are subject to the surrounding atmospheric conditions. The stability of the emulsion would therefore be determined at a constant 25°C.

Stability of emulsions: The stability of emulsions to sedimentation/creaming was assessed by monitoring the increase with time of the position of the clear water-emulsion interface. For the w/o emulsions, the downward movement of the oil/emulsion boundary was used as a measure of the stability to sedimentation and the position of the water/emulsion interface was used as an indicator of coalescence. The stability of the emulsions was assayed by measuring percent water separated after a fixed period of time.

RESULTS AND DISCUSSION

Effect of mixing time on FY and BL emulsions: From Table 1, the optimum resolution for the emulsions was at 2 min agitation. The rate of resolution increased as mixing time increased from 60 sec to 2 min while it decreased as mixing time increased from 2-6 min. At mixing time greater than 2 min, the size of the water droplets reduced as a result of prolonged agitation which also permits surface-active particles to reach the vicinity of the interfaces stabilize them.

The existence of inertia and shear forces is responsible for the reduction of the dispersed-phase particle size and the accompanying increase in interfacial area. However, the increase in the rate of resolution from 60 sec to 2 min is unexpected. This may be explained by the fact that this rate depends on the mechanisms governing instability. Creaming appears to have more preponderance over sedimentation at these low mixing times as revealed from the larger volumes of crude oil separated. This suggests formation of multiple emulsions at these mixing times. In general, at a constant shear, greater ease of resolution was observed with BL emulsions than with FY emulsions according to Stoke’s law for a smaller density difference.

Effect of mixing intensity on FY and BL emulsions: The effect of mixing intensity on emulsion stability was assayed by measuring percent water separated after 5 days of sedimentation from emulsion mixed at different intensities for two minutes. As mixing intensity increased beyond 5000 rpm, a higher energy input resulted in smaller water droplets and consequently a slower separation process. However, at 5000 rpm the degree of coalescence of droplets was highest (Table 2). Present deduction is that agitation must be of sufficient intensity to cause impacts that lead to coalescence of the very small droplets but must not be excessively vigorous since this would cause a shattering of the drops into still smaller droplets and enhance stability.

Table 1: Variation of mixing time vs. % water resolved for BL and FY emulsions

Settling time (days)	60 sec		90 sec		120 sec		150 sec		180 sec		210 sec		240 sec	
	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.5	3.0	0.1	5.0	0.2	9.0	2.0	7.0	0.3	5.0	0.3	3.0	0.2	2.5	0.3
1.0	6.0	0.6	8.0	0.8	12.0	4.0	9.0	1.1	6.8	0.4	5.7	0.5	4.6	0.6
1.5	10.0	1.0	12.0	2.0	17.0	6.0	12.0	3.0	8.6	1.0	7.4	1.0	6.2	1.0
2.0	13.0	3.0	15.0	5.0	22.0	10.0	13.0	5.0	10.0	4.0	9.0	4.0	8.0	3.0
2.5	16.0	5.0	18.0	7.5	25.0	17.0	15.0	9.0	12.0	7.0	11.0	6.0	10.0	5.0
3.0	17.0	9.0	20.0	12.0	29.0	21.0	17.0	12.0	13.0	9.0	11.0	8.0	8.0	8.0
3.5	19.0	11.0	22.0	13.0	35.0	24.0	20.0	15.0	13.0	11.0	12.0	10.0	10.0	10.0
4.0	20.0	16.0	24.0	18.0	43.0	30.0	24.0	19.0	15.0	12.0	13.0	15.0	12.0	15.0
4.5	20.0	18.0	24.0	21.0	50.0	40.0	32.0	32.0	16.0	16.0	14.0	14.0	13.0	13.0
5.0	21.0	20.0	25.0	24.0	62.0	50.0	40.0	40.0	18.0	18.0	15.0	13.0	14.0	12.0

Table 2: Effect of mixing intensity on percent water resolved from the emulsions

Mixing intensity (rpm)	% water resolved for BL emulsion	% water resolved for FY emulsion
1000	100	86
2000	100	87
3000	100	86
5000	100	90
8000	95	85
10000	91	60
13000	78	56
15000	69	52
18000	62	50

Table 3: Aqueous phase volume fraction vs. % water resolved (@13000 rpm)

Setting time (hrs)	0.2		0.4		0.5		0.6		0.7		0.8		0.9	
	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	10.0	5.0	0.0	0.0	35.0	18.0	0.0	0.0	0.0	0.0	2.0	0.0
6	0.0	0.0	15.0	7.0	0.0	0.0	43.0	23.0	0.0	0.0	0.0	0.0	3.0	1.0
12	0.0	0.0	25.0	15.0	10.0	3.0	54.0	29.0	3.0	0.0	2.0	0.0	5.0	2.0
15	0.0	0.0	28.0	18.0	12.0	6.0	54.0	29.0	5.0	2.0	5.0	2.0	8.0	5.0
18	0.0	0.0	28.0	19.0	20.0	14.0	54.0	30.0	6.0	3.0	10.0	4.0	10.0	8.0
21	2.0	0.0	28.0	19.0	41.0	27.0	55.0	30.0	6.0	4.0	10.0	4.0	25.0	15.0
24	10.0	4.0	28.0	19.0	48.0	32.0	56.0	31.0	6.0	4.0	10.0	4.0	25.0	15.0

Table 4: Effect of brine on % water resolved from BL and FY emulsions after 75 hrs

Brine concentrations (ppm)	%Water resolved	
	Bonny Light (BL)	Forcados Yörkri (FY)
0	28.0	23.0
100	27.0	22.0
1,000	27.5	20.0
10,000	28.0	21.0
50,000	26.5	20.5
100,000	27.0	20.0
150,000	27.0	21.0
200,000	27.0	20.0

Table 5: Effect of acid on % water resolved from the emulsions

Setting time (days)	pH					
	1	2	3	4	5	6
0	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
6	0	0	0	0	0	0
7	0	0	0	0	0	0
8	0	0	0	0	0	0
9	0	0	0	0	0	0

Aqueous phase volume fraction: As the volume fraction of water increased from 0.2 to 0.6 in Table 3, the emulsion produced became more flocculated changing color gradually from brown to cream and more agitation is necessary to emulsify the water completely. At higher volume fraction above 60%, the emulsion passes through the inversion point. As water volume fraction increases, viscosity decreases and turbulence is readily induced and fluid movement is transferred to parts of the fluid remote from the stirrer.

Nature of aqueous phase: Since emulsions are formed in a variety of environments, the stability of emulsions with other aqueous solutions as, for instance, brine, acidic and alkaline solutions was investigated.

Effect of brine: The fact that addition of electrolytes to the aqueous phase did not affect the emulsion stability as shown in Table 4 confirms that little influence should be ascribed to electric charges, as expected due to the low dielectric constant of the continuous medium (oil of organic solution). Electric charges cannot be expected to stabilize without emulsions of more than extremely low concentration. This is primarily due to the fact that in water-continuous emulsions, the thickness K^{-1} of the double layer generally equals about $10^{-3} \mu$, so that electrical interactions take place only at short distances^[7].

Effect of acid: Table 5 shows that the acidic aqueous phase produced very stable emulsions. Reduction in pH is likely to induce the precipitation of sludges and may be responsible for the stable emulsion produced. This stability may also arise because a rigid interfacial film formed by the presence of asphaltenes is strongest in acid pH.

Effect of alkali: The aqueous phase of emulsions formed with NaOH solution were slightly turbid, which may indicate some extent of oil solubilization in the aqueous phase and may be attributed to the extraction of surface active acidic fractions from the oil (Table 6), whose presence has been reported in the literature^[8].

Table 6: Effect of alkali on % water resolved from the emulsions

Settling Time (days)	pH 13		pH 12		pH 11		pH 10		pH 9		pH 8	
	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY	BL	FY
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	45.0	40.0
1	25.0	20.0	38.0	34.0	52.0	50.0	49.0	44.0	54.0	50.0	50.0	48.0
2	33.0	25.0	50.0	38.0	57.0	52.0	56.0	53.0	59.0	56.0	52.0	50.0
3	40.0	34.0	52.0	46.0	57.0	52.0	57.5	54.5	59.0	57.0	53.0	51.0
4	43.0	35.0	57.0	50.5	57.5	52.0	58.0	55.0	59.0	57.0	54.0	51.5
5	43.0	35.5	57.0	50.5	57.5	52.0	58.5	55.0	59.0	57.0	55.5	52.0
6	44.0	36.0	57.0	51.0	57.0	52.5	59.0	56.0	59.5	57.5	55.5	52.5
7	44.0	36.0	57.0	51.0	58.0	52.5	59.0	56.0	59.0	58.0	56.0	53.0
8	44.5	36.0	58.0	52.0	58.0	53.0	58.5	56.0	59.0	58.0	56.0	53.0

Table 7: Effect of aromaticity and paraffinicity on stability of FY emulsions

Dilution ratio (HEX,TOL)	Hexane		Toluene	
	FY	BL	FY	BL
1.1	4.0	4.0	30.0	20.0
1.3	5.0	31.0	50.0	18.0
1.6	0.0	0.0	24.0	10.0
2.0	0.0	0.0	24.0	10.0
2.7	0.0	45.0	50.0	40.0
4.0	35.0	47.0	50.0	45.0
8.0	50.0	59.0	99.0	50.0

Table 8: Effect of blending on stability after 3 days of sedimentation

Dilution ratio (FY+BL)/BL	% water resolved
0.0	29
1.1	25
1.3	20
1.6	19
2.0	11
2.7	10
4.0	9
8.0	6

Nature of organic phase:

Addition of toluene and hexane: In some of the experiments, FY and BL crude oil was diluted with various amounts of toluene/hexane to modify the aromaticity/paraffinicity of the oil phase. Toluene dilution of crude oil resulted in less stable emulsions. The effect on BL crude is less pronounced as shown in Table 7 because the effect of asphaltene dissolution is offset by steric hinderance offered by toluene. As the aromaticity of the oil phase increased, the asphaltene aggregates were dissolved and the stability of the emulsions reduced. Further, the foamability was also affected by the toluene addition. With an increase in the content of toluene in the oil phase, the capacity of the system to form foam decreased as a result of dissolution of stabilizing material. The results of this study inferred that adsorption of surface active particles at an oil/water interface depend on the nature of the oil. Aromatic oils such as toluene interacted more strongly with interfacial water than paraffinic ones such as hexane.

Effect of blending: From Table 8, as the dilution increases, stability also increases. Mixing more asphaltenic oil such as FY with less asphaltenic one such as BL resulted in more stable emulsions. Mixing of crude oils from different sources during production may cause aggregation effects that would lead to stability increase.

CONCLUSIONS

It may be concluded from the present study that the production of fine droplets by mechanical emulsification requires sufficient energy density $E V$; furthermore a critical power density $P V$, critical at about 5000 rpm has to be exceeded. The efficiency of droplet disruption increases from high API gravity (FY) to low API (BL) blends. Emulsions were most stable at dispersed phase concentration of 0.7 and in acidic solutions and paraffinic oils. In general, optimum pH for resolution of alkaline-based emulsions was between 10 and 11 and between 6 and 7 for brine. However, unstable emulsions were produced at high pH while at low pH, stable emulsions were formed. A comparison of BL and FY experimental results yields an understanding of their stability character. A decrease in the BL emulsion shelf life indicates that BL emulsion is less stable than FY over time and throughout the storage container.

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