Petroleum and Coal

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SURFACTANT BLENDING FOR QUICK WATER KNOCKOUT IN CRUDE OIL EMULSION RESOLUTION

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Received June 28, 2017; Accepted October 30, 2017

Abstract

The complex and dynamic interactions of crude oil emulsion constituents result to variations in the stability of the emulsions. Chemical demulsification methods permit the flexibility of varying the concentration or the type of demulsifier employed to mitigate these changes or achieve a desired objective for more efficient demulsification. We present in this work, a method of blending surfactants to formulate demulsifiers with quick water knockout potential. A composite water-in-crude oil emulsion was treated with 30mg/l of a formulation (PXPNG442) to attain 40% water knock-out in 1 hour using the bottle test method. The same concentration of a typical commercial demulsifier under the same condition and time amassed 7.8% water separation. Both the commercial demulsifier and the formulated demulsifier achieved 100% emulsion resolution in 48 hours. Higher rates of water knockout, 48 and 60% were respectively recorded for PXPN055 and PX001 formulations without a corresponding complete water separation in 72 hours and beyond. The formulations can be applied in demulsification processes that require quick water knockout such as treatment platforms that are close to separation tanks or when initial water knockout is required before further treatment for crude oil emulsions of high water content.

Keywords: Crude oil; Emulsion; Demulsification; Surfactants; Blending; Formulation.

1. Introduction

Crude oil deposits are mixtures of hydrocarbons, resins, asphaltenes and several other organic and inorganic materials associated with their geological formations. Water naturally cohabits with crude oil in their underground reservoirs; therefore, the process of producing oil to the surface leads to unavoidable mixing of the oil with the water in the form of emulsion [1]. Some production techniques such as water flooding also involve the deliberate introduction of water to the underground reservoir before lifting the resultant emulsion to the surface [2-5]. The water content of crude oil needs to be reduced to 0.5% or less to enhance its market value [2,6-7].

Crude oil emulsions are stabilised by some of its components (resins, waxes and asphalttenes), sands silts and other surface active materials that may have been introduced during drilling and production processes [1-2,8-9]. Demulsification process involves destabilising these inherent surfactants by single or combined processes of mechanical, thermal, electrical or chemical methods. The use of chemicals in crude oil emulsion demulsification is the most convenient and cost effective method and it involves using surfactants of higher hydrophile-lipophile-balance (HLB) values to counteract the resident surfactants in the crude oil emulsion [2, 10]

Due to the variations in the composition of different crude oil samples, their response to a particular chemical demulsifier also varies in terms of percentage water separation and the time required to achieve that. Depending on the desire of the operator, some treatment platforms may require quick water knockout especially for the ones that are close to the separation tanks. This was the aim of the work presented here.

1.1. Blending of surfactants in demulsifier formulation

Most demulsifiers are blends of two, three or more surfactants, which have been formulated to optimum cost/performance requirements. These blends may consist of chemical intermediates which possess vastly different chemical structures, surface active properties, and solubilities [11]. Although the demulsification characteristics of these individual chemical components can be loosely correlated to their chemical properties, the interactions of these chemicals with each other in the blends are complex.

Two demulsifier intermediates may exhibit similar or different demulsifying characteristics. Both intermediates may individually have fast water drop characteristics, for example, but when blended together, these chemicals can interact to drop water at the same, slower or faster rate. In the latter case, the chemicals are said to act synergistically with each other [12-13].

In another situation, one intermediate may exhibit good oil dehydration with poor water drop while another may drop water quickly but with poor oil dehydration. Blending these two chemicals may produce a formulation which exhibits the best characteristics of intermediate, that is, a blend which drops the water quickly and dehydrates the oil well.

The two major reasons for blending, therefore, are the synergistic effect of two intermediates which exhibit similar demulsifying characteristics and the combined effect of chemicals which exhibit complimentary treating characteristics [14]. Blending also reduces the number of synthesized intermediates required to produce demulsifiers for specific applications.

1.2. Evaluation and rating of demulsifier performance

The best demulsifier will be the compound which results in the most rapid and complete separation of the phases at a minimum concentration. Their performance can be assessed by physical observation of the following tests before a reliable recommendation can be expected.

1.2.1. Water drop rate

In a high water content system, a compound with a fast water drop is necessary to make the system function as it is designed to operate. When free water knockouts are involved, the speed of water drop may become the most important factor. It is noteworthy that compounds with fast water drop are sometimes incomplete in treatment. In low volume systems or those with more than normal residence time, the speed of water-drop may be of lesser significance in selecting the best demulsifier. In all cases, the speed of water-drop should be noted and recorded.

1.2.2. Sludge

When basic sediments agglomerate without breaking into water and oil, the result is commonly called sludge. In some systems, non-coalesced water drops will result in a loose agglomeration which breaks into water and oil causing no problem. Depending upon the system and sludge stability, interface sludge may or may not cause a problem. The sludge can be stabilised by finely divided solids and other contaminants to form pads. Loose interface sludge can be detected by swirling the test bottle about its vertical axis and, if the material is loose, it will be break up.

1.2.3. Interface

Kokal stated that the desired interface is one which has shiny oil at the interface devoid of hanging loose solids and this is referred to as a mirror interface [15]. In all instances, the interface should be as good as that formed by the compound being replaced, if not better especially where interface buildup in the treater is the problem.

1.2.4. Water turbidity

The turbidity of the water is very difficult to interpret in the bottle test and correlate to plant behaviour. When the chemical effects in the bottles are pronounced and reproducible, some correlation can be expected. Clear water is definitely the desired result [16].

1.2.5. Oil colour

One of the characteristics of an emulsion is its hazy appearance in contrast to the bright colour of treated oil. Consequently, the colour of the oil is expected to be brighter as the water phase separates. However, it will be erroneous to take brightening of the oil as the only criteria for selecting a demulsifier. While bright colour is not a guarantee for a successful compound, lack of it assures you that the compound is not worthy of further consideration.

2. Experimental

Reagents and equipment used are presented in Table 2.1. Composite crude oil emulsion and commercial demulsifier were provided by Shell Petroleum Development Company, Port Harcourt.

Table 2.1. List of chemicals and equipment used

S/No.	**Bench reagents**	Source/ Manufacturer
1.	Acetone (Analysis)	Lobie Chemie
2.	Isopropyl alcohol (Analysis)	Lobie Chemie
3.	Xylene (Analysis)	Lobie Chemie
	Surfactants	
1.	Ethylene glycol (EG)	Lobie Chemie
2.	Poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt (PGN)	Sigma Aldrich
3.	Polyvinylpyrrolidone (PVP)	Sigma Aldrich
4.	Glycolic acid ethoxylate lauryl ether (GLE)	Sigma Aldrich
5.	Poloxamer 407 (PLX)	Sigma Aldrich
6.	Commercial demulsifier (OPD)	
	Equipment	
1.	TW8 Water Bath	Julabo
2.	Centrifuge	Damon IEC

2.1. Determination of suitable solvents for the surfactants

The surfactants which were initially selected and purchased based on literature [17-22], were tested in order to choose most suitable solvent. Water, isopropanol and xylene (50 mL each) were separately measured into three 100 mL conical flasks in four sets. Four surfactants, PLX, PVP, GLE and PGN were added (10 g) into each set of the solvents and observed for dissolution. The ones that are not readily soluble were warmed in a fume hood with occasional swirling. The flasks were covered and the nature of the solutions formed was observed at the laboratory temperature of 23°C and recorded.

2.2. Crude oil treatment procedure

Graduated test tubes of 100mL capacity with caps (used for the bottle-test method of demulsifier screening) were used. The test tubes were filled to the 50mL mark with crude oil emulsion samples and the surfactants/demulsifiers were added using a 250 microlitre syringe. Each of the tubes was shaken 140 times in an 'up' and 'down' direction. This was to mimic the natural mixing of crude oil and demulsifier in the field as the crude flows through the pipes. The tubes were immersed in a water bath maintained at a temperature of 60°C, the average treating temperature in the field. After 30 minutes, the tubes were placed on the bench for observation and water drop-out recorded at 1, 24, 48 and 72-hour intervals.

2.3. Screening of single surfactants

Surfactants- PLX, PVP, GLE and PGN (5% w/v solution) were prepared in different solvents based on solubility profiles in Table 3.1. Composite crude oil emulsion samples (50 mL) of 25% BS&W were treated with 20 mg/l of each of the surfactants in their different solvents. The water drop-out observed for a period of 72 hours was recorded.

Table 3.1. Test for suitable solvents for surfactants at 25°C

Surfactant	Solvent Water	Isopropanol	Xylene
PLX	☑	☒	☑
PEP-PPG-PEG	☒	☑	☒
PVP	☑	☒	☒
GLE	☑	☑	☒
PGN	☑	☑	☑

Legend: (☑) Clear solution, (☒) Insoluble or cloudy solution

2.4. Blending of surfactants to formulate demulsifiers

From the result in Table 3.2, $GLE_{(p)}$, $PLX_{(x)}$, $PGN_{(x)}$ and $PVP_{(w)}$ were selected and a stock solution (10 %) of each was prepared. Using the relationship, $M_1V_1 = M_2V_2$, a concentration 50 mg/L in various ratios and combinations (Appendix A), was used to treat 50 mL of a composite crude oil emulsion containing 46% (23mL) water. One of the test tubes was left free of the surfactant blends to serve as blank while another was treated with the same concentration of the commercial demulsifier (OPD). Their performance in water separation observed within 72 hours was recorded. Lower concentrations (30 and 20 mg/litre) of blends with performances that are close to the commercial demulsifier were used to repeat the procedure and their results were recorded. The water content of the composite emulsion used for the 20 mg/L concentration is 12.0 mL.

Table 3.2. Water separation (ml) of surfactants in different solvents; water (w), xylene (x) and isopropanol (p)

	Water drop-out (mL) 1hr	24 hrs	48 hrs	72 hrs
Surfactant				
GLE (w)	0	0	0	0
PVP (w)	0	<0.5	<0.5	0.5
PGN (x)	0.5	3.0	3.0	4.0
PLX (x)	1.0	3.0	6.0	8.0
GLE (p)	<0.5	0.5	1.0	1.0
PGN (p)	0	0	0	0
PLX (p)	0.5	1.0	1.0	1.0
PGN (w)	0	0.5	0.5	1.0

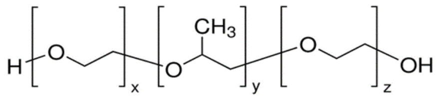
3. Results and discussion

3.1. Selection suitable solvents for surfactants

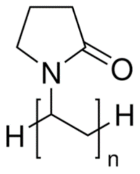
From Table 3.1, water was selected as the solvent for PVP. For GLE and PEG-PPG-PEG that are soluble in water and isopropanol, their isopropanol solutions were preferred [23]. If a surfactant is also soluble in xylene (PLX and PGN), the choice of xylene precedes the others due to its aromaticity [24] and added advantage that the more oil soluble xylene will be a distributor of the surfactant to the continuous phase of the W/O emulsion.

3.2. Screening of single surfactants

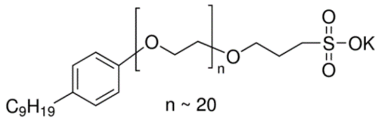
As shown in Table 3.2, the Xylene solution of PLX showed the highest water drop-out followed by PGN. This could be partly due to their structures (Figure 3.1) and partly due to the aromaticity of the solvents. Block copolymers such as PLX have been found to have improved demulsification efficiency due to their high molecular weight and HLB [19, 22]. The oil external phase of the emulsion will require compatible solvents in other to get to the dispersed water globules. This accounts for the less or zero water separation observed in PGN and GLE water solutions. However, for the required synergy, both the water and oil soluble surfactants will be used in final demulsifiers formulations.



PLX



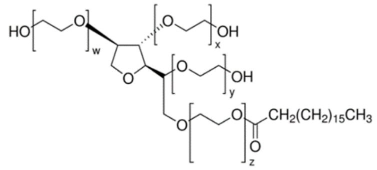
PVP



PGN

$HOCH_2CH_2OH$

EG



GLE

Figure 3.1. Molecular structure of some surfactants used

3.3. Blending of surfactants to formulate demulsifiers

At 50 mg/L concentrations, all demulsifiers performed a little below 100% separation. This may be as a result of overtreat. Generally, eight of the formulated demulsifiers achieved quicker water dropout than the commercial one in 24 hours (Table 3.3, Figures 3.2a and 3.2b). However, based on percentage and clarity of resolved water, 5 out of the eight (PX001, PXPN055, PXPNG442, PXPN073 and PXPN037) were selected and used to repeat the treatment at reduced concentrations of 30 and 20 mg/l alongside the commercial demulsifier (Table 3.4). The results (Figure 3.3) showed that complete separation was attained by formulation (PXPNG442) at the 30 mg/L concentration with initial water dropout that is 32% higher than the commercial demulsifier. Three other formulations, PX001, PXPN073 and PXPN055 achieved quicker water dropout rate, up to a period of 24 hours but lacked complete separation at their maximum performance.

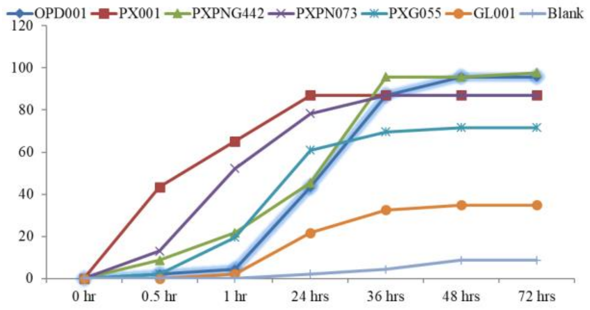


Figure 3.2a. Water separation (%) of comercial and 1st set of different formulated demu-sifiers at 50 mg/L concentration

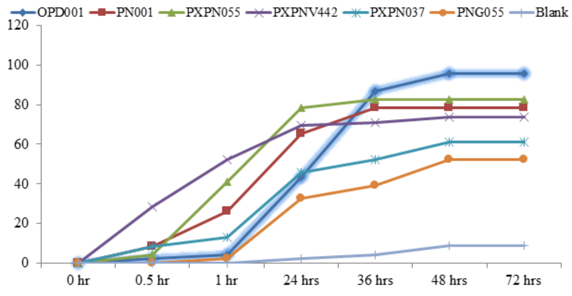


Figure 3.2b. Water separation (%) of comercial and 2nd set of different formulated demulsifiers at 50 mg/L concentration

Table 3.3. Water separation (ml) of composite crude oil emulsion using 50 mg/l of formulated and the commercial demulsifier

Demulsifier	Water drop-out (mL)					
	0.5 hr	1 hr	24 hrs	36 hrs	48 hrs	72 hrs
OPD001*	0.5	1.0	10.0	20.0	22.0	22.0
PX001	10.0	15.0	20.0	20.0	20.0	20.0
PN001	8.6	6.0	15.0	18.0	18.0	18.0
PXPN055	1.0	9.5	18.0	19.0	19.0	19.0
PXPNG442	2.0	5.0	10.5	22.0	22.0	22.0

Demulsifier	Water drop-out (mL)					
PXPNV442	1.5	12.0	16.0	16.4	17.0	17.0
PXPN073	3.0	12.0	18.0	20.0	20.0	20.0
PXPN037	2.0	3.0	10.7	12.0	14.0	14.0
PXG055	0.5	4.5	14.0	16.0	16.5	16.5
GL001	0	0.5	5.0	7.5	8.0	8.0
PNG055	0	0.5	7.5	9.0	12.0	12.0
Blank	0	0	0.5	1.0	2.0	2.0

**Commercial demulsifier*

Table 3.4. Water separation (ml) of composite crude oil emulsion using 30 mg/L of formulated and the commercial demulsifier

Demulsifier	Water drop-out (mL)					
	0.5 hr	1 hr	24 hrs	36 hrs	48 hrs	72 hrs
OPD001*	1.0	1.8	12.9	19.3	23.0	23.0
PX001	1.8	13.8	18.4	19.3	20.2	20.2
PN001	3.9	11.0	16.6	19.3	19.3	19.3
PXPN055	1.8	9.2	16.2	22.0	23.0	23.0
PXPNG442	0.7	9.2	13.8	18.4	18.4	18.4
PXPNV442	0.0	4.5	11.0	14.7	14.7	14.7
PXPN073	1.0	1.8	12.9	19.3	23.0	23.0
PXPN037	1.8	13.8	18.4	19.3	20.2	20.2
PXG055	3.9	11.0	16.6	19.3	19.3	19.3
GL001	1.8	9.2	16.2	22.0	23.0	23.0
PNG055	0.7	9.2	13.8	18.4	18.4	18.4
Blank	0.0	4.5	11.0	14.7	14.7	14.7

As shown in Table 3.5, none of the formulated demulsifiers could attain complete water separation at 20 mg/l concentration in comparison with the commercial demulsifier. The early quicker water dropout trend was however maintained by three of the demulsifiers (Figure 3.4).

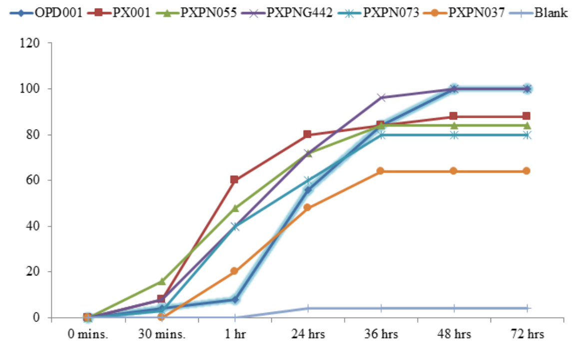


Figure 3.3. Water separation (%) using 30 mg/L of formulated and commercial demulsifiers

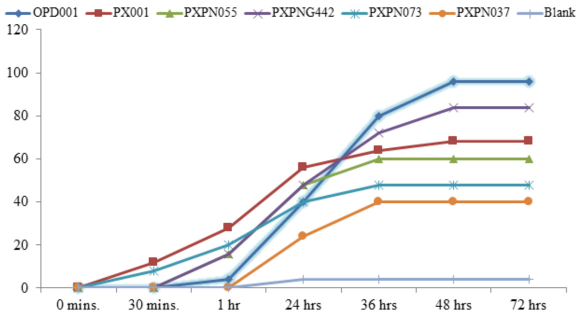


Figure 3.4. Water separation (%) using 20 mg/L of formulated and commercial demulsifier

Table 3.5. Water separation (mL) of composite crude oil emulsion using 20 mg/L of formulated and the commercial demulsifier

Demulsifier	Water drop-out (ml)					
	0.5 hr.	1 hr	24 hrs	36 hrs	48 hrs	72 hrs
OPD001*	0.0	0.5	5.0	10.0	12.0	12.0
PX001	1.5	3.5	7.0	8.5	8.5	8.5
PXPN055	0.0	2.0	6.0	7.5	7.5	7.5
PXPNG442	0.0	2.0	6.0	9.0	10.5	10.5
PXPN073	1.0	2.5	5.0	6.0	6.0	6.0
PXPN037	0.0	0.0	3.0	5.0	5.0	5.0
Blank	0.0	0.0	0.5	0.5	0.5	0.5

**Commercial demulsifier*

3. Conclusion

The formulation (PXPNG442) is therefore comparable with OPD001, a typical commercial demulsifier at 30 mg/L concentration with an advantage of higher rate of water knock-out. This property is highly desired in some operations of emulsion resolution. For example, treatment facilities that are close to settling tanks require a quick water knockout before it is mingled with other streams that have been treated earlier in other platforms. It will also be useful in some other operations where the emulsion contains a high percentage of water that will require initial knockout before further treatment. Formulations PXPN055 and PX001 will be more suitable for the later application considering that they lacked complete water separation but possess the advantage of an initial higher percentage of water knockout. It should be noted that the observed performances of the demulsifiers formulated here are with respect to the particular crude oil emulsion treated – a typical light crude of Niger Delta, Nigeria. The performance with any other crude oil sample may be higher or lesser depending on the crude's physical properties.

Further works will be carried out on the economics and toxicity of the formulations in comparison with the available commercial type(s).

Appendix A: Surfactants combinations used for demulsifier formulations

Surfactant combinations	*Ratio (%)*	*Code*	*Surfactant combinations*	*Ratio (%)*	*Code*
PLX	*100*	*PX001*	*PLX/PGN/EG*	*60/20/20*	*PXPNG622*
GLE	*100*	*GL001*	*PLX/PGN/PVP*	*40/40/20*	*PXPNV442*
PVP	*100*	*PV001*	*PLX/PGN/GLE*	*40/20/40*	*PXPNGL424*
PGN	*100*	*PN001*	*PGN/GLE*	*50/50*	*PNGL055*
PLX/PGN	*70/30*	*PXPN073*	*PLX/GLE/PVP*	*40/40/20*	*PXGLV442*
PLX/PGN	*30/70*	*PXPN037*	*PLX/GLE*	*50/50*	*PXGL055*
PLX/PGN	*50/50*	*PXPN055*	*PLX/GLE/EG*	*40/40/20*	*PXGLG442*
PLX/PGN/GLE	*40/40/20*	*PXPNGL442*	*PLX/PGN/GLE*	*30/30/40*	*PXPNGL*
PLX/PGN/EG	*40/40/20*	*PXPNG442*	*PLX/GLE/EG*	*60/20/20*	*PXGLG622*
PLX/PGN/EG	*40/20/40*	*PXPNG424*	*PLX/EG*	*50/50*	*PXG055*
PLX/PGN/EG	*30/30/40*	*PXPNG334*	*PGN/EG*	*50/50*	*PNG055*

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