

A Comparative Analysis of Decylamine and Phenol in Water-In-Oil Emulsion Demulsification Process

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ABSTRACT: Crude oil is seldom produced alone. (Lake & Fanchi, 2006). Its production will usually be accompanied by water (in the form of free water or emulsions). This causes increased corrosion of the pipelines, increased pumping costs, increased cost of transportation, et cetera. Therefore, there is a need to separate water from the crude oil in crude oil emulsions. This study employed the bottle test method to compare the performance of the chemical demulsifiers - decylamine and phenol – in the demulsification of water-in-oil crude oil emulsions. The crude oil emulsion sample used was taken from an offshore well located in the Niger Delta region of Nigeria (West Africa). Similar volumes of the emulsion sample were then collected in a series of graduated tubes and known amounts of the chemical demulsifiers were added to the tubes. The tubes were then centrifuged. The amount of water separated was measured and recorded for various dosages of the demulsifiers – 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, 1.0 ml, 1.2 ml and centrifugation times of 2, 4, 6, 8, 10, and 12 minutes respectively. Results obtained show that decylamine performs faster and separates a higher volume of water than phenol. It is therefore recommended that decylamine be selected over phenol in the demulsification of water-in-oil crude oil emulsions originating from the Niger Delta region of Nigeria.

KEYWORDS: Emulsion, Demulsifiers, Decylamine, Phenol, Niger Delta, Chemical Demulsification.

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I. INTRODUCTION

During crude oil production, the presence of produced water is the precondition for several problems, each of which can increase the unit cost of oil production, processing, and transportation. One of the challenges in the petroleum industry that results from the production of oil in association with water is that of emulsions (Lake & Fanchi, 2006). An emulsion is a two-phase system of two immiscible liquids, in which droplets of one of the liquids is uniformly and finely dispersed in the second liquid. The liquid whose droplets are dispersed is called the dispersed phase while the continuous phase is the liquid containing the dispersed phase (Khan, et al., 2011).

Oilfield emulsions are either classified as water-in-oil, oil-in-water, or complex (multiple) emulsions. Water-in-oil emulsions consist of water droplets in a continuous oil phase, and oil-in-water emulsions consist of oil droplets in a water-continuous phase. Complex or multiple emulsions consist of droplets suspended in a second (bigger) droplet which itself is suspended in a larger continuous phase. An example of a multiple emulsion is an oil-in-water-in-oil which contains oil droplets suspended in larger water droplets that are finally suspended in a continuous oil phase (Lake & Fanchi, 2006). In the oil industry, water-in-oil emulsion is the most common type of emulsion, so that oil-in-water emulsions are occasionally called reverse emulsions. However, both oil-in-water or reverse emulsions and water-in-oil emulsions may occur together. It is rare, but when a reverse emulsion occurs within an internal phase of a water-in-oil (regular) emulsion, a complex emulsion is formed (Grace, 1992).

Emulsions can occur inside the reservoirs, wellbores, and wellheads, at facilities for handling wet-crude, in separators, it can also occur in pipelines, and crude storage facilities (Kokal, 2005). The occurrence of emulsions usually results in increased corrosion of the pipelines, increased pumping costs, and an increased cost of transportation (Okereke, Ohia, & Obah, 2018).

Demulsification is the process by which an emulsion is separated into its component phases. Demulsification may be achieved using various methods. One such method is using heat. A novel innovative way of using heat for achieving demulsification is by the process known as Microwave demulsification (Nour,

Pang, & Omer, 2010). Experimental results from Chan & Chen, (2002) recorded successes in the demulsification of water-in-oil using microwaves. They were able to separate more than 80% of water under some conditions. Microwave seems to provide quicker separation than other conventional heating techniques (Chan & Chen, 2002). The electrical demulsification method using high voltage electricity (electrostatic grids) can also be very effective in breaking emulsions. When an electric field is applied, the water droplets which have a net charge move about rapidly, colliding with each other to induce coalescence. Electrical demulsification generally lead to reduced usage of chemicals for emulsion breaking. The limitation of electrostatic dehydration is arcing/shorting which mainly occurs when there is the presence of excess water. Mechanical method of demulsification involves the use of various equipment such as free-water knockout drums, two- and three-phase separators, settling tanks, desalters (Lake & Fanchi, 2006). The specifics about using such equipment in achieving mechanical demulsification may be read up in other materials.

In the petroleum industry, demulsification is preferably achieved using chemicals because of its applicability (Grace, 1992). Chemical demulsifiers that find application in the oil field are polymeric surfactants like ethoxylated phenols, amines, alcohols, nonylphenols, propylene oxides, copolymers, ethylene oxides, et cetera (Bhattacharyya, 1992). The addition of chemical demulsifiers enhances film drainage and reduces interfacial viscosity (Krawczyk et al, 1991; Bhardwaj & Hartland, 1994); thus making the film very thin, causing it to collapse and resulting in coalescence. Increasing the chemical demulsifier concentration, therefore, will generally cause a corresponding increase in the rate of demulsification. This is because higher concentration causes higher interfacial thinning, and increases the coalescence rate (Hajivand & Vaziri, 2015). However, increasing the concentration of the demulsifier causes an increased rate of demulsification only until the critical concentration (called the critical aggregation concentration) is reached. Higher concentrations above this critical concentration (overdosing of demulsifier) will either level the demulsification rate with further increase in chemical demulsifier concentration or reduce the demulsification rate with increasing concentration of the chemical demulsifier (Aveyard, Binks, Fletcher, & Lu, 1990; Mohammed et al, 1994).

This paper considered the use of two demulsifiers (Phenol and Decylamine) on a sample of crude oil emulsion from an offshore field in Niger Delta. Varying volumes of the demulsifiers were used to carry out demulsification on the emulsion.

II. MATERIALS AND METHODS

Bottle test procedure was applied for the demulsification process in this study. Bottle test is an empirical test in which demulsifiers are added to bottle samples of a crude oil emulsion to determine which demulsifier is the most efficient at separating the crude oil emulsion into its constituent oil and water.

Sample Collection and Analysis

The sample of crude oil was collected from an offshore well in the Niger Delta region. The samples were analyzed and the efficiency of the two chemical demulsifiers using bottle test techniques was determined. The laboratory equipment, apparatus, and chemicals, demulsifier properties, crude oil properties that were employed for this analysis are shown in the table below.

Table 1: Materials, apparatus, and chemicals used

S/N	Material Name	S/N	Material Name	S/N	Material Name	S/N	Material Name	S/N	Material Name
1	Funnel	5	Measuring Cylinder	9	Pipette	13	Spatula	17	Xylene (solvent)
2	Clock Timer	6	SETA Centrifuge	10	Flat bottom flask	14	Crude oil	18	Distilled water
3	Syringe	7	Thermometer	11	Centrifuge tubes (ASTM D-96)	15	Decylamine (demulsifier)		
4	Beakers	8	Hydrometer	12	Oswald Viscometer	16	Phenol (demulsifier)		

Table 2: Properties of the demulsifiers

Demulsifier	Molecular formula	Physical Properties	Density	Melting point	Boiling point
Decylamine	C ₁₀ H ₂₃ N	Colorless liquid	0.787g/cm ³	17.0°C	220.5°C
Phenol	C ₆ H ₅ OH	Transparent crystalline solid	1.07 g/cm ³	40.5 °C	182 °C

Table 3: Properties of the crude sample used for the study

S/N	Properties	Values
1	Specific gravity	0.812 g/cm ³
2	API gravity	42.76 ^o
3	Water content	6 %
4	Colour	Dark brown

Demulsification Procedure

The demulsification process as applied in this paper consists of the use of the bottle testing technique and procedure. The bottle test is an empirical test in which varying amounts of potential demulsifiers are added into a series of tubes containing a sample of an emulsion to be broken down. The demulsification test was carried out using a 15ml graduated centrifuge tube and at constant revolution per minute of 1500rpm as follows:

- 1) 5ml of the emulsion sample was centrifuged alone at a constant rpm and 77^oF without the addition of any demulsifier.
- 2) Another 5ml of the emulsion sample was centrifuged with the addition of 5ml of xylene at a constant rpm and 77^oF.
- 3) Two different tubes were filled to the 10ml mark, each containing 5ml of emulsion sample and 5ml of xylene solvent.
- 4) Increasing dosages of the demulsifiers were added in their concentrated states without dilution to the two tubes.
- 5) The dosages of demulsifiers added to the tubes were varied as follows for the two demulsifiers; 0.2ml, 0.4ml, 0.6ml, 0.8ml, 1.0ml, and 1.2ml.
- 6) Centrifugation was carried out for time intervals of 120, 240, 360, 480, 600 and 700 seconds for each demulsifier volume.
- 7) The tubes were agitated by using hand a given number of times, approximately 20times and then placed on the centrifuge for centrifugation after a new dosage of demulsifier was added.

III. RESULTS AND DISCUSSIONS

The table below shows the results for the centrifuge tests of the emulsion only at a constant speed of 1200 rev/min. The seta electronic centrifuge was set to maintain the specimen at a temperature of 85 °F

Results from the first control experiment (Emulsion only)

The emulsion used here contained no xylene and no demulsifiers at all. The emulsion sample alone was centrifuged.

Table 4: Results from the centrifugation of the emulsion sample only

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	0	0	0	0	0	0
Vol. of water separated (ml)	0.2	0.2	0.2	0.2	0.2	0.2

Results for control experiment 2 (50% vol. Emulsion + 50% vol. Xylene):

Here, the centrifuged sample contained 50% volume of emulsion and 50% volume of xylene

Table 5: Results from the centrifugation of the emulsion sample plus xylene

Time	120	240	360	480	600	720
Vol. of demulsifier (ml)	0	0	0	0	0	0
Vol of water separated (ml)	0.2	0.3	0.35	0.35	0.35	0.35

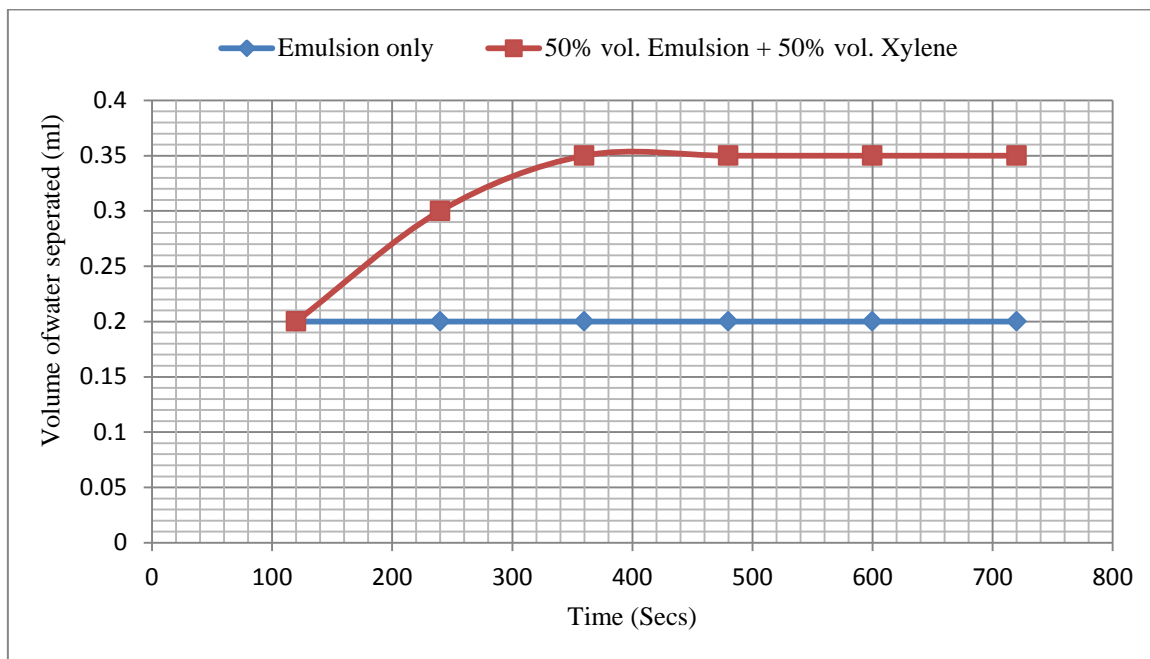


Figure 1: graph comparing centrifugation results obtained when xylene is applied to results obtained when only the emulsion is centrifuged

Results obtained after addition of chemical demulsifier

For the addition of 0.2 ml demulsifier:

Two samples, each containing equal volumes of emulsions plus 0.2 ml demulsifiers, were subjected to centrifugation. The results are shown below:

Table 6: Results obtained when 0.2 ml of the demulsifier was added

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	0.20	0.20	0.20	0.20	0.20	0.20
Vol. of water separated using Decylaminodemulsifier (ml)	0.55	0.65	0.70	0.75	0.75	0.75
Vol of water separated using Phenol Demulsifier (ml)	0.05	0.10	0.15	0.20	0.20	0.20

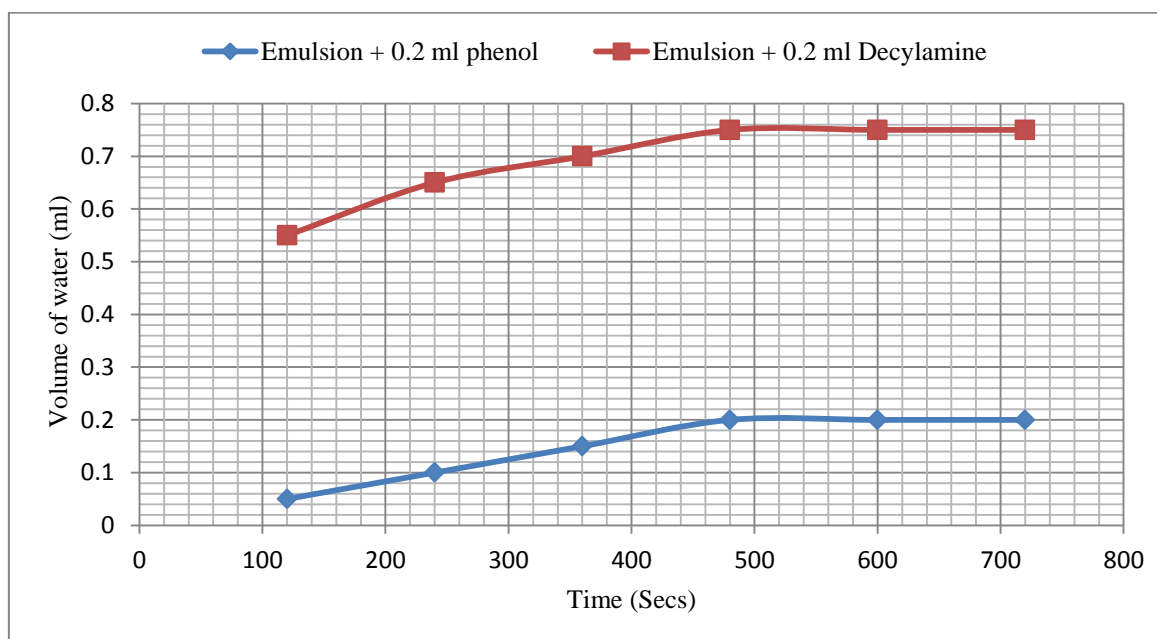


Figure 2: graph comparing results obtained when 0.2 ml of each demulsifier was added

For the addition of 0.4 ml demulsifier:

Here, 0.2 ml of both demulsifiers were added to the separate samples from the previous centrifugation to make them up to 0.4 ml. The results are shown below:

Table 7: Results obtained after addition of 0.4 ml of each demulsifier

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	0.40	0.40	0.40	0.40	0.40	0.40
Vol. of water separated using Decylaminedemulsifier (ml)	0.75	0.80	0.80	0.80	0.80	0.80
Vol. of water separated using Phenol Demulsifier (ml)	0.20	0.20	0.20	0.20	0.20	0.20

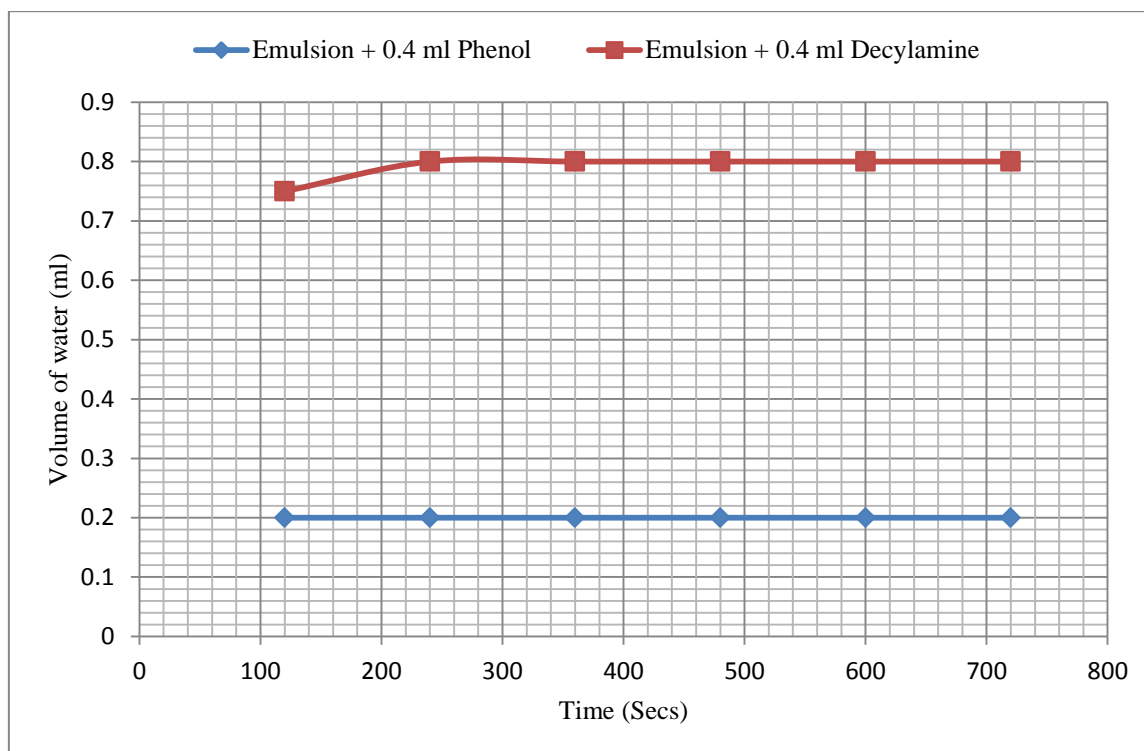


Figure 3: graph comparing results obtained when 0.4 ml of each demulsifier was added

The charts suggest that the volumes of water separated during the centrifugation of emulsion samples plus 0.4 ml of demulsifier is relatively constant when 0.4 ml of phenol and 0.4 ml of decylamine are used on the emulsion samples.

For the addition of 0.6 ml demulsifier:

Here, 0.2 ml of both demulsifiers were added to the separate samples from the previous centrifugation to make them up to 0.6 ml. The results are shown below:

Table 8: Results obtained after addition of 0.6 ml of each demulsifier

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	0.60	0.60	0.60	0.60	0.60	0.60
Vol. of water separated using Decylaminedemulsifier (ml)	1.00	1.00	1.00	1.00	1.00	1.00
Vol of water separated using Phenol Demulsifier (ml)	0.20	0.20	0.20	0.20	0.20	0.20

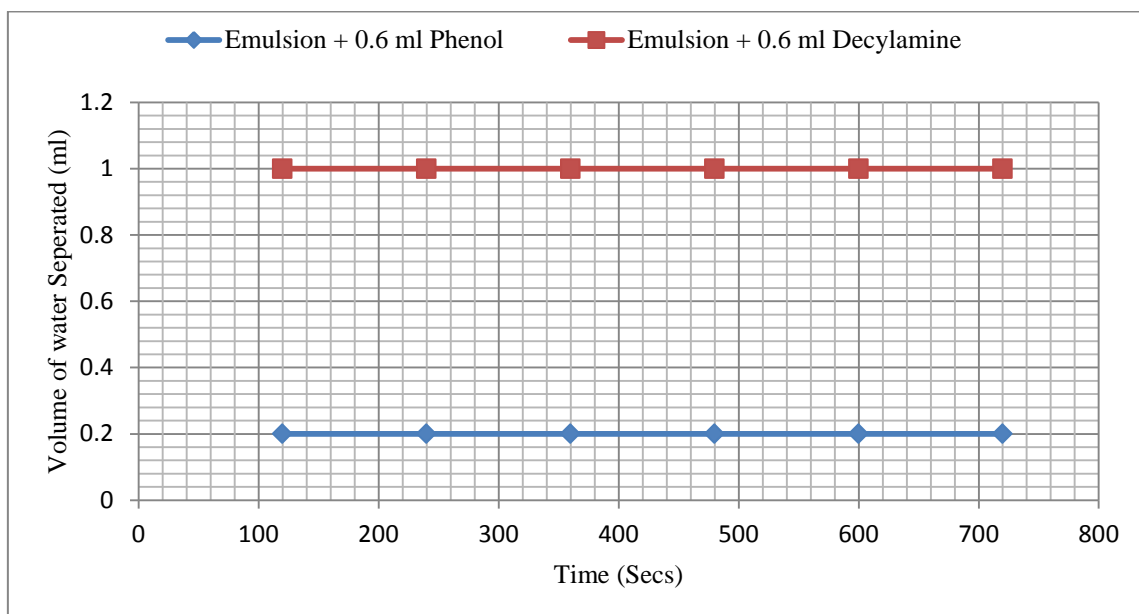


Figure 4: graph comparing results obtained when 0.6 ml of each demulsifier was added

There is no additional volume of water separated when the volume of phenol is increased.

For the addition of 0.8 ml demulsifier:

Here, 0.2 ml of both demulsifiers were added to the separate samples from the previous centrifugation to make the total volume of demulsifier in the samples up to 0.8 ml. The results are shown below:

Table 9: Results obtained after addition of 0.8 ml of each demulsifier

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	0.80	0.80	0.80	0.80	0.80	0.80
Vol. of water separated using Decylaminodemulsifier (ml)	1.10	1.10	1.10	1.10	1.10	1.10
Vol. of water separated using Phenol Demulsifier (ml)	0.20	0.20	0.20	0.20	0.20	0.20

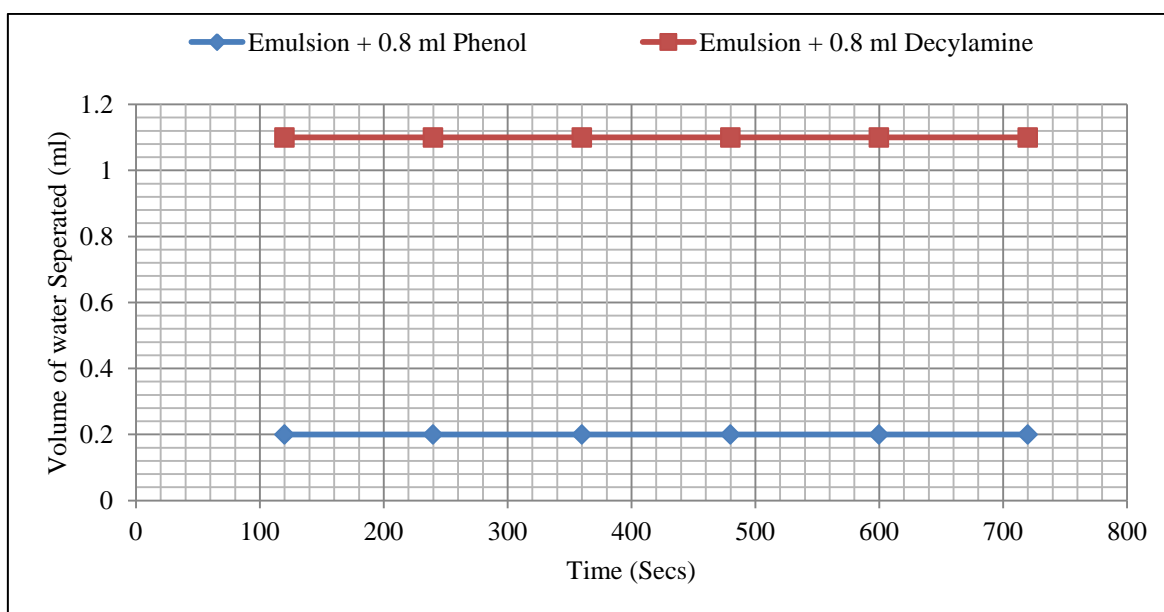


Figure 5: graph comparing results obtained when 0.8 ml of each demulsifier was added

For the addition of 1.0 ml demulsifier:

Here, 0.2 ml of both demulsifiers were added to the separate samples from the previous centrifugation to make the total volume of demulsifier in the samples up to 1.0 ml. The results are shown below:

Table 10: Results obtained after addition of 1.0 ml of each demulsifier

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	1.00	1.00	1.00	1.00	1.00	1.00
Vol. of water separated using Decylaminodemulsifier (ml)	1.10	1.20	1.25	1.25	1.25	1.25
Vol. of water separated using Phenol Demulsifier (ml)	0.20	0.20	0.20	0.20	0.20	0.20

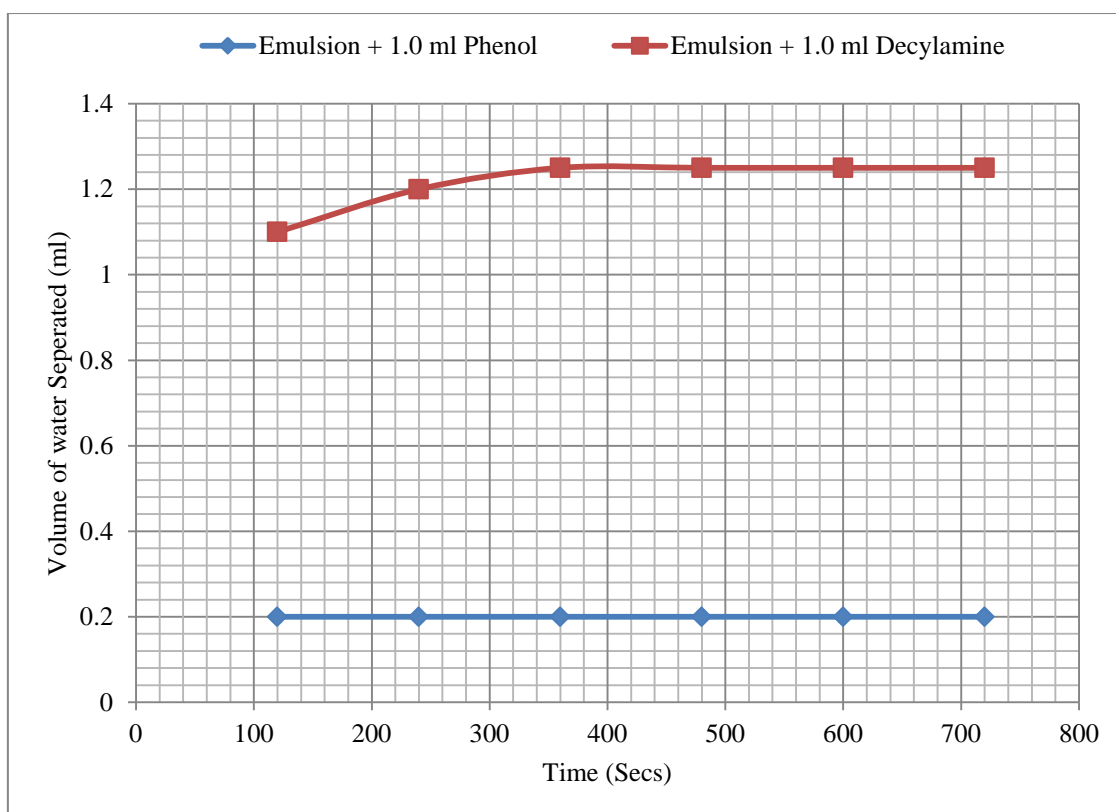


Figure 6: graph comparing results obtained when 1.0 ml of each demulsifier was added

There is no increase in the volume of water separated using Phenol, while for decylamine water separated increased.

For the addition of 1.2 ml demulsifier:

Here, 0.2 ml of both demulsifiers were added to the separate samples from the previous centrifugation to make the total volume of demulsifier in the samples up to 1.2 ml. The results are shown below:

Table 11: Results obtained after addition of 1.2 ml of each demulsifier

Time (Secs)	120	240	360	480	600	720
Vol. of demulsifier (ml)	1.20	1.20	1.20	1.20	1.20	1.20
Vol. of water separated using Decylaminodemulsifier (ml)	1.25	1.25	1.25	1.25	1.25	1.25
Vol. of water separated using Phenol Demulsifier (ml)	0.20	0.20	0.20	0.20	0.20	0.20

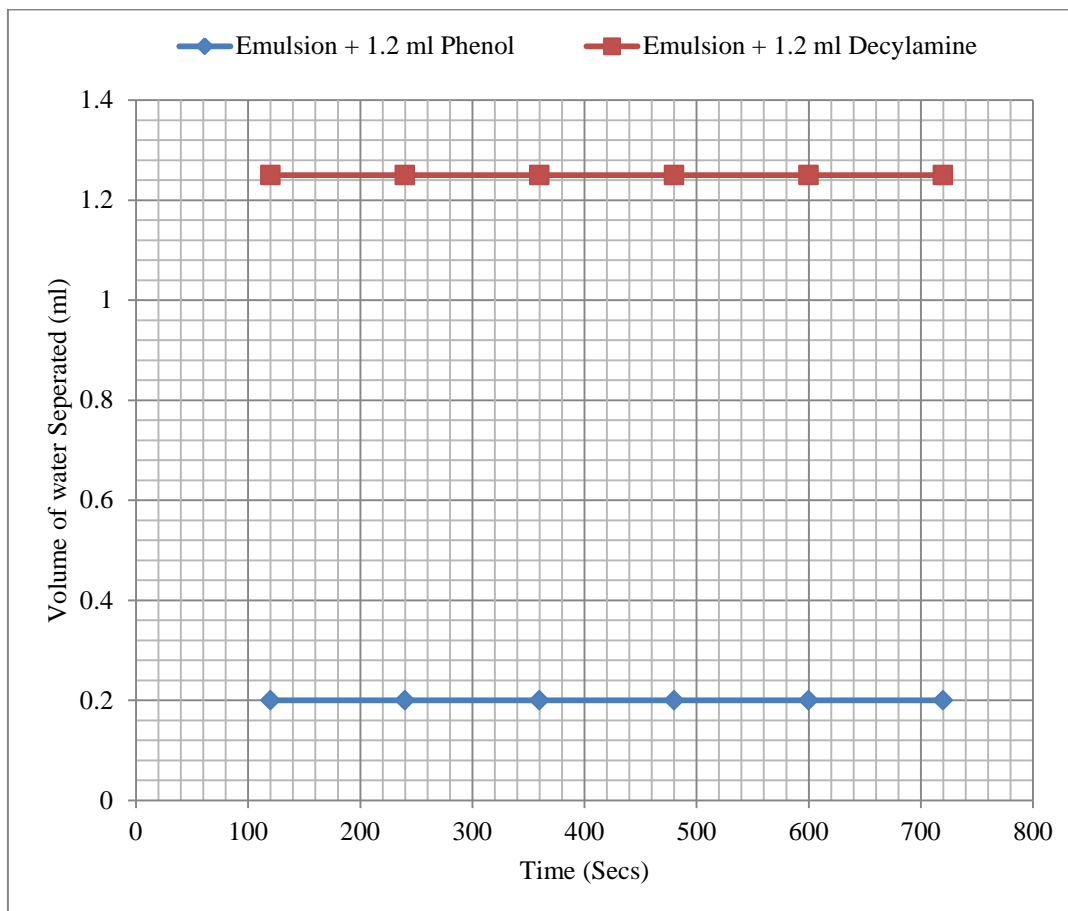


Figure 7: graph comparing results obtained when 1.2 ml of each demulsifier was added

IV. CONCLUSION

At the end of the study, the results generated showed that decylamine generally performed better than phenol. The results are explained in the following sections below.

Speed of action — the chemical demulsifier – decylamine acts faster than Phenol when both are used in water-in-oil crude oil emulsion systems like our samples.

Water separated — the decylamine causes more water separation to occur than an equal volume of Phenol when both are acting on similar samples of water-in-oil emulsions. However, it must be noted that the water phase separated by the decylamine is not as clear (distinct) as the one separated by phenol. With phenol, greater interface quality between the water separated and the crude oil from which it is separated is achieved.

Choice of demulsifier — If the speed of separation and amount of water separated are the key factors for consideration before selecting a chemical demulsifier, then decylamine should be chosen over phenol for the demulsification of crude oil emulsions originating from the Niger Delta.

Dosage of the demulsifier— an increase in amount of demulsifier used caused a corresponding increase in the amount of water separated until the critical aggregation concentration was reached. It is known in theory that the application of dosages of a demulsifier above the critical concentration will achieve is not good. Therefore, increasing the amount of any of the demulsifier beyond the critical concentration not achieve optimum separation and will at least be financially unreasonable.

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