Comparative Analysis of Polyethylene Glycol and Triethanolamine as Demulsifying Agents for Separation of Water-In-Oil Emulsion

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ABSTRACT - Emulsion problems is prevalent in the oil industry today and there is need to propose and adopt new techniques and materials that can compete with the conventional materials. The presence of impurities that is found within the crude oil is a cause of concern seeing that the presence of such impurities like immiscible liquids like water leads to further expenses on pumping or transporting water through pipeline or tanker, poisoning of downstream refinery catalysts and corrosion of pipelines, production equipment and downstream overhead distillation columns. This general leads to greater importance and practice of demulsification to solve such issues in the oil industry. This study seeks to carry out a comparative analysis of polyethylene glycol and triethanolamine as demulsifying agents as separators in water-in-oil emulsion. According to the results obtained from the experimental work, observations of the two demulsifier performance (polyethylene glycol and triethanolamine), it can be concluded that, there is an assured better interface quality when using polyethylene glycol as a demulsifier than using triethanolamine, also a better separation performance is gotten from the utilization of polyethylene glycol than that of triethanolamine, also water will separate clearly when using polyethylene glycol and a faster rate of separation is also achieved when using polyethylene glycol as a demulsifier.

Keywords: Bottle test method, Demulsification, Demulsifiers, Emulsion, Emulsifcation, Polyethylene Glycol, Triethanolamine, Toluene.

1.0 INTRODUCTION

The occurrence of emulsion in the oil and gas industry is a very common and major problem as engineers over the years have found out. Generally in reservoirs containing oil, the presence of oil and water is always found and oil appears to be at top and water below and this leads to an affluence of water during production. According to (Aamir, 1998; Sharif, 2010), the influx of water during oil production is defined as emulsion. African Journal of Pharmacy and Pharmacology Vol.5 (25), 30 December, 2011 also defined emulsion as a biphasic system comprising of two immiscible liquids, one of which (the dispersed phase) is finely and uniformly dispersed as globules throughout the second phase (the continuous phase). We can generally say emulsion is the mixture of two immiscible liquids which consist of a dispersed phase and a continuous phase. Emulsion is to be broken apart or separated before transportation or for further processes to meet up to economic standard and customers need. Emulsion has basically three (3) types which occur in the industry; they are;

I. Water in oil emulsion: In the industry, this emulsion has water as its dispersed phase and oil as the continuous phase
II. Oil in water emulsion: In the petroleum industry, this emulsion has oil as the dispersed phase and water as the continuous phase
III. Complex/multiple emulsion: In the industry, the complex/multiple emulsion is the combination of water in oil phase and oil in water phase.

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There are certain conditions that must be present in order for emulsion to occur;

1. Mixing(agitation)
2. Two immiscible liquids
3. Emulsifying agents

According to research (Bhardwaj and Hartland, 1998), crude oil emulsions are formed when two immiscible liquids (oil and water) are agitated together to disperse one liquid into the other in droplets form. This agitation is achieved through the flow of crude oil from the well to surface line, with either natural or artificial means like electrical submersible pumps (ESP).

It has been observed that crude oil obtained from different field location have different properties. Crude oil is a mixture of hydrocarbon. It ranges from naphthenes to parrafins and aromatics. It varies from clear to tar-black in colour and then from water to almost solid in viscosity. According to (Hyne, 2001) crude oil exists in the reservoirs in most cases as gas at the top followed by the oil then water at the bottom.

In most cases, crude oil emulsions result from the natural surfactants such as asphaltenes and resins contained in the crude oil which, when mixed with water, emulsifies the water into the oil (Sjoblom *et al*., 1992). In this study we concentrate or focus on the water in oil emulsion.

According to Emerging Nanotechnologies in Food Science, 2017, "emulsification is defined as a process of "dispersing one liquid (containing the bioactive compounds) in a second immiscible liquid by applying electrostatic, or hydrophobic, or hydrogen bonding interactions between the bioactive compounds and an encapsulating material".

"The dictionary of Biology 2004 originally published by Oxford University Press 2004" defined "Emulsification as the breakdown of fat globules in the duodenum into droplets, which provides a larger surface area on which the enzyme pancreatic lipase can act to digest the fats into the fatty acids and glycerol".

The formation of emulsion during oil production in the petroleum industry is viewed as a very costly problem either relating to lost production from increased pressure drop due to increased viscosity or lost production due to emulsion incurred processing system shut-down and also in terms of desired chemicals that are used for processing to achieve the desired product quality.

For emulsion to be formed when oil and water phases are brought together, there are two important factors that must be present which are the presence of a surface-active agent and an adequate mixing. In general, the larger the amount of mixture the tighter the emulsion and the smaller the amount of dispersed phase.

Another important factor in the formation of emulsion is the introduction of emulsifying agents which helps to dictate the type and tightness of the emulsion to owe to the amount and composition of the emulsifier.

2.0 FACTORS AFFECTING EMULSION

It is very important to take note of certain factors that are responsible for the stability of emulsion looking into the fact that interfacial films are primarily responsible for emulsion stability. The important factors include;

I. Temperature
II. The pH of the brine and brine composition
III. Droplets size and droplet-size distribution
IV. Heavy polar fractions in the crude oil
V. Solids including organic (asphaltenes) and inorganic (clays)

2.1 DEMULSIFICATION

In the petroleum industry, the separation processes of water, oil, and gas are very important.

Demulsification is defined as the breaking of crude oil emulsion into the water and oil phase. It can also be defined as a process that involves coalescences, flocculation, and separation of two immiscible liquids. To the oilfield personnel, they are interested in three basic aspects of the demulsification

I. Quality of separated water for disposal
II. Measure of remaining water left in the crude oil after separation
III. Rate or the speed at which this separation takes place

The oilfield producers are very much interested in the low value of residual water, the low value of oil in the disposed water and a very fast rate of separation as to meet up to company and pipeline specifications.

2.3 DEMULSIFIERS

Chemical demulsifiers are used in the chemical method. The use of the right demulsifiers is very essential in the separation of the emulsion. In the experiment to be carried out, the use of polyethylene glycol and triethanolamine are the demulsifiers used in the chemical method

3.0 MATERIALS AND METHODS

To achieve the objective and scope of this research, the demulsification process applied in this study consist of the use of bottle test technique.

3.1 MATERIALS

For this study to be carried out, some reasonable amount of crude oil sample was obtained from an offshore oil field in the Niger Delta region, Escravos, Warri, Delta state, Nigeria. The characteristic of the obtained crude oil is given in table 3.2. The selected chemical demulsifiers; polyethylene glycol and triethanolamine with its characteristic stated in table 3.3. The selected solvent for this experiment; Toluene as the selected solvent were also made available for use in the laboratory.

Table 3.1 Showing laboratory materials and apparatus

S/N	Material Name	S/N	Material Name
1	Centrifuge tube	9	Syringe
2	Beakers	10	Funnel
3	Hydrometer	11	Polyethylene glycol (demulsifier)
4	Manual centrifuge	12	Tri ethanolamine (demulsifier)
5	Clock timer	13	Pipette
6	Flat bottom flask	14	Crude oil
7	Hydrometer Cylinder	15	Toluene (solvent)

Table 3.2: Showing the properties of Crude oil used.

Crude oil properties	**Values**
Color	Black
API	30.03^{o}C
Specific Gravity	0.876

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3.2 EXPERIMENTAL APPROACH

In recent studies, it has been found out that there are various methods to carry out emulsion process. According to a research by "Mr. Saran Kumar Das and Ms. Deepika U, M. Pharm, Department of Pharmatics", the various method commonly used to prepare emulsion can be divided into two categories;

I. Trituration method and
II. Bottle method

For the cause of our experiment, we will focus on the use of the bottle test method. The bottle test method an empirical test whereby various amount of demulsifiers are added into the tubes containing samples of emulsion to be broken down at different dosage.

3.3 PROPERTIES OF CHEMICALS USED

The various chemicals used in the course of this study which are listed in table 3.1 which are; Polyethylene glycol, triethanolamine, and Crude oil.

I. Crude oil: The properties of the crude used in this study where gotten in the laboratory using a hydrometer and hydrometer cylinder.

II. **Toluene:** It is an aromatic hydrocarbon that is colorless and a water insoluble liquid. Also known as "Toluol" is a mono-substituted benzene derivative, consisting of a CH3 group attached to a phenyl group and has an IUPAC name of methylbenzene. Its chemical formula is C7H8. It has a sweet, pungent and benzene-like smell. It is used as a precursor to benzene, for nitration, oxidation and solvent. It is generally used for industrial purpose. Its isomers are shown below;

III. **Polyethylene glycol**: Also known as polyethylene oxide (PEO) or polyoxyethylene (POE) is a polyether with many applications from medicine to industrial purpose. Its chemical formula is C2nH4n+20n+1, has a density of 1.12g/cm3 and a molar mass 44.05n + 18.02g/mol. It is also considered biologically safe and inert. According to chemindustry.ru Polyethylene glycol (PEG) is produced by the interaction of ethylene oxide with water or ethylene glycol oligomers. The structural formula of PEG is shown below; It can be used to preserve objects that have been salvaged from underwater, in the medical sector it can be used as an excipient for pharmaceutical products, as a binder in the preparation of technical ceramics in the industry.

IV. **Triethanolamine:** Triethanolamine also known as Trolamine is a viscous organic compound that is a triol and also a tertiary amine. Its chemical formula isC6H15NO3 with density of 1.124g/mol-1 and a boiling and melting point of 335.40c and 21.60c respectively. It is a colorless compound though samples may appear yellow because of impurities. Triethanolamine is produced from the reaction of ethylene oxide with aqueous ammonia. It is primarily used in making surfactants such as for emulsifier and can also be used in cement production, cosmetics and medicine.

Table 3.3 Showing the Properties of demulsifiers (triethanolamine and Polyethylene glycol)

PROPERTIES	**POLYETHYLENE GLYCOL**	**TRIETHANOLAMINE**
Molecular formula	$C_{2n}H_{4n}+2O_{n+1}$	$C_6H_{15}NO_3$
Density	1.12g/cm^3	1.13g/cm^3
Boiling point	250^{0}C	360^{0}C
Physical properties	Clear to white semi solid	Colorless liquid
Melting point	Softening point (-65^{0} to -50^{0}C)	21.2^{0}C

3.4 PREPARATION OF EMULSION

The crude oil used for this experiment was measured with a measuring cylinder and poured into the centrifuge tube and spun for a regulation time of 2mins with a manual centrifuge after which we confirmed that the crude was an emulsion so formation of emulsion was not needed as the crude gotten was an emulsion itself.

3.5 DEMULSIFIER PREPARATION

In the course of this research, the use of triethanolamine and polyethylene glycol were used in the laboratory. The chemicals are measured with a syringe or pipette to get the correct dosage needed for the experiment and was transferred or placed into a beaker during the experiment.

3.6 DEMULSIFICATION PROCEDURES

In this study, the use of the bottle test technique was applied to carry out the demulsification process. The use of a 15 ml cylinder was used during the process as follows:

1. The emulsion sample was added to the centrifuge tube
2. A dosage of solvent (toluene) was added to the centrifuge tubes
3. The tubes were agitated by shaking for some time by hand and set to spin for a given time
4. The required dosage of demulsifier was added to initiate demulsification
5. The tubes were agitated again at room temperature and set to spin for a given time.
6. The amount of water separation was recorded or measured in time-2, 4, 6, 8, 10 minutes.
7. The steps are carried out for different dosages of 0.2, 0.4, 0.6, 0.8, and 1.0 mls.
8. The same procedures were repeated on the two chemical demulsifiers

3.7 SAFETY PRECAUTIONS

During the course of this experiment, some safety measures were taken which are;

A. Errors due to parallax were avoided when taking the readings/values
B. A proper dosage of demulsifier were taken to avoid un-resolved emulsion
C. When shaking the centrifuge tube it was done below eye level to avoid contact with the eye and also oil spillage.
D. Proper PPE was provided to be worn during the course of the experiment
E. Made use of measuring cylinder to avoid splashing of crude oil

4.0 RESULTS AND DISCUSSION

From the experiments carried out, the test results of the demulsification process are presented in the tables below. Tables 4.11 to 4.15 displays the volume of water separated from 2mins to 10mins, when Polyethylene glycol and triethanolamine were added.

Table 4.1 Result of demulsification process for 0.2 ml demulsifier dose

Demulsifier	Time (mins)				
	2	4	6	8	10
Triethanolamine separated water (ml)	0.9	1.0	1.1	1.1	1.1
Polyethylene glycol separated water (ml)	1.0	1.1	1.1	1.1	1.1

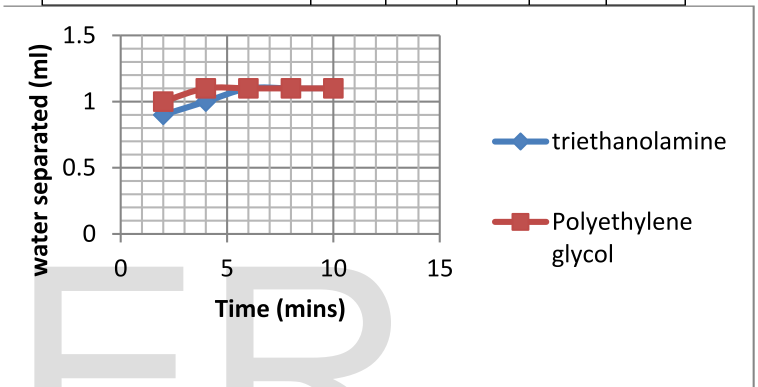

Fig 4.1 Plot of water separation in 0.2 ml demulsifier dose

Table 4.2 Result of demulsification process for 0.4 ml demulsifier dose

Demulsifier	Time (mins)				
	2	4	6	8	10
Triethanolamine separated water (ml)	1.4	1.45	1.45	1.45	1.45
Polyethylene glycol separated water (ml)	1.4	1.4	1.4	1.4	1.4

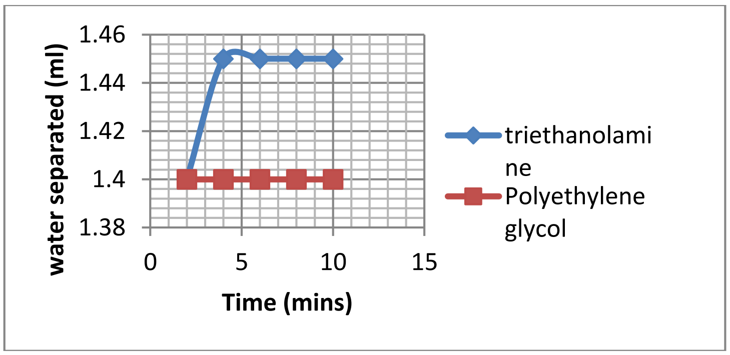

Fig 4.2 Plot of water separated in 0.4 demulsifier dose

Table 4.3 Result of demulsification process for 0.6 ml demulsifier dose

DEMULSIFIER	TIME (MINS)				
	2	4	6	8	10
Triethanolamine separated water (ml)	1.6	1.65	1.7	1.7	1.7
Polyethylene glycol separated water (ml)	1.6	1.65	1.7	1.7	1.7

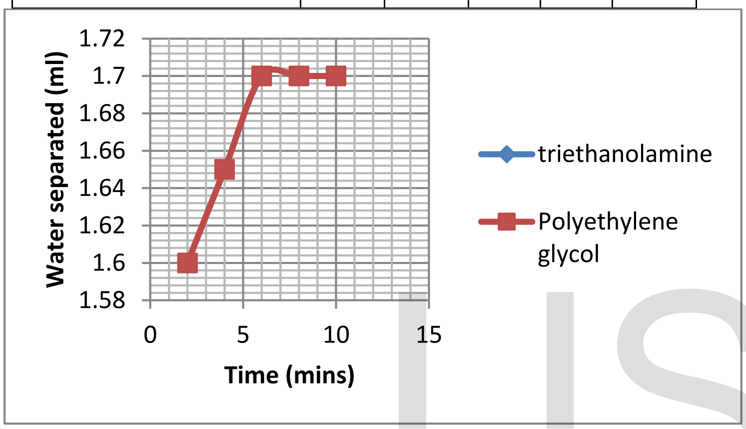

Fig 4.3 Plot of water separated in 0.6 demulsifier dose

Table 4.4 Result of demulsification process for 0.8 ml demulsifier dose

DEMULSIFIER	TIME (MINS)				
	2	4	6	8	10
Triethanolamine separated water (ml)	1.8	1.9	1.95	1.95	1.95
Polyethylene glycol separated water (ml)	1.9	1.95	2.0	2.0	2.0

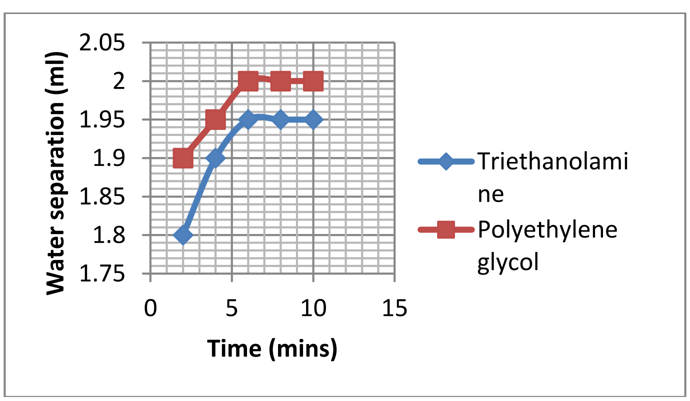

Fig 4.4 Plot of water separated in 0.8 demulsifier dose

Table 4.5 Result of demulsification process for 1.0 ml demulsifier dose

DEMULSIFIER	TIME (MINS)				
	2	4	6	8	10
Triethanolamine separated water (ml)	2.1	2.2	2.2	2.2	2.2
Polyethylene glycol separated water (ml)	2.1	2.2	2.2	2.2	2.2

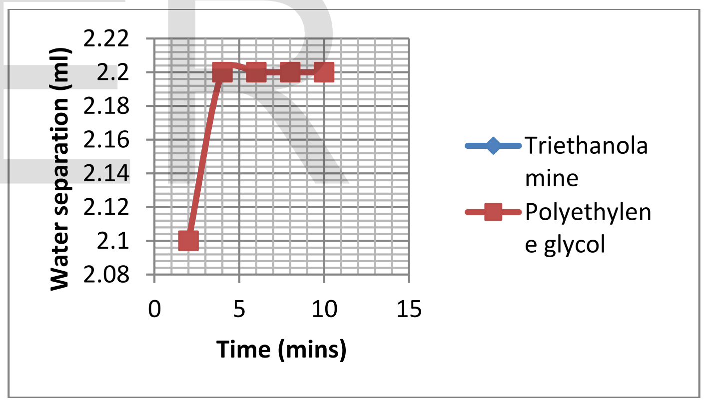

Fig 4.5 Plot of water separated in 1.0 demulsifier dose.

4.1 DISCUSSION OF RESULT

The results gotten from the experiment shows that polyethylene glycol and triethanolamine are almost similar in terms of separating water in an emulsion. It was observed that at demulsifier dose of 0.6 and 1.0 ml, the volume of water separated was the same for both demulsifiers at the different time intervals which they were conducted but taking note of the first addition dose of demulsifier it was noted that polyethylene glycol separated water faster than triethanolamine as it took till 6mins for triethanolamine to separate the same volume of water polyethylene glycol did at an interval of 4mins. It was also noticed that at a dose of 0.4 ml triethanolamine did separate water faster than polyethylene glycol but from the general results it was observed that polyethylene glycol

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separated water from the emulsion better and faster than triethanolamine. The interface quality of polyethylene glycol as a demulsifier was far better than the interface quality obtained by the use of triethanolamine. Also putting into consideration the cost of both demulsifiers, polyethylene glycol is less expensive than triethanolamine.

The use of polyethylene glycol has more advantage in areas such as better separation performance, better interface quality and also less expensive to triethanolamine which are some areas of interest for the oil industry as well as the production engineers producing the crude oil. Therefore optimal crude recovery having similar properties sampled from an emulsion, the best option of demulsifier to be used is polyethylene glycol based on the highlighted result

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

According to the results obtained from the experimental work, observations of the two demulsifier performance (polyethylene glycol and triethanolamine), it can be concluded that, there is an assured better interface quality when using polyethylene glycol as a demulsifier than using triethanolamine, also a better separation performance is gotten from the utilization of polyethylene glycol than that of triethanolamine, also water will separate clearly when using polyethylene glycol and a faster rate of separation is also achieved when using polyethylene glycol as a demulsifier.

5.2 RECOMMENDATION

i. Further research work should be carried out using a Seta centrifuge to apply different rpm in order to enhance the study between the two demulsifiers used.
ii. Further research work should be carried out attempting to compare more demulsifiers with the ones used in this study.
iii. The use of crude oil gotten from different locations should be carried out in this study to enhance and improve the accuracy of the best demulsifier to be used.
iv. Finally, it is recommended that polyethylene glycol be used in the separation of water-in-oil emulsion as a demulsifier in crude oil with same properties of the sample used in this study.

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