EXPERIMENTAL ANALYSIS OF CHEMICAL DE-EMULSIFICATION USING POLYMERIZATION AND SULFONATION METHODS ON NIGER DELTA CRUDE OIL

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ABSTRACT: *This technical paper evaluates the effects of salt concentrations and P^H on water separation efficiency. The laboratory measurements were carried out on chemical de-emulsification using polymerization and sulfonation methods on the Niger Delta crude oil. Chemical de-emulsification was then carried out at the temperature of $65^O C$, using different salt concentrations for 120 minutes. And the results depicts that water separation increases with decrease in salt concentration but increases with the PH of the solution. Also, Heavy Alkyl Benzene Sulfonated (HAS) and Linear Alkyl Benzene Sulfonated (LAS) gave 90% and 88.3% of water separation respectively. PPA prepared by polymerization gave 75%. This shows that HAS is the best followed by LAS while PPA is the least in terms of water separation efficiency.*

KEYWORDS: Salt Concentrations, P^H, Separation Efficiency, De-emulsification, Polymerization, Sulfonation.

INTRODUCTION

In order to minimize the production problems related with crude oil emulsions and environmental concerns, petroleum operators need to prevent emulsion formation or to break it (Gafonova, 2000). The treatment of water-in-crude oil emulsions involves the application of mechanical, thermal, electrical, and chemical processes(Grace, 1992). An emulsion is usually defined as a system in which one liquid is relatively distributed or dispersed in the form of droplets, in other substantially immiscible liquids. The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients introduce sufficiently high mechanical energy input (shear forces) to disperse water as droplets in the oil phase. The dispersed phase is sometimes referred to as the internal phase, and the continuous phase as the external phase (Aske, 2002). In the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase called water-in-oil emulsion (W/O). Conversely, if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion. In addition to the usual emulsion types, multiple emulsions for instance, water droplets dispersed in oil droplets that are in turn dispersed in a continuous water phase (W/O/W) can occur (Paul, 2001). Crude oil is found in the reservoir in association with gas and saline formation water. The number of wells, now co-producing water with crude oil is steadily increasing, these immiscible fluids are readily emulsified by the simultaneous action of pressure drop at the well head (Bhattacharyya, 1992).

De-emulsification or emulsion breaking of water-in-crude oil emulsion is carried out by using either four methods such as mechanical, thermal, chemical and electrical Gafonova, 2000. The

knowledge of the properties and characteristics of the emulsion and the mechanisms that are taking place during coalescence of water droplets are required for fast separation (Ese et al., 2006). Chemical de-emulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and it involves the use of chemical additives (de-emulsifiers) to accelerate the emulsion breaking process. The stability of emulsions is largely affected by the nature of the interface/film and surfactant adsorption mechanisms. The most common method of de-emulsification in both oil-field and refinery application is the combination of heat and application of chemical design to neutralize and eliminate the effects of emulsifying agents (Grace, 1992).

The method of determining relative emulsion stability for lab-scale is the simple bottle test. The bottle test is an empirical test in which varying amounts of potential de-emulsifiers are added into a series of tubes or bottles containing sub sample of an emulsion to be broken. After some specific time, the extent of phase separation and appearance of the interface separating the phases are noted (Auflem,2002).

Chemical de-emulsification is a dynamic process since it is a phenomenon that occurs under non-equilibrium conditions. This de-emulsification activity promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity. Since the stability of emulsions can be traced to the presence of surfactant films at the water/oil interface, the rupture of the thin film separating droplets in a water-in-oil emulsion is affected primarily by de-emulsifier. The role of the de-emulsifier is the suppression of the interfacial tension gradient in addition to the lowering of interfacial viscosity, thus causing accelerated film drainage and coalescence (Fiocco, 1999). Different types of de-emulsifiers will give different ways in de-emulsification process. Knowledge of formation and stability of crude oil emulsions, types of de-emulsifiers, de-emulsification mechanisms are very important since it can be useful in the de-emulsification process of crude oil emulsions. Thus, it is frequently observed in studies of parameters that can affect the formation of stability of the crude oil emulsion. P^H is one of the parameters that are being identified to affect de-emulsifiers performance.

The oil-in-water emulsions are preferential at low pH value ranging between 4 to 6, while water-in-oil emulsions are favored at high pH values that are between pH 8 to 10. Tambe and Sharman, 1993 showed that the stability of oil-in-water emulsion formed increased as pH was increased from 4 to 6, but further increasing in pH, from 6 to 8 and finally 10 resulted in formation of relatively less stable oil-in-water emulsions and more stable water-in-oil emulsions. Dodd, 1954 concluded that the de-emulsifiers that are soluble in both phases are effective in breaking crude oil emulsions, provided that very small amounts of hydrochloric or Sulfuric acid are also added. He suggested the use of Phenol and Sulfuric acid. Salager, 1990 showed that, the most effective mechanism for destabilization of an (O/W) or (W/O) emulsion is removal of the surfactant from the water –oil interface by trapping of the former in a micro emulsion. He also pointed out that, the physical and chemical phenomena involved in dehydration processes can be interpreted by simulating both the surfactant which occurs naturally in the crude oil and the addition of a chemical de-emulsifiers, to produce extremely unstable emulsions. Sjoblom et al., 1990 investigated two synthetic (W/O) emulsion model systems and real crude oil emulsions. They made a qualitative comparison in describing the interaction between de-emulsifiers and these model interfaces. Staiss et al., 1991 presented a new emulsion breaker (de-emulsifier), generally polyester amines. Their advantages

over classic de-emulsifiers are more complete migration to the interface, improved emulsion breaking and coalescence, improved water quality and partial corrosion inhibition. They also observed that the advantages of the combination of the new de-emulsifiers with classic emulsion breakers. Aamir, 1998 showed that the mixture of phenol and sulfonic acid was the best chemical additive used to separate water from the crude oils. Hanapi, 2006 investigated that the combination of oil soluble de-emulsifiers and water-soluble de-emulsifiers produced great result in water separation. He also observed that the formulation de-emulsifiers is better than other commercial de-emulsifier.

MATERIALS/METHODOLOGY

This is a laboratory measurements on de-emulsification using polymerization and sulfonation methods on Nigerian crude oil with the physical properties as shown in table1 below.

Table 1: Physical Properties of the Niger Delta crude oil

Properties	Crude Oil Data
Sp.Gr. at 15.6^{o}C	0.8849
API	28.4
Salt content (%wt.)	0.0006
Water and Sediment content (%vol.)	0.05
Asphaltene (%wt.)	2.22
Ash content (%wt.)	0.0151
Sulfur content (%wt.)	2.1
Viscosity (cp) at 20°C	50
Conductivity (mS)	0

Apparatus Used in Experiments

The equipment used were: Water bath with temperature controller type (Haak-G and Haak-D) made in Germany, Water bath type (Gerhardt Bonn EV2) connects with thermocouple, Batch reactor with stirrer, Electrical mixer with standard turbine impeller type (RL10 M 24684). The mixer calibrated using Dual Digital Tachometer (DT-2268) made in Germany, Electronic balance type (Ntrols mod. Mark 2200) with ± 0.05g accuracy, Digital pH meter type (90 Metrohm AG CH -9100 Herisau) with accuracy (± 0.01), Conductivity meter type (YK-43CD),Clock timer, Thermometer, Cylinders (10 ml) and Beakers (100 ml), Separator funnel, Burette,
Two types of de-emulsifiers were used in the laboratory measurements and they are:
1. PAA prepared by polymerization method.
2. LAS and HAS prepared by Sulfonation method.

Table 2: Properties of LAB and HAB (ARADET Company, Iraq).

Substance	Molecular Weight	Density at 20°C	Viscosity at 20 ^{o}C	Flash point ^{o}C
Linear Alkyl benzene LAB	242	0.8573	7.7	145
Heavy Alkyl benzene HAB	—	0.8825	95	188

Emulsion Preparation
In this research, the brine solution was used in preparing the emulsion system. The brine solution was prepared by dissolving 3gm NaCl in 100 ml water in order to obtain the required salinity similar to crude oil field. The emulsion was prepared by adding water 30% vol. (3% wt. NaCl) to the crude oil at room temperature. The de-emulsification was carried out by using a mixer at a speed of 5000 rpm for 60 minutes to until a stable emulsion was obtained.

Chemical De-emulsification Method (Bottle test)
The de-emulsification tests were performed on emulsion and the de-emulsifiers were then tested by using bottle test method (Lissant, 1983).The purpose of this testing process is to test the effectiveness of de-emulsifiers in breaking the Niger Delta crude oil as per the API procedures stated below:

Three beakers of capacity 100ml each, was filled with the (W/O) emulsion samples, de-emulsifier or chemical compound was added in different concentrations (10-80)ppm to the contents of the beakers. A series of three condensers were joined with water bath. The water was pumped from the reservoir tank at 65 ^{o}C into condensers, at the same time the contents of the beakers were added to the condensers to separate water from crude oil emulsion for 120 minutes.

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Polymerization of Acrylamide
Polymerization of acrylamide takes place in distilled water. The acrylamide monomer and a small amount of the initiator (Persulfate Potassium) at 70°C and 15 minutes reacted to form the polymer. This corresponds to the use of acryl amide as a water thickener, although the solution becomes dense (Robert A, 1999).

Sulfonation of Alkylbenzene
It is required to sulfonate alkyl benzene using sulfuric acid (H_2SO_4 conc. 95-98% vol.) as sulfonating agent to produce sodium alyklbenzene sulfonate which is the pave for production of solid detergent (De Groot, 1991). The procedure of preparation is: 195 gm of sulfuric acid (conc.

98% vol.) was added to 130 gm alkyl benzene with continuous mixing. Water bath was used to control the heat of sulfonation conversion and the temperature maintained at 55ºC, the time of reaction was one hour. Distilled water was added carefully while mixing so that the temperature should not exceed 60 ºC. The reaction mixture was placed in separating funnel for two hours. The mixture then separated into two layers. The upper was the sulfonating layer while the lower is the spent acid layer. The sulfonated product is neutralized with NaOH (5N) solution under control temperature (55ºC).

RESULTS AND DISCUSSION

This is about the water separation efficiency (for breaking the crude oil emulsion) and the influence of operating variables studied on the pH of aqueous phase and salt concentrations in (W/O) emulsion. The results are shown in tables 3 and, plotted in figures 1 and 2.

Effect of Salt content on Water Separation
Figure1 below shows the effect of salt content on water separation efficiency using prepared de-emulsifiers. it can be observed that the separation of water efficiency increases with decreased salt concentration for the three types of prepared de-emulsifiers, where maximum water separation efficiencies were 90%, 88.3% and 75% for HAS, LAS and PAA respectively. The reason of decreasing salt concentration in the oil phase with increasing of water separation efficiency, attributed to the chemical activity of hydrophilic and hydrophobic group present in the de-emulsifier molecular weight.

Table3: Effect of salt concentrations on water separation efficiency at 120 minutes for the three types of de-emulsifiers (PAA, LAS and HAS), Temperature(65ºC) and water content 30%vol. (3%wt. NaCl).

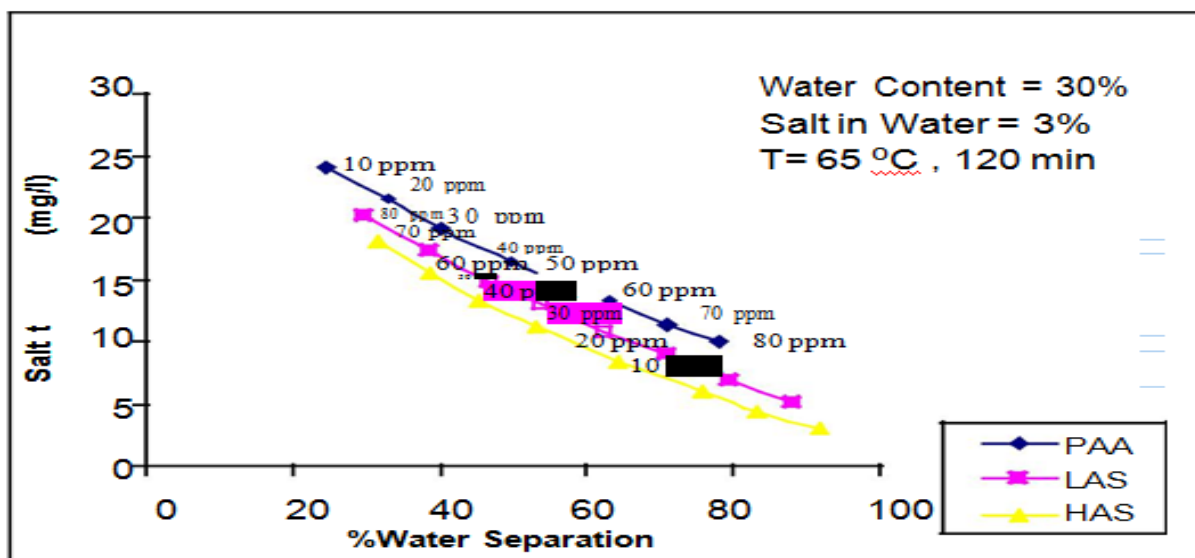| Salt Concentrations (ppm)			Separation time 120 minutes		
			Water separation (%)		
PAA	LAS	HAS	PAA	LAS	HAS
21	20.2	20.1	32.7	35.6	35.7
16.8	16.4	11.6	46.9	48.2	64.1
13.9	13.7	11.4	56.5	57.3	64.5
12.3	11.9	11.3	61.8	63.7	65.3
11.1	11.1	10.5	65.7	65.9	68
9.8	8.8	7.5	70.1	73.5	78
8.7	6.9	4.7	73.8	77.1	87.1
8.4	4.4	3.9	75	88.3	90

Figure 1: Effect of Salt Concentrations on Water Separation Efficiency Using PAA, LAS and HAS

Effect of pH on Water Separation Efficiency
The (W/O) emulsions are stabilized by absorbed film of organic acids and bases at a given
concentration. The films are strongly influenced by adding the acids and bases. Consequently, the
physical properties of the interfacial film were also affected (Strassner, 1968 and Einar, 1989). It
can be observed from figure2 below that water separation efficiency increases with increasing of
pH up to 90% was obtained at pH of 7.6 for HAS. This behavior is similar to the trend obtained
by Aamir, 1998. It can easily be seen from the figure 2 that the increasing of water separation
causes an increase in pH of the solution.

Table4: Effect of pH on water separation efficiency at 120minutes for the given de-emulsifiers
(PAA, LAS and HAS), Temperature 65°C, and water content 30%vol. (3%wt. NaCl)

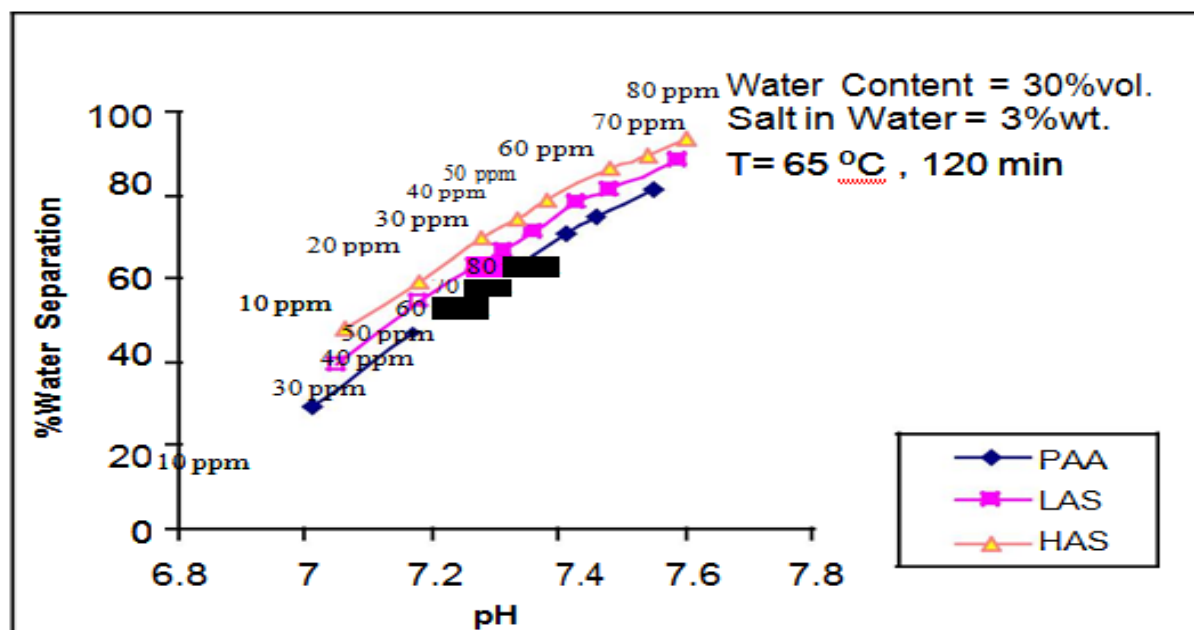| pH | | | Separation time 120 minutes | | |
| | | | Water separation (%) | | |
PAA	LAS	HAS	PAA	LAS	HAS
7.01	7.06	7.06	32.7	35.6	35.7
7.17	7.18	7.18	46.9	48.2	64.1
7.26	7.27	7.28	56.5	57.3	64.5
7.32	7.34	7.35	61.8	63.3	65.3
7.36	7.36	7.38	65.7	65.9	68
7.41	7.43	7.48	70.1	73.5	78
7.44	7.48	7.56	73.8	77.1	87.1
7.46	7.59	7.60	75	88.3	90

Figure 2: Effect of pH on Water Separation Efficiency Using PAA, LAS, and HAS

CONCLUSIONS

The following conclusions could be obtained:
Water separation efficiency increases with decrease in salt concentration.
Water separation efficiency causes an increase in P^H of the solution.
Chemical de-emulsification by Sulfonation gave a higher separation efficiency for both Linear Akyl Benzene (LAB) and Heavy Alkyl Benzene (HAB) than the Polymerization method (PAA).

CONTRIBUTION TO KNOWLEDGE

Sulfonation method of de-emulsification to be recommended when de-emulsifying Niger Delta crude oil than the Polymerization method.

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