

The Effects of Molecular Weight of Polyester Based De-Emulsifiers on the De-Emulsification Process of Crude Oil Emulsions.

¹Efeovbokhan, Vincent, Hymore, ²Fredrick Kofi ³Ayoola Ayodeji, ⁴Adesanya Olarewaju

^{1,2,3,4}Chemical Engineering Department, Covenant University, Km 10 Idi-Iroko Road, Canaan Land Ota

Abstract

The effect of molecular weight of polyester based de-emulsifiers on the de-emulsification of Nigerian crude has been carried out. It was observed that initially, as the molecular weight of the polyesters (de-emulsifiers) increased, there was a corresponding fourth order polynomial increase in its performance when they were used to screen the Nigerian Crude Oil Emulsion (NCOE). It was further observed that beyond a molecular weight value of 7500g/mol it tended towards an asymptote at 30.6% performance. Beyond this point, further increase in the molecular weight of the de-emulsifier did not produce any significant increase in performance on the de-emulsification process of the NCOE. The performance of the de-emulsifiers also increases as the time of de-emulsification increases. For all the de-emulsifier samples, performance was highest after 10 minutes.

Key Words: De-emulsifiers, Molecular weight, de-emulsification, performance and Nigerian crude.

Date of Submission: 12,February 2013



Date of Publication:26,February 2013

1. INTRODUCTION:

Emulsions of crude oil and water can be encountered at many stages during drilling, production, transportation and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation systems and refineries [1]. According to Grace [2] emulsions of oil and water are one of many problems directly associated with the petroleum industry, both oil-field production and refinery environments. The water and oil phases are co-produced during oil production and transportation. The dispersion of water droplets in oil or oil droplets in water will be formed by sufficient mixing energy from the refinery [3]. Crude oil is a complex fluid comprising colloidal particles such as asphaltenes and resins dispersed in a mixture of aliphatic and aromatic solvents. Asphaltenes is the heaviest and most polar fraction in the crude oil and responsible in rising up the variety of nuisances. It is the interfacial active agents in the crude oil such as asphaltenes, resins and naphthenic acid that may accumulate at the water-oil interface and hinder the droplets to separate. Among these components, asphaltenes are believed to be the major causes in stabilizing the emulsion. This is because they tend to adsorb at water-in-crude oil interfaces to form a rigid film surrounding the water droplets and protect the interfacial film from rupturing during droplet-droplet collisions [3]. An emulsifying agent must be present to form stable water-in-crude oil emulsions [4]. Such agents include clay particles, added chemicals or the crude oil components like asphaltenes, waxes, resins and naphthenic acids [4]. The basic physics of water-in-oil emulsification was understood in the surfactant industry, but not in the oil spill industry [5]. In the late 1960's, Berridge and his co-workers were the first to measure several physical properties of emulsions [5]. They described the formation of emulsions due to the asphaltene and resin content of the oil [5]. Mackay and McAuliffe (1988) also stated that the main factors affecting the stability of the emulsion are the presence of substances like crude oil resins, asphaltenes, and natural wax. These components combine with organic and/or inorganic solids producing emulsion-stabilizing films at oil-water interface, and contribute to the formation of stable emulsions [6]. There are four classes of stability which include stable, meso-stable, unstable, and entrained water [7]. Generally, the emulsifier will help to prevent water separation from a given w/o emulsion [8]. Demulsification is defined as a process of breaking emulsions with intention to separate water from oil [9]. Emulsion breaking is one of the most complex processes in the oil industry. Breaking of water in crude oil emulsions involves chemical, thermal, electrical, or a combination of these processes depending on the characteristics and properties of the emulsion [10]. Various methods of de-emulsification, like centrifugation, sedimentation, heating, use of dispersants and emulsion breakers have been examined [11]. Amongst these

techniques, heating and centrifugation did not gain much acceptance due to the high cost and energy requirements. The realization that dispersants cannot deal with higher viscosity emulsions, encouraged the investigation of the possible application of emulsion breakers [7]. The addition of chemical de-emulsifiers in small quantities can greatly facilitate oil-water separation [9]. Though, there is no chemicals de-emulsifier that is applicable to break all kind of crude oil emulsion [13]. According to Nordvik et al (1996), the main advantages of using emulsion breakers are: Breaking of such emulsions which also requires introduction of some turbulent energy [14]. The energy requirement is variable and depends upon the type of energy induction and the type of emulsion breaker used [14]. The main objective of the emulsion breaker/de-emulsifier is to displace the naturally occurring emulsifying agents from the oil-water interface [7]. Nordvik et al. (1996) stated that the efficiency of the emulsion breakers depends upon: (a) The efficiency of the product (b) Oil characteristics (c) Environmental conditions (d) Application method (e) Time of application. Emulsion breaking must be attempted at the earliest possible opportunity in the oil spill response process [6]. Lots of different emulsion breakers are available in the market and the choice of the most efficient one is a time consuming and difficult process. For economic and operational reasons, it is necessary to remove water completely from the crude oil emulsion before refining and transporting those [16]. This water (and salt) must be removed from the crude oil prior to refining. If the majority of the water and salt are not removed, the emulsion creates problems in oil field industry. They might increase the cost of production and also transportation, accumulate in the refinery tank age, pipeline corrosion, equipment failure, plugged pipeline and also decrease through put [17]. Locally formulated polyester based de-emulsifiers have been investigated by Efeovbokhan et al and were found very effective in breaking crude oil emulsions [18]. Hence the current investigation is to further establish the optimal molecular weight conditions of these polyesters on the de-emulsification process of Nigerian hydrocarbon crude.

II. Materials And Methods

The sample of crude oil emulsion used for this study was obtained from an oil processing plant in Kwale, Delta state Nigeria. The sample was a stable emulsion gotten from the wellhead of the rig site. The chemicals polypropylene glycol, maleic anhydride and Phosphoric acid used are all of analar grade.

2.1 Experimental Methods

The experimental set up as described by Efeovbokhan et al was employed except that reaction conditions were completely varied as given in table 1 below:

Table 1: Reaction Time and Temperature for each Formulated Sample

Sample	Reaction time(hr)	Reaction temperature (°C)
A1	3	120
A2	5	120
B1	3	183
B2	5	183
C1	3	162
C2	5	162

2.2 De-Emulsifier Screening

The de-emulsifiers were screened using the bottle test method. The bottle test is an empirical test in which varying amounts of potential de-emulsifiers are added into a series of centrifuge tubes containing the sample of the emulsion to be broken. Here, four centrifuge bottles were used for the precise data obtained in the experiment. 10ml each of emulsion samples were measured and 40ppm of de-emulsifier was added to each sample. The sample was then stirred rigorously for 1minute for proper mixing. The bottles were then contacted in a water bath whose temperature was preset to 60°C and then placed in the centrifuge. The centrifuge was set at 1200 rpm at different time intervals. The volume of water expelled from the emulsion system was measured as a function of time for all the de-emulsifier samples.

2.3 Measuring the molecular weight of the prepared de-emulsifier (polyester)

In measuring the molecular weight of the various samples, vapour pressure measurement method was employed. The vapour pressure lowering is measured by the help of a differential manometer. One arm of the manometer was connected to the solution and the other to pure solvent. The manometer liquid should be of low density since the pressure differential expected would be very small. The difference in vapour pressure is

determined directly from the difference in level of the liquid in the two arms. The system was placed in a water bath with the temperature set to 50.5°C. This was to increase the time required to measure the vapour pressure lowering and also the difference in level between the two arms. The relationship between the molecular weights and the vapour pressures is described by the formula below:

$$M_2 = \frac{P^0}{\Delta P} \left(\frac{W_2}{W_1} \right) M_1$$

Where

M_2 and M_1 are the molecular weights of the solute (de-emulsifier) and solvent (PPG) respectively.

W_2 and W_1 are the quantities (g) of the solute and solvent respectively.

P^0 is the vapour pressure of the pure solvent.

ΔP is the difference in vapour pressure of the two liquids.

III. Results and Discussion Of Results

Table 3.1: De-emulsification of Crude Oil Sample using Sample A1

Separation Time (minutes)	Volume of oil emulsion used (mL)	Volume of water separated (mL)	% water separation (performance)
0	10	0	0
2	7.7	2.3	23
4	7.6	2.4	24
6	7.55	2.45	24.5
8	7.5	2.5	25
10	7.45	2.55	25.5

Table 3.2: De-emulsification of Crude oil Sample using Sample A2

Separation Time (minutes)	Volume of oil emulsion used (mL)	Volume of water separated (mL)	% water separation (performance)
0	10	0	0
2	7.7	2.3	23
4	7.65	2.35	23.5
6	7.5	2.5	25
8	7.45	2.55	25.5
10	7.4	2.6	26

Table 3.3: De-emulsification of Crude Oil Sample using Sample A3

Separation Time (minutes)	Volume of oil emulsion used (mL)	Volume of water separated (mL)	% water separation (performance)
0	10	0	0
2	7.5	2.5	25
4	7.45	2.55	25.5
6	7.35	2.65	26.5
8	7.3	2.7	27
10	7.2	2.8	28

Table 3.4: De-emulsification of Crude Oil Sample using Sample A4

Separation Time (minutes)	Volume of oil emulsion used (mL)	Volume of water separated (mL)	% water separation (performance)
0	10	0	0
2	7.1	2.6	26
4	6.95	2.65	26.5
6	6.85	2.75	27.5
8	6.8	2.8	28
10	6.7	2.875	28.75

Table 3.5: De-emulsification of crude oil sample using Sample A5

Separation Time (minutes)	Volume of oil emulsion used (mL)	Volume of water separated (mL)	% water separation (performance)
0	10	0	0
2	7.4	2.6	26
4	7.3	2.7	27
6	7.15	2.85	28.5
8	7.1	2.9	29

10	7.075	2.925	29.25
----	-------	-------	-------

Table 3.6: De-emulsification of Crude oil Sample using Sample A6

Separation Time (minutes)	Volume of oil emulsion used (mL)	Volume of water separated (mL)	% water separation (performance)
0	10	0	0
2	7.3	2.7	27
4	7.2	2.8	28
6	7.05	2.95	29.5
8	7.075	2.925	29.25
10	6.95	3.05	30.5

Table 3.7: Variation of Molecular Weight with Performance after 10 Minutes

Sample of De-emulsifier	Molecular weight M_2 (g/gmol)	Performance (%)
A1	1346.723	25.5
A2	1484.244	26
A3	1860.647	28
A4	2485.61	28.75
A5	3739.099	29.25
A6	7492.442	30.5

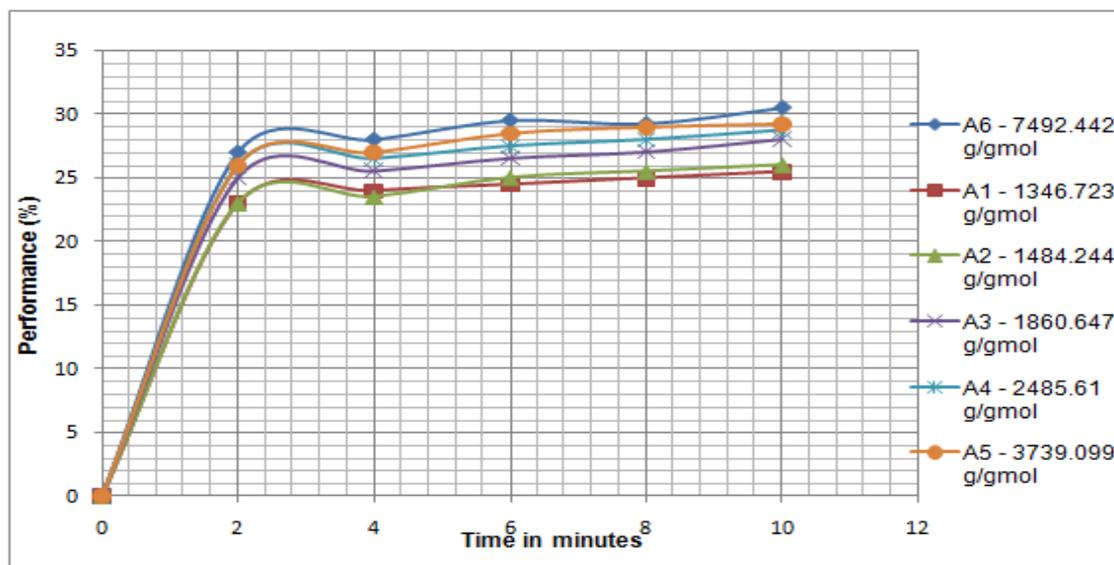
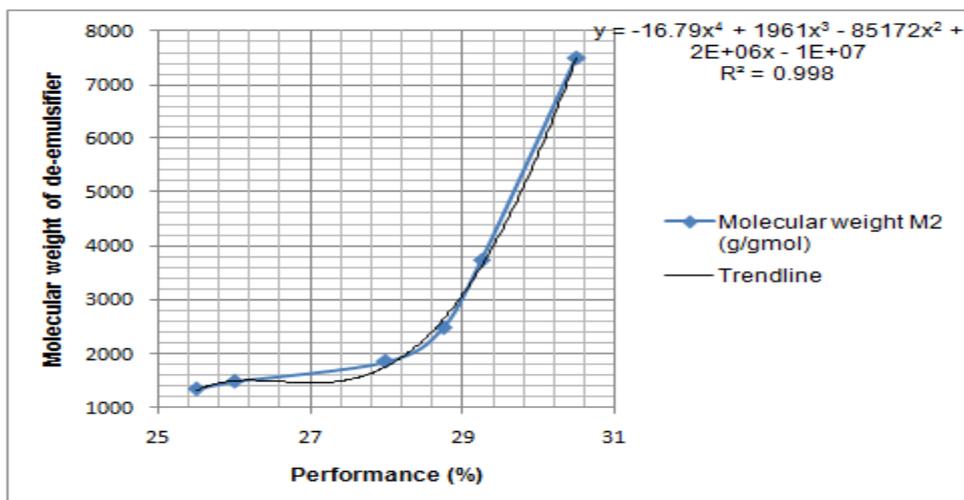


Fig 3.1: Effect of Molecular Weight and Separation Time on Emulsion Treatment**Fig. 3.2: Variation of Molecular Weight of Formulated De-emulsifiers with Performance**

Each sample of the formulated de-emulsifier was used to de-emulsify the crude oil emulsion at 60°C and at constant concentration of 40 ppm. The volume of water separated from the emulsion system at the given operating conditions, was used as a measure of the performance of the de-emulsifier samples. Meaning that the higher the percentage of water separation, the more effective the de-emulsifier used in separating that emulsion system. The performance of the de-emulsifiers increased steadily within the time allowed for de-emulsification. The highest performance was recorded for each sample of de-emulsifiers at 10 minutes

3.1 Effect of Molecular Weight of De-Emulsifiers on Performance

Tables 3.1–3.7 show the different samples of de-emulsifiers used to examine the effects of their molecular weights on rate of separation of the crude oil emulsion system. It was generally observed that as the molecular weight of de-emulsifier increased, their performance also increased. From figure 3.1, it was observed that sample A₆ with molecular weight of 7492g/gmol gave the highest performance of about 31% while sample A₁ with the least molecular weight value of about 1347 g/gmol gave the least performance of 26%. Fig. 3.2 illustrates the effect of molecular weight on the performance of the formulated de-emulsifiers. The figure shows that for a given separation time, concentration and de-emulsification temperature, there was a polynomial relationship between performance of de-emulsifier and its corresponding molecular weight. The polynomial is of the 4th order and has a correlation coefficient of 0.998. The yield of water from the separation process increased as the molecular weight increased. However, it was observed that as the molecular weight increased, the ascending curve tends to form an asymptote. This result is indicative of the fact that further increase of molecular weight beyond a certain value of 7500g/gmol would not have any remarkable effect on its performance.

IV .Conclusion

The de-emulsification performance of a Nigerian crude oil emulsion using formulated polyesters (or de-emulsifiers) reveals that:

- As the molecular weight of the de-emulsifier increases there was a corresponding increase in the de-emulsifier performance.
- The performance of the de-emulsifiers also increases with the time of de-emulsification.
- A fourth order polynomial relationship between the molecular weight of the de-emulsifiers and its performance with a correlation co-efficient of 0.998 was obtained.
- At molecular mass greater than 7,500 g/mol, performance of the de-emulsifier is almost independent of the molecular weight.

References:

- [1] Langevin, D, Poteau, S, Hénaut, I, Argillier, J.F. 2004. Crude Oil Emulsion Properties and their Application to Heavy Oil Transportation. *Oil & Gas Science and Technology* 59, 5, 511-521
- [2] Sjöblom, J. (2001) *Encyclopedic Handbook of Emulsion Technology*, Marcel Dekker, New York.
- [3] Ahmed, N.S., Nassar, A.M., Zaki, N.N. and Gharieb, K.H (1999) Stability and Rheology of Heavy Crude Oil-in-Water Emulsion Stabilized by an Anionic-Nonionic Surfactant Mixture. *Petroleum Science and Technology*, **17**, 553-576.
- [4] Sjöblom, J., Aske, N., Auflem, I. H., Brandal, Ø., Havre, T. E., Saether, Ø, Westvik, A., Johnsen, E. E., Kallevik, H., 2002. Our current understanding of water in crude oil emulsions. Recent characterization techniques and high pressure performance. *Advances in Colloid and Interface Science* 100-102, 399-473.
- [5] Fingas, M. and Fieldhouse, B., 2003. Studies of formation process of water-in-oil emulsions. *Marine pollution bulletin* 47, 9-12, 369-396.
- [6] Cormack, D., 1999. Response to marine oil pollution – review and assessment. Dordrecht, The Netherlands.
- [7] Fingas, M., Fieldhouse, B., 2004. Formation of water in oil emulsions and application to oil spill modeling. *Journal of Hazardous Materials* 107, 37-50.
- [8] Ghannam, M.T. 2005. Water-in-crude oil emulsion stability investigation. *Petroleum Science and Technology*. **23**: 649-667
- [9] Fan, Y., Simon, S. and Sjöblom, J. 2009. Chemical destabilization of crude oil emulsion: Effect of nonionic surfactant as emulsion inhibitors. *Energy & Fuel*.
- [10] Mohammed, R. A., Bailey, A. I., Luckham, P. F., Taylor, S. E., 1993. Dewatering of crude oil emulsions. 1. Rheological behaviors of crude oil-water interface. *Colloids and surface* 80, 223-235
- [11] Kim, B. Y., Moon, J. H., Sung, T. H., Yang, S. M., Kim, J. D., 2002. De-emulsification of water in crude oil emulsions by a continuous electrostatic dehydrator. *Separation Science and Technology* 37 (6), 1307-1320.
- [12] Poindexter, M. K., Lindemuth, P. M., 2004. Applied statistics: Crude oil emulsions and De-emulsifiers. *Journal of Dispersion Science & Technology* 25 (3), 311-320
- [13] Alwadani, M.S. 2009. Characterization and rheology of water-in-oil emulsion from deepwater fields. M. Sc. Thesis. Rice University, Texas. U.S.
- [14] Lane, P., 1995. The use of chemicals in oil spill response. Philadelphia, Pennsylvania
- [15] Abdurahman, H. N, Yunus, R. M. and Anwaruddin, H. 2007 Water-in-crude oil emulsions: Its stabilization and demulsification. *Journal of Applied Sciences*. 7 (22): 3512-3517.
- [16] Souleyman, A.I. 2007. *Stability and demulsification of water-in-crude oil emulsions via microwave heating*. Universiti Teknologi Malaysia, Skudai.
- [17] Efevbokhan V.E, Hymore F.K, Akinola, T., 2010. Performance evaluation of formulated de-emulsifier samples and a commercially available sample in the de-emulsification of a Nigerian crude oil emulsion. *American Journal Of Scientific And Industrial Research*. 1.3.629.635

Author Biography



Efevbokhan, Vincent Enontiemonria is both a Lecturer and a researcher in the Department of Chemical Engineering, Covenant University, Ota Nigeria. He had his first and second degrees in Chemical Engineering from the Federal University of Technology, Owerri (Nigeria) and the University of Benin, Benin City (Nigeria) respectively. He is a registered Engineer with the Council for the Regulation of Engineering in Nigeria (COREN) and a corporate member of two professional bodies. Some of the courses he teaches amongst others include Engineering Mathematics, Chemical Engineering Process Analysis, Chemical Reaction Engineering etc. His research interests are in renewable energy, product development and bio-chemical engineering. He has published ten papers in International Journals, one conference paper and featured in a number of exhibitions and fairs to display numerous new products he has developed.