Formulation and Evaluation of Eco-Friendly Water-in-Crude Oil Emulsion Breakers from Cashew Nutshell Liquid

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Abstract In this study Cashew Nut Shell Liquid (CNSL), was extracted from cashew nutshells using n-hexane and modified with Dibromoethane, Ethanolamine (EA), Diethanolamine (DEA) and Triethanolamine (TEA) in a one-pot synthetic pathway. Their emulsion breaking efficiency was investigated. Physicochemical characterization of extracted CNSL was also studied, chemical modifications of the extracted CNSL were confirmed via FTIR analysis. Physicochemical characterization of laboratory formulated seawater and sampled crude oil were performed in-line with ASTM standards. Water-in-crude oil emulsion at different water to crude oil ratios (10:90, 30:70 and 50:50) were simulated, and the performance of the modified CNSL as emulsion breaker were assessed at varying concentrations (10 – 50 ppm) and temperatures (30 ℃, 40 ℃ and 60 ℃) in isopropyl alcohol and toluene respectively for 3 hours using the laboratory bottle testing method. The demulsification ability of all formulated emulsion breakers were compared with that of the control (Phase Treat-12172) under same conditions. Data obtained showed that all formulated emulsion breakers are good demulsifiers, and their efficiency followed the order; $E_o > E_6 > E_5 > E_4 > E_3 > E_2 > E_1$ It was also observed that increase in concentration of emulsion breaker, temperature and water content of the emulsion resulted in corresponding increase in the percentage water separation. The results also showed that isopropyl alcohol is a better solvent system for CNSL and the formulated derivatives, whereas toluene is a better solvent system for the conventional Phase Treat-12172.

Keywords Emulsion breaker, CNSL, water-in-crude oil emulsion, phase treat-12172

1. Introduction

The formulation of stable water-in-crude oil emulsion is always noticed at diverse stages of production and processing of crude oils [1]. The formation of these emulsions is the general consequence of the presence of resins and asphaltenes in the crude oil, which carries out the function of a natural emulsifiers, so also are the wax and solid particles component of crude oil [2-4] All these above-mentioned components can align and form rigid films at the oil/water interface [5-6]. It is paramount to separate water completely from produced crude oil, water-in -crude oil emulsion must be broken for economic and operational reasons. As water in produced crude oil leads to increased cost of pumping, crude oil containing significant amount of emulsified water pressure build-up at the pump head due to high viscosity of emulsion, risk of corrosion of refinery equipment, water dissolved salt can poison catalyst in the downstream processes [7].

The process of breaking breaking down water-in-oil emulsion or oil-in-water emulsion [8]. There are various methods for breaking water-in-crude oil emulsion, which includes: electro-sedimentation, supersonic demulsification, centrifugation and chemical demulsification [9]. Emulsion breaking process is a crucial

industrial process, used solely for removing water and salts from crude oil. When water is dispersed as small droplets in crude oil forming water-in-crude oil emulsion, there are possibilities of salts dissolving in the water droplets in crude oil. And if these impurities are eliminated, they could lead to corrosion and fouling in the heat exchanger and desalting equipment. For proficiency, water content should be less than 0.5–3% after demulsification.

The step-wise processes of demulsification and the role of emulsion of emulsion breakers have been investigated by many researchers [10]. Emulsion breakers decreases the surface elasticity of the interfacial film by creating the film drainage phenomenon, which then leads to the coalescence of the water droplets [11]. It has been proven that molecules with an equal partitioning between the aqueous and the oil phase (Amphophilic molecules) are the best emulsion breakers [12].

Cashew nutshell liquid (CNSL) is a renewable material and an agricultural waste found as thick reddish-brown oil in the interior sponge part of the Cashew nut shell (CNS) from the cashew plant (*Anacardium occidentale*), is cheap and available phenolic liquid characterized by specific gravity, moisture content, iodine value, total volatile content, viscosity, and polymerization hardening time. Which makes it applicable in vast industrial processes [13-14]. Naturally occurring CNSL composes of four major compounds anacardic acid, cardanol, cardol, and 2-methyl cardol. They are monohydric or dihydric phenols with a long C_{15} alkyl side-chain at the meta-position (Figure 1).
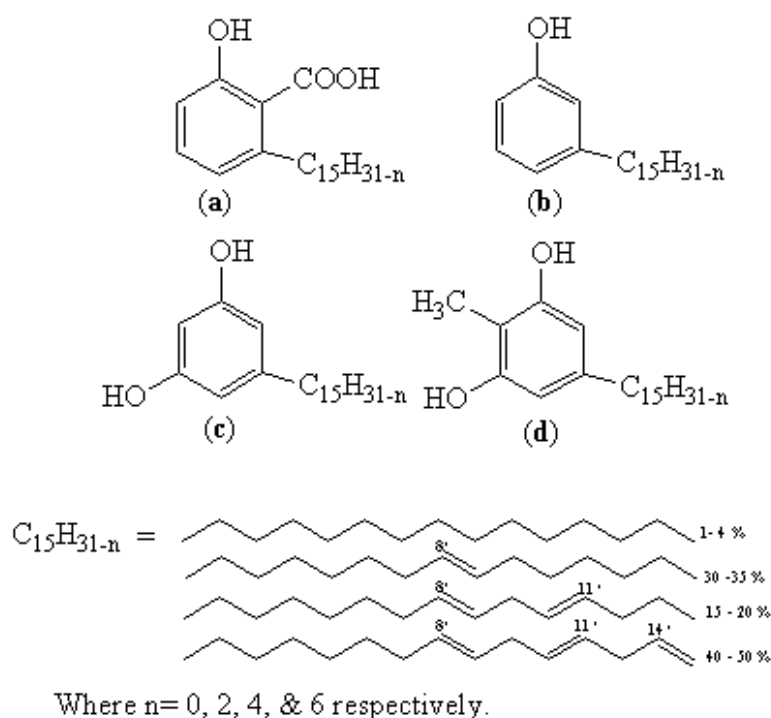

Figure 1: Chemical composition of CNSL: (a) anacardic acid, (b) cardanol, (c) cardol, (d) 2-methylcardol

Structurally, the constituents of CNSL are fitting for application as surface active agents in oilfield operations and other industry-related applications, and they also exhibit peculiar characteristics which makes it useful in numerous applications [15]. The merits of using CNSL for industrial operation such as (as emulsion breakers, pour point depressant *etc*) relative to synthetic materials includes; its low cost, availability, sustainability, and its ecofriendly nature, hence, it is a renewable raw material.

The laboratory bottle test analysis use in evaluation of emulsion breaking capacity of demulsifier, is not an ideal method, but owing to trial and error and the fact that it can be carried out under both static and controlled conditions, hence it remains the only suitable method for the valuation and selection of potential emulsion breaker for a particular well or field [16]. However, this test method is appropriate in determination of treatment temperatures and water separation times that can be applied for designing oilfield operations [17]. The

appropriate temperatures applicable for a laboratory-scale emulsion breaking test falls within the range of 50 to 70 ℃, which reflects the actual field practice temperature [1]. Studies on the impact of solvents, especially aromatic solvents which includes; cymene, toluene, xylene, ethylbenzene, tert-butyl benzene etc, on emulsion firmness, have reveal that aromatic solvents with greater carbon content are more efficient in the breaking of emulsions [18], the few demerits attached to the use of aromatic solvents on emulsion breakers includes; hike in cost, flammability, and toxicity etc. Hence, emulsion breakers applied with non-aromatic solvent would possess great advancement in the science of demulsification [19]. This paper focuses on the evaluation of the emulsion breaking ability of modified CNSL in comparison with that of commercial demulsifier using an aromatic solvent (Toluene) and a non-aromatic solvent (isopropyl alcohol) in the treatment of water-in-crude oil emulsions.

2. Materials and Method
2.1 Materials
2.1.1 Cashew Nut Shell Liquid (CNSL)
Cashew nutshell (CNS) was obtained from a vendor at Anyigba Kogi state, Nigeria. Sample pre-treatment of the CNS was carried out by washing and sun drying to a constant weight. The treated CNS was then crushed using a hydraulic press at the Chemical Engineering laboratory University of Port Harcourt Choba, River State.
2.1.2 Crude oil
Crude oil was obtained from a storage tank at Port Harcourt Refinery Eleme Rivers State, Nigeria. Analysis of the physicochemical properties of the sampled crude oil was carried out at the Quality control laboratory as shown in Table 1.
2.1.3 Seawater
Formulated seawater used for this analysis was synthesized in accordance to the report of Falode *et al.*, [20] with slight modification. NaCl was dissolved in tap water to obtain a salinity related to that of the average Niger-Delta field. Physicochemical characterization of the formulated seawater was carried out at the Quality control laboratory of Port Harcourt Refinery as shown in Table 2.
2.1.4 Chemicals
All chemicals and reagents used in this study were purchased analytical grade from a vendor and no further test or purification was carried out on them. Chemicals and reagents used includes; Sodium hydroxide (BDH, 99%), Potassium hydroxide (BDH, 99%), Sulfamic acid, Ethanolamine (Luba chemie, 98%), Diethanolamine (Luba chemie, 98%) and Triethanolamine (CDH, 98%), Dibromoethane (Luba chemie, 99%), Hydrochloric acid, Phenolphthalein, Ethanol (JHD, 99%), Chloroform, Wij's solution, Sodium thiosulphate, Potassium chromate, silver nitrate ($AgNO_3$) and n-Hexane (JHD, 99%).
2.1.5 Emulsion Breakers
 In this study, modified CNSL (EA modified (E_1 & E_2), DEA modified (E_3 & E_4), TEA modified (E_5 & E_6) and Dibromoethane modified (E_0)) and Commercial demulsifier Phase treat (PT) 12172 (used in most SPDC flow stations) were applied.

2.2 Methods
2.2.1 Extraction of CNSL
Crushed CNS (1000 g) was served into a Soxhlet extractor thimble and refluxed at 65-75 ℃ with n-hexane solvent. The extract was then subjected to solvent recovered using Rotary evaporator at 40 ℃ and the crude CNSL was analyzed for its physicochemical characterization as shown in Table 3.
2.2.2 Coupling of CSNL (E_0)
Two molecules of CNSL were coupled together using dibromoethane as the cross-linking agent via Williamson reaction as reported by Puchot [21]. To a pre-weighed 50 ml round bottom flask, CNSL (0.058 mol; 20.0 ml), KOH (0.058 mol; 3.23 g) and dibromoethane (0.029 mol; 2.49 ml) were introduced, and refluxed in an oil bath at 120 ℃. The reaction process was checked through the water volume collected in the dean stark trap (the reaction came to completion when water volume in the dean and stark trap is constant). The reaction mixture was filtered to remove the crystals of KBr formed and filtrate (the oil) allowed to stand for 24 hours in a desiccator (Figure 2).
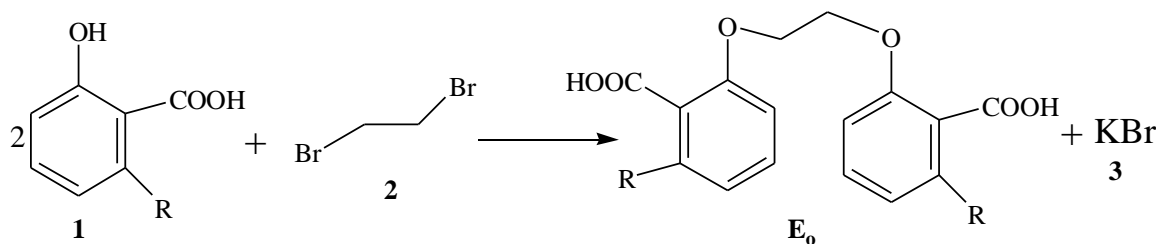
1 = CNSL, 2 = Dibromoethane, 3 = Potassium bromide & E_o = Dibromoethane CNSL derivative

Figure 2: Reaction pathway for coupling of CNSL

2.2.3 Modification with Ethanolamine (E_1 & E_2)

Coupled CNSL (E_o) was subjected to modification via an esterification reaction with ethanolamine, the reaction procedure adopted is same as that reported by Victor-oji *et al.,* [22]. E_o and EA in a (1;1 & 1:2 mol) molar ratios for E_1 and E_2 respectively were introduced into a pre-weighed 150 ml round bottom flask and refluxed in an oil bath to a temperature of 120 ℃. At temperature 120 ℃ an heterogeneous catalyst (sulfamic acid) was then added and refluxing continued till the reaction was brought to an end. The reaction progress was monitored by measuring the volume water trapped in the dean stark trap. The product was filtered and then placed in a desiccator for 24 hours to remove all traced water molecule (Figure 3).

2.2.4 Modification with Diethanolamine (E_3 and E_4)

The reaction procedure is same as that of ethanolamine modification. From E_o and DEA in a (1;1 & 1:2 mol) molar ratios, E_3 and E_4 were produced respectively (Figure 3).

2.2.5 Modification with Diethanolamine (E_5 and E_6)

The reaction procedure is same as that of ethanolamine modification. From E_o and TEA in a (1;1 & 1:2 mol) molar ratios, E_5 and E_6 were produced respectively (Figure 3).

$R' = C_{15}H_{31-n}$
$R = R_1 = H$; ethanolamine
$R = H$ & $R_1 = C_2H_5OH$; diethanolamine
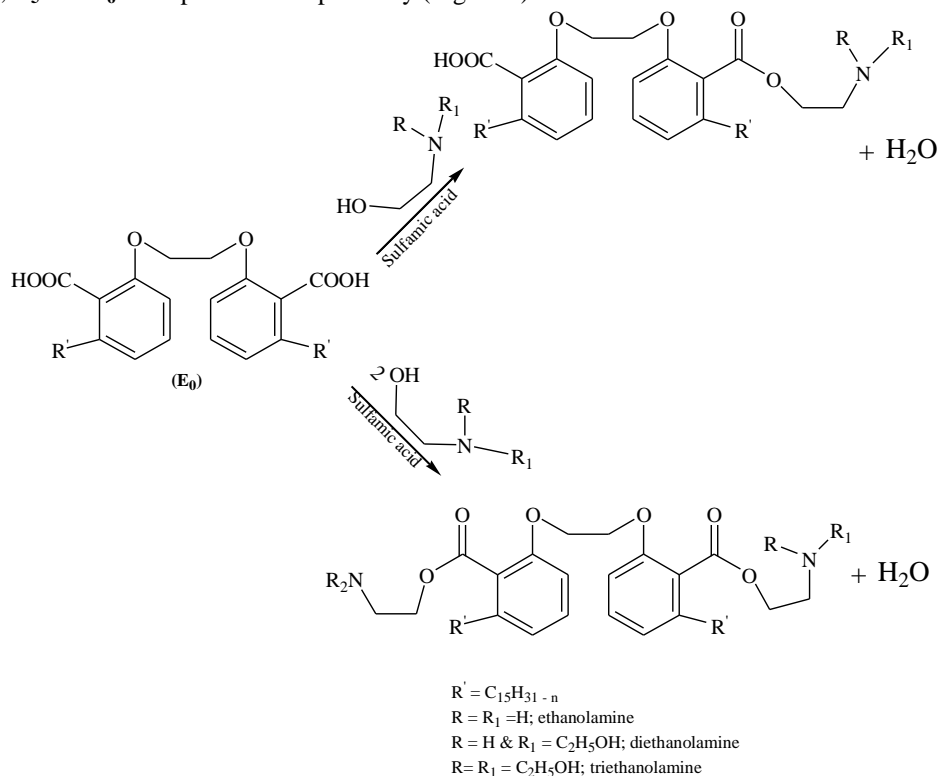$R = R_1 = C_2H_5OH$; triethanolamine

Figure 3: Reaction scheme for modification of E_0 with (1:1 & 1:2) molar ratio ethanolamine, diethanolamine and triethanolamine

2.3 Functional group Characterization
Structural Elucidation was carried using Agilent FTIR spectrophotometer scanning in the $4000 – 650$ cm^{-1} range at the Multi-User Research Laboratory Ahmadu Bello University Zaira.

2.4 Hydrocarbon oil characterization
Physicochemical properties of the sampled petroleum were carried out at the Quality control laboratory of the Port Harcourt Refining Company Eleme, River State, Nigeria.

● *Water cut:*

The percentage of water present in the sampled crude oil was estimated in accordance to ASTM D4006-1 using the Dean-Stark distillation method. To a 250 ml round bottom flask, 200 ml of crude oil and toluene was added in 1:1 volume ratio and the resulting mixture was homogenized. A dean stark trap was attached to the flask and the mixture was refluxed. The percentage water content in the sampled crude oil was therefore calculated from the recorded volume of water in the trap (when a constant volume was noted over a period of time) using the equation (1):

$$Water\ content = \frac{Volume\ of\ water\ in\ the\ trap}{Volume\ of\ crude\ oil\ used} \times 100 \quad (1)$$

● *Kinematic viscosity*

Kinematic viscosity of sampled crude oil was determined at 40 ℃ and 100 ℃ using Rigo PSH425-0019 viscometer bath in accordance to ATM D445-09 standard. 100 ml Crude oil sample was introduced into a centrifuge tube and oscillated for 10 mins at 50,000 rpm. The resulting sample was carefully sent into a viscometer tube corked at the smaller opening and was partially immersed into the viscometer bath to stand for 30 mins at 40 ℃. The corked end was then opened and the oil was allowed to flow with gravity, and the time taken for the oil to flow down from the upper neck mark to the lower mark was recorded. This procedure was repeated at temperature 100 ℃. Kinematic viscosity was thus calculated using the equation (2):

$$Kinematic\ viscosity\ (cSt) = Reflux\ time \times Calibration\ constant \quad (2)$$

● *Sulphur content*

The sulphur content of the crude oil sample was estimated in accordance with ASTM D4294 using an automated Tanaka Sulphur meter RX-360SH.

● *Specific gravity and API gravity*

The specific gravity (60/60 ℉) of the sampled crude oil was measured according to ASTM D1298-12b using Hygrometer and API gravity calculated using the equation (3):

$$API\ gravity = \frac{141.5}{Specific\ gravity} - 131.5 \quad (3)$$

● *Base sediment and water (BS&W)*

The BS&W composition of the sampled crude oil was determined in accordance to ASTM D4007-11 standard using a centrifuge. 100 ml solution of Crude oil and toluene (1:1 ml) volume ratio was fed into a centrifuge tube. The mixture was agitated carefully in a to and fro manner and the tube was fixed into the centrifuge and oscillated for 15 mins at 50,000 rpm.

● *Pour point*

The pour point of the sampled crude oil was measured in accordance to ASTM D97-12b standard using an automated Tanaka mini pour point/cloud point tester (MPC102L-T).

2.5 Seawater Characterization
● *Specific gravity*

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Specific gravity of the laboratory stimulated seawater was measured in line with ASTM D1298-12b standards and calculated using equation (4):

$$Specific\ gravity = \frac{density\ of\ seawater}{density\ of\ water} \qquad (4)$$

● *Salinity*

The salinity test of the formulated seawater was determined in line with ASTM D4458-15 standard (Victor-oji *et al.,* 2019). Seawater solution was made by dissolving 0.1 ml seawater in distilled water (25 ml). The seawater solution was then titrated against 0.0140 M $AgNO_3$ solution using 0.25 ml of potassium chromate (5 % w/v) was added to the mixture as indicator. The end point indicated by a colour change in the solution from yellow to brick red, and the volume of the $AgNO_3$ used was recorded. A blank titration was also performed and the Chloride ion concentration (Cl^-), and salinity in mg/L were calculated using equation (5a&b):

$$[Cl^-] = \frac{(Vt - Vb) \times M \times 35450}{Vs} \qquad (5a)$$

$$Salinity = [Cl^-] \times 1.8066 \qquad (5b)$$

Where Vt is the volume of $AgNO_3$ used up by the test solution, Vb is the volume of $AgNO_3$ used up by the blank solution, M is the molarity of the $AgNO_3$ solution and Vs is the volume of seawater used.

● *pH*

The pH of the sea water was measure using Hanna digital pH meter according to ASTM D1293-99 standard.

● *Total dissolved solids (TDS)*

The TDS of the formulated seawater was determined using Thermo Scientific Orion Star A212 meter according to ASTM 5907-13 standard.

● *Resistivity and conductivity*

Conductivity and resistivity of formulated seawater was determined using Thermo Scientific Orion Star A212 meter according to D1125-14 standard.

2.6 Emulsion formulation

Laboratory stimulated emulsion used in this study was formulated in line with the report of Victor-oji *et al.,* (2019). Formulated seawater was gradually introduced into the crude oil kept under high-speed stirring with the aid of a Hamilton beach mixer for proper homogeneity of the resulting emulsion. This was done for 45 mins, after which the emulsion was allowed to stand for 24 hours to attest for the homogeneity of the emulsion. This procedure was carried out for three different ratios of stimulated emulsions crude oil to seawater emulsions (90:10, 70:30 & 50:50).

2.7 Demulsifier formulation

5000 ppm stock solution of the formulated demulsifier was prepared by dissolving 5 % weight in grams (500 mg) of the synthesized compounds in 0.1 L (100 ml) of isopropyl alcohol and toluene respectively. Afterward, a serial dilution procedure was followed to obtained the desired concentrations of 10, 20, 30, 40 and 50 ppm were obtained for each solvent used (toluene and isopropyl alcohol) using equation (6):

$$C_1 V_1 = C_2 V_2 \qquad (6)$$

Where C_1 is the concentration of the stock, V_1 is the volume of the stock needed for further dilution, C_2 is the desired concentration needed to be prepared (which is 10, 20, 30, 40 and 50 ppm for this study) and V_2 is the volume desired. This was also repeated for the commercial demulsifier obtained (Phase Treat 12172).

2.8 Demulsification Process

Demulsification of the stimulated emulsion was done using the bottle testing method as described by Atta et al., (2018); Al-Sabagh et al., (2013) & Victor-oji et al., (2019) with modifications. The stimulated emulsions (20 ml, 70:30) were feed into calibrated bottles and was dosed with (0.3 ml, 10ppm) formulated demulsifiers respectively. The resulting mixture was allowed to homogenize by careful agitation for 2 mins and was placed in a thermostatic water bath for 3 hrs at 60 ^{o}C, and the water separation was observed and recorded for every 30

mins interval. This experiment was repeated using 50:50 and 90:10 crude oil and water emulsion and also for 20, 30, 40 and 50 ppm concentrations of demulsifiers. A blank test was also carried out for each case as a control. The efficacy of the demulsifiers was thus assessed based on the volume of water separated and percentage separation calculated using equation (7):

$$\% \, Water \, Separation = \frac{Volume \, of \, separated \, water \, (ml)}{Volume \, of \, water \, in \, the \, emulsion \, (ml)} \times 100 \qquad (7)$$

3. Result and Discussion

Table 1: Physicochemical properties of extracted CNSL

Properties	Value
Colour	Dark Brown
Specific gravity (25 ^{o}C g/ml)	0.955
pH	4.7
Kinematic Viscosity (40 ^{o}C, cP)	40.56
Dynamic Viscosity (40 ^{o}C, cSt)	40.04
Acid Value (mg KOH/100g)	10.60
Saponification Value (g KOH/100g)	39.20
Yield (%)	33
Iodine Value	232.0

Table 2: Physicochemical properties of crude oil sample

Parameters	Value
Specific gravity at 60/60ºF (g/ml)	0.8647
API gravity at 60/60ºF	32.1406
Sulphur content (% w/w)	0.1653
Water content (%)	0.3
Base sediment and water (%)	0.3
Pour point (^{o}C)	-14.0
Kinematic viscosity at 40 ^{o}C (cP)	13.7407
Kinematic viscosity at 100 ^{o}C(cP)	4.4221

Table 3: Physicochemical properties of formulated seawater

Parameters	Value
Specific gravity (g/ml)	1.0214
Density (g/ml)	1.0214
Salinity	28800
Resistivity (ohm)	0.0216
Conductivity (mS/cm)	46.28
Total dissolved solid (ppm)	22680
pH	7.9

3.1 FTIR assays and interpretations

For E_o (Figure 4), at 3350.9 cm^{-1}, a broad band observed for O-H vibration of the carboxylic acid. C–H stretching vibration due to alkene groups observed at 3011.7 cm^{-1} and C–H vibrations of aliphatic group (methylene and methyl groups) was also observed at absorption bands at 2922.2 cm^{-1} and 2855.1 cm^{-1}. Absorption band at 1722.0 cm^{-1} indicated the acid C=O group attached to aromatic ring. The aliphatic alkene C=C stretching vibration occurred at 1654.9 cm^{-1}, while the band at 1580.4 cm^{-1} corresponded to C=C aromatic stretching vibrations., Ar-O-C absorption band was also observed at 1252.4 cm^{-1}. The absorption band at 842.4 cm^{-1} corresponded to the 1,2,3-trisubstitution on the aromatic ring. For E_1 and E_2 absorption bands are same as that of E_o except for adsorption bands at 3298.5 cm^{-1} which corresponds to the N-H stretch vibration of the

amine group. 1371.2 cm^{-1} which represents the C-N stretch vibration of an Amine and 1155.5 cm^{-1} representing the C-O stretch vibration of an esters. For E_3 and E_4 a broad adsorption band was observed at 3295.0 cm^{-1} and 3296.0 cm^{-1} which corresponds to the N-H vibration which overlaps with the O-H of alcohol. 1371.2 cm^{-1} which represents the C-N stretch vibration of an Amine and 1155.5 cm^{-1} representing the C-O stretch vibration of an esters. All other bands correspond to those of E_o. For E_5 and E_6, adsorption bands at 3298.7 cm^{-1} and 3309.9 cm^{-1} respectively were observed and this corresponds to the O-H vibration of the carboxylic acid and that of the alcohol respectively. 1371.2 cm^{-1} which represents the C-N stretch vibration of an Amine and 1155.5 cm^{-1} representing the C-O stretch vibration of an esters. All other bands correspond to those of E_o.

3.2 Evaluation of the efficiency of formulated demulsifiers

Water separation capacity of formulated demulsifiers and that of the commercial demulsifier (PT12172) were analyzed on a laboratory stimulated emulsions of different oil to water ratios using isopropyl alcohol and toluene respectively, and different concentration of demulsifier 10, 20, 30, 40 and 50ppm at 60 ^{o}C. The water separation was measured and recorded, and presented in Tables 4 and 5. Factors such as solvent effect, effect of water content, effect of concentration and temperature was studied.

3.2.1 Effect of Concentration of emulsion breaker

In analyzing the effect of concentration of emulsion breakers on the water separation capacity, different concentrations (10 - 50 ppm) of all formulated emulsion breaker and Phase Treat 12172 in isopropyl alcohol and toluene were prepared, and tried on stimulated emulsions prepared at three different water to crude oil ratios at 60 ^{o}C, and the water separation was monitored for a duration of three (3) hours. Plots of water separation capacity against concentration of emulsion breaker for all formulated emulsion breakers and Phase Treat 12172 in isopropyl alcohol and toluene respectively at 60 ^{o}C, and on different water to crude oil emulsion ratios are presented in Figures 8 and 9. It was detected from the plots, that increase in the concentration of the emulsion breakers result in an equivalent increase in the water separation capacity for all cases. Maximum water separation percentage was recorded at concentration of 50 ppm for all cases in isopropyl alcohol and toluene with exceptions to E_o for 30:70 emulsion ratio in toluene and E_6 at 10:90 emulsion ratio in isopropyl alcohol, which gave a maximum water separation efficiency at 40 ppm. This observation is related to the trend observed by Attah *et al*., [23] and Victor-oji *et al*., [22].

3.2.2 Effect of water content

The amount of water present in a water-in-crude oil emulsion is a basic factor that impacts the firmness of an emulsion; and thus, influences the water separation capacity. Strength and stability of emulsions are not just hooked on the asphaltene, resin and paraffin content but also primarily on the emulsion water content. Therefore, emulsions with low water concentration experiences stronger external pressure of the continuous (oil) phase, which is greater than the internal pressure of water droplets [2]. This in turn, results in an amplified mechanical stability of the interface film making the breaking of this strong interfacial film more difficult, and hence require high temperature and highly efficient emulsion breakers. On the other hand, high percentage water emulsions experience weaker external pressure than the internal pressure, resulting in an increased weakening of the interface film, creating greater possibilities for flocculation and coalescences of water droplets (Al-Sabagh *et al*., 2013). The influence of water content of the various laboratory stimulated emulsions was investigated for 50 ppm of all formulated emulsion breakers and PT-12172 in isopropyl alcohol and toluene respective at 60 ^{o}C and from the records obtained it was revealed that increased in water ratio of the stimulated emulsion results in a corresponding increase in the emulsion breaking capacity of the emulsion as shown in figure 10.

3.2.3 Effect of solvent

To investigate the influence of solvents on the emulsion breaking capacity of the formulated emulsion breakers and PT-12172, isopropyl alcohol and toluene solvents were used. From the results obtained (Table 4 & 5) showed that all formulated emulsion breakers performed better in isopropyl alcohol than in toluene. However, for PT-12172 a better separation was recorded in toluene than in isopropyl alcohol. Solvent adsorption deteriorates and breaks interfacial film resulting in increased coalescences and greater water separation, and this

may be associated with the common ion effect of the -OH group in the isopropyl alcohol and the formulated emulsion breakers [22].

3.2.4 Effect of temperature

The major impact of temperature is always reflected in the time taken for maximum separation. Increased in temperature results in decrease in time taken for maximum demulsification [24]. The influence of temperature on the emulsion breaking capacity of all formulated emulsion breakers and the control (PT-12172) were evaluated at a concentration of 50 ppm in toluene and isopropyl alcohol respectively at 30, 40 and 60 ^{o}C and for 3 hours on 50:50 water-in-crude oil emulsion. From records generated (Figure 11), increase in temperature leads to a corresponding increase in water separation.
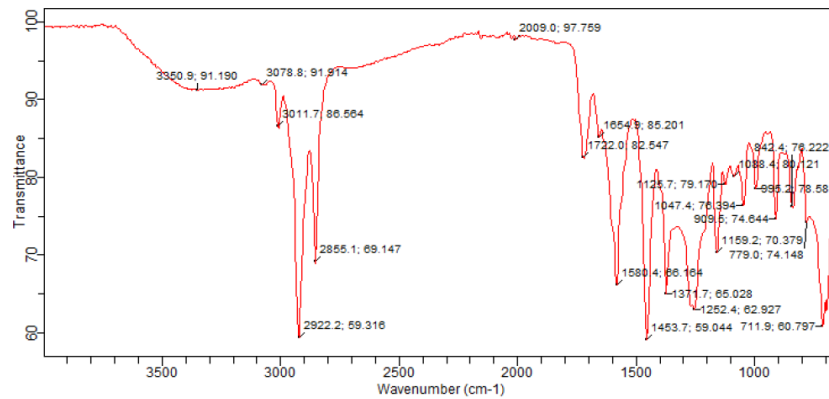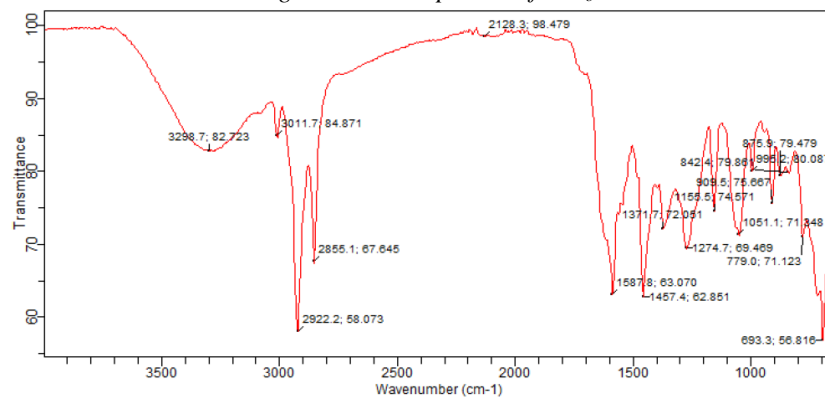

Figure 4: FTIR spectrum for E$_o$

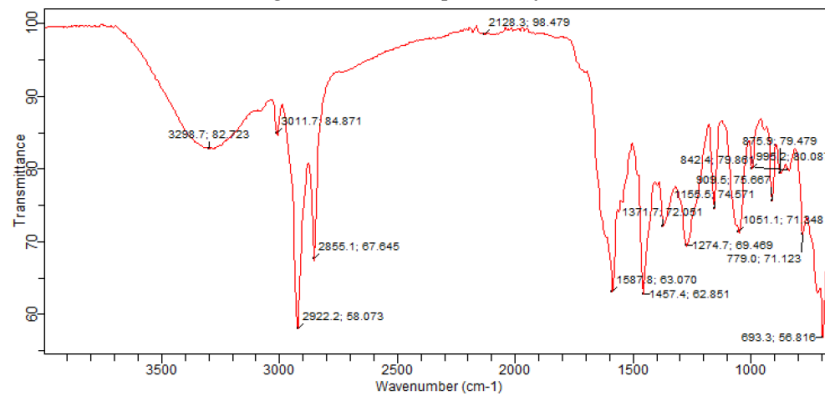

Figure 5a: FTIR spectrum for E$_1$
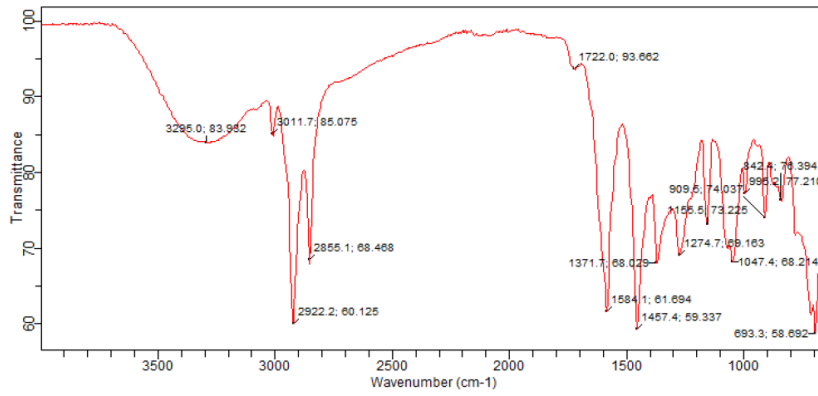

Figure 5b: FTIR spectrum for E$_2$

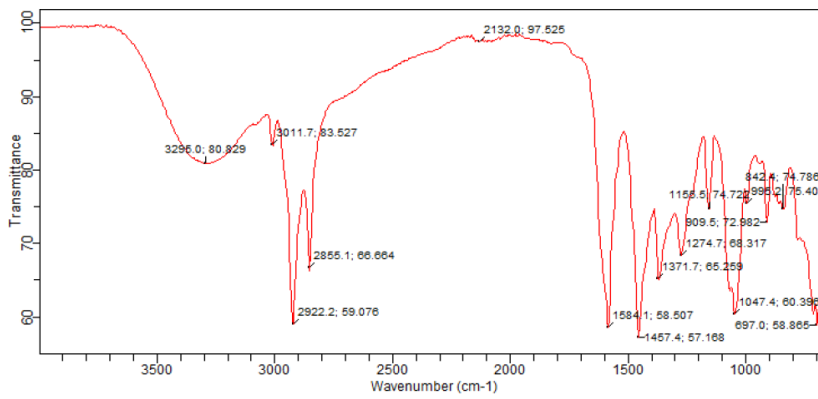*Figure 6a: FTIR spectrum for E₃*
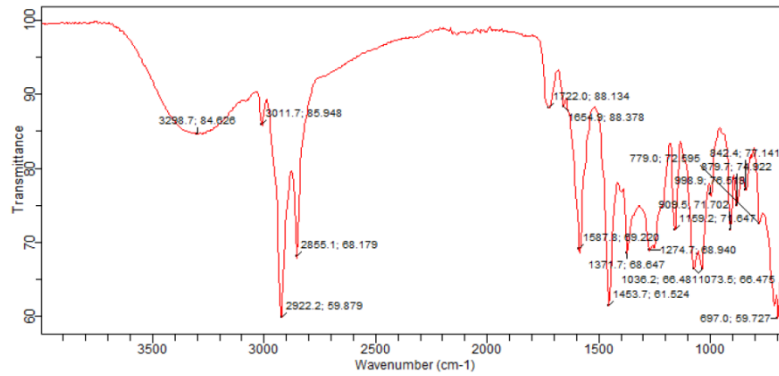

Figure 6b: FTIR spectrum for E₄
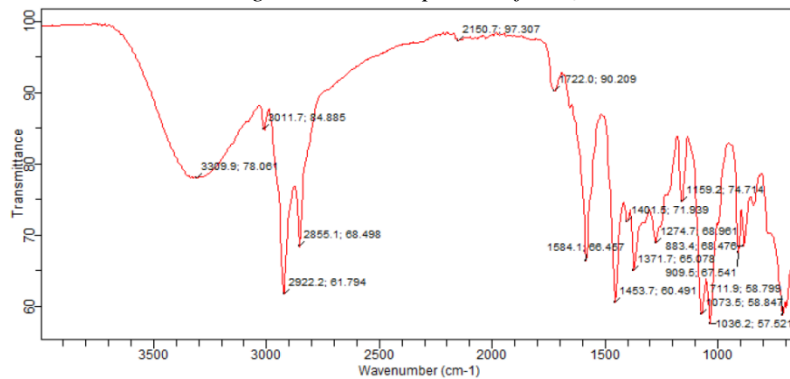

Figure 7a: FTIR spectrum for E₅

Figure 7b: FTIR spectrum of E_6

Figure 8a: Effect of concentration of emulsion breaker on water separation capacity for 10:90 W/O formulated emulsion at 60 ^oC in isopropyl alcohol

Figure 8b: Effect of concentration of emulsion breaker on water separation capacity for 30:70 W/O formulated emulsion at 60 ^oC in isopropyl alcohol
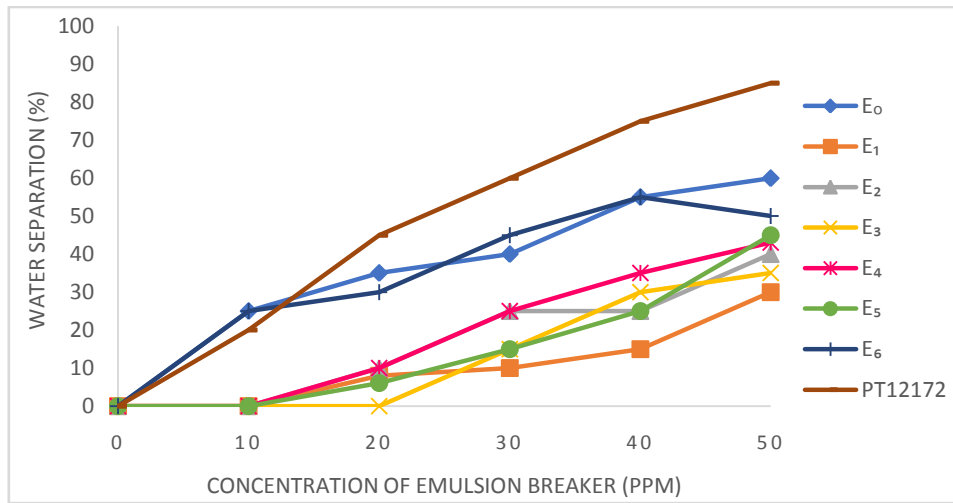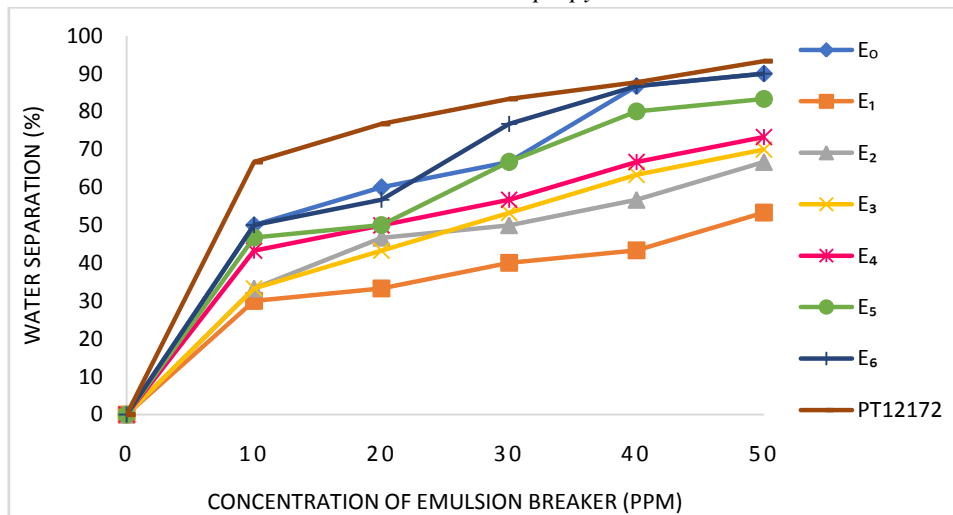
Figure 8c: Effect of concentration of emulsion breaker on water separation capacity for 50:50 W/O formulated emulsion at 60 ^{o}C in isopropyl alcohol
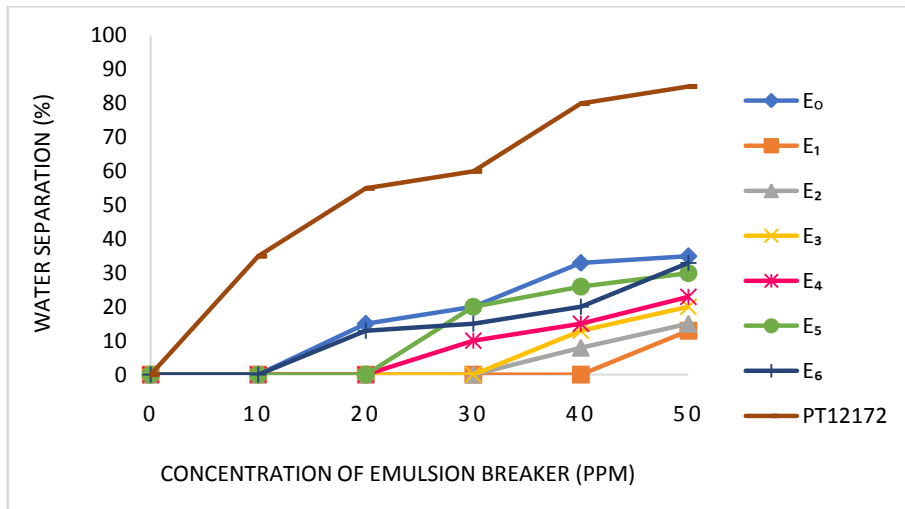
Figure 9a: Effect of concentration of emulsion breaker on water separation capacity for 10:90 W/O formulated emulsion at 60 ^{o}C in toluene
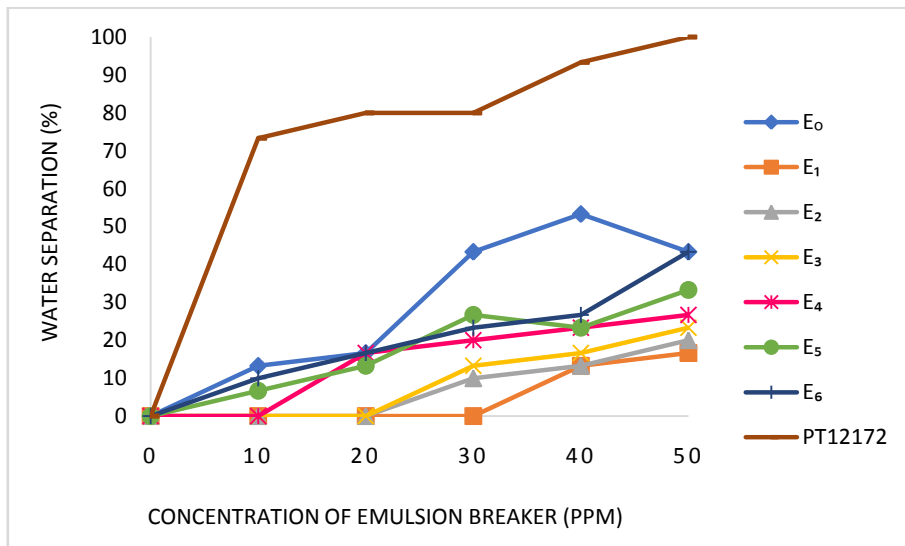
Figure 9b: Effect of concentration of emulsion breaker on water separation capacity for 30:70 W/O formulated emulsion at 60 ^{o}C in toluene
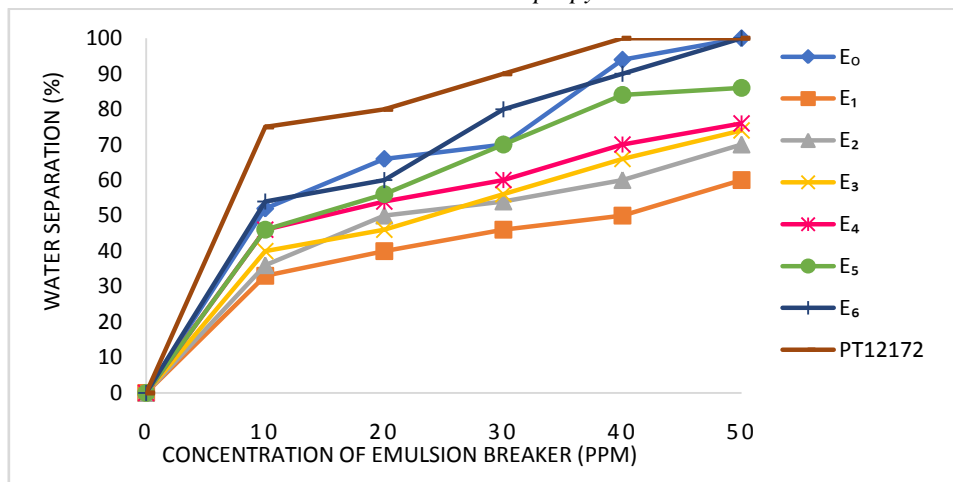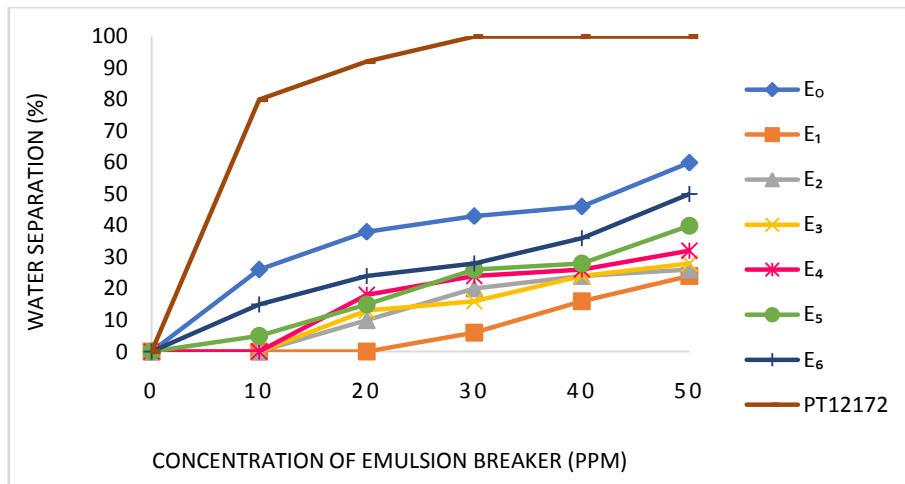
Figure 9c: Effect of concentration of emulsion breaker on water separation capacity for 50:50 W/O formulated emulsion at 60 ^{o}C in toluene
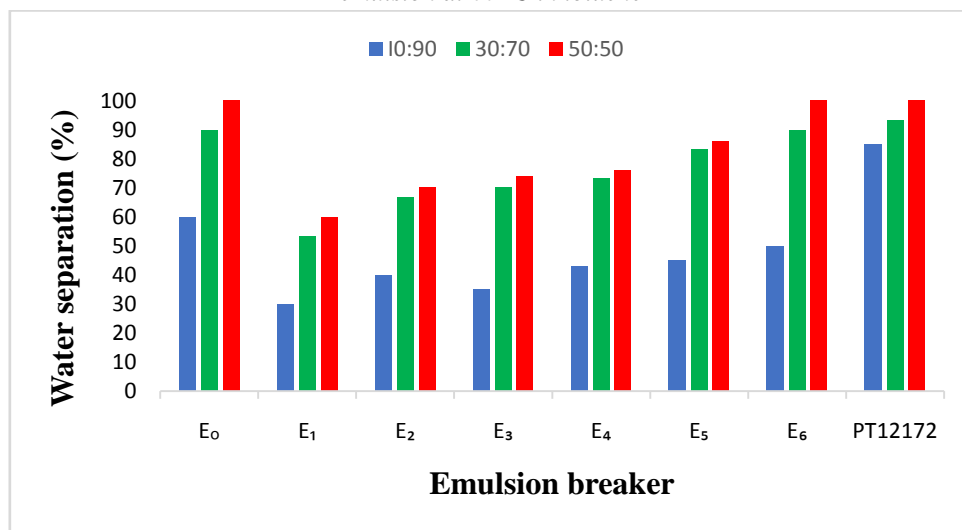
Figure 10a: Effect of amount of water content on emulsion breaking capacity for 50 ppm of formulated emulsion breakers and PT 12172 in isopropyl alcohol at 60 ^{o}C.
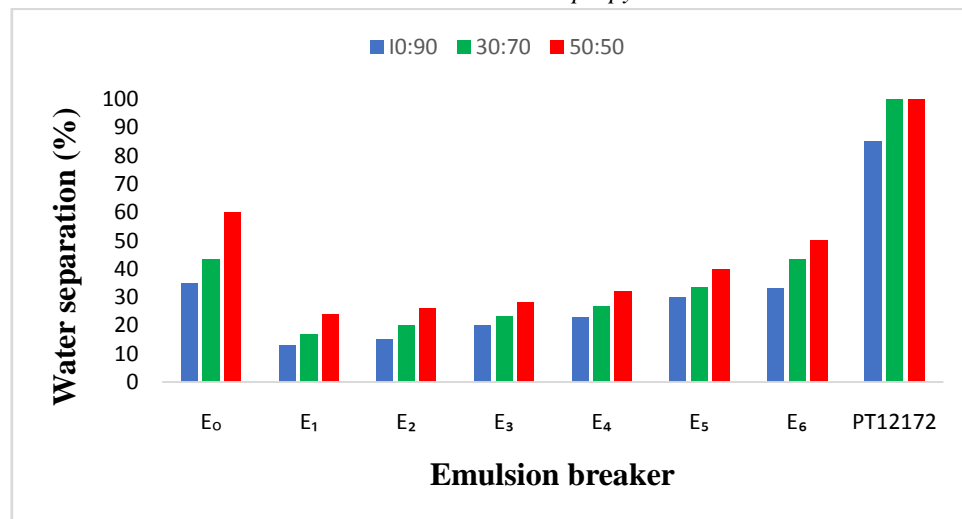
Figure 10b: Effect of amount of water content on emulsion breaking capacity for 50 ppm of formulated emulsion breakers and PT 12172 in toluene at 60 ^{o}C
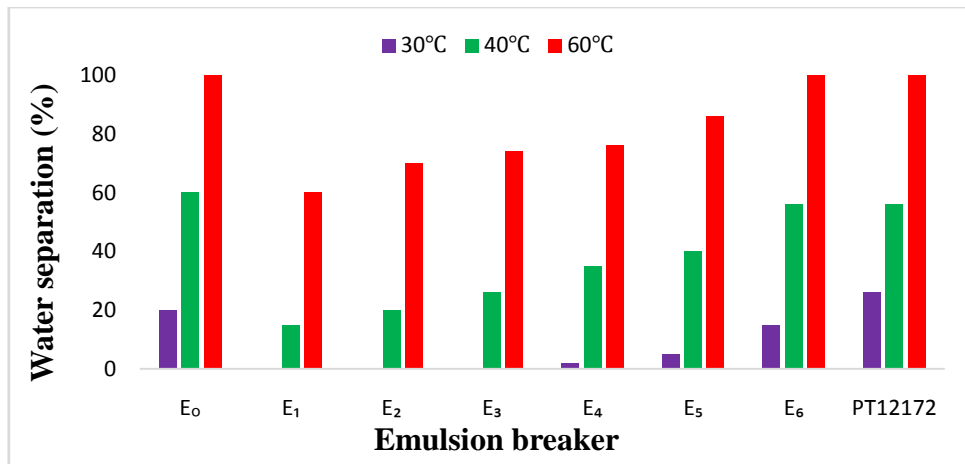
Figure 11a: Effect of temperature on the percentage water separation of formulated emulsion breaker and PT 12172 in isopropyl alcohol at 3 hours for 50 ppm and 50:50 water-in-crude oil stimulated emulsion
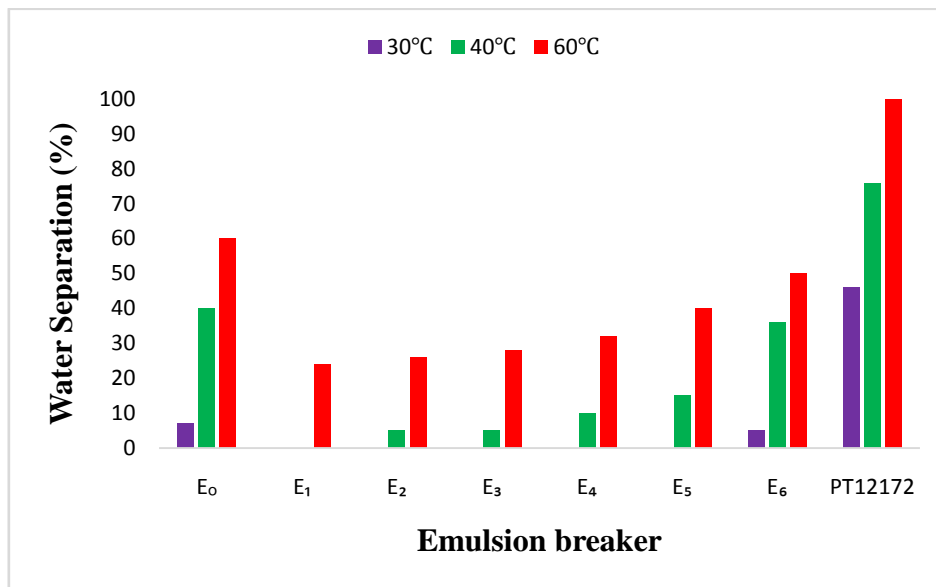
Figure 11b: Effect of temperature on the percentage water separation of formulated emulsion breaker and PT 12172 in toluene at 3 hours for 50 ppm and 50:50 water-in-crude oil stimulated emulsion

Table 4: Demulsification capacity of formulated emulsion breaker and Phase Treat 12172 in isopropyl alcohol at 180 hours and 60 ^{o}C.

| Demulsifier code	Concentration (ppm)	Water Separation Efficiency (%)					
		water: crude oil ratio (10:90)	TIME (min)	water: crude oil ratio (30:70)	TIME (min)	water: crude oil ratio (50:50)	TIME (min)
Phase Treat 12172 (control)	0	-	180	-	180	-	180
	10	20.0	150	66.7	90	75.0	180
	20	45.0	150	76.7	60	80.0	180
	30	60.0	180	83.3	60	90.0	30
	40	75.0	150	87.7	30	100.0	60
	50	85.0	150	93.3	60	100.0	30
E_o	0	-	180	-	180	-	180
	10	25.0	150	50.0	180	52.0	150

Demulsifier code	Concentration (ppm)	(10:90)	TIME (min)	(30:70)	TIME (min)	(50:50)	TIME (min)
	20	35.0	150	60.0	180	66.0	150
	30	40.0	120	66.7	180	70.0	180
	40	55.0	180	86.7	120	94.0	180
	50	60.0	150	90.0	150	100.0	150
	0	-	180	-	180	-	180
	10	-	60	30.0	120	33.0	180
E_1	20	8.0	90	33.3	180	40.0	180
	30	10.0	180	40.0	180	46.0	180
	40	15.0	150	43.3	180	50.0	180
	50	30.0	180	53.3	180	60.0	180
	0	-	180	-	180	-	180
	10	-	150	33.3	150	36.0	150
E_2	20	10.0	150	46.7	120	50.0	180
	30	25.0	120	50.0	150	54.0	150
	40	25.0	180	56.7	180	60.0	120
	50	40.0	150	66.7	180	70.0	120
	0	-	180	-	180	-	180
	10	-	60	33.3	150	40.0	120
E_3	20	-	90	43.3	180	46.0	150
	30	15.0	180	53.3	180	56.0	150
	40	30.0	150	63.3	180	66.0	120
	50	35.0	180	70.0	180	74.0	120
	0	-	180	-	180	-	180
	10	-	180	43.3	180	46.0	120
E_4	20	10.0	90	50.0	180	54.0	180
	30	25.0	120	56.7	150	60.0	180
	40	35.0	180	66.7	180	70.0	180
	50	43.0	150	73.3	180	76.0	180
	0	-	180	-	180	-	180
	10	-	180	46.7	180	46.0	120
E_5	20	6.0	180	50.0	180	56.0	150
	30	15.0	120	66.7	120	70.0	180
	40	25.0	150	80.0	180	84.0	180
	50	45.0	180	83.3	150	86.0	180
	0	-	180	-	180	-	180
	10	25.0	150	50.0	180	54.0	150
	20	30.0	150	56.7	180	60.0	150
E_6	30	45.0	120	76.7	180	80.0	180
	40	55.0	180	86.7	120	90.0	180
	50	50.0	180	90.0	150	100.0	180

Table 5: Demulsification capacity of formulated emulsion breaker and Phase Treat 12172 in Toluene at 180 hours and 60 ^{o}C

Demulsifier code	Concentration (ppm)	Water Separation Efficiency (%)					
		water: crude oil ratio (10:90)	TIME (min)	water: crude oil ratio (30:70)	TIME (min)	water: crude oil ratio (50:50)	TIME (min)

Phase Treat	0	-	180	-	180	-	180
12172	10	35.0	180	73.3	180	80.0	180
(control)	20	55.0	180	80.0	180	92.0	90
	30	60.0	150	80.0	180	100.0	90
	40	80.0	180	93.3	180	100.0	30
	50	85.0	150	100.0	180	100.0	180
E_o	0	-	180	-	180	-	180
	10	-	180	13.3	150	26.0	120
	20	15.0	150	16.7	150	38.0	180
	30	20.0	180	43.3	180	43.0	150
	40	33.0	180	53.3	180	46.0	180
	50	35.0	120	43.3	150	60.0	120
E_1	0	-	180	-	180	-	180
	10	-	180	-	180	-	180
	20	-	180	-	180	-	180
	30	-	150	-	180	6.0	180
	40	-	180	13.3	180	16.0	180
	50	13.0	180	16.7	180	24.0	180
E_2	0	-	180	-	180	-	180
	10	-	180	-	120	-	180
	20	-	180	-	180	10.0	180
	30	-	180	10.0	180	20.0	150
	40	8.0	150	13.3	180	24.0	180
	50	15.0	180	20.0	180	26.0	180
E_3	0	-	180	-	180	-	180
	10	-	180	-	120	-	150
	20	-	180	-	150	14.0	120
	30	-	180	13.3	180	16.0	180
	40	13.0	180	16.7	180	24.0	180
	50	20.0	150	23.3	180	28.0	180
E_4	0	-	180	-	180	-	180
	10	-	180	-	150	-	120
	20	-	150	16.7	150	18.0	180
	30	10.0	180	20.0	180	24.0	150
	40	15.0	180	23.3	180	26.0	180
	50	23.0	120	26.7	150	32.0	120
E_5	0	-	180	-	180	-	180
	10	-	180	6.7	180	5.0	180
	20	-	180	13.3	150	14.0	180
	30	20.0	180	26.7	180	26.0	150
	40	26.0	180	23.3	180	28.0	150
	50	30.0	180	33.3	150	40.0	180
E_6	0	-	180	-	180	-	180
	10	-	180	10.0	180	14.0	180
	20	13.0	180	16.7	180	24.0	180
	30	15.0	180	23.3	180	28.0	150
	40	20.0	180	26.7	180	36.0	150
	50	33.0	180	43.3	180	50.0	15

4. Conclusion

This study has shown that modified CSNL exhibits demulsifying ability, and its water separation efficiency is greater in isopropyl alcohol solvent than in toluene solvent. Increased in temperature, concentrations of emulsion breaker and water content of the stimulated emulsion resulted in corresponding increase in the demulsification capacity. The emulsion breaking efficiency of all modified derivatives in this study followed the order;

$$E_o > E_6 > E_5 > E_4 > E_3 > E_2 > E_1$$

From the performance evaluation, all formulated emulsion breakers relative to that of the Phase Treat 12172, all seven (7) modified CNSL in this study can be used as a replacement for Phase Treat-12172 as regards to the abundant availability of cashew nutshell, low cost, simple and straightforward synthetic pathway and its ecofriendly nature.

Acknowledgement

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