Synthesis and Evaluation of Ethanolamine-Cashew Nut Shell Liquid Products as Crude Oil Emulsion Breakers

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Authors' contributions

The work was carried out in collaboration among all authors. Author COV designed the study, performed the analysis, wrote the protocol and wrote the first draft of the manuscript. Author UJC managed the analysis of the study. Author OA managed the literature searches. All authors read and approved the final manuscript.

Article Information

Original Research Article

ABSTRACT

Cashew Nut Shell Liquid (CNSL), a natural phenolic liquid, was extracted from cashew nut shells using acetone and derivatized using Ethanolamine (EA) and Diethanolamine (DEA) in varying molar ratios via a one-pot process into anacardic acid-based ethanolamine esters and evaluated for use as crude oil emulsion breakers. The CNSL extract was characterized for its physico-chemical properties, FTIR spectral analysis for CNSL and the derivatives confirmed its chemical modification. Medium heavy crude and seawater sampled and characterized with ASTM standards were used in producing laboratory-simulated crude oil emulsions at varying crude oil: water mixing ratios of 90:10, 70:30 and 50:50. Performance of the anacardic acid-based CNSL extract and derivatives as demulsifiers were evaluated based on variation in dosage (10 ppm – 50 ppm), water content (10%, 30% and 50%), and solvent types (xylene and butanol, BuOH) at 60℃ within a 3-hr period via bottle testing. The performance of effective demulsifier formulations were compared with a commercial demulsifier, Phase Treat-4633, PT-4633, under similar conditions. Results obtained

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showed that water separation increases with demulsifier concentration and emulsion water content respectively, though water seperation varied among the demulsifiers as concentration and water content increased. PT-4633 in butanol achieved efficient water separation with an optimal seperation (100%) observed after 5 minutes at 40 ppm and 50 ppm, 50% and 60℃. In conclusion, the evaluated ethanolamine-CNSL products possess emulsion breaking potential using BuOH as solvent at shorter times. This behaviour may be due to the synergetic effect of BuOH as a solvent, thus, BuOH should be considered as solvent substitute for xylene due to low cost and toxicity levels, unlike xylene which is toxic and expensive.

1. INTRODUCTION

Water commonly co-exists in crude oil, an outcome of the mixing which occurs throughout oil production. The commingling of water with crude oil is regarded as an oil emulsion, which arises when dual immiscible liquids are mixed together. Two basic forms of emulsions exist namely; oil-in-water (o/w) and water-in-oil (w/o) emulsions [1]. These emulsions are one of the recurring problems encountered during oil production processes. Water-in-oil emulsions, formed as a result of the interfacial barrier that exists between oil and water, can lead to an array of problems which include; decrease oil quality and production, interference in oil refining processes, corrosion of pipelines and production equipment thus hindering the handling capacity which consequently increases oilfield capital and operation costs. It is pertinent to produce water-free crude, which is achievable by utilizing demulsifiers in treating emulsified crudes, as they help increase cost-effectiveness in oil production and refining to attain mandatory quality parameters for crude oil and water. Three demulsification methods used are namely: mechanical, electrical and chemical methods, however, destabilization mechanisms using demulsifiers is complex as no specific demulsifier can be employed in breaking various oil emulsions [2,3]. The desire to reduce operational cost and apparent space constraint in most production fields for treating equipment has made chemical demulsification the favored choice amongst other methods.

Most emulsion breakers utilized are generally polymeric surface-active agents formulated in solvents such as short-chain alcohols, aromatics, etc. and they are precisely formulated to meet water-oil seperation requirements at the oil production zone. Two demulsifier types are essentially used in oil-field processes namely; Water-soluble demulsifiers and Oil-soluble demulsifiers. As the name implies, the former, are solvable in oil, water, and can be varied with water in any ratio, ensuing in emulsion formation when comingled with water, while the latter, are solvable in crude oil and organic solvents such as benzene, ethanol, methylbenzene etc. instead of water. The demulsifier quality used is reliant on the chemical type used in its formulation, hence, demulsification rate of emulsions is solely reliant on the chemicals utilized in demulsifier formulation. Therefore, utilizing suitable demulsifiers can improve oil quality produced in an oilfield, minimizing production costs and complementary processes like refining, as crude oil properties differ from well to well and field to field [4].

Demulsifier selection is crucial in an emulsion-breaking process and testing procedures which aid selection of appropriate chemicals exist and they include: bottle tests, actual plant tests, and dynamic simulators. Bottle tests provide data concerning the required quantity of chemical and an estimation of the settling time for a treating vessel. Here, water separation is observed as a function of time. It is pertinent to note that static bottle tests cannot model these dynamic conditions; however, field trials should be done to ascertain the chemical's ability to operate in a dynamic system because the actual conditions are dynamic [4]. They are usually carried out to select a suitable demulsifier that will most effectively break emulsions from a given well, as demulsifiers are generally specific for specific emulsions (crude-oil type) thus may be completely ineffective for another. The bottle tests results are an indication of the ratio of the demulsifier to the emulsion needed to achieve high-quality oil. They also provide; an estimate of retention times and treating temperatures utilized for operation and design, are excellent for screening different emulsion samples for relative tightness, evaluation of prospective demulsifiers and effects of variables on emulsion resolution. Simulations are also a valuable tool in order to understand the role of surfactants in the stability

of the emulsions. Some basic rules should be adhered to in the course of standard bottle testing which include: samples must be chemical free and characteristic of the emulsion to be treated, the sample must be fresh to avoid emulsion aging which affects their demulsification, and mixing, heat, retention time and dosing conditions, should be simulated close to field operational conditions [5].

The suitable temperatures considered for a laboratory-scale demulsification experiment lie between 50℃ to 70℃, which is similar to the actual operational temperature [2,6]. Some studies have investigated the influence of solvents, mainly aromatics, such as; benzene, toluene, xylene, ethylbenzene, tert-butyl benzene and cymene, on emulsion stability and results have shown that most aromatic solvents (with higher aromatic carbon content) are more effective in demulsification [7,8]. The disadvantage of having organic solvents in a demulsifier formulation include increased cost, flammability, and toxicity among others, therefore, a demulsifier formulation which does not include organic solvents would represent an advance in the art of demulsification [9].

Cashew Nut Shell Liquid (CNSL), a dark brown thick phenolic fluid, is a useful by-product of cashew nut processing and has boundless possibilities as an industrial precursor for diverse

applications, as it offers much scope and varied opportunities for developing other specialty polymers as seen in its diverse and extensive application in the making of special paint types, shielding lacquers (in the electrical industry), distinct adhesive cement types, abrasion and brake linings, coating and epoxy resins, neoprene compounding resins, polyurethane-based polymers, surface- active agents, foundry chemicals and as a chemical intermediate for production [10,11,12]. CNSL has been developed as a valuable commodity and bio-renewable material for the production of different compounds due to it phenolic composition. It is composed mainly of anacardic acid, cardol, 2-methyl cardol and cardanol in varying proportions dependent on the extraction method used as shown in Fig. 1 and Table 1 [13].

CNSL is a sustainable source for naturally occurring substituted phenols and a cheaper alternative for unsaturated phenols [13]. Its products are renewable in nature and have significant advantage over synthetics as its constituents possess special structural features that makes for transformation into specialty chemicals and high value polymers [14]. Different methods exist by which CNSL is extracted namely; mechanical, roasting and solvent extraction, of these methods, CNSL gotten by solvent extraction is rich in anacardic acid and regarded as high quality.
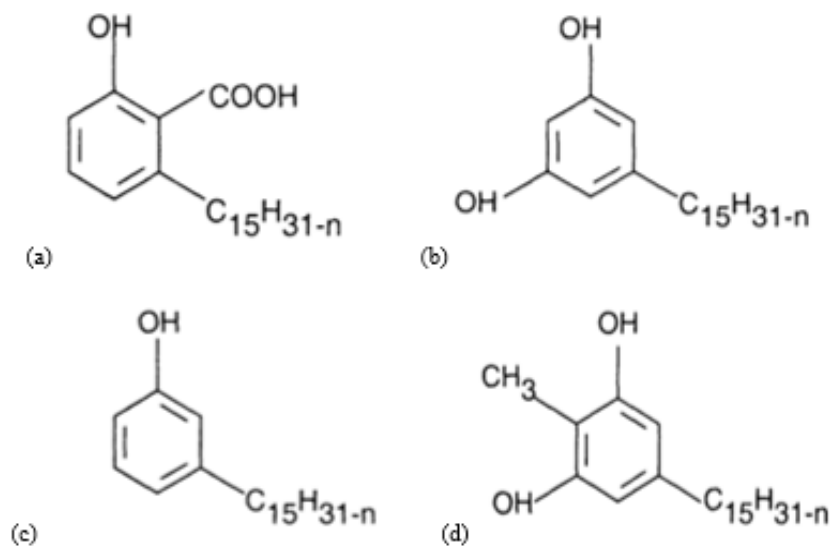

Fig. 1. Components of CNSL: (a) Anacardic acid, (b) Cardol, (c) Cardanol, and (d) 2-methyl cardol. Where n= 0, 2, 4, 6 [13]

Table 1. Phenolic compositions of natural and technical CNSL (in wt.%) [13]

Component	Natural CNSL	Technical CNSL
Cardanol	1.2	62.86
Cardol	11.31	11.25
2-methyl cardol	2.04	2.08
Polymer	20.3	23.8
Anacardic acid	64.93	_

This paper is focused on the efficiency of Ethanolamine ester derivatives of CNSL as crude oil emulsion breakers in xylene and butanol.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Cashew Nut Shell Liquid (CNSL)

Whole cashew nuts (CN) were procured from Ihube village in Okigwe Local Government Area of Imo State, Nigeria. The CN was pre-treated by washing and sun drying for 2 days to remove impurities, after which they were cut lengthwise, dekernelled and crushed using a hydraulic press (to increase the surface area for extraction). Three hundred grams (300 g) of crushed CNS was packed in the Soxhlet extractor thimble using a Whatman filter paper and extracted by refluxing with acetone at 60-70℃ until the solvent becomes clear in the thimble. The Natural CNSL (NCNSL) extract was recovered from the solvent by distillation technique.

2.1.2 Seawater

Seawater was sampled from the Gulf of Guinea, labelled accordingly and dispatched to the laboratory for further analysis. Its physicochemical characterization is as shown in Table 2.

2.1.3 Crude oil

Medium heavy oil sampled from a flow station located within the Niger Delta region, was labelled accordingly and dispatched to the laboratory for further analysis. Its physicochemical characterization is as shown in Table 3.

2.1.4 Demulsifiers

The commercial demulsifier used in this study was Phasetreat (PT) 4633, used in most flow stations within the industry.

2.1.5 Chemicals

The chemicals used include; Industrial grade acetone, ethanolamine, diethanolamine, Sulphamic acid, xylene and butanol (Analar grade Aldrich Chemicals). All chemicals were used as received without further purification.

2.2 Methods

2.2.1 Cashew Nut Shell Liquid (CNSL) assay

The CNSL extract was characterized for appearance/colour, pH, density, specific gravity (ASTM D-1298-12b), acid value (Wijs method), iodine value and saponification value [15]. FTIR analysis was conducted with an Agilent spectrophotometer scanning in the 4000 – 700 cm^{-1} range.

2.2.2 Synthesis of CNSL derivatives

The derivatives of CNSL used as demulsifiers in this study were chemically modified in an esterification reaction with Ethanolamine (EA) and Diethanolamine (DEA) respectively using an heterogenous catalyst.

2.2.2.1 Modification with ethanolamine (EA)

The CNSL extract and EA (1:1 molar ratio) were charged into a pre-weighed 250 ml round bottom flask (the reactor vessel). The solution mixture was heated under reflux in a paraffin bath until the oil bath attained 120℃. Stirring commenced on addition of the heterogenous catalyst and the reaction progress monitored by volume of water condensed into the dean and stark trap for one hour (the end of reaction is reached when water volume in the dean and stark trap is constant). After which, the resulting mixture was cooled and the product weighed using analytical weighing balance.

2.2.2.2 Modification with diethanolamine (DEA)

The CNSL extract and DEA (1:1 and 2:1 molar ratio respectively) was charged into pre-weighed 250 ml round bottom flasks. The mixture was

heated under reflux in an oil bath until the oil bath attained a temperature of 120℃. Stirring of the mixture commenced on addition of the catalyst and the progress of the reaction was monitored by the water collected in the dean and stark trap for an hour (the end of reaction is reached when the volume of water in the dean and stark trap is constant). At the end of the reaction, the mixture is cooled and the product was weighed using analytical weighing balance.

2.2.3 FTIR characterization of CNSL and its derivatives

The CNSL extract and its modified derivatives were characterized using their FTIR spectra. The FTIR analysis was conducted with an Agilent spectrophotometer scanning in the 4000 – 700 cm^{-1} range.

2.2.4 Crude oil assay

2.2.4.1 Water cut

Water-cut was determined by Dean-Stark distillation according to ASTM D4006-11 method. Homogenize sample by agitation and measure 100 ml into a round bottom flask. Add an equivalent amount of xylene to the flask, fix the dean and stark receiver trap to the condenser and heat for one hour. Record the reading of water collected in the trap and estimate the water cut with the equation below:

$$Water\ cut\ (\%) = \frac{Volume\ of\ water\ collected\ in\ the\ trap}{Volume\ of\ sample} \times 100$$

2.2.4.2 Kinematic viscosity

Kinematic viscosity was determined at 40ºC and 100ºC using ASTM D455-12 method with Stanhope-Seta KV-8 Viscometer bath. A 100 ml centrifuge tube was filled to mark with the crude oil sample and positioned in the centrifuge at 50,000 revolution per minute (rpm) for 15 mins. The water-free centrifuged sample was poured into a viscometer tube, already corked with a stopper at the smaller opening, fitted to a viscometer tube handler and positioned in the viscometer bath. A thermometer was dipped into the sample to ascertain when the appropriate temperature (40℃ or 100℃) is attained, the cork is detached and the oil left to flow. Once the oil reached the first line above the upper neck of the small bulb, the timer clock is switched on till the oil reaches the line above the big bulb. The efflux time (in secs) is recorded and the kinematic viscosity in centistokes (cSt) calculated using the equation below:

$$Kinematic\ viscosity\ (cSt)\\ = Calibration\ constant\ (c)\\ \times Efflux\ time\ (in\ secs)$$

2.2.4.3 Sulphur content

Sulphur content of the crude was determined according to ASTM D4292-16 using a Horiba Sulphur-in-oil analyzer.

2.2.4.4 Specific gravity and API gravity

Specific (60/60ºF) of the sample was determined according to ASTM D1298-12b. and API gravity calculated using the equation below:

$$API\ gravity = \frac{141.5}{Specific\ Gravity} - 131.5$$

2.2.4.5 Pour point

Pour point was determined with a Stanhope-Seta Pour Point refrigerator using ASTM D5853-17a method. The crude oil was pre-heated to 45℃ in the test jar, in a thermostatic water bath, after which it was positioned in the pour point refrigerator. The test jar was gently removed from the refrigerator to check for flow repeatedly until the pour point was reached. Three degrees Celsius (3ºC) was added to the final pour point value obtained.

2.2.4.6 Base, sediment and water (BS&W)

The BS&W content of the crude was determined according to ASTM D4007-11 by Centrifuge method. Fifty millilitres of sample was transferred into a centrifuge tube (100 ml), an equivalent volume of xylene was added. Five (5) drops of demulsifier (0.5 ppm equivalent) was introduced into the mixture and mildly agitated 10 times in a to and fro motion. The tube was positioned in a thermostatic water bath set to 60ºC for a 15 mins duration then, centrifuged for 10 mins and readings taken from.

2.2.5 Seawater assay

2.2.5.1 Specific gravity and density

The specific gravity and density were determined according to ASTM D1429-13 method using a hydrometer and density calculated via the specific gravity- density relationship in the equation below.

$$Specific\ Gravity = \frac{Density\ of\ liquid}{Density\ of\ water} = \frac{\rho_{liquid}}{\rho_{water}}$$

2.2.5.2 Total dissolved solids (TDS)

Total dissolved solid was determined according to ASTM D5907-18 method. The crucible was preheated to constant weight at 180°C and placed in the desiccator for two hours before weighing. One hundred millilitres (100 ml) of seawater sample was vacuum-filtered through a 45 μ filter paper into a receiving flask. The constant weight crucible was filled with the seawater filtrate and placed on a water bath. The filtrate was left to evaporate to dryness, oven dried and weighed. The total dissolved solids can be calculated using the equation below.

$Total\ Dissolved\ Solids\ (ppm)$
$$= \frac{(weight\ of\ crucible + filtrate) - (weight\ of\ crucible)}{volume\ of\ sample} \times 10^6$$

2.2.5.3 Resistivity and conductivity

The electrical resistivity and conductivity were determined according to ASTM D1125-14 method using a YSI 3200 conductivity instrument and the electrical resistivity calculated using the equation below.

$$Resistivity = \frac{1}{Conductivity}$$

2.2.5.4 Salinity

The salinity was determined according to ASTM D4458-15 method. A sample aliquot (0.1 ml) was introduced into a measuring cylinder (25 ml) and filled to mark with distilled water, which was subsequently transferred into an Erlenmeyer flask (50 ml). 0.25 ml of 5% w/v potassium chromate indicator was added and titrated using 0.0140 N silver nitrate ($AgNO_3$) solution as titrant to the equivalence point (which is pinkish yellow or brick red). The titrant volume was recorded and the chloride content, Cl⁻, and salinity in mg/L, calculated using the equations below.

$Chloride\ content$
$$= \frac{(mL\ AgNO_3\ used - Blank) \times molarity\ of\ AgNO_3 \times 35450}{volume\ of\ sample}$$

$$Salinity = Cl^- \times 1.8066$$

2.2.5.6 pH

The pH was determined according to ASTM D3875-03 using Thermo Scientific Orion Star A211 pH meter.

2.2.6 Demulsifier preparation

Five percent weight per weight (5%w/w) of the demulsifiers were dissolved in 100 g volume equivalent of Xylene and Butanol respectively to give 50000 ppm stock solution. Two millilitres of stock solution (1000 ppm equivalent) was pipetted into the 100 ml volumetric flask and filled to mark with the respective solvents.

2.2.7 Preparation of crude oil emulsions

Laboratory simulated emulsions was prepared using the method described by Attah *et al.* [16,17] with slight modification. The crude oil was mixed at high speed using a Hamilton Beach Commercial mixer for a 30 mins duration with gradual addition of seawater until both phases are completely homogenized. Different emulsions were gotten by varying mixing ratios of crude oil to water of; 90:10, 70:30, 50:50 respectively.

2.2.8 Crude oil emulsion breaking

The method used in breaking the crude oil emulsions was the bottle testing method, as described in Atta *et al.* [16] and Al-Sabagh et al. [18,12] with slight variation. The bottle testing method was used to assess the efficiency of the demulsifier-in-solvent formulation in the simulated crude emulsions. The simulated emulsions varying in seawater volumes were poured into graduated 100 ml Teflon-stoppered bottles and dosed with the formulated demulsifiers dosed at 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm respectively. A blank was used for each experimental set. The bottle was agitated 100 times in a 'to' and 'fro' motion (mimicking natural mixing of crude oil and demulsifier in the flow station) and placed in the thermostatic water bath set to 60°C, and water seperation observed for the initial 5 minutes and subsequently at every 10-minute interval for 3 hrs. The demulsifier performance was assessed based on its water seperation rate, quality of interfacial layer and water separated. Water seperation was estimated using the equation below.

$Water\ seperation\ (\%)$
$$= \frac{Volume\ of\ seperated\ water\ in\ ml}{Total\ volume\ of\ water\ in\ the\ emlusion\ in\ ml} \times 100$$

3. RESULTS AND DISCUSSION

3.1 Sea Water Assay

The physico-chemical properties of the seawater sampled from the Gulf of Guinea are presented in Table 2.

3.2 Crude Oil Assay

The physico-chemical properties of the crude oil used in the study are presented in Table 3. The API (American Petroleum Institute) gravity classification shows that the crude is a medium heavy crude.

3.3 CNSL Assay

The physico-chemical properties of the extracted CNSL are presented in the below table.

3.4 FTIR Analysis of CNSL and Its Derivatives

The FTIR spectrum of anacardic rich-CNSL extract and its ethanolamine esters shows characteristic peaks corresponding to the functional groups in anacardic acid as presented in their spectra on Figs. 2-5. For CNSL, a strong and broad absorption band observed at 3400 cm^{-1} due to O-H vibration of the phenol group overlaps with that of carboxylic acid. The C–H stretching vibration due to alkene groups occurs at 3011.7 cm^{-1}, wavelength absorption bands at 2922.2 cm^{-1} and 2855.1 cm^{-1} are due to the C–H vibrations of methylene and methyl groups of the meta substituted hydrocarbon chain respectively. The acid C=O attached to aromatic ring absorbs at 1699.7 cm^{-1} while 1300.8 cm^{-1} is the acid C–O stretching vibration. The alkene C=C stretching vibration occurs at 1643.8 cm^{-1} while the band at 1602.8 cm^{-1} matches C=C aromatic stretching vibrations. Methyl C–H deformation vibrations occur at 1449.9 cm^{-1} and 1300.8 cm^{-1} while the absorption band at 708.2 cm^{-1} matches the alkene C–H deformation vibration. For the ethanolamine monoester (CNSL-EA), a broad absorption band observed at 3160.8 cm^{-1} due to the amine N-H vibration which overlaps the O-H of alcohol. Other absorption bands observed 3011.7 cm^{-1}, 2922.2 cm^{-1}, 2855.1 cm^{-1} and 1699.7 cm^{-1} complement the peaks already interpreted in pure CNSL. However, alkene C=C stretching vibration occurs at 1580.4 cm^{-1} while the absorption band at 1453.7 cm^{-1} corresponds to aromatic C=C vibrations. Methyl C–H deformation vibrations occur at 1371.7 cm^{-1} and 1323.2 cm^{-1}, appearance of an absorption band at 1271.0 cm^{-1} matches the ester C-O stretching vibration while the band observed at 711.9 cm^{-1} matches alkene C–H deformation vibration. For the diethanolamine monoester (CNSL-DEA) and diethanolamine diester (2CNSL-DEA), broad absorption band observed at 3220.4 cm^{-1} and 3216.7 cm^{-1} respectively is the amine N-H vibration which overlaps with the O-H of alcohol. Disappearance of the band originally at 1699.7 cm^{-1} shows that the acid group are used in ester bond formation. Other absorption bands observed at 3011.7 cm^{-1}, 2922.2 cm^{-1}, and 2855.1 cm^{-1} complement peaks already interpreted for CNSL while those observed at 1580.4 cm^{-1}, 1453.7 cm^{-1}, 1371.7 cm^{-1}, 1323.2 cm^{-1}, 1271.0 cm^{-1} and 711.9 cm^{-1} complement peaks already interpreted for CNSL-EA.

Table 2. Characterization of seawater sample

Parameter	Method	Seawater sample
Total Dissolved Solids (ppm)	ASTM D 5907	32653
Resistivity (Ohm) @ 19℃	ASTM D 1125	0.0181
Conductivity (mS/cm) @ 19℃	ASTM D 1125	55.41
Density (g/ml)	ASTM D 1429	1.0189
Salinity (ppm)	ASTM D 4458	35931.12
Specific Gravity	ASTM D 1429	1.0189
pH @ 26℃	ASTM D 3875	8.18

Table 3. Physico-chemical properties of crude oil sample

Parameter	Method	Value
Specific Gravity (60/60ºF)	ASTM D 1298	0.9030
API Gravity@ 60ºF	ASTM D 1298	25.1999
Kinematic Viscosity at 40℃ (c.St.)	ASTM D 455	13.7506
Kinematic Viscosity at 100℃ (c.St.)	ASTM D 455	3.1469
Water cut (%)	ASTM D 4006	0.0250
Sulphur content (wt.%)	ASTM D 4292	0.3082
Base, Sediment and Water (%)	ASTM D 4007	0.025
Pour Point (℃)	ASTM D 5853	-30

Table 4. Physico-chemical properties of extracted CNSL

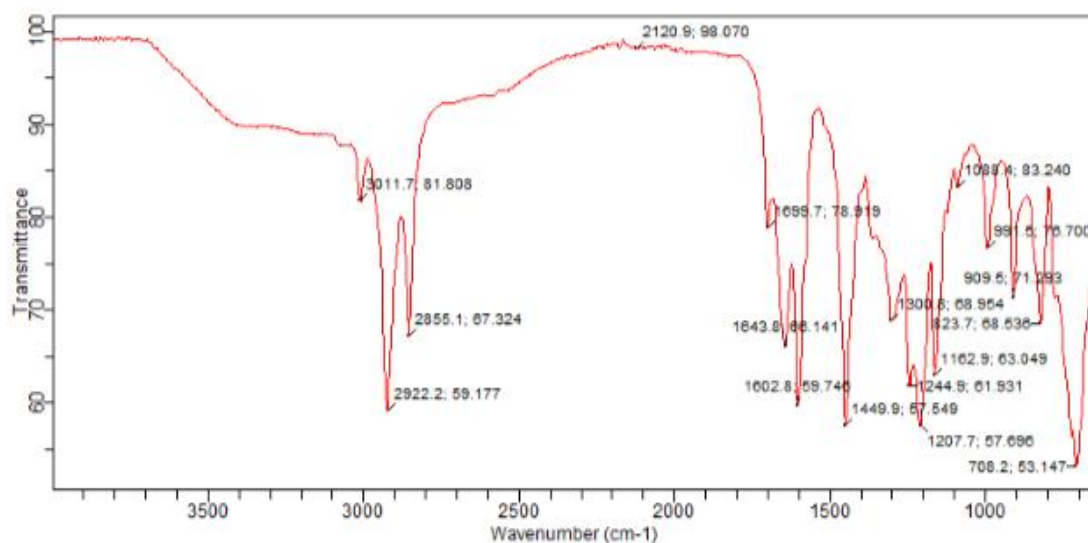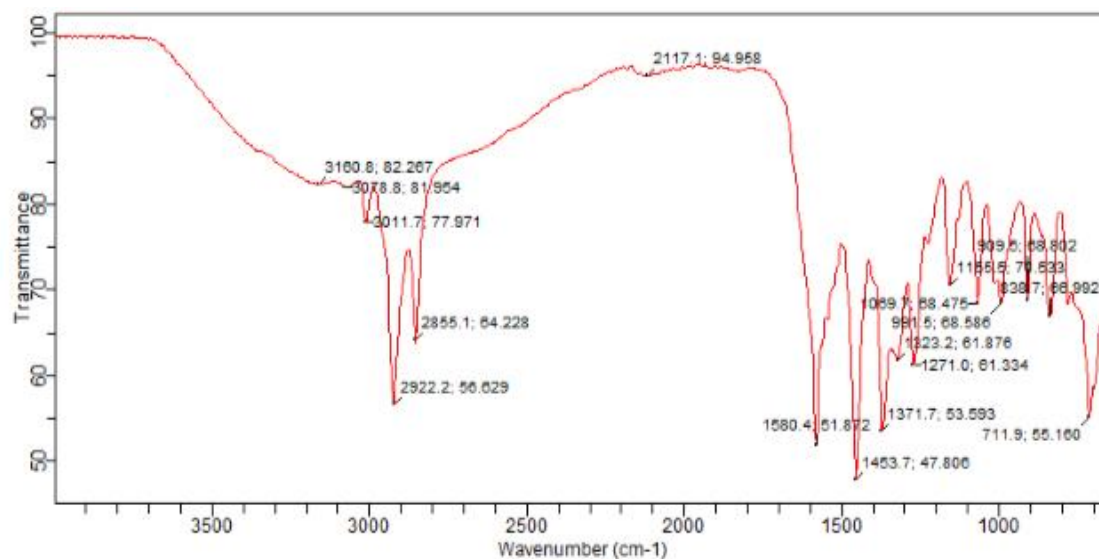| Property	Value
Colour	Dark Brown
pH	4.06
Specific Gravity (22.5ºC)	0.870
Density(g/mL)	0.870
Acid value (mg KOH/g)	1.63
Iodine value	71.76
Yield	35%
Saponification value (mg KOH/g)	173.44

Fig. 2. FT-IR Spectrum of CNSL
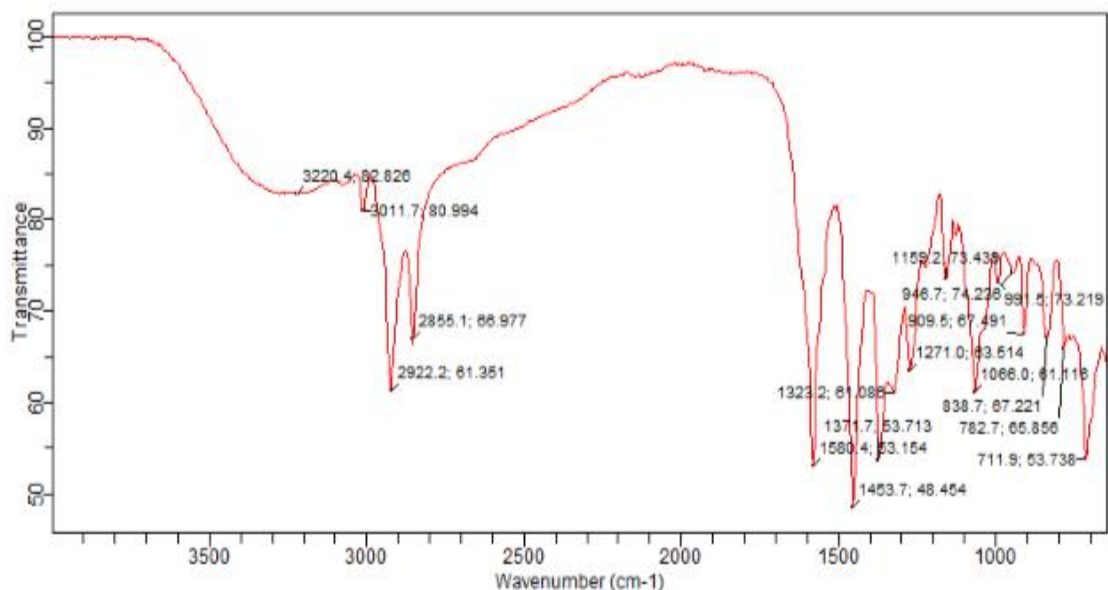

Fig. 3. FT-IR Spectrum of CNSL-EA

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**Fig. 4. FT-IR Spectrum of CNSL-DEA**
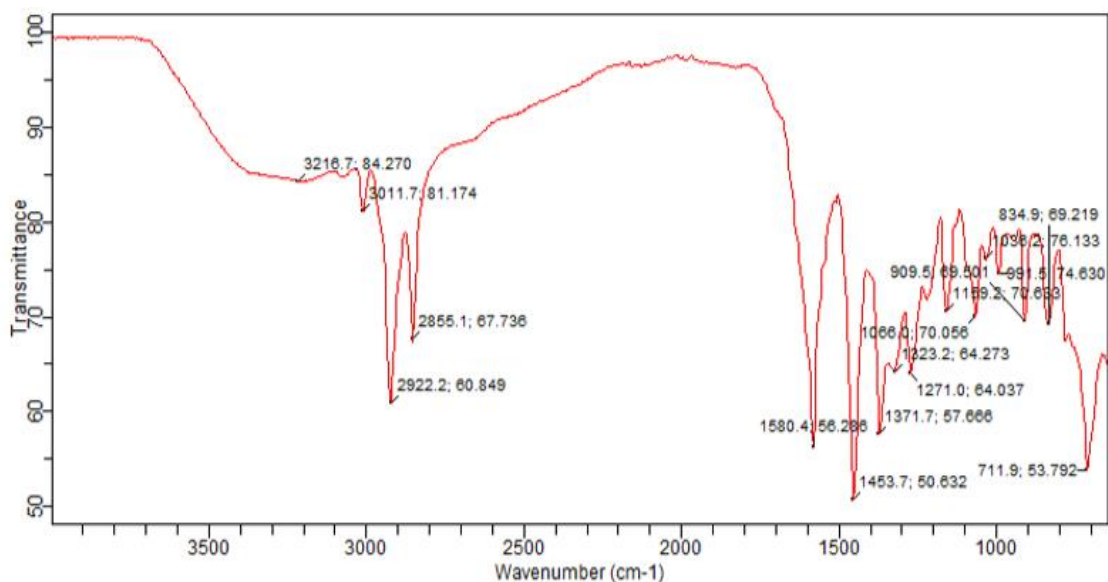
Fig. 5. FT-IR Spectrum of 2CNSL-DEA

3.5 Performance Evaluation of Formulated Emulsion Breakers IN XYLENE and Butanol

Ethanolamine-CNSL products assigned compound codes; CNSL-EA, CNSL-DEA, and 2CNSL-DEA respectively, were evaluated for their emulsion breaking potentials and efficiency in xylene and butanol using laboratory simulated crude oil emulsions at varying crude oil: water ratios of 90:10, 70:30 and 50:50, and different concentrations of 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm, at 60℃. The bottle testing data for water seperation in Xylene and BuOH are shown in Appendix 1 and 2, while water seperation plots at varying concentration and water content are shown in Figs 6(a)– 20(a) for Xylene and Figs. 6(b) – 20(b) for BuOH respectively. Some factors which influence emulsion breaking were studied and are discussed as follows:
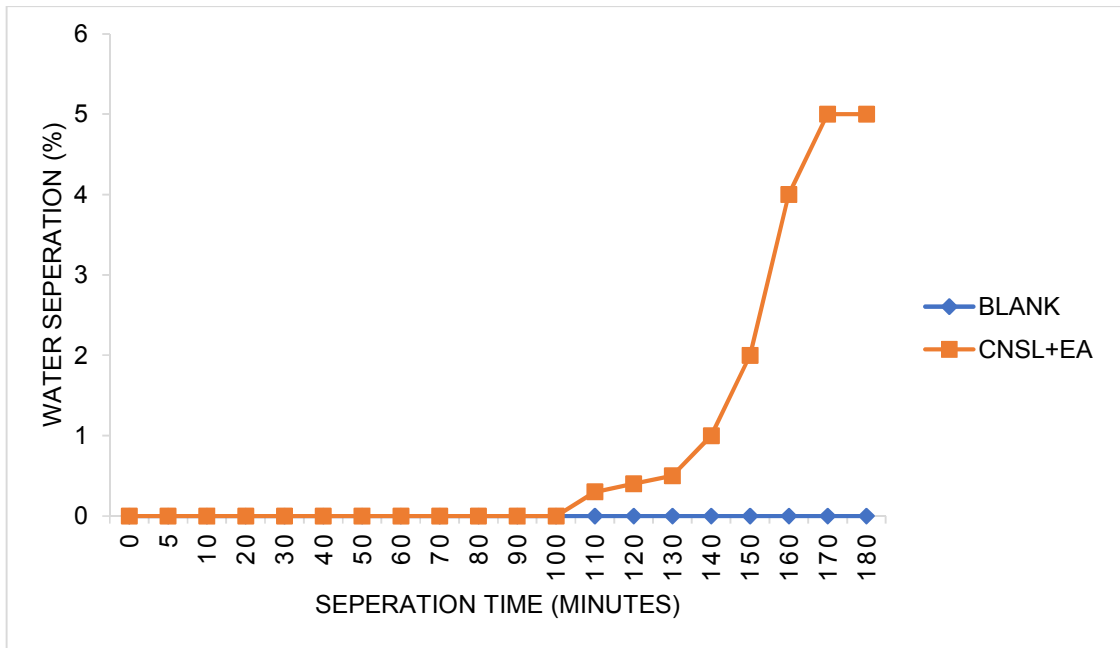
(a)
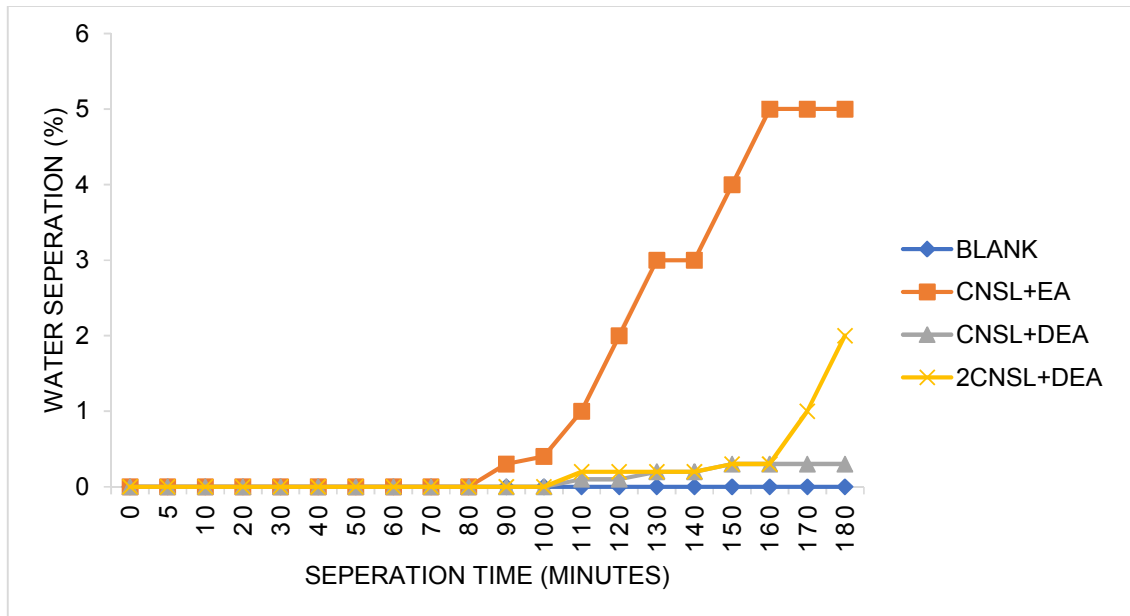
(b)

Fig. 6. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 10% water content and 10 ppm and 60℃

3.5.1 Effect of concentration

Several sets of experiments were done to evaluate the effect of concentration on water seperation, as this parameter governs adsorption of demulsifiers at the interface. The results are presented in Figs. 6 to 20 for the formulated emulsion breakers in xylene and BuOH at

10

different water content and concentrations of 10-50 ppm at 60℃ respectively. The plotted data revealed that increasing demulsifier concentration, increases water seperation for the ethanolamine esters of anacardic acid, this trend follows for formulated emulsion breakers in
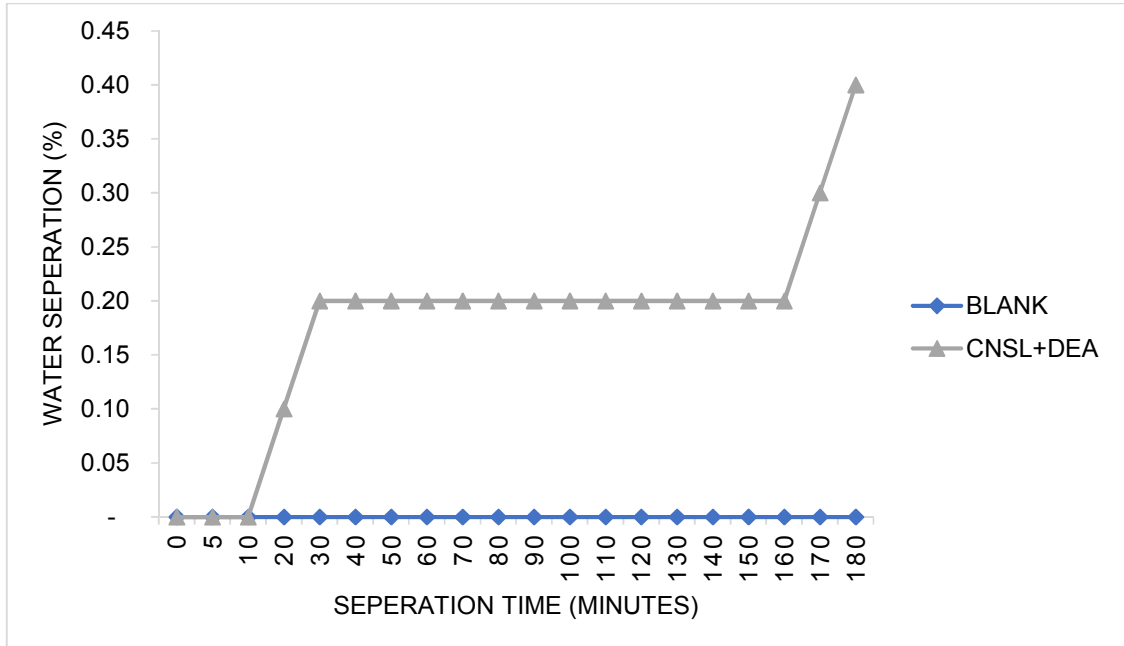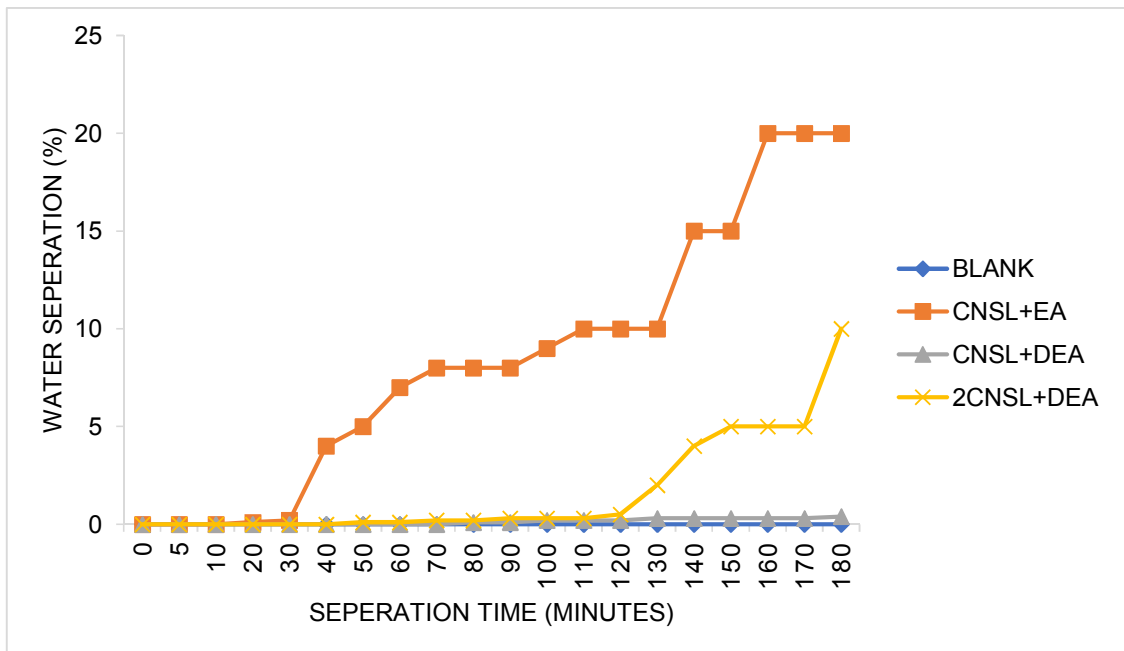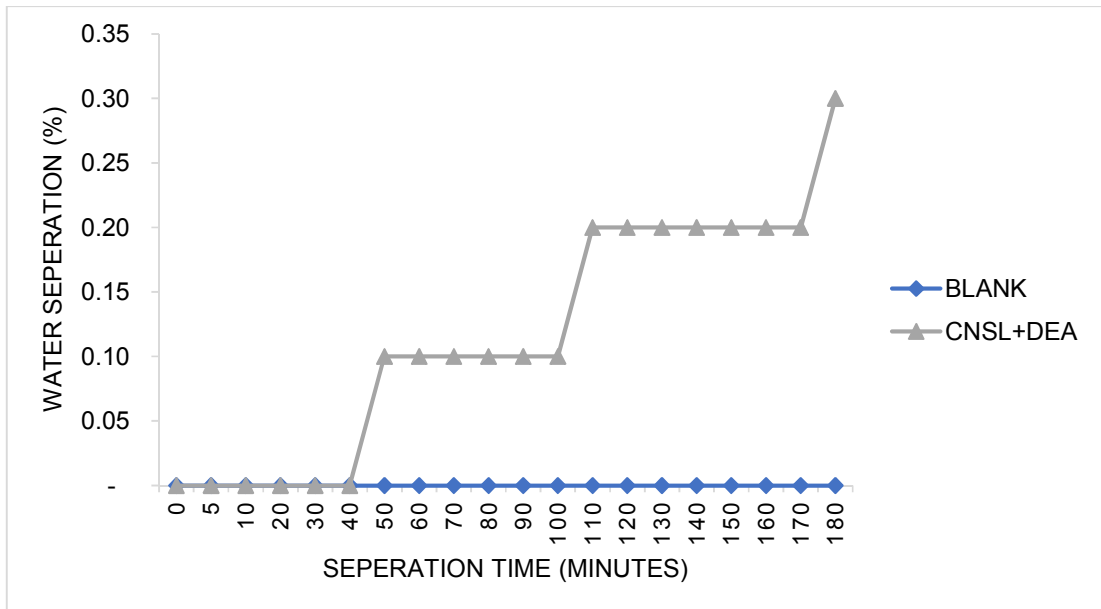

(a)

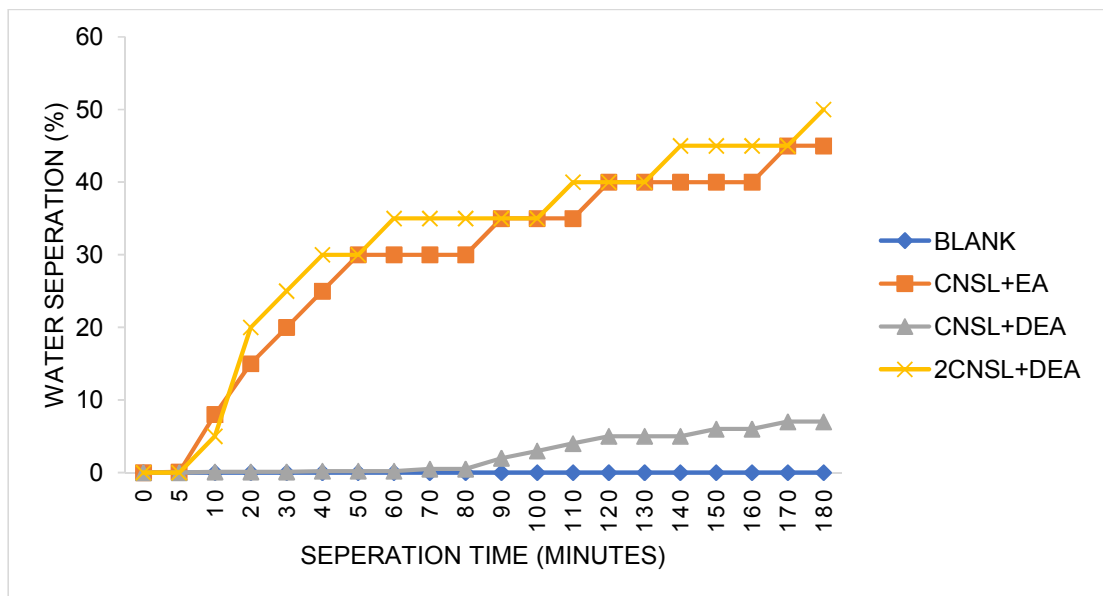**(b)**

Fig. 7. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 10% water content and 20 ppm and 60 ℃

(a)

b)
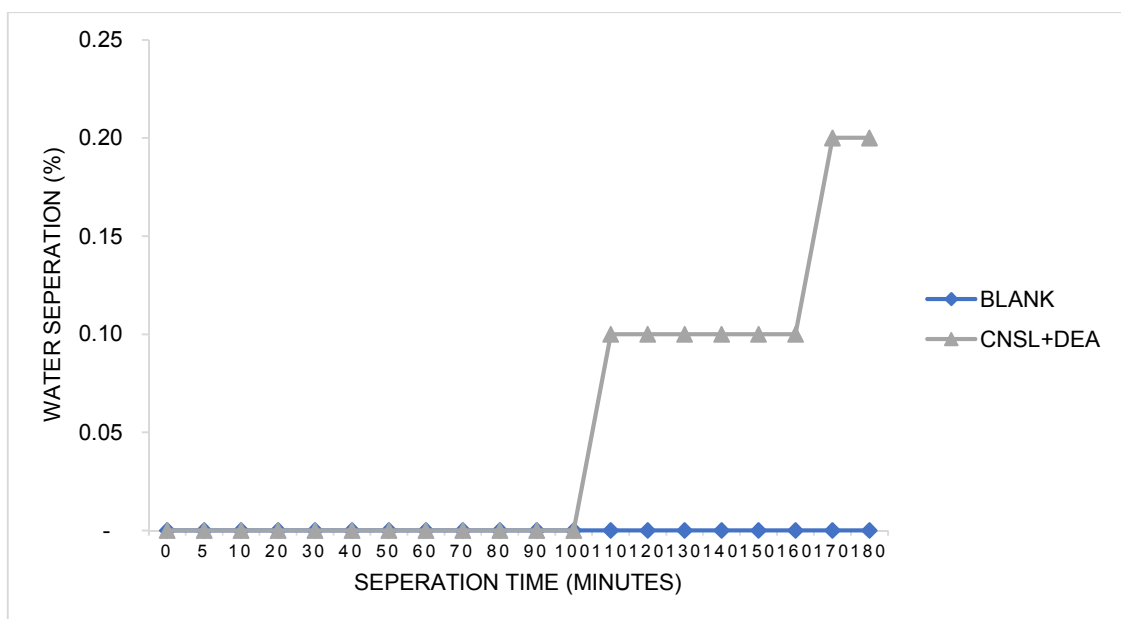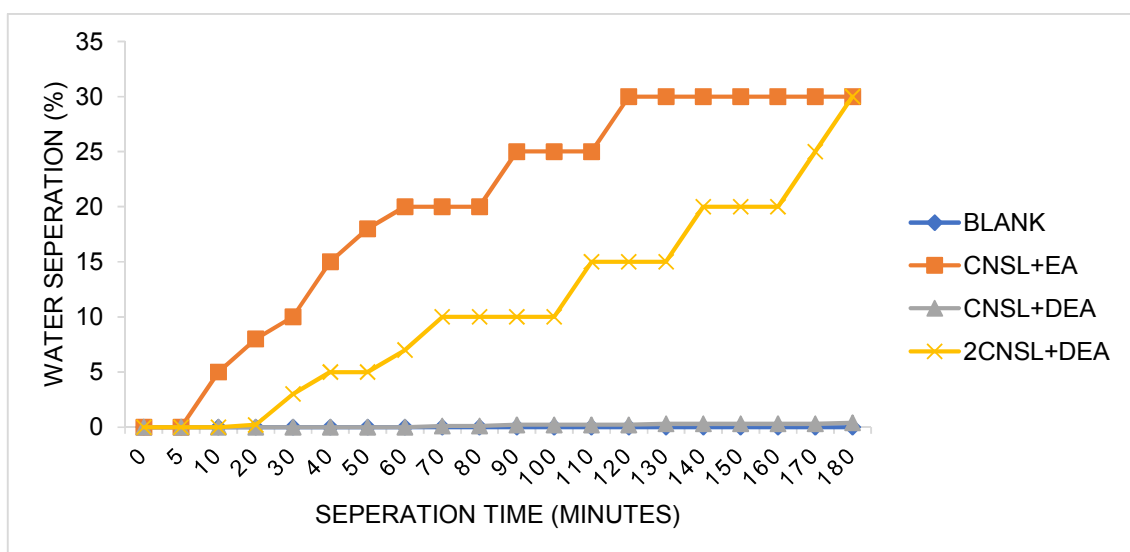
Fig. 8. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 10% water content and 30 ppm and 60 ℃

BuOH, however, in xylene, it is non-existent, as little or no seperation is observed for the emulsion breakers despite increase in concentration. This decrease in seperation time may be due to increased partitioning which further increases adsorption of demulsifier molecules at the emulsion interface [19]. In xylene, at 10 ppm– 50 ppm no seperation was

observed for all or some formulated demulsifiers, and where seperation occurred it was minimal, with difference in their seperation time, which may be due to differences in their chemical structures. In butanol, seperation was observed for all demulsifiers at 10 ppm - 50 ppm and 10% water content, however, at 20 ppm – 50 ppm concentrations, all formulated demulsifiers

showed improvement in water seperation rates compared to their rates in xylene. The demulsification performance of PT-4633 demulsifier in xylene and butanol increases as the concentration increases, with an optimal seperation of 100 % achieved at 50 ppm in lesser time. In comparison to water seperation observed for CNSL-EA, CNSL-DEA, and 2CNSL-DEA, PT-4633 achieved higher water seperation in xylene and butanol at 40 ppm and 50 ppm, except in BuOH where it achieved little or no water seperation at 10 ppm and 20 ppm as illustrated in Figs. 21-25. Generally, for the studied demulsifier formulations, as demulsifier
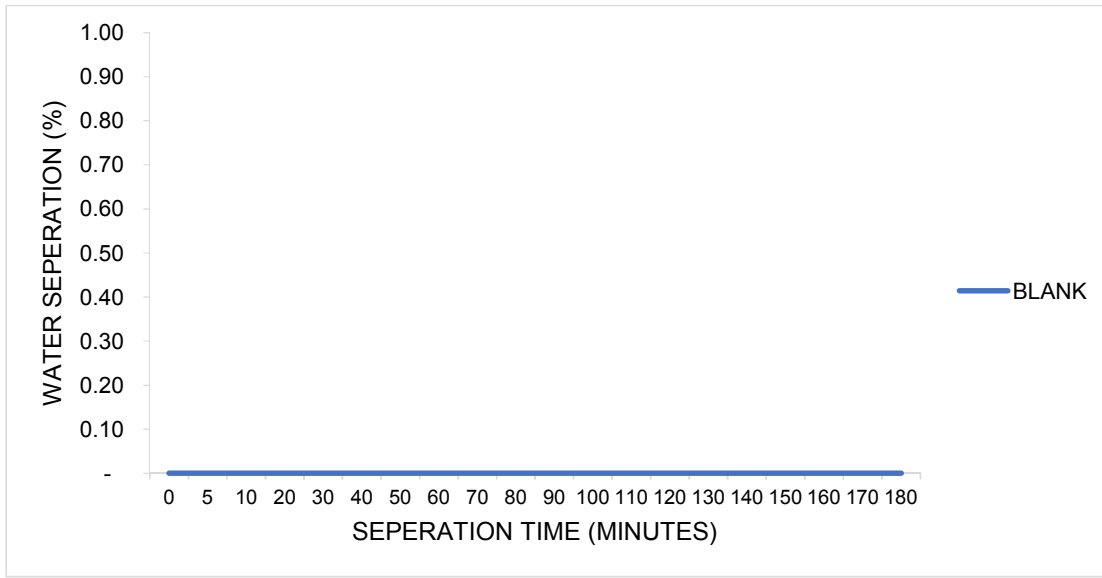
(a)
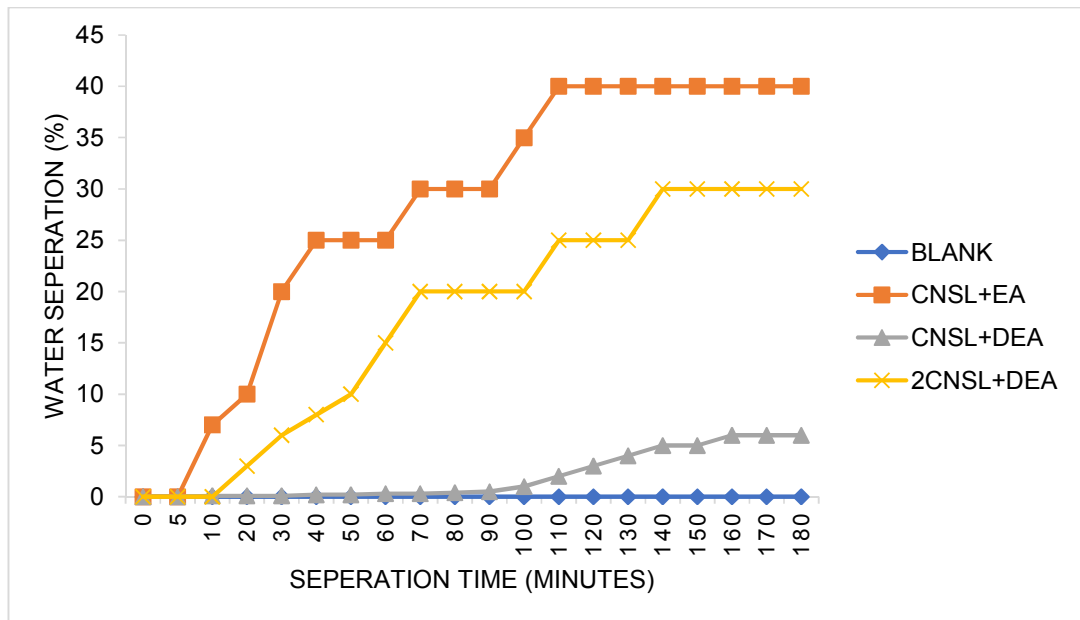
(b)

Fig. 9. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 10% water content and 40 ppm and 60 ℃

(a)

(b)

Fig. 10. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 10% water content and 50 ppm and 60 ℃

concentration increases, interfacial tension of the emulsion decreases, thus increasing percentage of water seperation [18].

3.5.2 Effect of solvent

To investigate the effect of solvents on the demulsification efficiency; the demulsifiers;

CNSL-EA, CNSL-DEA, and 2CNSL-DEA, and PT-4633, were used in two solvents, xylene and BuOH. The data obtained were compared and it showed that water seperation for the formulated demulsifiers was poor in xylene as it took longer times for little or no seperation to occur, as seen in Figs. 6(a)–20(a). However, in butanol, water

14

seperation rate is increased as seen in Figs. 6(b) – 20(b), as it took lesser time to achieve water seperation, indicating that BuOH is a better solvent in optimizing water seperation. Solvent adsorption weakens and ruptures the interfacial film making coalescence rapid and leading to

increased water seperation attributed to the synergetic (common ion) effect of the -OH group in butanol. With BuOH, water seperation was achieved in shorter times compared to xylene. Interfacial quality of the emulsions was examined and w/o interface was cloudy for bottle tests
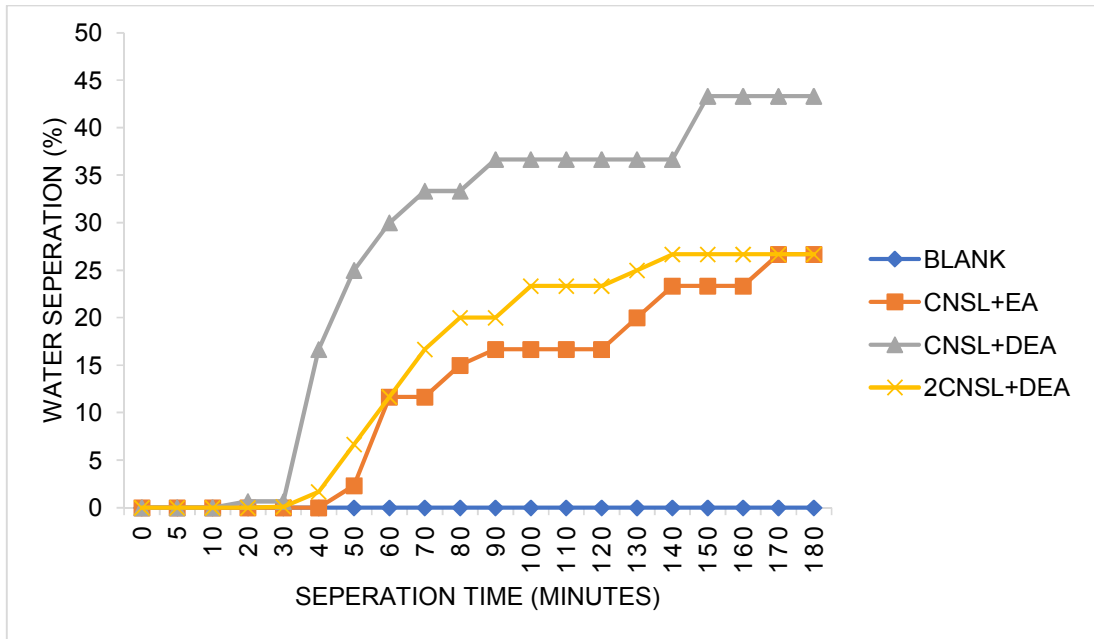
(a)
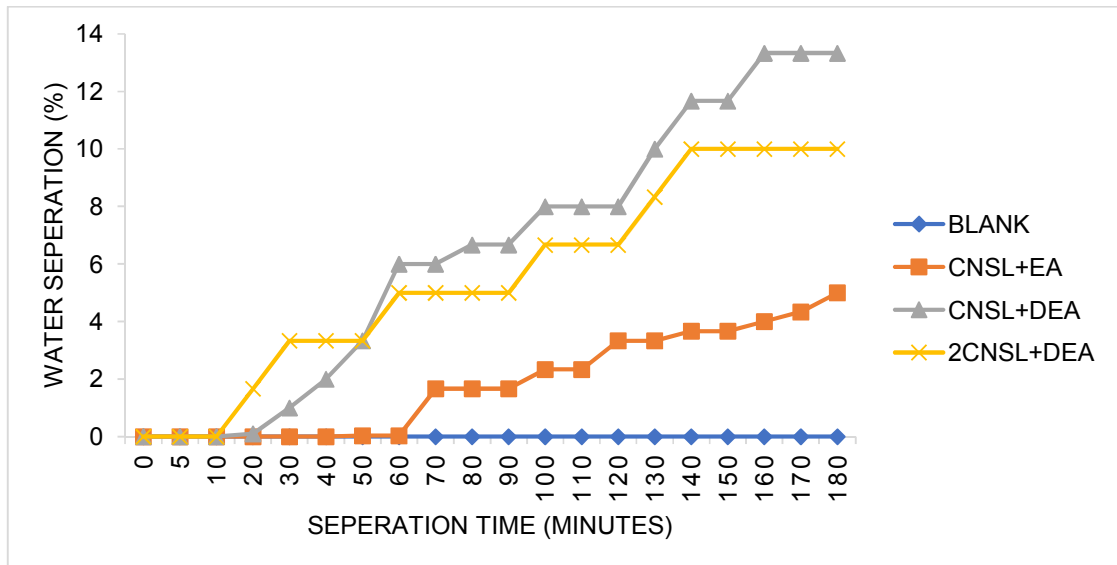
(b)

Fig. 11. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 30% water content and 10 ppm and 60℃
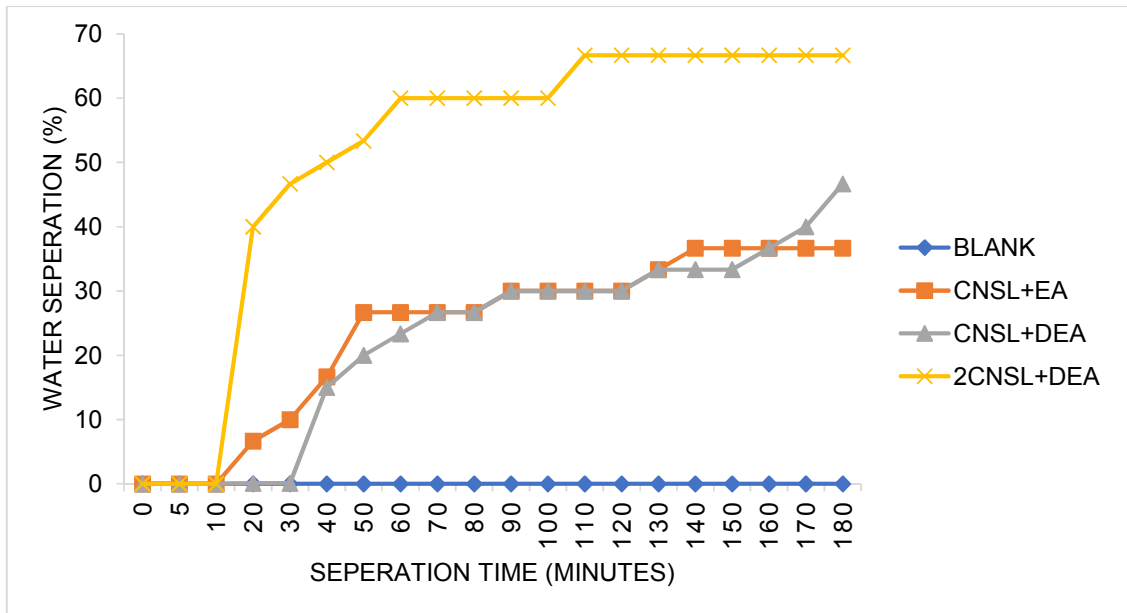
(a)

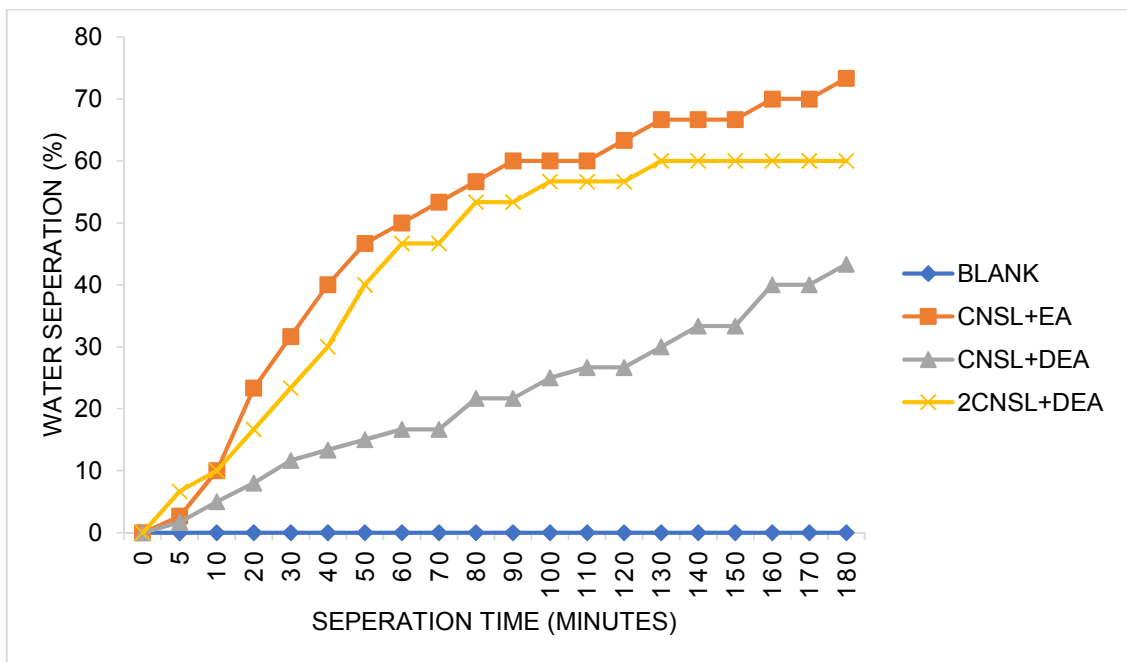**(b)**
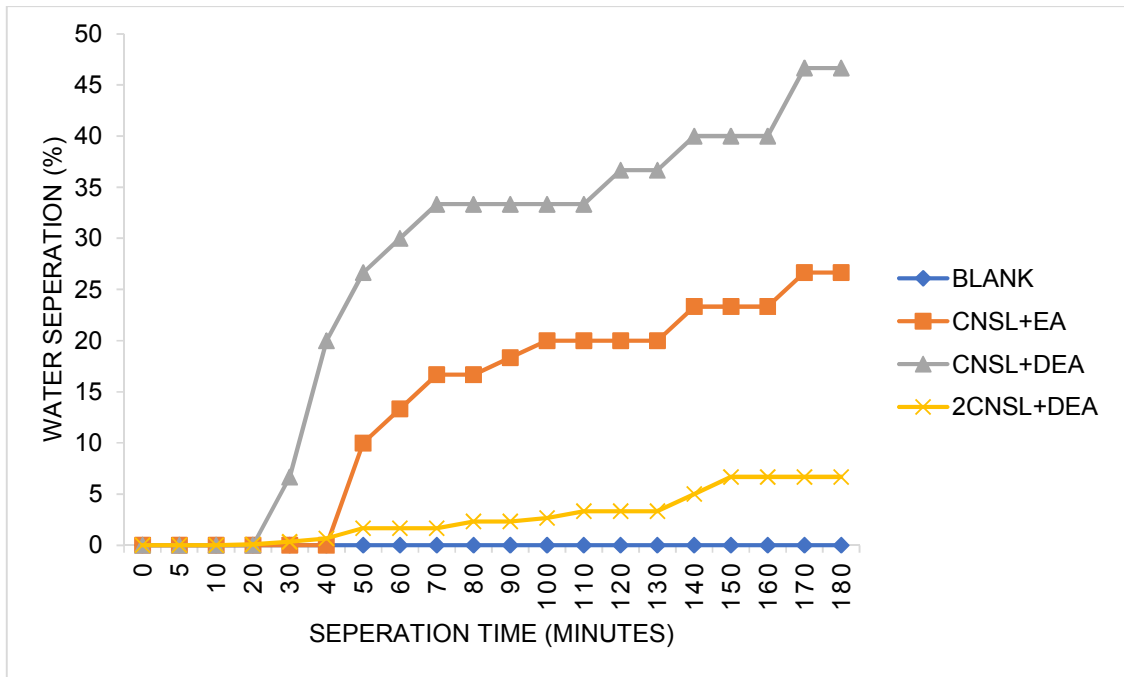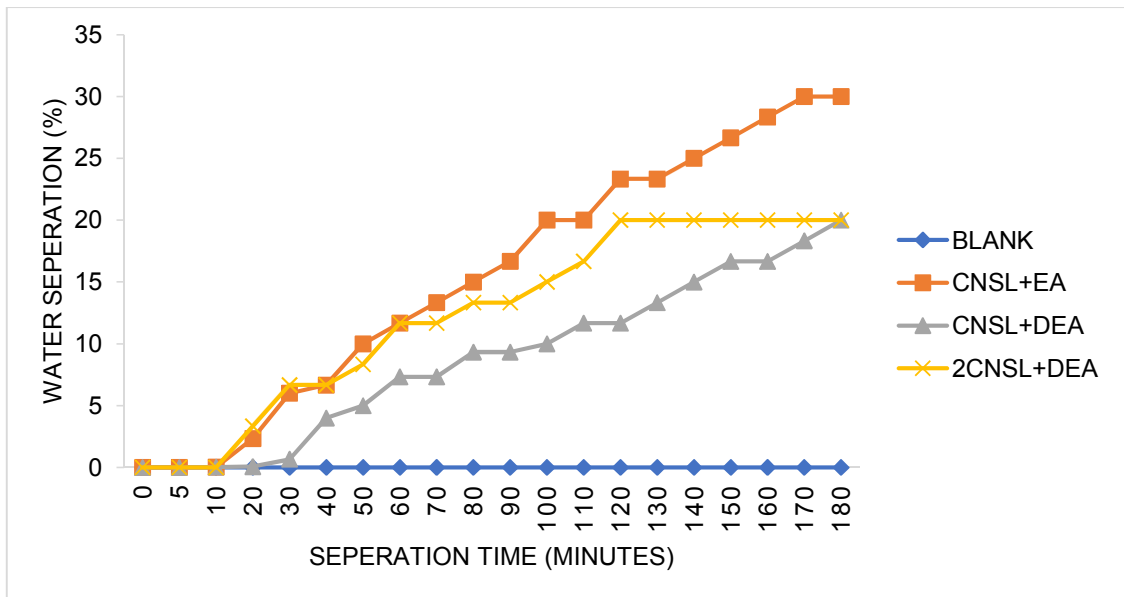
Fig. 12. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 30% water content and 20 ppm and 60 ℃

using the formulated demulsifiers in xylene, while for BuOH, the w/o interface was distinct and the water phase was very clear as seen in bottle test results illustrated in Appendix 3 and 4.

3.5.3 Effect of water content

Emulsion water content plays an imperative role on demulsifier performance. Varying proportions

of crude oil: water mixing ratios, 90:10, 70:30 and 50:50, to produce different degrees of w/o emulsions were used to investigate this parameter. By inspection of data illustrations in Figs. 6–20, water seperation rates for formulated demulsifiers increased with increase in water content. This is because water drop-out/seperation becomes very difficult at low water content, because external pressure of the oil is greater than the internal pressure of the water droplets leading to increased interfacial film firmness, making it difficult for coalescence of
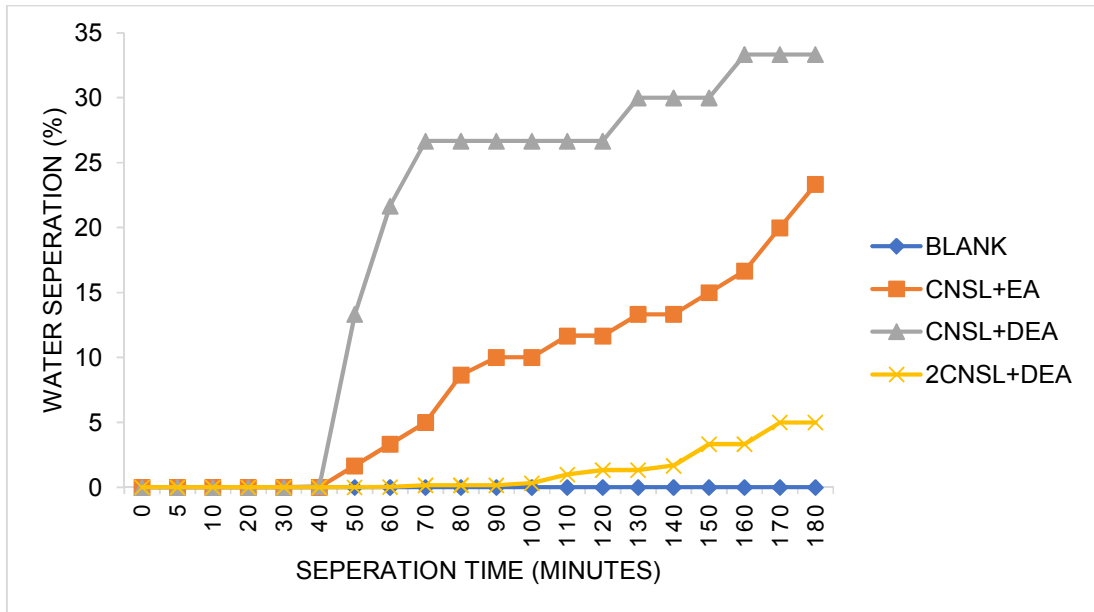
(a)
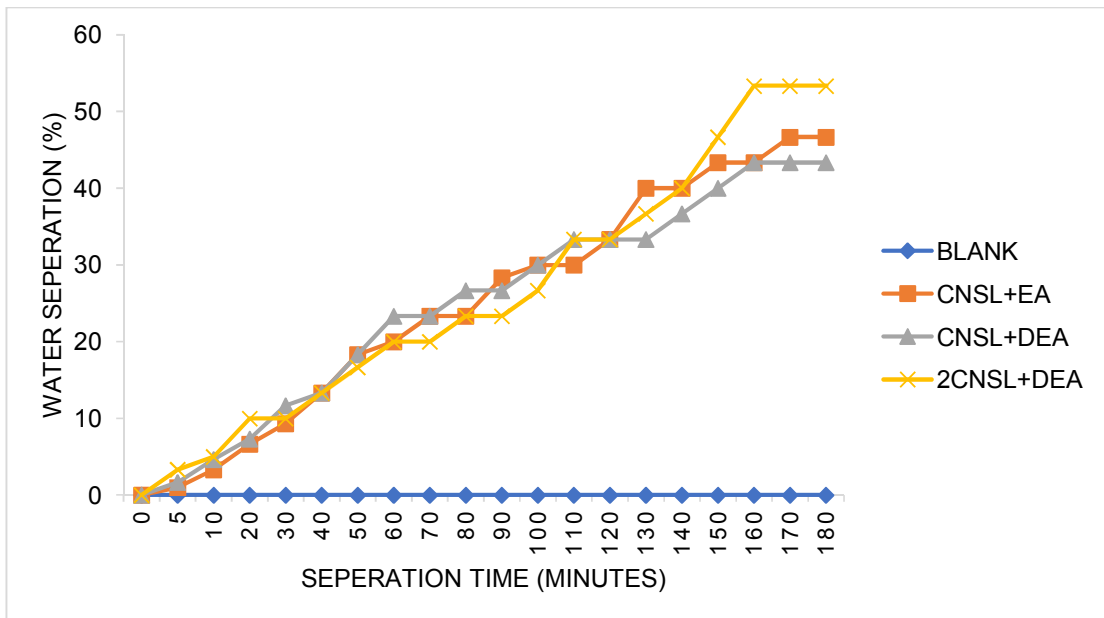
(b)

Fig. 13. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 30% water content and 30 ppm and 60 ℃

(a)

(b)

Fig. 14. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 30% water content and 40 ppm and 60 ℃

water droplets to occur. At increased water content, the external pressure of the water droplets is less the internal pressure of the oil, leading to increased interfacial film thinning thus

enhancing coalescence [19,20,21,22]. However, at 10% water content, water seperation for PT-4633 increases as concentration increases, compared to the formulated demulsifiers

irrespective of solvent type. At 30% water content, PT-4633 shows little or no seperation at 10 ppm and 20 ppm in BuOH, however as concentration increases, the water seperation increases. At 50% water content, high water seperation at high concentrations of 40 ppm and 50 ppm at shorter times was observed for PT-4633 in xylene as shown in Figs. 21–25.
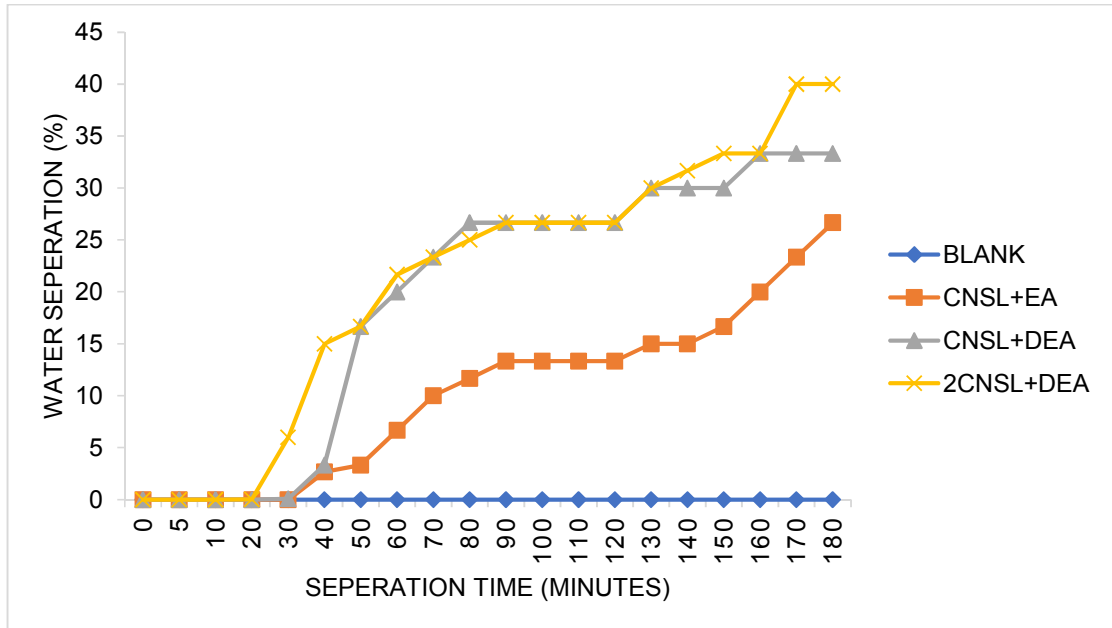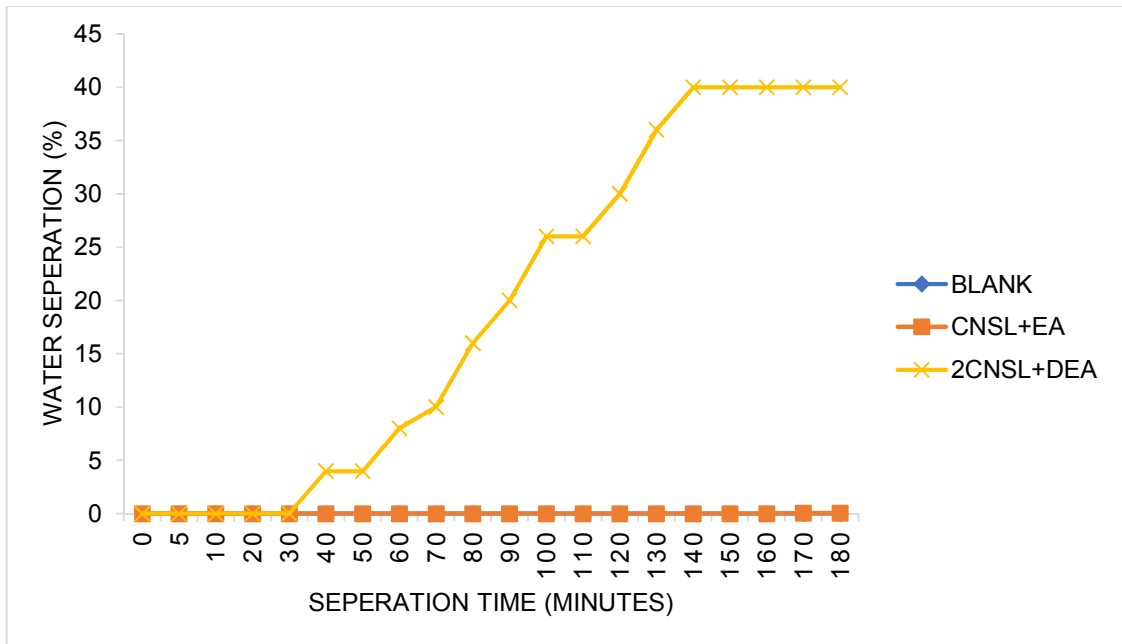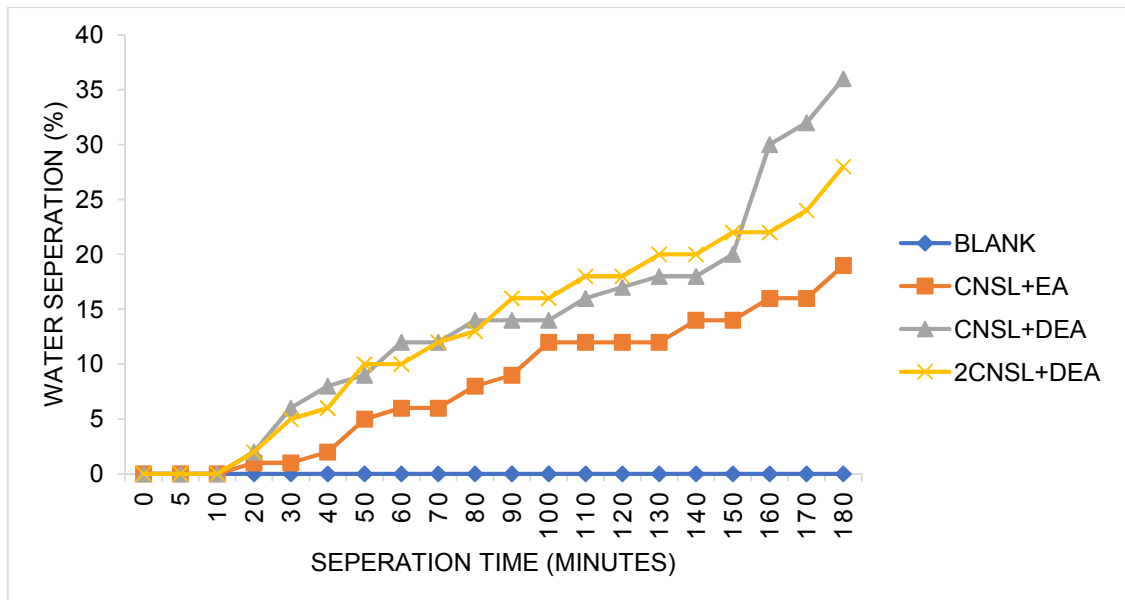

(a)
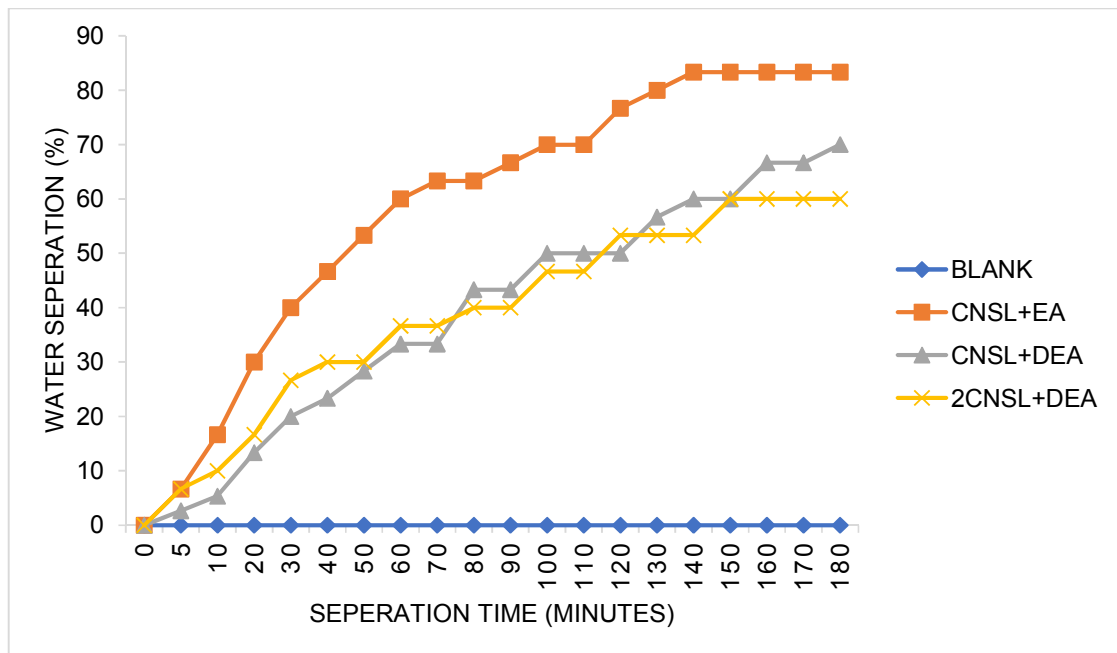
(b)

Fig. 15. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 30% water content and 50 ppm and 60 ℃

(a)

(b)

Fig. 16. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 50% water content and 10 ppm and 60 ℃

3.5.4 Effect of chemical structure

Chemical demulsification method, involves the use of chemicals (mostly surfactants) to treat emulsions. Studies have shown that these surface-active agents, can be produced through various methods; changing acceptor ratio, quantity and arrangement of water-loving and oil-loving groups [16,18,19,21,23,24]. Chemical structures of most effective emulsion breakers

20

contain a hydrophobic backbone and a more hydrophilic head-group side chain. The hydrophobic ends match natural emulsifiers in the emulsion (asphaltenes) thus enhancing demulsification efficiency. The data plots in Figs. 6–20 show that water seperation decreases with increasing water content, concentration and varies from demulsifier to another, due to differences which exist in their structures, which is of great importance in the adsorption of the demulsifier molecule on the emulsion interface [25]. The demulsifier performance also varied in both solvents, however, water seperation is improved with butanol.
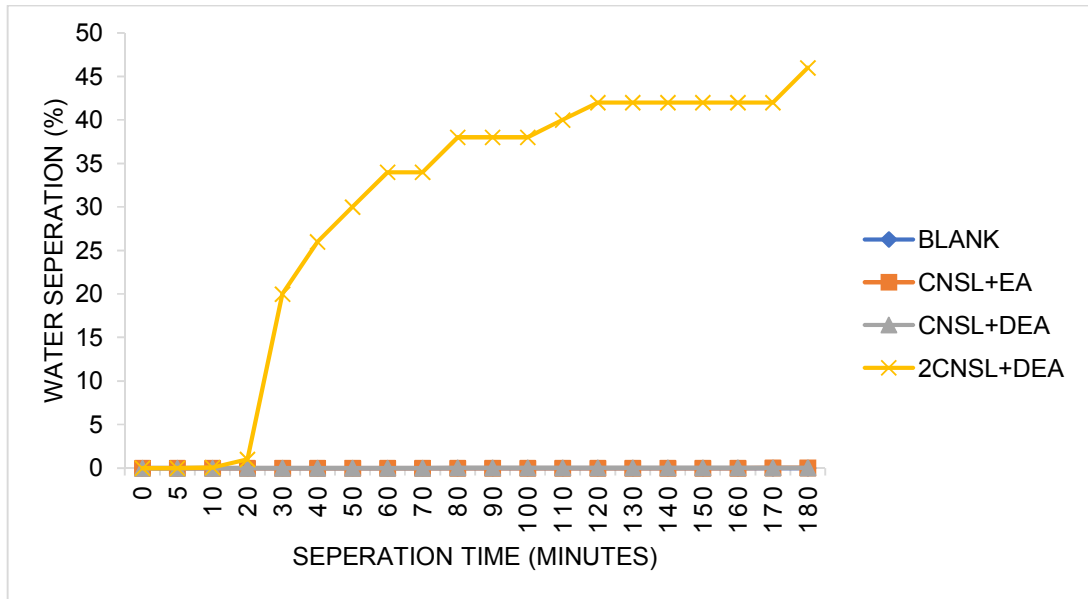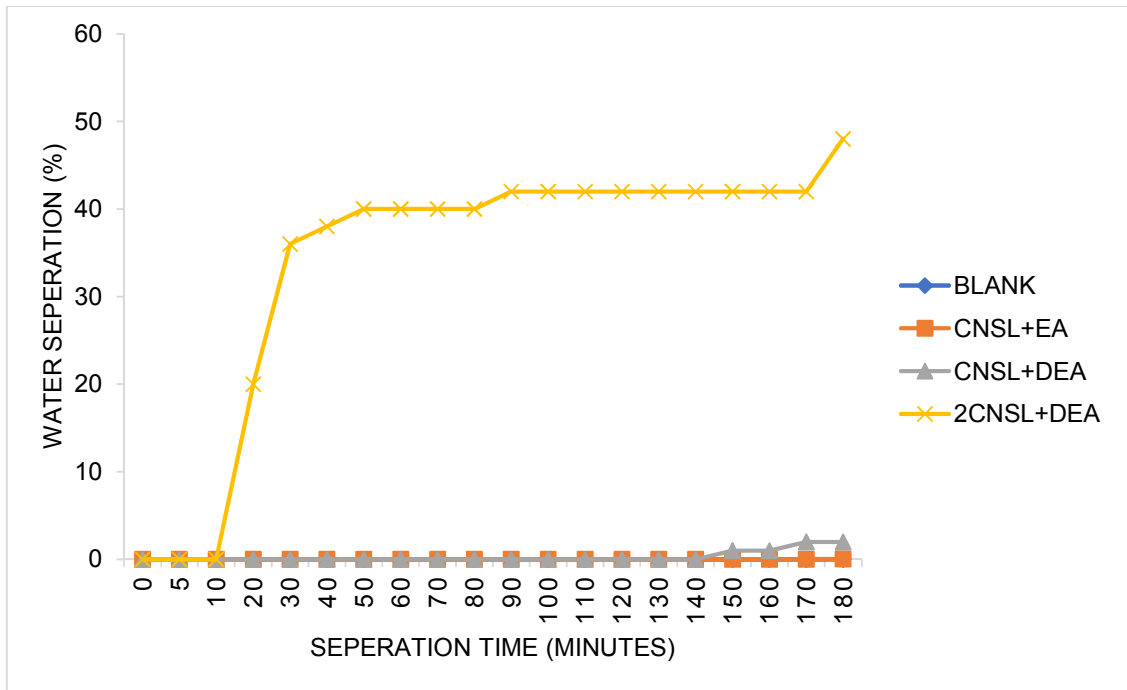

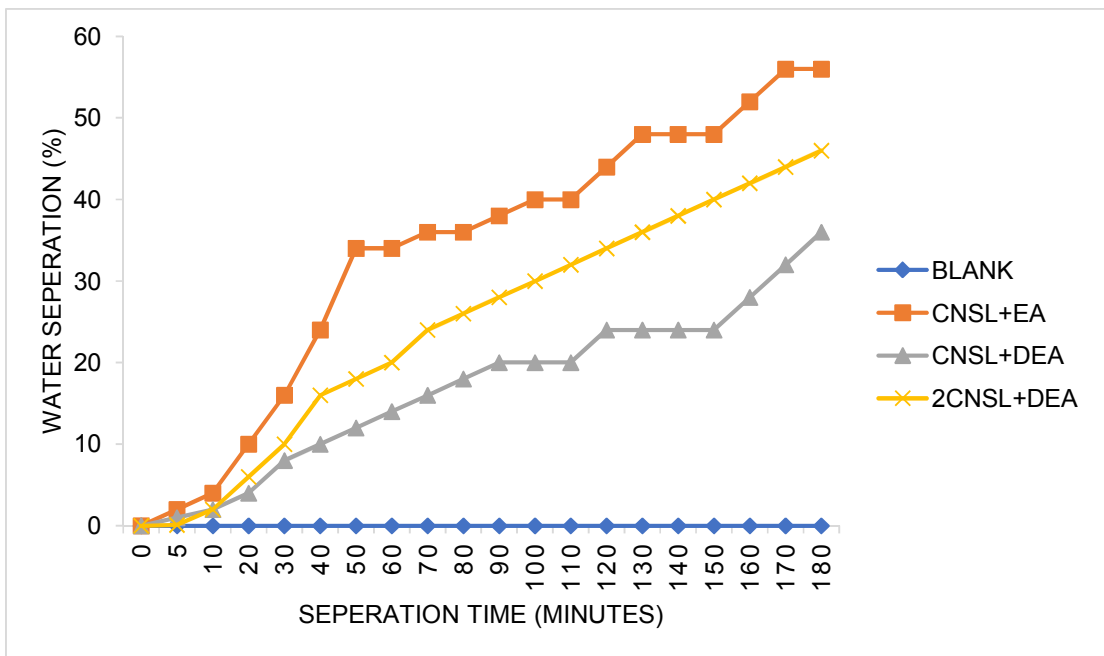**(a)**
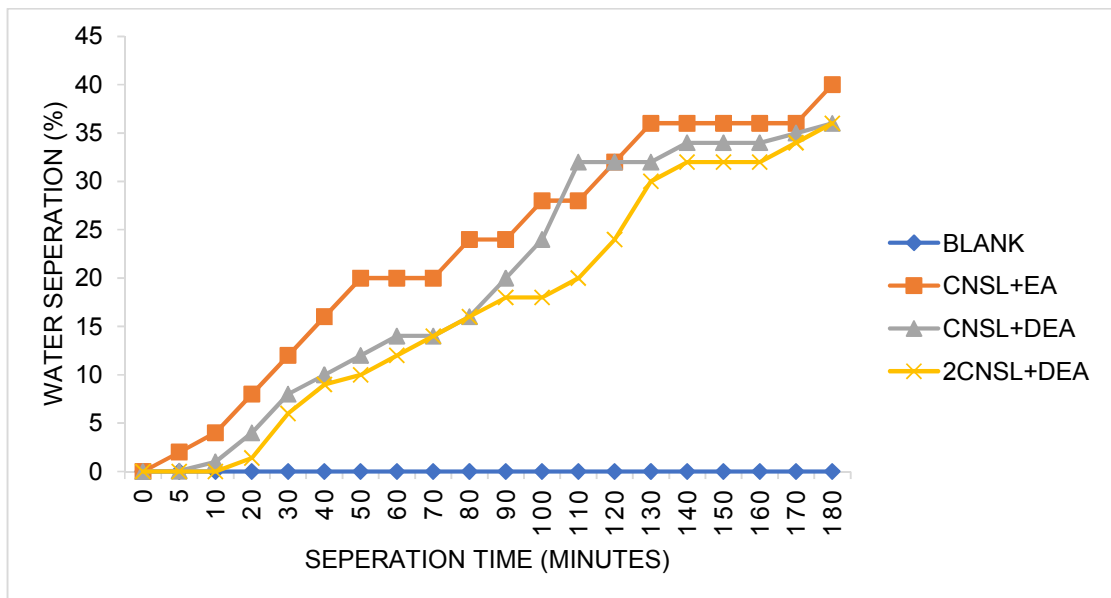
(b)

Fig. 17. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 50% water content and 20 ppm and 60 ℃
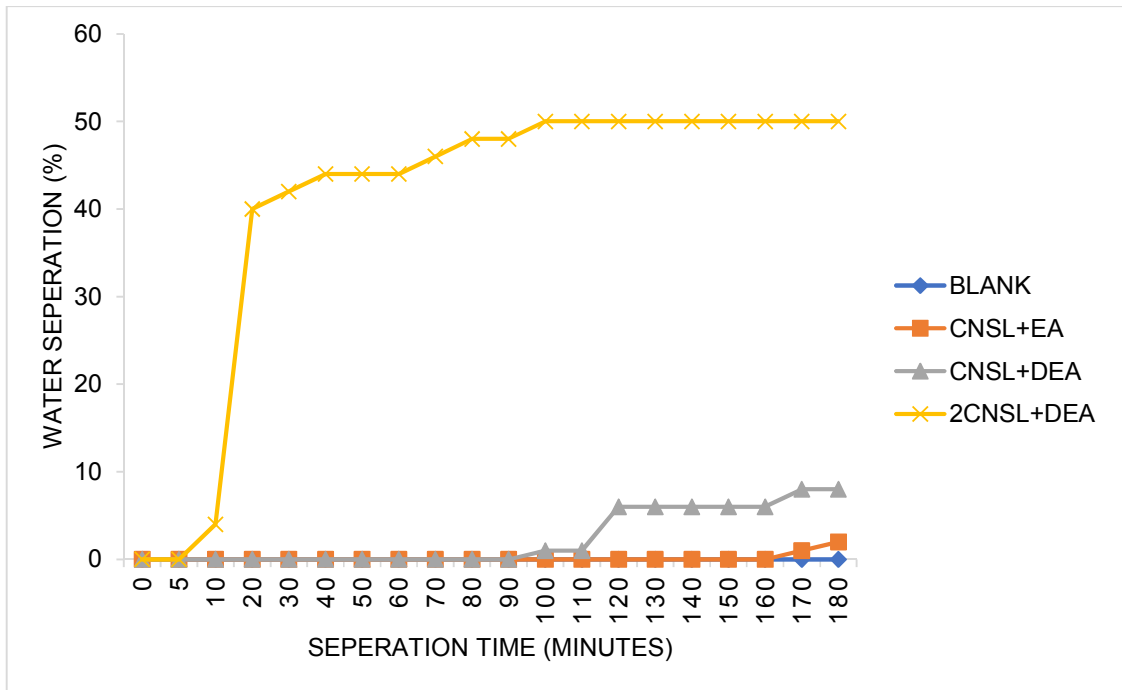
21

(a)

(b)

Fig. 18. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 50% water content and 30 ppm and 60 ℃

(a)

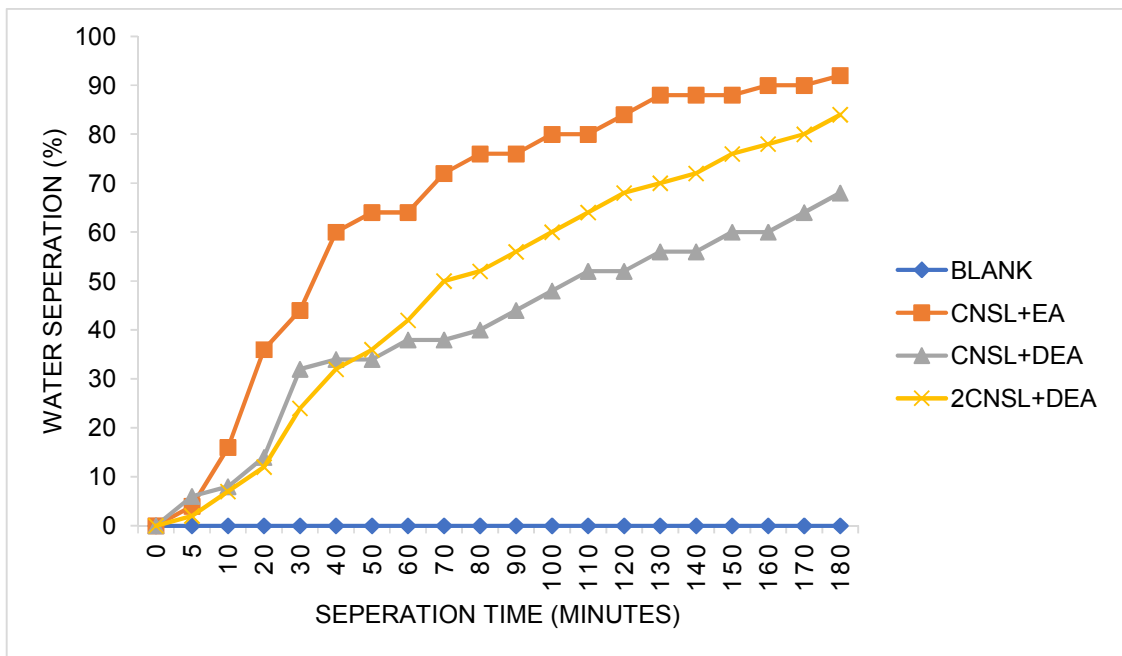**(b)**

Fig. 19. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 50% water content and 40 ppm and 60 ℃
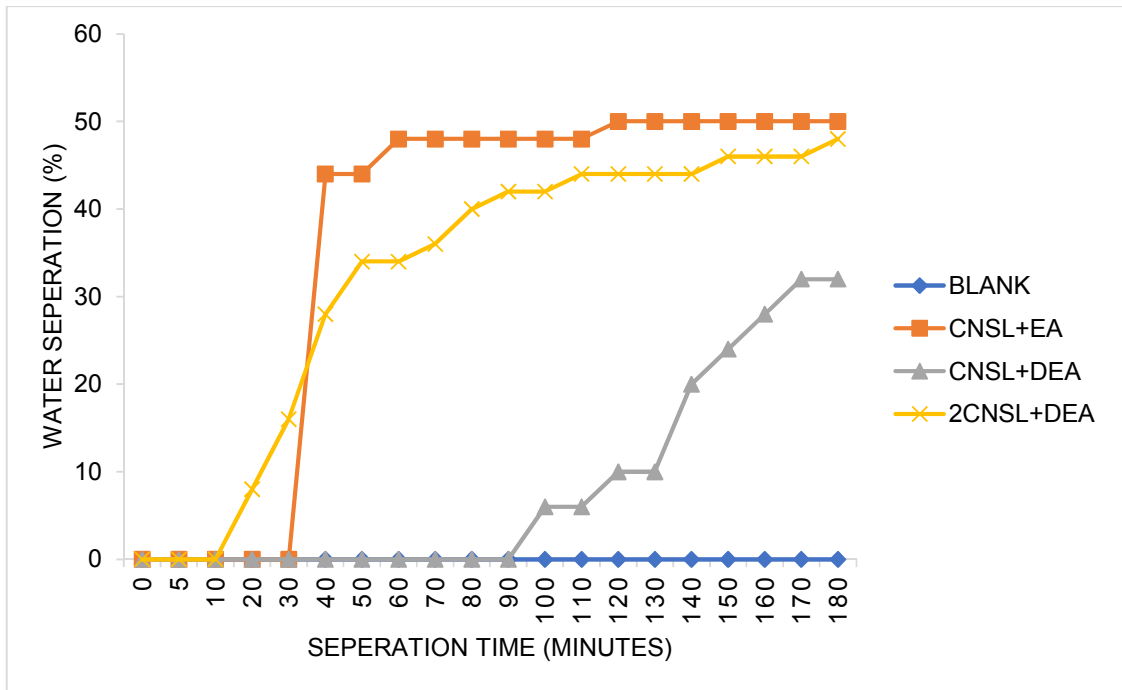
(a)

(b)

Fig. 20. Water seperation (%) of the formulated emulsion breakers in (a) Xylene, and (b) BuOH at 50% water content and 50 ppm and 60 ℃
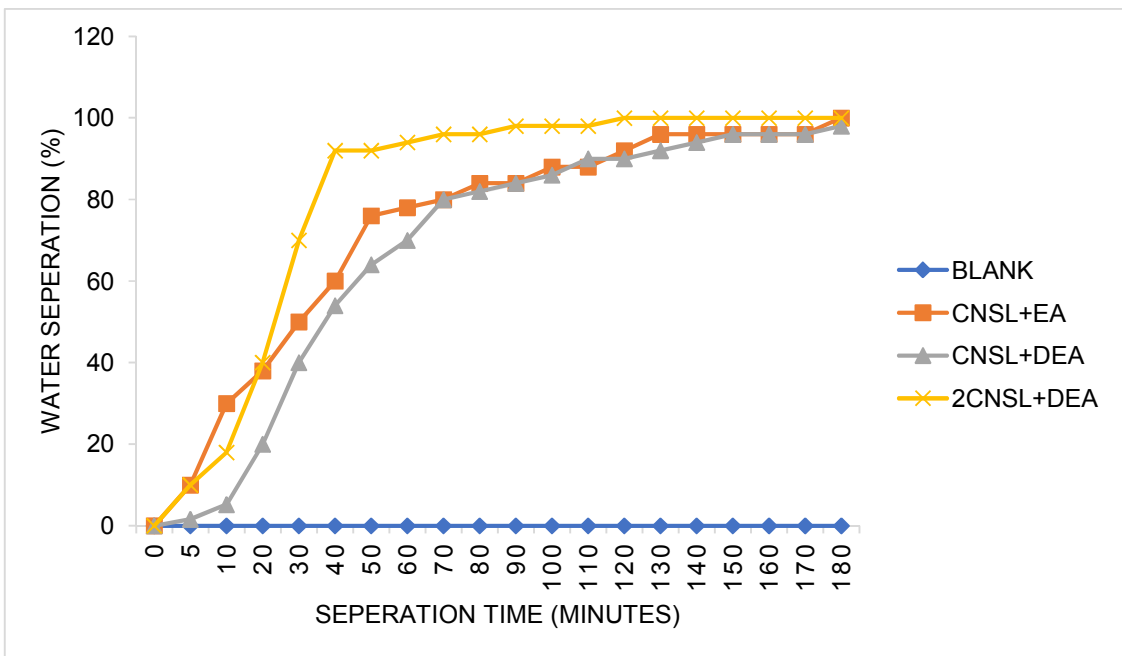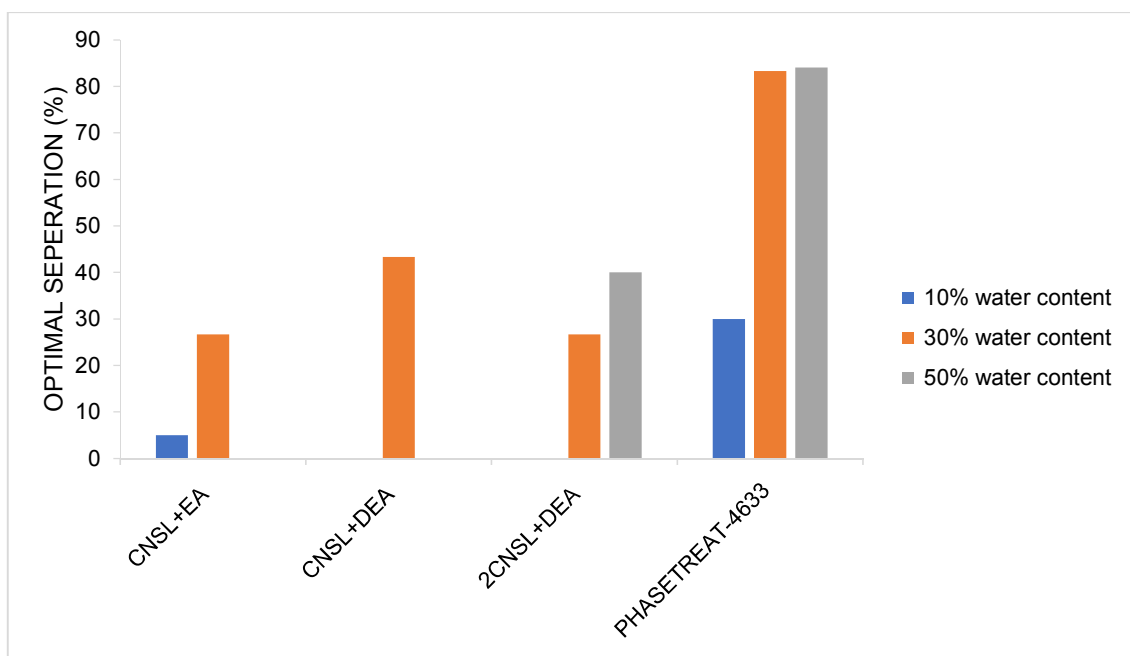
(a)
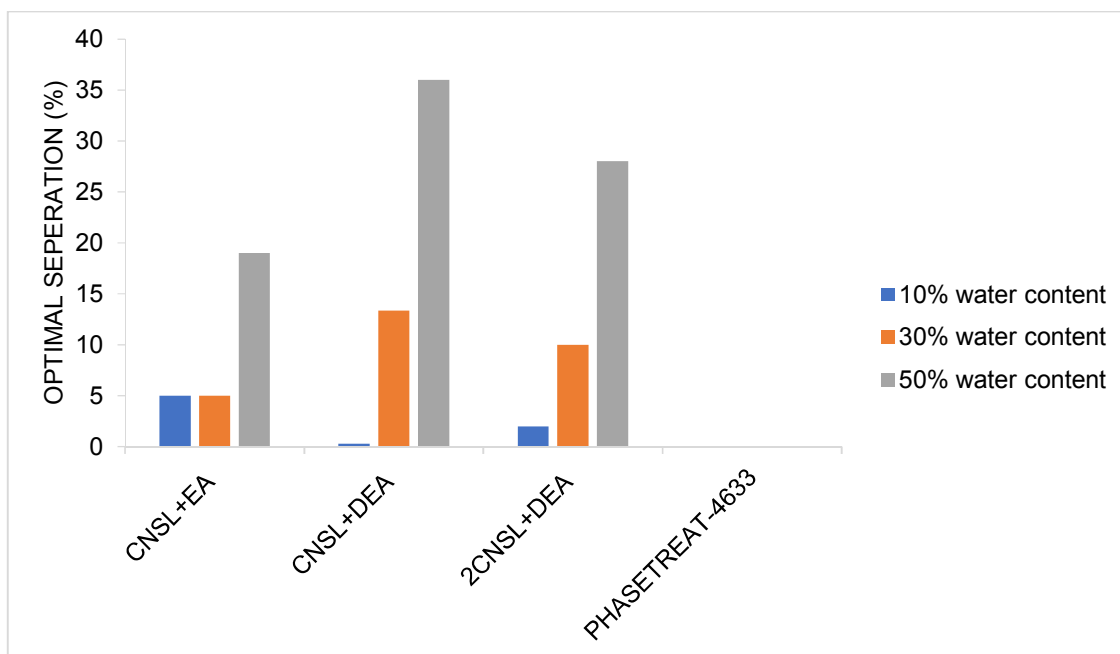
(b)

Fig. 21. Comparison of Optimal Water seperation (%) of formulated emulsion breakers and Phasetreat-4633 in (a) Xylene, and (b) BuOH at 10 ppm and 60 ℃

(a)

(b)

Fig. 22. Comparison of Optimal Water seperation (%) of formulated emulsion breakers and Phasetreat-4633 in (a) Xylene, and (b) BuOH at 20 ppm and 60 ℃

(a)

(b)

Fig. 23. Comparison of Optimal Water seperation (%) of formulated emulsion breakers and Phasetreat-4633 in (a) Xylene, and (b) BuOH at 30 ppm and 60 ℃

(a)

(b)

Fig. 24. Comparison of Optimal Water seperation (%) of formulated emulsion breakers and Phasetreat-4633 in (a) Xylene, and (b) BuOH at 40 ppm and 60 ℃
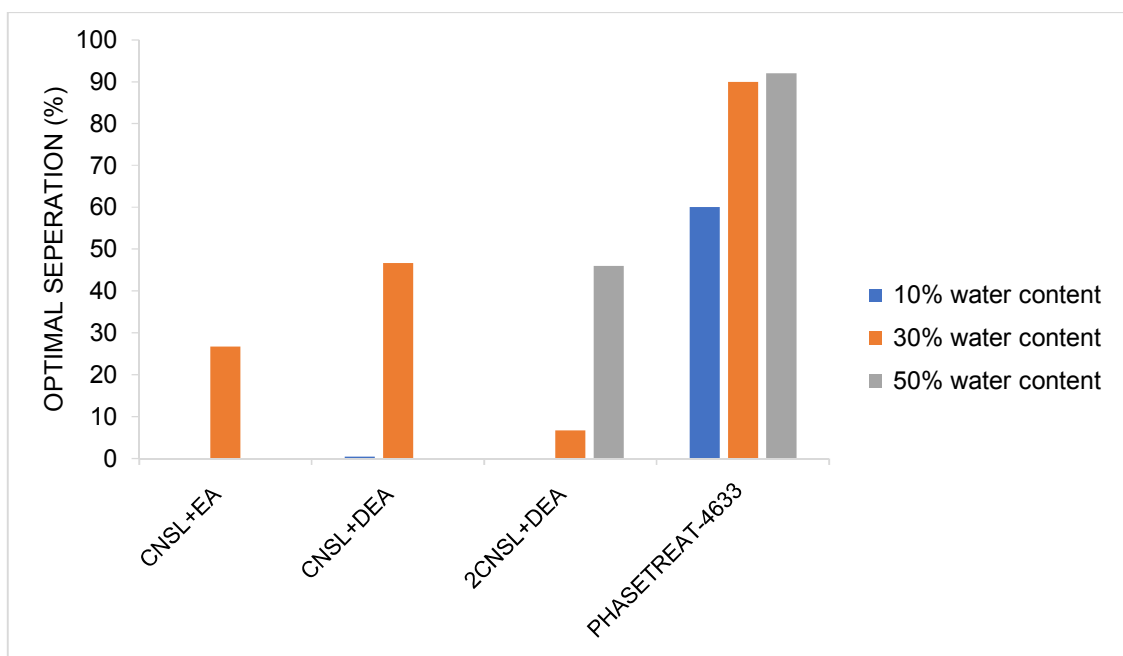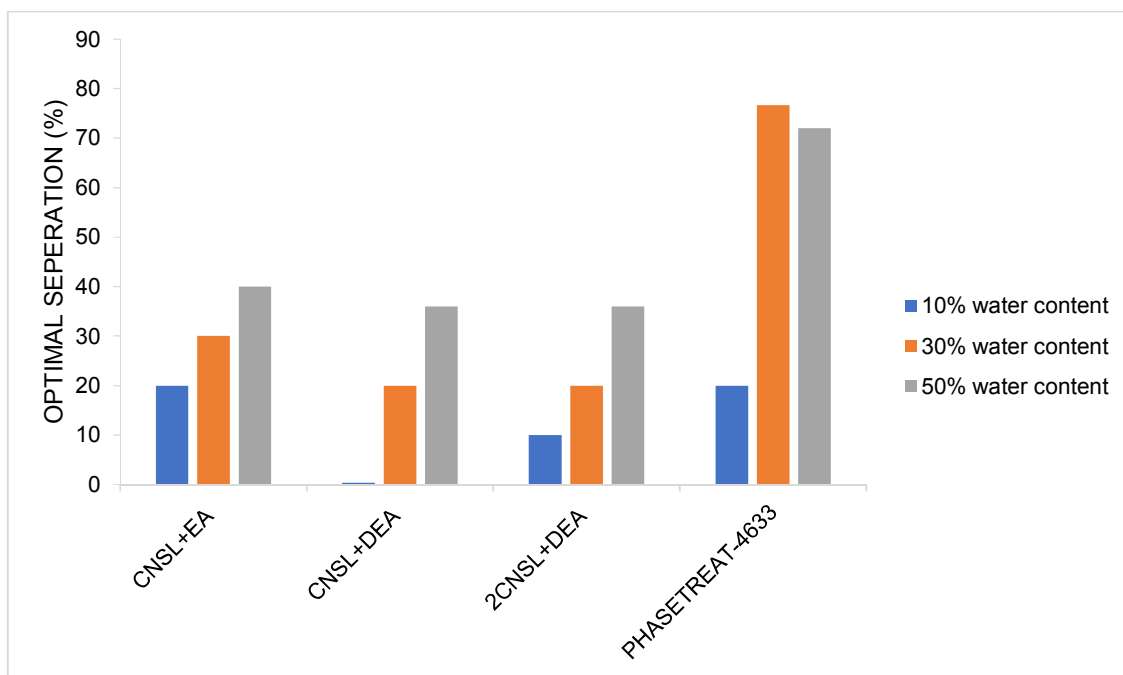
(a)

(b)

Fig. 25. Comparison of Optimal Water seperation (%) of formulated emulsion breakers and Phasetreat-4633 in (a) Xylene, and (b) BuOH at 50 ppm and 60 ℃
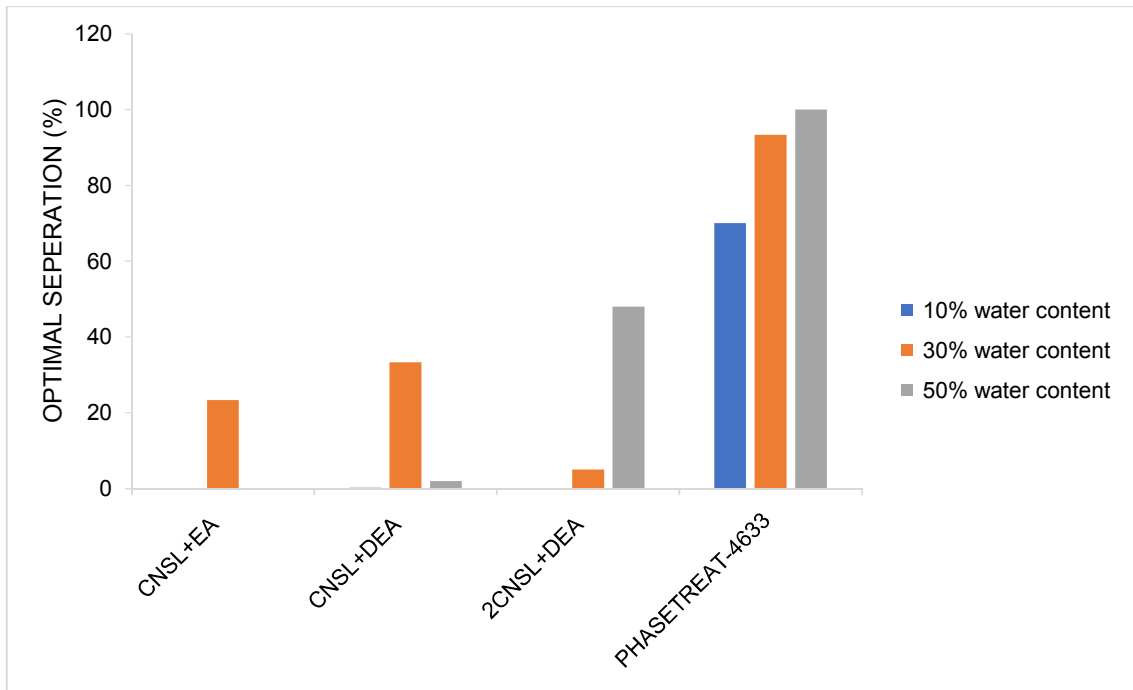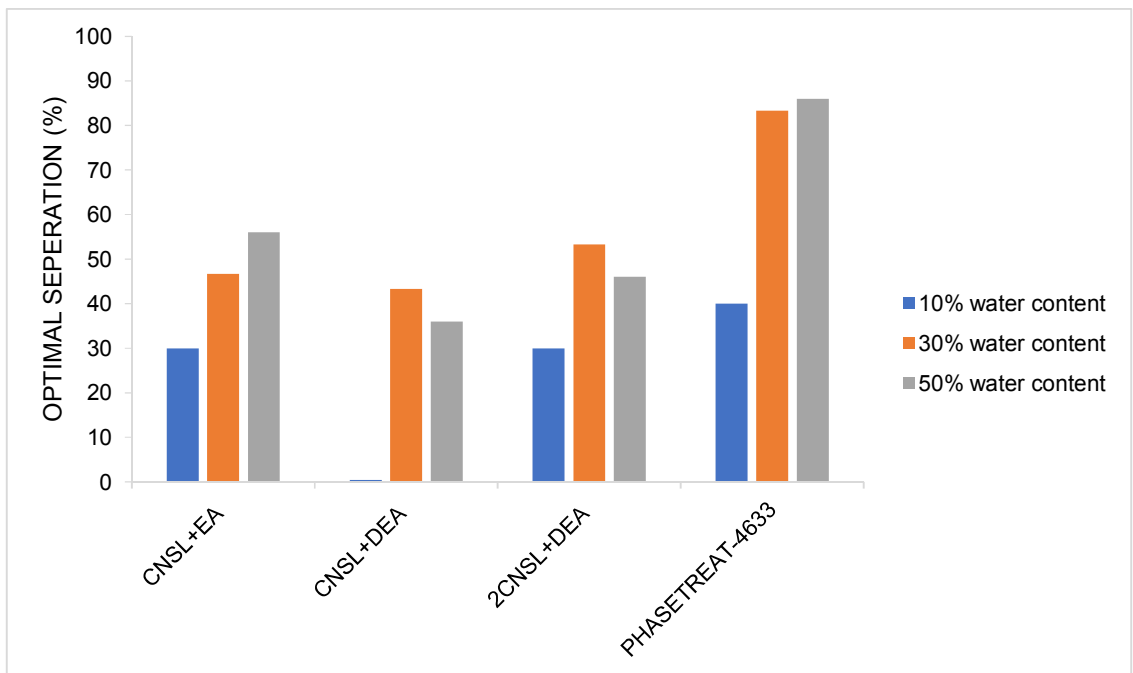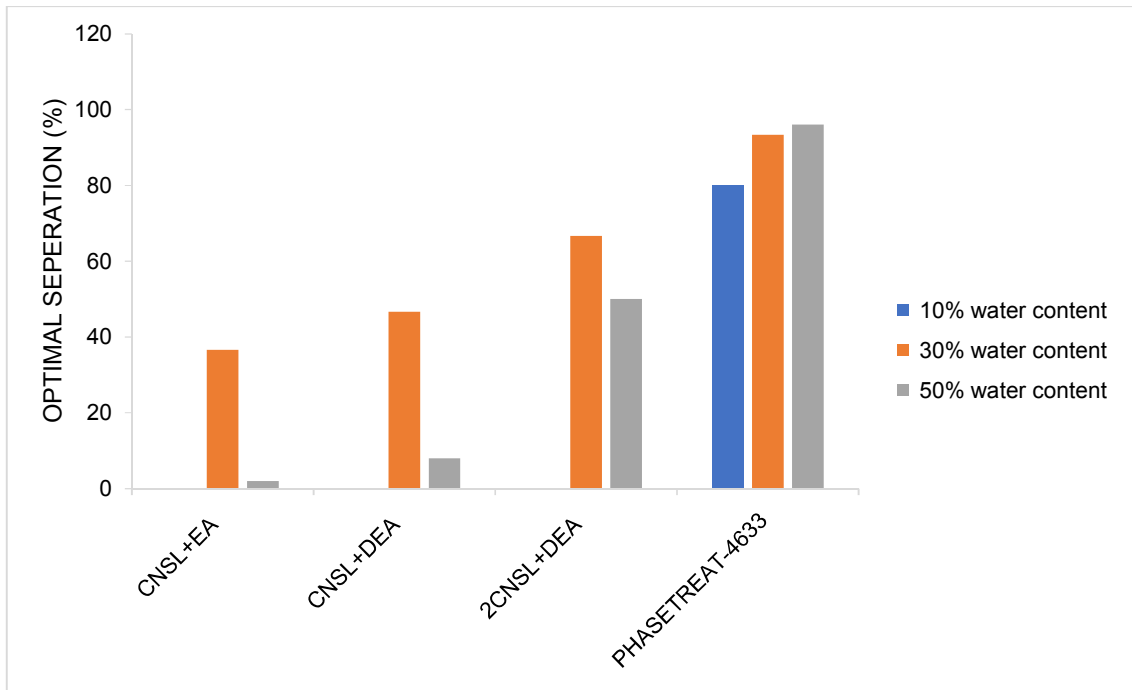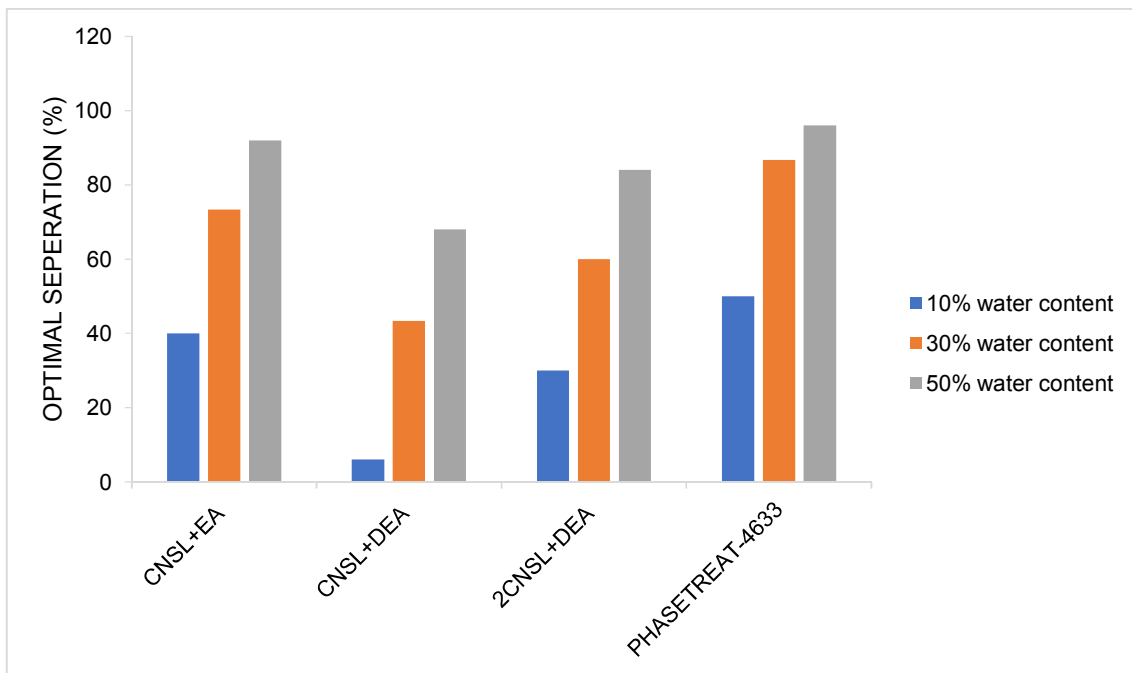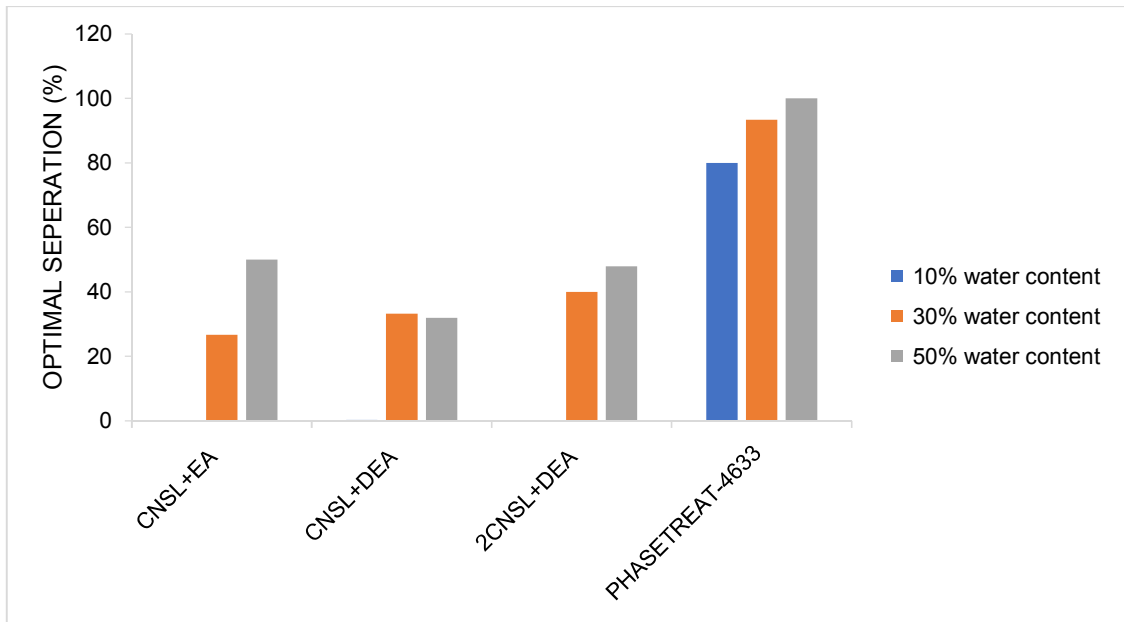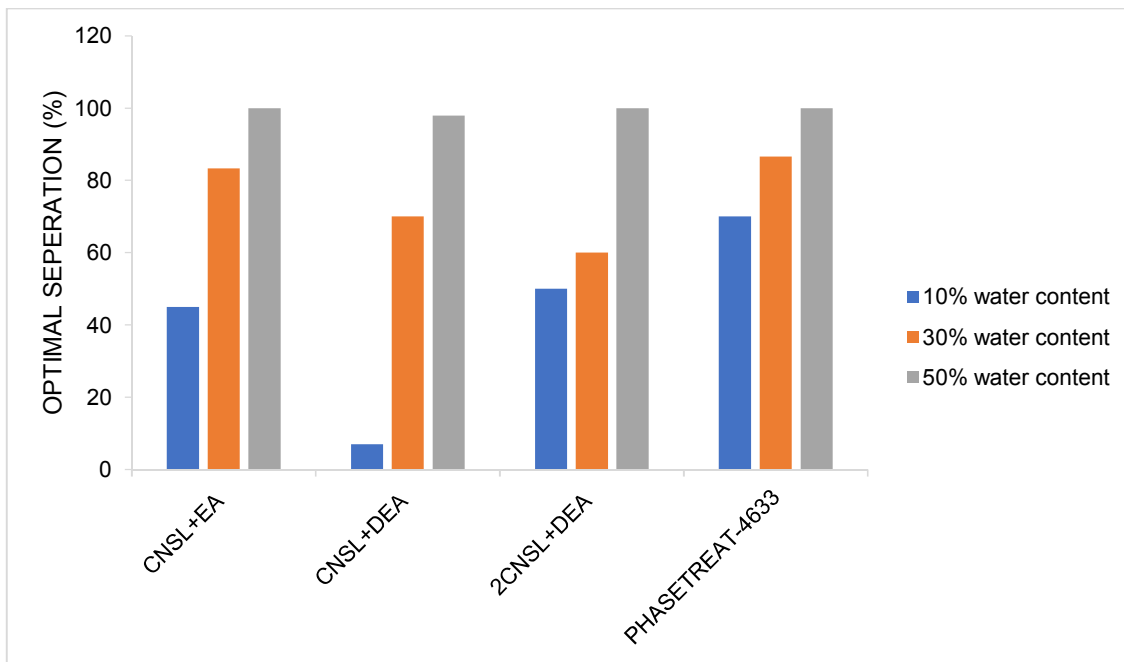
4. CONCLUSION

From the study, the following conclusion(s) can be deduced:

1. The synthesized ethanolamine-CNSL products function as crude oil emulsion breakers.

29

2. Increasing demulsifier concentration (from 10 ppm to 50 ppm) and water content of the emulsion increases water separation.

3. Performance evaluation of the formulated demulsifiers showed that the effective emulsion breakers in both solvents across the concentrations studied are in this order: CNSL-EA > 2CNSL-DEA> CNSL-DEA.

4. The comparative evaluation with a commercial demulsifier formulation (PT-4633 in xylene) revealed that the efficiency of the commercial demulsifier in butanol is better at increased water content and concentration than the currently used formulation.

5. The chemical structure of the formulated emulsion breakers and solvent type, may have increased the partitioning between emulsion phases which enhanced demulsification performance.

6. Optimal water seperation of 100% was achieved by PT-4633 and Ethanolamine-CNSL products in butanol which is because of the attributive synergetic effect of the hydroxyl group.

Though the demulsification performance of the ethanolamine-CNSL product is low compared to PT-4633, it should be considered as substitute for petroleum-based demulsifier chemicals, due to the availability of CNSL, and reduced cost advantage. Also, butanol should be considered as a solvent substitute for xylene, due to its attributive synergetic (common ion) effect, low cost and low toxicity levels. We recommend further works on the economics and toxicity of demulsifier formulations with ethanolamine-CNSL products, and comparison of same with other available commercial demulsifier(s) in the field.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Appendix 1. Water seperation rate of the formulated demulsifiers and PT-4633 in Xylene at varying water content and concentration at 60℃

Demulsifier Code	Concentration (ppm)	10% water content		30% water content		50% water content	
		Water Seperation (%)	Time (mins)	Water Seperation (%)	Time (mins)	Water Seperation (%)	Time (mins)
CNSL-EA	0	-	180	-	180	-	180
	10	-	180	26.67	170	0.06	170
	20	-	180	26.67	170	0.04	180
	30	-	180	23.33	180	0.04	180
	40	-	180	36.67	40	2	180
	50	-	180	26.67	180	50	120
CNSL-DEA	0	-	180	-	180	-	180
	10	-	180	43.33	150	-	180
	20	0.4	180	46.67	170	0.04	80
	30	0.2	170	33.33	160	2	170
	40	-	180	46.67	180	8	170
	50	0.3	180	33.33	160	32	170
2CNSL-DEA	0	-	180	-	180	-	180
	10	-	180	26.67	140	40	140
	20	-	180	6.67	150	46	180
	30	-	180	5	170	48	180
	40	-	180	66.67	110	50	100
	50	-	180	40	170	48	180
PT-4633	0	-	180	-	180	-	180
	10	30	170	83.33	170	84	160
	20	60	160	90	180	92	80
	30	70	140	93.33	180	100	80
	40	80	170	93.33	180	96	20
	50	80	160	93.33	180	100	170

Appendix 2. Water seperation rate of the formulated demulsifiers and PT-4633 in Butanol at varying water content and concentration at 60℃

Demulsifier	Concentration (ppm)	10% water content		30% water content		50% water content	
		Water Seperation (%)	Time (mins)	Water Seperation (%)	Time (mins)	Water Seperation (%)	Time (mins)
CNSL-EA	0	-	180	-	180	-	180
	10	5	160	5	180	19	180
	20	20	160	30	170	40	180
	30	30	120	46.67	170	56	170
	40	40	110	73.33	180	92	180
	50	45	170	83.33	140	100	180
CNSL-DEA	0	-	180	-	180	-	180
	10	0.3	150	13.33	160	36	180
	20	0.4	180	20	180	36	180
	30	0.4	180	43.33	160	36	180
	40	6	160	43.33	180	68	180
	50	7	170	70	180	98	180
2CNSL-DEA	0	-	180	-	180	-	180
	10	2	180	10	140	28	180
	20	10	180	20	120	36	180
	30	30	180	53.33	160	46	180
	40	30	140	60	130	84	180
	50	50	180	60	150	100	120

Demulsifier	Concentration	10% water content		30% water content		50% water content	
PT-4633	0	-	180	-	180	-	180
	10	20	150	76.67	70	72	170
	20	40	150	83.33	20	86	160
	30	50	160	86.67	30	96	20
	40	70	150	86.67	30	100	5
	50	80	150	86.67	50	100	5

Appendix 3. Plates showing bottle test results for effective demulsifiers in Xylene at 60℃

Appendix 4. Plates showing bottle test results for effective demulsifiers in Butanol at 60℃